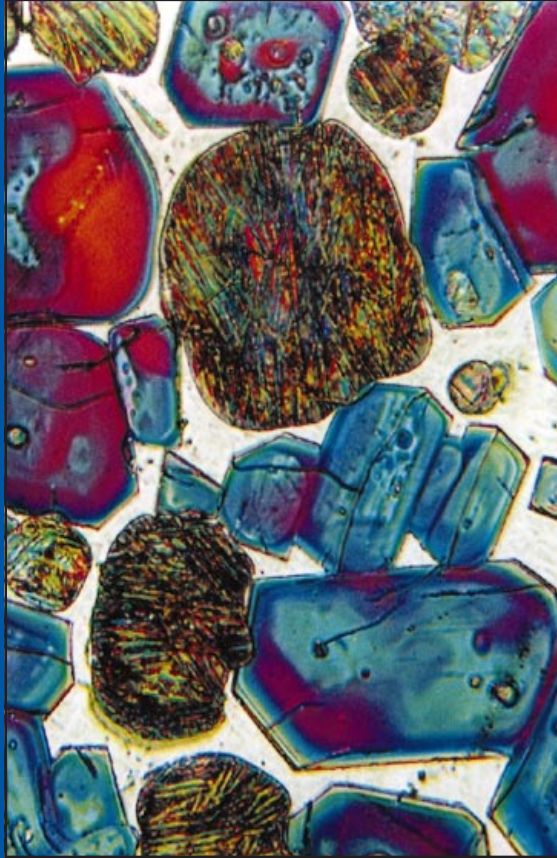
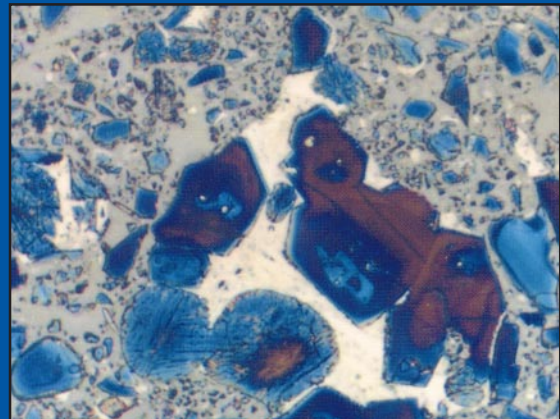
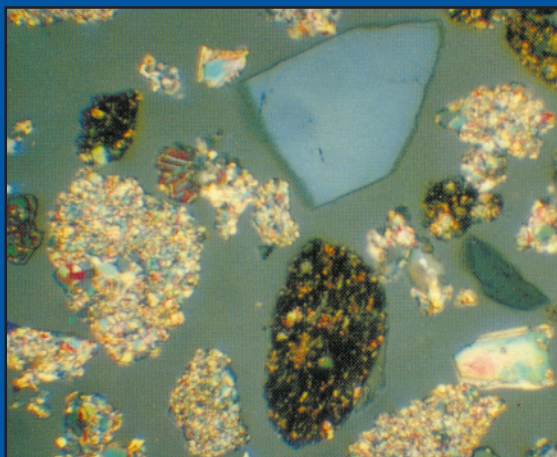




MICROSCOPICAL EXAMINATION AND INTERPRETATION OF PORTLAND CEMENT AND CLINKER

by Donald H. Campbell, Ph.D.

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Microscopical Examination and Interpretation of Portland Cement and Clinker

Second Edition

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Cover Photo:

Upper left: Polished section of portland cement clinker at 400X

(see also page 79). (S#A6636)

Lower left: Feed particles in thin section

(see also page 120). (S#A6715)

Right: Polished section of cement in epoxy

(see also page 68). (S#A6622)

Warning: Contact with wet (unhardened) concrete, mortar, cement, or cement mixtures can cause SKIN IRRITATION, SEVERE CHEMICAL BURNS (THIRD-DEGREE), or SERIOUS EYE DAMAGE. Frequent exposure may be associated with irritant and/or allergic contact dermatitis. Wear waterproof gloves, a long-sleeved shirt, full-length trousers, and proper eye protection when working with these materials. If you have to stand in wet concrete, use waterproof boots that are high enough to keep concrete from flowing into them. Wash wet concrete, mortar, cement, or cement mixtures from your skin immediately. Flush eyes with clean water immediately after contact. Indirect contact through clothing can be as serious as direct contact, so promptly rinse out wet concrete, mortar, cement, or cement mixtures from clothing. Seek immediate medical attention if you have persistent or severe discomfort.

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PREFACE TO THE FIRST EDITION

The aim of this handbook is to improve economical production and quality control of portland cement. Samples of clinker, cement, and raw materials can be prepared for microscopical examination with relative ease and rapidity. Virtually immediate improvements in the production process can result, quickly justifying the costs of optical equipment and personnel training. Use of the microscope, therefore, readily translates into energy savings and production of a competitive cement while facilitating control of cement quality. The underlying variables in the equation of cement quality and performance are essentially those of many other chemical (mineral) industries: nature of the raw materials, efficiency of treatment of those raw materials during product manufacture, and the proper use of the product. Consequently, the answer to the question "How can we improve the quality of portland cement?" lies, to a great extent, in the sciences of mineralogy and chemistry.

The primary purposes, therefore, of this publication are

1. To describe the methods of sample preparation for microscopical study and to recommend the use of certain methods of analysis and microchemical techniques
2. To describe the common phases in portland cement clinker
3. To present a set of microscopical observations (illustrated with photomicrographs where possible) with corresponding genetic interpretations drawn, for the most part, from published sources.

An effort has been made to present information valuable in day-to-day cement manufacture and to separate microscopical observation from interpretation. Even though some interpretations may be somewhat contradictory from author to author, such contradictions point out directions for further research. The compilation of optical data and interpretations is therefore considered preliminary and should serve as the basis for continued study of clinker phases, preferably with statistical methods.

The publication is not meant to cover the theory of light transmission in solid crystalline and noncrystalline media or optical mineralogy. These subjects are discussed by Midgley* in Taylor (1964), Wahlstrom (1969), and Kerr (1977). The reader's working knowledge of polarized-light and reflected-light microscopy is assumed. College or industrial courses or private study and experience in light microscopy are required to derive optimum benefit from this material, which, for the most part, evolved from a course in cement and clinker microscopy given for several years at the Portland Cement Association (PCA), Skokie, Illinois. Consequently, this handbook was written for the practicing microscopist in the cement plant or in the research laboratory.

Most of the photomicrographs were taken by the writer as part of a PCA research project (HR-1404, Microscopical Analysis of Clinker) in which samples of raw feed, clinker, and cement from approximately 51 North American kilns were studied and interpreted.

One should not assume, however, that interpretive cement microscopy has an unalterable foundation in optical fact, for much research remains to be done in describing and defining the correlations between microscopical observation and the production regime. Extensive systematic research is needed on the nature of portland cement phases (in particular, the polymorphic varieties) discerned through *combined* observations utilizing transmitted- and reflected-light microscopes, scanning and transmission electron microscopes, electron microprobe, and X-ray diffraction. An appreciation of the techniques, problems, and applicability of these complementary modes of analysis adds immeasurably to the depth of one's competence in clinker interpretation and consequently increases one's value in the economics of cement production. Modern methods of cement production, therefore, require modern techniques of microscopy and chemical analysis.

* See references at the back of this publication.

PREFACE TO THE SECOND EDITION

Many reports concerning raw feed, clinker, and cement microscopy have been published since the first edition of this book in 1986. Most of the publications are in the annual Reviews of the General Meetings of the Japanese Cement Association (JCA), the monthly journal of Zement-Kalk-Gips (ZKG), the Proceedings of the International Cement Microscopy Association (ICMA), and a few other journals. Thus considerable space, describing some of the salient results of research that have application to or involve microscopy, is required to bring the revised edition of this book up to date. Selected information from these publications has been inserted into the relevant contexts throughout the second edition. Time and the requirements of other projects, unfortunately, have not permitted a review of all the available literature and, regrettably, some probably very informative articles have been unintentionally omitted.

The strong influence of the meritorious work of Yoshio Ono of Chichibu Onoda Cement Company is seen not only in the Japanese literature but also in the basic and practical research from workers in other countries, some of whom have challenged Ono while others have defended and, to some degree, verified Ono's broad interpretations of kiln conditions in laboratory and plant studies. Ono recently summarized much of his more than 40 years of industrial research in a Chichibu Onoda publication (1995), "Ono's Method, Fundamental Microscopy of Portland Cement Clinker," in which he emphasized the use of polished sections and etching degree to evaluate clinker. Ono's kiln interpretations, based largely on transmitted- and reflected-light characteristics of the clinker silicates, appears to be of optimum use in cement plants characterized by relative uniformity of the major pyroprocessing variables, and during start up.

Illustrating the complexity of clinker phase crystal chemistry and microscopy, the basic research work of Iwao Maki at the Nagoya Institute of Technology, Nagoya, Japan, is especially illuminating and definitive.

Recognition of the profound effects of raw feed particle size, mineralogy, and homogeneity in controlling many clinker silicate characteristics has come to the forefront in clinker interpretations in recent years. As the reader will undoubtedly observe in this book, the separation of raw feed and clinker phase microscopy and interpretation is exceedingly difficult because of their many complex relationships. Thus, one might expect to find discussions of alite crystal size in terms of nodulization, feed mineralogy / particle size, SO_3 , etc. Indeed this complexity makes for continuing interest. Consequently, the microscopy of raw feed is given major emphasis in the Second Edition, forming a newly added Chapter 10. Most of the added references, observations, and interpretations in the second edition deal with correlations of raw feed characteristics with clinker microscopy. A new classification of belite, based on internal microstructure, and a classification of matrix crystal size are proposed. A few of the previously published clinker photographs have been eliminated, improved, or replaced, and many photomicrographs of raw feed particles have been added.

As we look to the future, we see an increasing application of electronic controls in clinker and cement production, expensive automated systems that, theoretically, eventually provide a higher-quality product at a reasonable price. The essential value and use of microscopy in the cement industry, however, have not changed. The light microscope remains an economical, practical, easily applied means of *material quality control from the quarry to the construction*. It should be a complementary tool amidst other equally valued instruments of analysis. But, as in mastery of the piano, the virtuoso must "practice, practice, practice." One can always make better observations, tighter correlations, and more explanatory interpretations.

Thus it is to my fellow microscopical practitioners, my friends and colleagues, those who recognize the tremendous value of the microscope, that I dedicate this book.

For this second edition, I am particularly indebted to Mr. Steven H. Kosmatka of the Portland Cement Association in Skokie, Illinois (USA), for his congenial, editorial thoroughness and tenacity, to Diane Vanderlinde who masterfully re-keyed the entire manuscript, to Natalie Holz for her meritorious editorial efforts, and to the staff at Construction Technology Laboratories, particularly F. M. Miller and Fulvio Tang who ably assisted me on numerous occasions in the pursuit of answers. Gratitude is also extended to Walt Rowe (Centex Construction Products), Hung Chen (Southdown Inc.), and Paul Tennis (PCA) for their thorough thoughtful reviews.

Donald H. Campbell, Ph.D.

Conversion factors—

$\text{kg/cm}^2 (14.22) = \text{psi}$

$\text{psi} (0.006894) = \text{MPa}$

$\text{kg/cm}^2 (0.09807) = \text{MPa}$

ACKNOWLEDGMENTS

The writer is particularly grateful to the late George J. Vanisko of PCA who introduced the author to the subject of clinker and cement microscopy and who participated in the teaching of that subject in a course given at the PCA laboratories in Skokie, Illinois. Vanisko was particularly fortunate to have had instruction from Yoshio Ono and persevered in the mastery of what he learned.

The writer is indebted to Stewart Tresouthick, past director, Chemical-Physical Research Department, CTL, and Jack Prout, St. Marys Cement Company, Toronto, Ontario. Gratitude is also extended to G. R. Long of the Blue Circle Research Laboratories in Greenhithe, England, for assistance at numerous times, especially for information on the calcium silicosulfates, and to Dr. Peter Hawkins, California Portland Cement Company, for procedure utilizing the Babinet compensator to determine alite birefringence. Yoshio Ono (formerly of Chichibu-Onoda Cement Company, Tokyo), Rong Far Lee (Taiwan Cement Corporation, Taipei), and Iwao Maki (Nagoya Institute of Technology, Japan) have been particularly helpful through correspondence on several occasions. I am grateful to Hugh Love for valuable assistance in the scanning electron microscopy and Jean Randolph, for aid in typing many of the observations and interpretations. My wife, Karen, kindly provided expertise on text and photograph formats, and assisted in editing and checking references.

INTRODUCTION

The fundamental use of the microscope in portland cement clinker analysis is to bring to the observer a visual appreciation of phase identities, sizes, conditions, and mutual relationships. With only a basic assemblage of equipment, microscopical analysis can be easily performed, in many cases within a few minutes. The rapidity with which potentially energy-saving information can be acquired clearly renders the analysis economically justifiable, especially in routine quality-control and trouble-shooting situations. In addition, the microscope has obvious value in scientific research in the manufacturing process.

Study of the polished section or thin section of portland cement clinker, for example, quickly reveals several details of crystal size, morphology, abundance, and distribution, leading almost intuitively to interpretations relating these data to certain features of the raw material and burning conditions. The microscopical method of analysis, using polished sections or thin sections of clinkers, is uniquely advantageous because the investigator can see individual crystals, virtually undisturbed, in their place of origin, and can interpret these observations in terms of the microenvironment developed in that clinker nodule. These observations are related to characteristics of the raw feed particles and the burning conditions in the kiln. For example, nests of tightly packed belite crystals form in silica-rich areas of the clinker and suggest the possibility of coarse quartz grains in the raw feed. Alite crystal sizes of 10 to 15 μm may indicate an undesirably rapid rate of temperature rise in the clinker as it passes through the kiln. Large clusters of free lime suggest coarse limestone particles.

Following are some of the many aspects of portland cement production in which microscopy can play an analytical and quality-controlling role:

1. Analysis of Raw Materials
 - A. Quarry rock analysis

- (1) Areal and volume distribution of rock types
 - (2) Mineralogy and chemistry
 - (3) Potential grindability
 - B. Raw-mix analysis
 - (1) Mineralogy and chemistry of size fractions and individual phases
 - (2) Efficiency of grinding and homogenization processes
 - (3) Estimation of burnability
2. Clinker and Cement Examination
 - A. Phase changes and phase concentrations at various stages in the pyroprocessing system (including buildups, rings, coatings, and clinker-refractory reactions)
 - B. Temperature profile—burning efficiency relationships in the calcining and burning zones of the kiln
 - (1) Rate of heating (rate of temperature change in the kiln feed through the approximate range of 1200°C to 1600°C)
 - (2) Maximum clinker temperature (above approximately 1450°C)
 - (3) Time of clinker retention at high temperature (length of time above approximately 1400°C)
 - (4) Rate of clinker cooling (rate of temperature change from maximum to approximately 1200°C)
 - C. Grinding and storage
 - (1) Prediction of clinker grindability
 - (2) Efficiency of clinker-grinding process (mineralogy of size fractions, estimate of Blaine surface area)
 - (3) Clinker weathering during storage
 - D. Prediction of cement performance
 - (1) Hydration characteristics

- (2) Strength gain
 - (3) Sulfate resistance
- 3. Analysis of Other Materials
 - A. Dust mineralogy and chemistry
 - (1) Stack emission
 - (2) Bag-house collection
 - B. Coal
 - (1) Mineralogy
 - (2) Fineness
 - (3) Grindability
 - C. Constitution of coal ash and slag
 - (1) As blended material in cement
 - (2) As a raw material for kiln feed
 - D. Gypsum and other sulfates
 - (1) Purity (byproduct or natural deposit)
 - (2) Size distribution (grinding efficiency)
 - (3) Alterations in silo storage and grinding effects
 - E. Metallography
 - (1) Kiln chain examination
 - (2) Grinding-ball examination

Optimum use of the microscope requires certain skills of the microscopist. Above all, one must be patient in the proper preparation of samples and diligent in perfecting those analytical techniques that give reliable data. Of prime importance is the microscopist's ability to quickly recog-

nize many phases that are routinely investigated without resort to the time-consuming process of gathering large amounts of optical data. In other words, sight identification of phases with a minimum of data is clearly an asset. With accumulated experience, most of which comprises long hours at the microscope, an ability for sight identification of the common phases is attained, interpretations are refined, knowledge is acquired, and the microscopist can confidently state the results of his or her analysis. A critical eye, an appreciation of optical mineralogy, and a knowledge of the chemical nature of the portland cement production process, therefore, are the primary requirements for optimum use of the microscope in the cement industry.

Up-to-date photographic or electronic equipment to provide a permanent record is practically mandatory. A video or photographic camera attached to the microscope can be quite helpful in presenting microscopical data to others, especially in an instructional and recordkeeping context. Complementary use of X-ray diffraction and the scanning electron microscope (with microprobe) add to the versatility of the microscopist, providing structural and compositional details not otherwise available, thus strengthening and widening the interpretations.

CHAPTER 1

History of Clinker Microscopy

Microscopical descriptions of clinker phases had their origins in 1887 with the work of the French chemist LeChatelier. Following the methods of microscopical analysis of rocks developed by the English geologist H.C. Sorby, founder of petrography and metallography, LeChatelier reported the presence of the following constituents in a portland cement clinker thin section:

1. Clear, colorless, angular crystals with a low birefringence, identified as tricalcium silicate
2. Rounded, turbid, yellowish crystals with moderate birefringence, identified as dicalcium silicate
3. A dark brown intermediate substance of irregular and ragged form with a lime-iron-aluminate composition (later shown to be calcium aluminoferrite)
4. Another material, which, he inferred chemically, should be tricalcium aluminate.

Although it is not clear whether LeChatelier examined cement made by Joseph Aspdin, who patented portland cement in England in 1824, a few comments on the nature of the Aspdin cement appear relevant to the history of clinker microscopy.

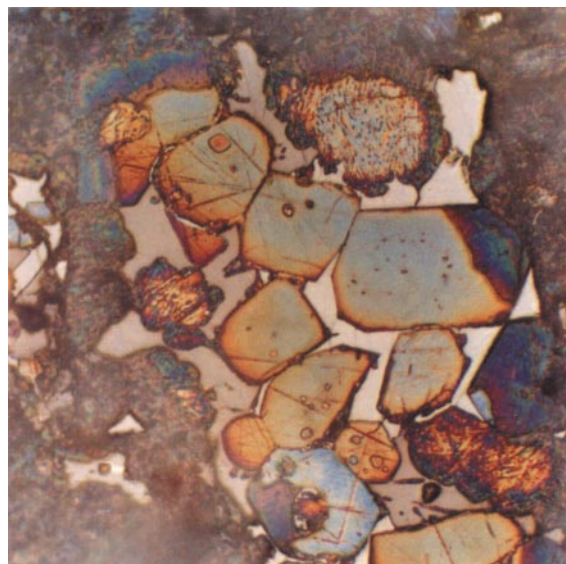
In 1978 a sample of hardened paste was given to the writer by Norman Gregg of R. H. Harry Stanger, Ltd., Hertfordshire, United Kingdom. Gregg reported that the paste represented several barrels of cement (made by William Aspdin, son of Joseph Aspdin) that had been aboard a ship that sank in the River Thames in 1848 near Sheerness, Kent, England. The story of these barrels of cement and other early cements is told by Blezard (1984).

A polished thin section of the hardened Aspdin paste (Photographs 1-1 through 1-4) was examined by the writer and found to contain approximately 10 percent unhydrated portland cement clinker (UPC)

PHOTOMICROGRAPHS OF ASPDIN PASTE

Photograph 1-1 Portland cement clinker particle in Aspdin paste. Subhedral to euhedral pale-green alite; raggedy, round multicolored belite; coarsely crystalline brightly reflecting ferrite; and gray aluminate (left center). Edge of particle shows pseudomorphous hydration effects. (S#A6606)

Polished section*
KOH followed by nital etch
FD (Field Dimensions) = 0.21x0.21 mm

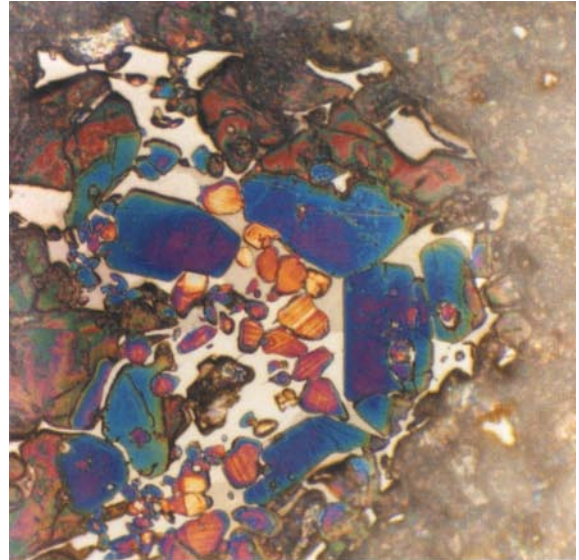


* Polished section photomicrographs were taken in reflected light unless otherwise indicated.

PHOTOMICROGRAPHS OF ASPDIN PASTE

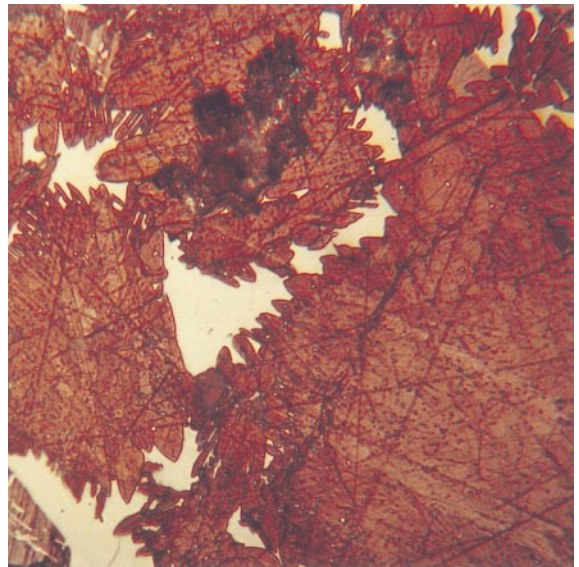
Photograph 1-2 Unhydrated portland cement clinker (UPC) in Aspdin paste. Large, blue-green, angular alite; small, tan-orange round belite (Type II, Insley); brightly reflecting ferrite; and pinkish-gray aluminate, presumably C_3A . (S#A6607)

Polished section
Nital etch
FD = 0.21x0.21 mm



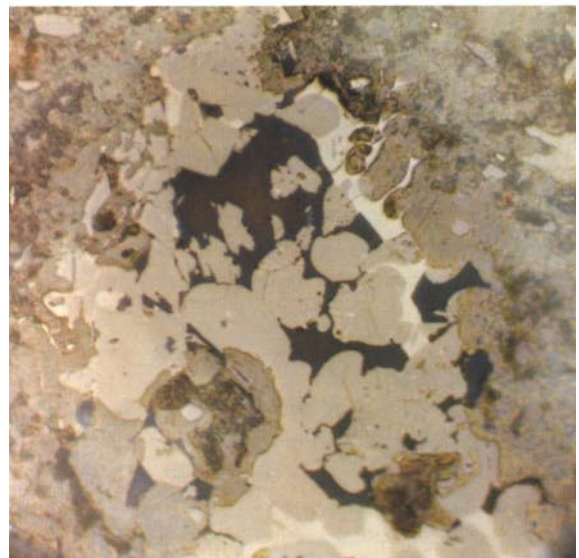
Photograph 1-3 Unusually large belite in UPC in Aspdin paste. Note prominent lamellar extensions into ferrite matrix. Probably an effect of CaO resorption during slow cooling. (S#A6608)

Polished section
Nital etch
FD = 0.21x0.21 mm



Photograph 1-4 UPC in Aspdin paste. Water etch reveals dark-blue, coarsely crystalline aluminate, presumably C_3A . (S#A6609)

Polished section
FD = 0.21x0.21 mm



particles. Although the UPCs are far from identical to those of modern production, they clearly contain, among other phases, the four principal phases typical of portland cement (alite, belite, aluminate, and ferrite). Glassy particles were also observed in the Aspdin paste and appear similar to those described by Idorn and Thaulow (1983), who described some of the microscopic characteristics of a precast concrete wall placed in front of Portland Hall, Gravesend, Kent, England, in 1847. The wall is said to have been built for William Aspdin. Further discussion of this wall and the nature of the UPCs is given by Blezard (1981 and 1984), who shows photomicrographs suggesting a coarsely crystalline clinker that was slowly heated and slowly cooled. Cements similar to this Aspdin cement may have comprised some of the samples studied by LeChatelier and other early workers in clinker microscopy.

Scrivener (1988) studied the Aspdin paste with backscattered electron imaging (BSE), showing clearly the development of hydration products pseudomorphic after the original clinker crystals and drawing attention to the occurrence of layers of hydration product ("inner product").

In 1897 Törnebohm, a Swedish investigator, possibly realizing that because of compositional variation mineral names might be better suited for clinker phases than chemical formulas, clearly described the optical features of the principal clinker phases in thin sections and powder mounts and coined the terms *alite*, *belite*, *celite*, *felite*, and also *glassy residue*. Törnebohm stated that "*belite*" has two or three sets of cross striations and "*felite*" has one set of parallel striations formed at low temperature. Törnebohm related microscopical data to burning conditions, stating:

1. Well-burned clinkers are less porous and contain better-crystallized colorless alite and dirty-green to muddy belite.
2. Brownish-orange celite functions as a flux, promoting the development of the silicates.
3. Underburned clinker disintegrates because of atmospheric moisture combining with residual lime.

Törnebohm also made notable contributions to the microscopical understanding of cement hydration, a topic that must be left for future discussion.

Richardson (1903-1905) summarized theories on the chemistry of portland cement and demonstrated the use of a polarized-light microscope in the prediction of cement quality from clinker examinations. Richardson stated: "If the structure is coarser and the elements are more segregated, the cement from such

a clinker will be less reliable." Most of Richardson's work, however, was in the laboratory where, with numerous sintering experiments, he made frequent use of powder mounts and thin sections to study the products. Richardson, undoubtedly, developed an extensive and systematic body of knowledge that formed foundation for later work by others.

Bates in 1912, describing some of the cement chemistry work at the National Bureau of Standards, stated (p. 369) "It was recognized from the first, that in order that the studies, which were to be made, might be complete, a petrographer with a complete outfit for petrographic studies must be installed. All burns would then be examined for their constitution according to the most approved and exacting methods."

Rankin and Wright (1915), although they were not particularly concerned with the interpretation of burning conditions, firmly established the optical properties of pure compounds and the principal phases in commercial cements. These authors systematically investigated approximately 1000 combinations of lime, alumina, and silica with fully 7000 heat treatments and microscopical examinations.

Using Törnebohm's classification, Guttman and Gille in 1928 tabulated the basic optical properties of clinker phases and the common hydration products. In 1931, Guttman and Gille summarized the 50-year controversy over the nature of alite and demonstrated conclusively that alite is C_3S .*

According to Insley (1936), polished section examination of portland cement clinker was reported by Stern (1908) and by Wetzel (1913); but, largely due to poor technique, the metallographic method was abandoned until Tavasci's very detailed paper in 1934 in which reflected-light microscopy was combined with that from transmitted light.

Tavasci (1934) believed that clinker was composed primarily of alite, belite (alpha and beta), and celite (a fine mixture of $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$), with free lime as a frequent additional phase. With a series of etches, including nital, oxalic acid, hydrofluoric acid, water, and others, Tavasci carefully described the various effects of these solutions on clinker phases and other synthetic compounds. Tavasci presented rather meticulous descriptions of the forms of belite, suggesting a martensite-type separation in the transformation of alpha to beta.

Tavasci classified belite into three morphological types: I, II, and III. Belite I was said to show striations, sometimes like twinning, prevalently in two directions. The striae were described as being relatively

* An abbreviated chemical symbolism in which C = CaO, S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 , K = K_2O , and N = Na_2O .

thick but not very "fitte" (a term believed by the present writer to mean "etching resistance"). Upon etching with alcoholic nitric acid (nital) the striae were hollowed out with respect to the rest of the grain. Belite II crystals were generally large, containing very "fitte" striae, the dark striae showing relatively less attack by alcoholic nitric acid than the bright striae. Belite III was comparatively small and appeared to be an external zone over a core formed by belite I or II. Coarse striation did not occur in belite III, but fine parallel striations were observed like those in belite II. Belite III was said to contain "a kind of veining formed by inclusions which at high magnification appear white and in strong relief."

In 1936 Insley (about whom much more is said later) clearly showed that (1) alite is tricalcium silicate (C_3S), (2) two different habits of dicalcium silicate (C_2S) comprise belite and felite, and (3) celite is tetracalcium aluminoferrite (C_4AF). Insley's descriptions and illustrations of clinker phases remain the basis for much of succeeding publications by others.

Among the many historically important contributors to the microscopy of portland cement clinker, Levi S. Brown deserves special recognition for his observational skills and interpretive acumen. Brown worked for Lone Star Research Laboratory in Hudson, New York, in the 1930s and in 1940 joined the research staff at the Portland Cement Association, where he spent approximately 25 years in cement and concrete investigations. Most of his scientific efforts were dedicated to the microscopical interpretation of clinker burning, cement hydration, and concrete deterioration. An unpublished report (Brown, 1936) contains the following interesting observations:

1. C_3A and C_3S were discriminated in thin sections and powders mounted in Hyrax, "a synthetic resin with index of refraction" of approximately 1.710.
2. Differences in optical properties of C_3S were defined and birefringence and morphology were observed to show wide ranges; crystal zoning was not clearly understood.
3. Optical characteristics of C_2S , particularly the discrimination between polymorphic varieties (alpha, beta, and gamma), were described. The "better burned" clinkers were said to contain relatively clear crystals.
4. Optical characteristics of C_4AF , especially the color variations, were related to burning conditions, magnesium oxide content, and a reducing environment, the latter indicated by a honey-brown C_4AF color and weak pleochroism. The darkening and strong pleochroism of C_4AF were correctly thought to be due to incorporation of magnesium oxide.

5. The morphologic and volumetric changes in the transformation of calcite to lime in a portland cement raw mix were described.
6. Large crystals of periclase were described and explained as an effect of annealing of commercial clinkers.
7. Gehlenite, found sparingly in practically all portland cement clinkers, was detected by examination of floating particles that have a uniaxial character and perfect basal cleavage in an oil of approximately 1.71 refractive index. Gehlenite was said to be suggestive of underburning.
8. Sulfate minerals in clinkers, observed as floating particles in refractive index oil, were said to occur abundantly in underburned clinker. Optical characteristics of clinker sulfates compared with sulfate phases formed in the laboratory led to the conclusion that the low-index mineral in clinker is an alkali sulfate with a variable but small amount of calcium sulfate held in solid solution.
9. Free lime was seen to increase with raw feed particle size and decrease with increasing burning time (flame length).

Brown and Swayze in 1938 published a paper describing the application of the microscope to autoclave problems, namely, free lime and magnesia in portland cement. Three forms of free lime were defined: (a) light-burned (quicklime), (b) hard-burned, and (c) air-slaked. The latter type was described as a "heretofore unidentified form of calcium hydroxide" having optical properties different from normal calcium hydroxide (portlandite) and thought to be the "Epezit" which was defined by Guttman and Gille in 1928a and 1928b. Epezite was said to differ from portlandite in optical sign and refractive indices as follows:

Epezite	Portlandite
Uniaxial (+)	Uniaxial (-)
Epsilon = 1.55 - 1.56	Epsilon = 1.545
Omega = 1.54 - 1.55	Omega = 1.574

Epezite typically forms tiny popcornlike crystals. Portlandite crystallizes in pore spaces as tablets and platelets. The growth of epezite was thought to be responsible for clinker disintegration in open storage (even in supposedly tightly sealed containers on the

* Hyrax (no longer available) is briefly described in Chapter 4 under the heading "Techniques with Hyrax."

** Unless otherwise stated, the indices of refraction given in this book refer to sodium light.

laboratory shelf) due to the 97% volume change when free lime combines with atmospheric moisture, hence the term *air-slaked*.

Brown's most widely known published work is his *Microscopical Study of Clinkers* (1948) in which 21 different lots of clinkers were microscopically studied at the Portland Cement Association laboratories in order to correlate mineral composition with what Brown termed the "degrees" of burning in the cement kiln and concrete durability. Although Brown's description and interpretation of what he termed the "glass" and "dark prismatic" phase may be questionable in the light of recent research, his work in clinker and concrete microscopy was seminal. Brown contributed significantly to the discussion of clinker phases in a book by Insley and Fréchette (1955).

Brown summarized his philosophy of microscopy in 1959 when he discussed the two primary modes of specimen examination (transmitted and reflected light); the phase rule in relation to the microscope; the nature of cement hydration and its effects on strength, water-cement ratio, dimensional stability, durability, and other concrete properties.

Tavasci (1978) elaborated on the three forms of belite (I, II, III), relating them to C_2S polymorphs (alpha, alpha prime, beta, and gamma), and attempted to show the analogy with the austenite-martensite conversion in high-carbon, hardened steel. Belite I was said to contain alpha lamellae (etching relatively light colored in nital) and alpha prime lamellae (narrow and etching dark in nital). Belite II was said to contain alpha and beta; the alpha prime, having originally formed from alpha, was transformed to beta upon further cooling. Alpha remained as an included phase. Belite III differed from belite II in having sharper and less-regular separation of the alpha inclusions.

Also among the many major historical contributions in clinker microscopy are the works of Parker and Nurse (1939); Taylor (1943); Gille (1955); Krämer (1960); Nurse, Midgley, and Welch (1961); Midgley (1964); Butt and Timashev (1974); and others. Most of these authors are mentioned again in Chapter 7, "Microscopical Interpretation of Clinkers."

Three publications of European origin are considered required reading for cement microscopists:

1. *Mikroskopie des Zementklinkers, Bilderatlas*, F. Gille, I. Dreizler, K. Grade, H. Krämer, and E. Woermann (1965, Verein Deutscher Zementwerke),
2. *Microstructure of Portland Cement Clinker*, Friedrich Hofmänner (1973, Holderbank), and
3. *Microscopy of Cement Raw Mix and Clinker*, Erling Fundal (1980, F.L. Smidth).

As will be evident, the present writer has drawn

heavily on the above three publications, plus several Japanese reports, particularly the work of Yoshio Ono (1995), whose detailed studies demonstrate the practicality of transmitted-light microscopy in the cement plant. Ono's Method is discussed in Chapter 6.

A commendable effort to bring cement and concrete microscopists together for the purposes of sharing knowledge and promoting the use of the microscope in the construction industry is seen in the founding of the International Cement Microscopy Association (ICMA) in 1980.* Published proceedings of their annual meetings have helped immeasurably in spreading knowledge of various microscopical methods and have generally stimulated growth in cement quality control through microscopy in North America.

Illustrating quality-control methods in well cements, polarized-light microscopy and fluorescent microscopy have been applied to the analysis of oil-well cement blends containing pozzolans, bentonite, potassium chloride, friction reducer, modified pozzolan, fluid-loss addition, silica flour, and other materials (Reeves, Bailey, and Caveny, 1983). Examination of cement polished sections has shown a relationship of oil-well cement thickening times and retardation rates (Caveny, Weigand, and Bailey, 1983). Caveny and Weigand (1985) described a good oil-well cement as having well-formed alite (40 to 50 microns), no surficial deterioration of silicates, low free lime (less than 0.5%), and being free of metallic iron.

Relatively recent contributions to oil-well cement microscopy include Polkowski (1987) who concluded that four cements with less than ideal microscopical characteristics still performed acceptably with different loadings of admixtures.

Carruthers, Livesay, and Wells (1994) describe some of the burning conditions required for production of a Class H (HSR) oil-well cement: (1) hot burning zone and long retention time (dendritic belite), (2) high burning zone temperature and long burning zone (cannibalistic alite, wrap-around belite), (3) lengthening of burning zone and increasing temperature (belite beginning to disperse, silicate enlargement, and clarification of matrix), (4) dust recirculation (zoning in alite), slow cooling from extension of burning zone farther back in the kiln (ragged belite), and others. Desirable properties of the Class H (HSR) cement include a dead burned clinker with large alite, cannibalistic alite, amoeboidal belite, wrap-around belite, and finely crystalline C_3A .

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The desirable characteristics of Class H well cement were listed by Arbelaez (1990): free lime levels less than 0.5% with a uniform distribution, C_3A less than 6.5%, no weathered clinker, using only the 12.7- to 38.1-mm clinker fraction for the cement, relatively hot burning without production of cannibalistic alite, and avoidance of ragged belite by rapid cooling.

The subject of clinker grindability also has microscopical aspects and the most complete literature survey, to date, is that of Hills (1995) who enumerated most of the prevailing agreed-upon relations (such as decreasing alite crystal size increasing grindability). Other variables on which the interpretations were not as clear cut (such as percent liquid phase) were also listed.

Tachihata, Kotani, and Jyo (1981), in a laboratory study of the relationships between rate of heating, raw meal fineness, and other factors, concluded that clinkers with large crystal sizes in a narrow size range showed unfavorable grindability, and that cracks within the crystals and at the boundaries were some of the most important factors in grindability.

Viggh (1994) studied clinker grindability and other related cement characteristics, concluding, among other things, that better grindability results with increase in liquid and alite percentages, and a decrease in alite crystal size. Poorer grindability resulted when belite percentage and crystal size increased. A decrease in setting time and improvement in strength development follow from better grindability. Cement flowage was said to be dependent on the amount of gypsum.

Theisen (1993) described a rapid method of microscopical determination of alite and belite size and approximation of visible pore space by recording the number of intercepts along a line of traverse in successive fields of view. The intercept numbers were used with Bogue calculations and related to power consumption (kwh/t) in grinding. Data can be gathered in less than an hour.

Many additional recent publications linking microscopy to a wide range of performance-related properties of cement are given in the following chapters.

CHAPTER 2

Sampling and Sample Storage

SAMPLING

Taking the clinker sample for microscopical examination has, as yet, no formally accepted procedure and several techniques are currently used, largely dependent on the purpose of the investigation. Because of time constraints during clinker analysis, the clinker sample must necessarily be small and, therefore, the conclusions must be cautiously drawn. A grab sample is preferable to composite samples for most investigations.

Hofmänner (1973) recommends the following sampling technique:

1. At intervals of five minutes or less take three 2-kg samples, mix, and quarter down to 500 g.
2. Crush the 500-g sample to 5-mm particles.
3. Quarter until a sufficient amount remains for encapsulation with resin in a 25-mm-diameter cup. Two encapsulations are recommended to get a "representative average of the random sample."

Ono (1981) recommends a grab sample every eight-hour shift during clinker production; hourly samples are taken during kiln startup.

Hicks and Dorn (1982) recommend the Ono test (except birefringence) once per day and every time a change is made in the burning process and, once per week, a polished-section examination of the 0.84- to 0.59-mm (No. 20- to 30-mesh) granulated clinker.

For determination of the phase content of clinker, Chromy (1983) utilized polished sections made from the quartered residue from 0.5 kg of clinker ground to a particle size passing a 1.0-mm sieve. A 20-mm-diameter polished section of particles embedded in epoxy was prepared.

One of the most popular methods involves crushing a random clinker sample of roughly a liter volume (1 to 2 kg) to approximately 2- to 4-mm-diameter par-

ticles, from which a few particles are randomly selected or riffled (1) for encapsulation in epoxy for reflected-light examination and (2) for further crushing to a powder for immersion in oil on a microscope slide for examination in transmitted polarized light. Several encapsulations can be made, thereby increasing the probability of studying particles representing most of the original clinker sizes. One should be aware that different size fractions of crushed clinkers may have different phase abundances (some alite-rich, others belite-rich).

J.D. Dorn (personal communication, 1985) stated that clinkers less than approximately 25 mm are virtually the same and that larger clinkers exhibit effects of different cooling rates. Dorn recommended passing a liter of clinker through a crusher, producing particles of approximately 5-mm diameter, followed by riffling to a volume of 1/4 liter and pulverizing to less than 0.59 mm. The 0.59- to 0.30-mm (No. 30- to 50-mesh) fraction is used for a polished section.

Centurione (1993) recommends an initial 15-kg clinker sample, which is then quartered to 2.5 kg and sieved. The sieved fractions are crushed, sieved into 2.4-, 0.6-, and 0.3-mm fractions, and blended. A 50-gram sample is taken for microscopy, XRF, and chemical determination of free lime.

One problem with the crushing of clinker prior to examination is that microcracks seen in polished-section or thin-section study are ambiguously interpreted. Microcracks that are not artifacts of sample preparation may, in some investigations, be related to strain caused by thermal stress (Hornain and Regourd, 1980), crystal reorganization, hydration, and expansion.

If the clinker is extremely sandy or dusty, crushing prior to sieving may not be necessary. A random spoonful taken from a well-mixed sample will likely be adequate.

Other workers prefer to sieve the clinker sample, after which representative portions of arbitrarily

defined coarse, medium, and fine fractions are selected for analysis. Whole or crushed clinkers are encapsulated in epoxy and polished sections are prepared. Powders for study in transmitted light can be made from representative portions of the same sieve fractions.

Long (1982a) stated that the sampling technique must be dependent on the kind of problem under investigation. A constant cement-quality problem might be studied with a clinker grab sample. However, for analysis of process variations of several days, for example, a combination of several clinker samples to form a composite might provide an abundance of information, particularly if the clinker shows variability. Hourly samples may also be studied as kiln modifications take place. Long recommends taking a 15-kg sample, crushing it to less than 6 mm, then riffing or quartering and separating the 2- to 4-mm fraction for microscopical study. Dusty or sandy clinker should be sieved into a coarse fraction (greater than 2 mm) and a fine fraction (less than 2 mm). The coarse fraction is then crushed to supply the 2- to 4-mm-size material for microscopical study as a companion to the fine fraction. Whole clinker nodules can also be studied. These should proportionally represent the sizes of the nodules in the grab sample and typically number 10 to 12.

The sampling method normally followed by the author is to restrict the microscopical investigation to clinkers from only a broadly defined modal-size class from which a number of clinker nodules (at least 30) are randomly selected and crushed to 1.0 to 2.0 mm, some fragments for encapsulation in epoxy and others further crushed and treated with KOH-sugar solution for powder-mount examination and X-ray diffraction (see Chapters 4 and 5). The broadly defined modal class is presumed to represent that part of the clinker size population that volumetrically supplies most of the cement and, therefore, has the dominant influence on the cement's hydraulic characteristics. Thus, by neglecting the largest and smallest clinkers, one studies the most common clinker sizes that perhaps more accurately reflect the burning conditions and the nature of the raw mix. Sampling just downstream from the cooler is also recommended because the clinkers represent a relatively narrow range of kiln conditions, simplifying the interpretation.

The sampling of cements appears to present no major problems. Care should be taken, however, to avoid bias from samples unduly rich in coarse or fine particles, or samples representing areas that might be affected by moisture condensation—unless incipient hydration is the object of the investigation.

In conclusion, sample volumes and sampling techniques appear to be largely the arbitrary choice of the

microscopist, with objectivity and relevance to the aim of the investigation as the primary considerations. A standard practice for sampling and sample preparation is needed for routine microscopy. For certain studies, clinker nodules can be halved, one half for microscopy, the other half for chemistry and X-ray diffraction (XRD). Only one kiln should be represented in a single clinker or cement sample. A composite clinker sample can be somewhat confusing due to the possible variety of burning conditions represented.

Systematic microscopical analyses of the clinker with its corresponding raw mix and cement are highly recommended. It is not uncommon for the writer to place a portion of the greater than 45- μ m cement and raw mix in the same cup with the clinkers for epoxy impregnation and polished thin-section examination.

SAMPLE STORAGE

Preventing atmospheric hydration and carbonation of cement and clinker is a difficult but, for most microscopical studies, not an insurmountable problem. Sample contact with water, atmospheric or otherwise, should be minimized. For long-term storage, glass jars or vials with corks or screwtops that have been sealed with molten wax appear to be moderately effective. During routine examinations, the author stores cement or crushed clinker sieve fractions (after wet sieving with an isopropyl alcohol spray) in 15-mL screwtop glass vials. Only the less than 75- μ m size (No. 200-mesh sieve) is retained. To help prevent hydration, the vials can be stored over Drierite™ or similar hydrophilic material in a vacuum jar. Various types of plastic bags with sealable tops are available and may suffice for temporary storage. However, pinholes produced by abrasion are not uncommon if the samples have been subjected to jostling or other types of rough handling. Metal cans with tight-fitting lids (the type in which paint is supplied) are also relatively satisfactory for sample storage.

Regardless of the type of clinker storage container, if a significant quantity of free lime is present in the clinker, disintegration of the clinker nodules will probably occur as a result of lime hydration (air slaking) forming calcium hydroxide. A dry (humidity-controlled) storage room or cabinet is recommended.

STORAGE OF PREPARED SPECIMENS

Polished sections and thin sections can be protected during storage by mounting the cover glass with a drop of epoxy (without hardener) on the prepared section surface. A small dropper bottle containing

epoxy resin (without hardener) is kept at approximately 40°C on the slide warmer for the purpose of mounting cover glasses. Keeping the resin at this temperature in the bottle seems to minimize the crystallization that may occur at room temperature. The cover glass can be easily removed for several months, but even the epoxy (without hardener) will eventually bond the cover glass to the section. Then the problem becomes one of trying to remove the cover slip with a razor blade or by grinding. The polished surface can be protected with an acrylic spray, which can be removed by gentle rubbing with an acetone- or xylene-soaked rag. An acrylic spray eventually cracks, however, and does not prevent hydration of free lime exposed on the section surface.

Immersion of epoxy-encapsulated materials in polished sections in an anhydrous lightweight oil (preferably odorless) in a wide-mouth glass jar with a screwtop lid effectively minimizes, but does not eliminate, hydration. If the specimen is re-examined microscopically, the oil appearing on the polished surface can be removed with a sonic cleaner containing isopropyl alcohol, followed by a forceful isopropyl alcohol spray. Dorn and Adams (1983) used Freon in a sonic cleaner to remove residual oil on polished-section surfaces. In the writer's experience, oil droplets on a polished section can be removed with a brief application of acetone, followed by an alcohol spray wash, and blow drying.

CHAPTER 3

Stains and Etches

The techniques of imparting color to various crystalline phases preferentially are well known in geology (see Carver, 1971, and Hutchison, 1974). Stain differentiation between plagioclase and potash feldspars and between various carbonate minerals is commonplace, using particles, thin sections, and polished slabs. Stains and etches are those liquids or vapors that, when applied to the polished cross section of a clinker or to a sample of portland cement, preferentially color or dissolve certain phases observed in reflected or transmitted light. The colors mainly result from the refraction, reflection, and interference of light within the thin layer of reaction product formed on the clinker phases. Stains and etches are used to bring out microstructural details of individual crystals. Both stains and etches can be related to the relative reactivities of various clinker phases. Photographs 3-1 through 3-6 illustrate some of the effects of a few stains and etches.

Perhaps the most thorough treatment of the subject of stains and etches is the work of Ellson and Weymouth of Australia (1968). Their paper lists approximately 43 reagent solutions and their effects on portland cement and blast furnace slag phases in terms of (a) reaction type (stain or structural etch), (b) time required for the desired effect, (c) recommended temperatures, and (d) concentrations. Futing summarized the application of many varieties of etches in 1986.

Much of the information given in this chapter was extracted from the work of John Marlin of the Oklahoma Cement Corporation (now a subsidiary of Lone Star Cement Company, Greenwich, Connecticut). Many of his recipes and results (1978 and 1979) are reproduced in this chapter with only slight modification but only a few have been tried by the present writer. Marlin recommends making fresh solutions every two months for most of these stains and etches. Most of the solutions described in the following pages have simultaneous staining and etching effects, and,

unless stated otherwise, the tests are carried out at room temperature. It will be obvious that the effects of various etches and stains are also functions of time and clinker phase composition.

Relative reactivities of silicates among several clinker samples, or comparison of the phase percentages of clinkers from different daily productions or different cement companies, can be determined by etching and staining several polished sections simultaneously at the same temperature. To facilitate this technique, one can combine several polished sections with a rubber band, immersing the assemblage in the etchant for the required length of time. Thus all sections are exposed simultaneously for the same length of time, at the same temperature, and relative rates of reaction can be evaluated according to the colors produced. Similar tests can be performed with 0.2% nital and 0.01% aqueous ammonium chloride. CDTA in successive 15-second applications with examinations after each is particularly good to evaluate the relative rates of silicate reactivities in a suite of samples etched simultaneously. Reaction rates can be increased by heating the polished section with the hair dryer for a few seconds prior to application of the etchant.

Another helpful procedure in polished section examination is to immerse only one half of the polished surface in water, for example, holding the section with a pair of forceps, spray wash the sample with isopropyl alcohol, dry, and then rotate the sample 90° immersing half of the section in nital. Thus the surface is divided by this procedure into quarters: one quarter with only water, one quarter with water plus nital, one quarter with only nital, and a quarter remaining with no etch.

ALUMINATES AND FREE LIME

- A. **Potassium hydroxide—ethyl alcohol solution** (5%) is placed in contact with the polished sec-

tion for no more than 20 seconds. Wash the section surface in a 1:1 ethyl alcohol-water solution followed by a wash in isopropyl alcohol, and buff for approximately 15 seconds on Microcloth™^{*,**} wetted with isopropyl alcohol. Wash with isopropyl alcohol. C₃A turns blue.

- B. **Sodium hydroxide—ethyl alcohol solution** is prepared with 2.5 g of sodium hydroxide plus 40 mL of water plus 10 mL of ethyl alcohol. If the contact of the polished surface with the solution is more than roughly 20 seconds, a deposit from a reaction between hydroxide and aluminate forms that buffing will not remove. C₃A turns blue. If determination of alkali sulfates is desired, stain only one time for approximately 10 seconds, washing with 1:1 ethyl alcohol-water solution, followed by isopropyl alcohol. Do not buff. This treatment will darken alkali sulfates slightly and with prolonged treatment (as for C₃A) will dissolve the alkali sulfate, producing a dark void.
- C. **Potassium hydroxide solution** (0.1 molar aqueous) can be applied in single drop fashion or in a small puddle on a polished surface for 30 seconds. Rinse with an isopropyl alcohol spray and dry with forced warm air. C₃A and alkali-aluminate stain blue-brown, alkali sulfate darkens, and free lime turns brown.
- D. **Boiling sodium hydroxide solution** (10% by mass) will turn calcium aluminate blue or brown in 20 seconds in a high-alumina cement. Etching 30 seconds with a 1% borax solution turns C₁₂A₇ gray (Long, 1983).
- E. **Warm distilled water** (40°C) in 5 to 10 seconds turns aluminates blue to brown, alite light tan, free lime multicolored, and does not affect belite.

SILICATES

- A. **Dilute salicylic acid stain** is mixed as follows: 0.2 g salicylic acid plus 25 mL of ethyl alcohol plus 25 mL of water. After a 20- to 30-second immersion, followed by an alcohol spray wash, alite and belite are blue-green. A modification of this stain is 0.2 g of salicylic acid plus 25 mL of isopropyl alcohol plus 25 mL of water, which, after 20 to 30 seconds, reveals that alite stains 50 percent faster than belite and which, therefore, can be used to distinguish the two phases. A precise immersion time for a series of samples aids in their comparison.
- B. **Salicylic acid etchant** is made by dissolving 0.5 g of salicylic acid in 50 mL of methyl alcohol. After a 45-second etch the alite and belite are clearly seen, the latter showing its lamellar struc-

ture. Longer contact with the solution degrades belite lamellae. Alite is more strongly etched than belite. This etchant can be used prior to ammonium nitrate for alite-belite differentiation with very little effect on the matrix phases. Reaction of salicylic acid in ethyl alcohol is 50 percent that of methyl alcohol and attacks alite about twice as fast as belite. With isopropyl alcohol, however, the reaction is less than 25 percent that of methyl alcohol, and alite is intensely and rapidly attacked, with belite almost nonreactive.

- C. **Nital** is perhaps the most common etchant and stain for silicates and improves with age. Nital is 1.5 mL of nitric acid (HNO₃) in 100 mL of ethyl, methyl, isopropyl, or amyl alcohol. The author routinely uses a solution of 1 mL of HNO₃ and 99 mL of anhydrous isopropyl alcohol. The solution quickly reacts in 6 to 10 seconds with alite and belite. At a 0.05% dilution the reaction time is 20 to 40 seconds. Ono (1995) relates alite reactivity to color produced with 0.2% nital. Depending on the relative reactivity of silicates, alite normally turns blue to green, belite is brown to blue—both silicates showing details of internal structure. Nital superimposed on a 20-second potassium hydroxide etch turns C₃A light brown and colors the silicates.
- D. **Acetone-water solution** (in a 1:1 proportion) can be used as a rinse because it reacts slowly on silicates. A 120-second stain time reveals well-stained alite and belite. C₃A is also visible.
- E. **Isopropyl alcohol solution** (10%) is an easily made stain (10 mL of isopropyl alcohol plus 90 mL of water) that reacts strongly with alite and weakly with belite in 30 seconds to 2 minutes. C₃A exhibits a weak reaction. Compare with HF vapor.
- F. **Maleic acid** attacks alite and belite at about equal rates and a little faster than salicylic acid. When followed by NH₄NO₃, it does not give color distinction to alite and belite.
- G. **Ammonium chloride** (saturated, aqueous) colors a hexagonal section of alite (perpendicular to the threefold crystallographic axis) light yellow. The slender hexagonal section of alite (parallel to the c axis) is colored blue. Zoned crystals in the slender hexagonal section show light-blue cores and dark-blue rims. Ono (1995) recommends an

* Microcloth™ is a tough, feltlike, rayon polishing cloth with a low nap marketed by Buehler Ltd., of Lake Bluff, Illinois.

** Manufacturers and products are listed for reference or to assist in locating various products; this does not imply Portland Cement Association endorsement or approval.

aqueous ammonium chloride solution (0.2 to 2.0%) for etching of polished sections. He related the thickness of the film produced by etching to the color of the resulting reflected light with the equation $R = 2d(n)$, where R is retardation, d is the thickness of the thin film of etching product, and n is approximately 1.5. Thus $R =$ approximately $3d$. A table of etch colors is presented in relation to different values of R and d , using a well-burnt clinker and 0.5% ammonium chloride. Likewise, alite etch colors produced with 0.2% HNO_3 -alcohol are presented in relation to location in the clinker, R , and d . Many of Ono's photomicrographs, however, indicate etching for 20 seconds with water followed by 5 seconds with 2% aqueous ammonium chloride.

Uchikawa (1992) summarized the quality-control techniques for cement and concrete and presented a numerical etch-color scale from 0 to 16, relating each clinker phase reactivity to etch color, using 0.01% aqueous ammonium chloride. The interpreted reactivities were said to be relevant to the initial and early stages of hydration, as well as the sintering conditions. Alite was reported to be more easily etched with "the increase in heating rate, the decrease in burning temperature, the coarsening of the particles of raw materials, and the burning atmosphere approaching reducing." Interstitial microstructure (ferrite and aluminate crystal sizes, and ferrite crystal shape factor) and the etch colors of alite were correlated with heat of hydration, mortar flow, and setting time. Relatively slowly cooled matrix was hydraulically more reactive but led to lower, more variable, mortar flow and lower fluidity. The more easily a clinker was etched, the shorter the initial setting time, which was also shortened by 40 minutes when free lime was increased by only 0.5%. Slowly cooled belite (Type IIIb variety showing extended lamellae and remelting) was shown to be colorless and, on a color basis, indistinguishable from quickly quenched belite. Alite with high amounts of impurities and high $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio correlated with low 28-day strength. Under reducing conditions, triclinic alite and partial transformation of belite to the gamma polymorph were produced, along with smaller alite, larger belite, and lower strength development.

Dorn and Adams (1983) have described the various etch rates of alite and belite in relation to hydraulic activity. A blue color on alite after a 15-second nital etch was said to represent an active alite.

- H. Another variety of the **ammonium chloride stain** is made as follows:

1 g NH_4Cl + 20 mL H_2O
+ 20 mL ethyl alcohol + 10 mL acetone
+ 150 mL isopropyl alcohol

Effects of this stain are very similar to those of NH_4NO_3 except the NH_4Cl stain is approximately 25% faster. Alite turns brown in 10 to 20 seconds; belite is unaffected. This stain can be used directly as a belite indicator by extending the submersion time to 30 to 45 seconds. Alite turns yellow to yellowish green and belite to brown. The effects of this NH_4Cl solution are not as clear for belite lamellae as NH_4NO_3 following salicylic acid.

- I. **Ammonium nitrate solution** is composed of the following ingredients:

1 g NH_4NO_3 + 20 mL H_2O + 20 mL ethyl alcohol
+ 10 mL acetone + 150 mL isopropyl alcohol

Alite is colored in 25 to 30 seconds. With increasing treatment time, the colors on the silicates progressively range from light brown to brown to purplish brown to blue to blue-green to green to yellow-green. Normally, when alite is stained yellow-green, belite will be brown. This solution can be applied following the salicylic acid stain to show alite and belite with an approximately 30-second submersion time.

- J. **Hydrofluoric acid (HF) vapor**, used to etch and stain a polished clinker, has been a very informative technique (Long, 1982a). Almost all the clinker phases can be differentiated with an HF vapor etch. The HF is kept at a temperature of 20°C to 22°C . A finely polished surface is held for 5 to 10 seconds in HF vapor and, after waiting a minute or two for the excess HF fumes to leave the polished surface, the section is examined in reflected light. Belite turns blue and alite is brown. With practice at varying the etch times one can develop reliable HF-vapor etch criteria for other phases such as the alkali sulfates. Prout reported (personal communication, 1984) that a temperature differential between fume and specimen enhances etching. The specimen can be cooled or the HF warmed. Incidentally, C_2AS (melilite) is colored with HF vapor and occurs in high-alumina cement (Long, 1983). *NOTE:* Care must be taken to avoid damaging the microscope objective lens with HF vapors emanating from a freshly etched polished section. Waiting a few minutes before examination is recommended. Because of the extreme danger in skin contact with HF, suitable precautions with gloves and ventilated hood are strongly advised.
- K. **Distilled water** was described by Brown (1948) as an etch that enabled one to discriminate nine clinker phases after a relief polish. With the use of present-day materials and equipment, Brown's

procedure is as follows: (1) Final polish on Microcloth™ or nylon with 0.05 μm alumina. (2) A removal etch, using distilled water at pH 6.8 to 7.0, is developed by holding the polished surface with moderate pressure on a rotating saturated Microcloth™ for two to three seconds while the distilled water is poured onto the Microcloth™. (3) Wash quickly with isopropyl alcohol and dry with forced warm air. Periclase remains topographically high due to its relative hardness. Free lime etches dark to iridescent green and blue. C_3A turns dark blue. What Brown called “dark prismatic” (actually, alkali aluminate) and ragged dark interstitial material turn faint blue. Alite becomes brown, and belite is recognized morphologically. Alkali sulfates are dark.

- L. **Dimethyl ammonium citrate (DAC) solution** is prepared by dissolving 192.6 g of citric acid in 1 L of warm water. The solution is cooled and brought to 2 L by adding 891 mL of aqueous dimethyl ammonium solution (33 percent). A 5- to 10-second application of DAC on a polished surface structurally etches alite strongly and belite slightly. An optional preparatory etch with water for five seconds will aid in the identification of aluminate.
- M. **Borax solution** is used for etching pleochroite (approximately $C_{22}A_{13}F_3S_4$). This mineral occurs in some high-alumina cements and characteristically has a bladelike habit. It is etched by boiling in a 1-percent borax solution (Long, 1983).
- N. **Cyclohexanediaminetetraacetic acid disodium salt, Hexaver Chelant* (CDTA) solution** is mixed as follows: 5 g CDTA in 100 mL distilled pure water plus 100 mL denatured ethyl alcohol. The polished section is covered with the etchant and two drops of etchant are added every 10 seconds until 60 seconds have elapsed. The surface is rinsed with ethyl alcohol. Alite is blue, green, pastels, and other colors; belite is not highly colored; ferrite remains brightly reflecting; aluminate appears as gray flecks or spots; free lime is high colored (Caveny and Weigand, 1985). Dorn (1985) stated that lime-rich alite with a CDTA-type etchant (30 seconds) quickly turns blue; an average lime-rich belite burns bluish gray. Blue, relatively lime-rich belite crystals occur on the periphery of some belite nests.

The writer has found that etching and examination with CDTA at successive 15-second intervals reveals information about relative rates of alite reactivity, for example, when comparing clinkers from different production periods. The polished sections are bound together with a rubber band and etched simultaneously, or the clinkers can be encapsulated in a multichambered container.

CALCIUM FLUOROALUMINATE

A staining procedure for calcium fluoroaluminate (rare in normal clinker) was developed by microscopists in the 1960s at the PCA laboratories. It is based on the slightly different activities of C_3A and $C_{11}A_7CaF_2$. A polished surface of clinker, etched for 3 seconds in distilled water with a pH of 6.5 to 7.0, reveals C_3A as a bluish color. The surface is then given a second polish and a 30-second etch with a 0.1-molar potassium hydroxide solution that reveals $C_{11}A_7CaF_2$ as a deep brownish-purple hue. Comments on each of these etches follow.

- A. **Water etch (distilled water)** in the pH range of 6.5 to 7.0 reacts rapidly with C_3A to form an interference film on the C_3A that produces a bluish color when viewed through a reflected-light microscope. The procedure must be followed closely because other colors may appear with shorter etch times or slightly different acidities. Although the fluoroaluminate compound sometimes also reacts to produce a faintly visible brownish purple hue, this particular reaction is not used for positive identification.
- B. **Potassium hydroxide** is used for detection of fluoroaluminate. The section surface should be repolished after the water etch. The freshly polished clinker surface is then exposed to 0.1-molar potassium hydroxide solution for 30 seconds. The fluoroaluminate compound is identified by the definitive brownish purple interference color that is deeper in hue and sharper in outline than the one that, as mentioned, is sometimes visible after the 30-second distilled water etch.

The 30-second period of etching with the potassium hydroxide solution apparently is not critical since similar results have been obtained with etch periods of 25 to 35 seconds or longer. Any reaction product of C_3A with potassium hydroxide, if present, will not interfere. C_3A is more reactive in basic solutions than the fluoroaluminate, and the 30-second reaction time will produce a relatively thick and very irregular orange-colored reaction product on the C_3A . This reaction product does not have a uniform interference color; much of the reflected light is irregularly scattered to produce a generally nondescript area of both positive and negative relief, often giving the appearance of a void in the clinker.

Experimental work on the microscopical staining method also reveals that fluorine-modified alite could

* CDTA is available from Hach, Inc., Loveland, Colorado, USA.

be identified with the 30-second potassium hydroxide etch. In that case, the characteristic pseudohexagonal outlines of individual alite crystals would become ragged and indefinite and the crystals would assume a faint brownish purple hue similar to that seen on the ternary compound after the 30-second distilled-water etch. In all cases thus far, little or no fluoroaluminate compound has been seen when the fluorine-modified alite was present.

It should be pointed out that the potassium hydroxide method should be applied to materials representing only the compositional field where the usual portland cement phases and fluoroaluminate can occur, as identification does not rely on unique optical properties of the various phases.

EXAMINATION OF STAINED CEMENT

A stain technique proposed by Poole and Thomas (1975) for detecting sulfates in aggregates has been modified and found to be quite appropriate for gypsum, plaster, and anhydrite in portland cement and, to some extent, alkali sulfates in clinker. The 6% stain solution is made from an aqueous mixture of BaCl_2 and KMnO_4 in a 2:1 ratio.

A few milligrams of cement or crushed clinker are immersed in a puddle of the stain solution in a small beaker for 1 minute, after which the mixture is washed with isopropyl alcohol into a 75- μm (No. 200) sieve, and finally into a watch glass. Excess alcohol in the watch glass can be drawn off with a paper towel. The residue is slowly dried in the watch glass at a temperature of approximately 40°C, under a heat lamp or on the slide warmer, and examined with oblique or transmitted light on the stage of a polarized-light microscope. Oblique light illuminates the particles from a point beside the microscope objective. Sulfate minerals retain a prominent pink to red color. A white paper background accentuates the color contrast while viewing the stained particles with oblique lighting. Refractive-index oils as mounting media can be used with transmitted light; however, the alteration of some sulfates during the staining may interfere with the refractive-index determinations.

The following easy method for concentrating some of the sulfates in cement or crushed clinker for microscopical examination has been developed. (1) Place a small portion of sample into a watch glass and flood with isopropyl alcohol. Swirl the mixture in the watch glass for a few seconds to concentrate the white-to-clear sulfate particles in the center. (2) Draw the liquid off with a paper towel and dry the remaining powder in the watch glass under a heat lamp or on the slide warmer (no hotter than 40°C). (3) Using a thin metal spatula, scrape off the top-central area of the residue in the watch glass and place it on a microscope slide for examination in oil with a selected index of refraction (n).

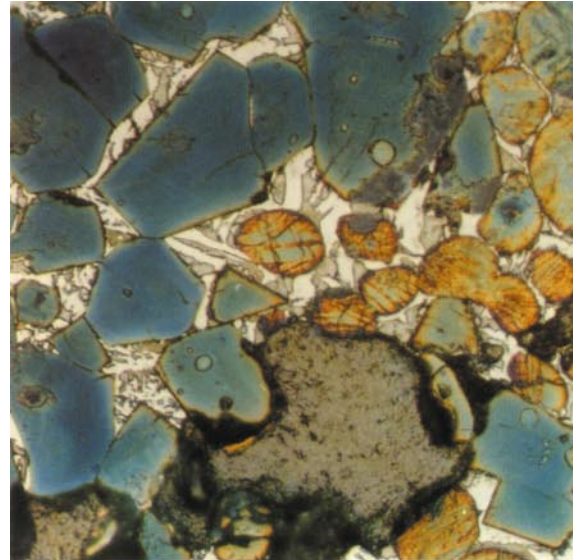
Although the mount is impure (contains several phases), in an oil with a refractive index of 1.54, gypsum ($n = 1.52$ to 1.53) and plaster ($n = 1.55$ to 1.57) can be distinguished. Gypsum has inclined extinction, but the extinction of plaster is straight (Lea, 1970). Anhydrite ($n = 1.57$ to 1.61) also shows straight extinction, cleavages at right angles, and relatively high birefringence. Extinction angles to differentiate gypsum from plaster, however, are difficult to apply due to the very finely microcrystalline structure common in gypsum and plaster particles. This microstructure appears to be a product of recrystallization due to relatively high temperature, grinding stress, or both, which convert the previously continuous atomic structure into a myriad of minute polygonal crystalline units. Dorn (personal communication, 1985) reported that sulfates such as gypsum and plaster float in refractive-index oil ($n = 1.71$) and can be skimmed aside for study in a powder mount; anhydrite may sink in the liquid. A simple heavy liquid-centrifuge method appears to be an efficient technique for separation of cement sulfates for microscopical examinations and x-ray diffraction, leading, perhaps, to a quantitative determination of phase abundance.

Gypsum, plaster, alkali sulfates, and epeizite float in refractive index liquid ($n=1.715$) and accumulate just beneath the cover glass.

PHOTOMICROGRAPHS OF EFFECTS OF STAINS AND ETCHES

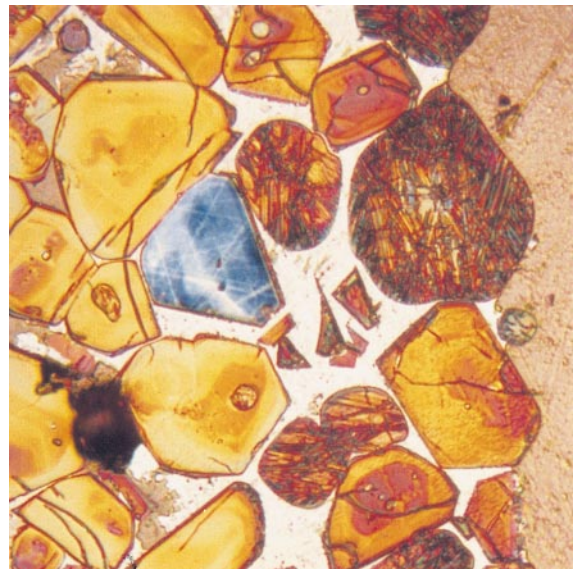
Photograph 3-1 Coarsely crystalline clinker from coarse seashell feed. Angular subhedral to euhedral blue alite, round tan-to-brown belite with wide lamellae, and matrix of dark aluminite (C_3A) and brightly reflecting ferrite (C_4AF). Coal- and coke-fired, semidry process kiln, 1850 tons/day. High maximum temperature, long burning time, slow heating rate, quick to moderately quick cooling, 44.1 MPa. (S#A6610)

Polished section
Nital on KOH etch
Field dimensions = 0.21x0.21 mm



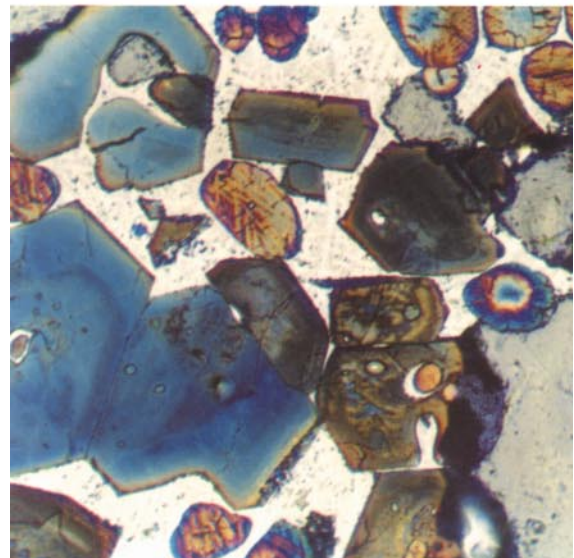
Photograph 3-2 Blue coloration on alite with an otherwise uniform tan color on alite crystals. Possible explanations include differences in crystallographic orientation, chemical composition, structural state (for example, monoclinic versus triclinic), or perhaps combinations of these. (S#A6612)

Polished section
Nital etch
Field dimensions = 0.21x0.21 mm



Photograph 3-3 Differential coloration by nital etch on angular alite and round belite. Coarsely crystalline clinker from coarse raw feed. Coal- and coke-fired, semidry process kiln, 1850 tons/day. High maximum temperature, long burning time, slow heating rate, quick to moderately quick cooling. (S#A6613)

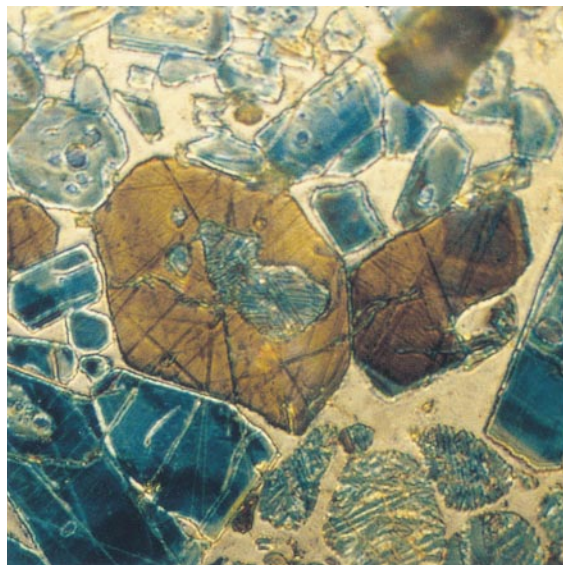
Polished section
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF EFFECTS OF STAINS AND ETCHES (CONTINUED)

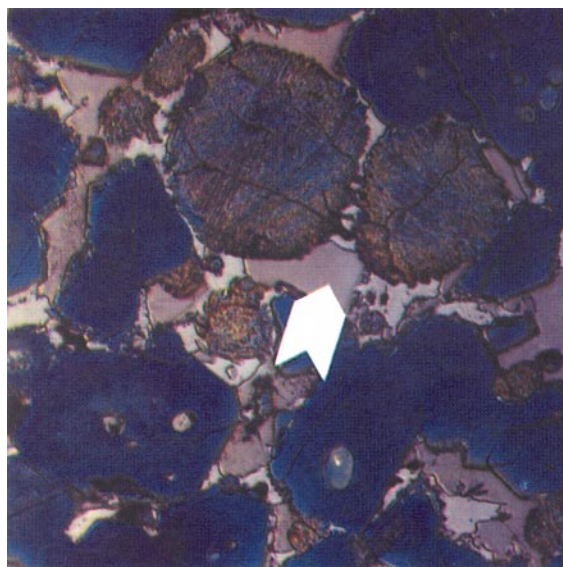
Photograph 3-4 Aqueous NH_4Cl etch (30 to 40 seconds). Sections perpendicular to the c crystallographic (three-fold axis) of alite are brown. Sections parallel to c are blue. (S#A6614)

Polished section
Field dimensions = 0.12x0.12 mm



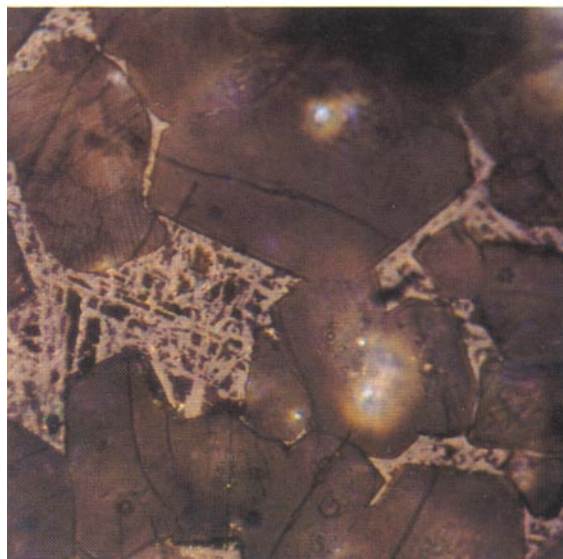
Photograph 3-5 Large, round, slightly ragged belite; blue subhedral to anhedral alite; and matrix of aluminate (C_3A , arrow) and ferrite. Superimposed nital over KOH produces increased clarity in matrix phase definition. (S#A6615)

Polished section
Reflected light with stop
Field dimensions = 0.21x0.21 mm



Photograph 3-6 Well-differentiated, finely microcrystalline matrix of aluminate (C_3A) and ferrite (C_4AF) in nital-etched polished section. (S#A6611)

Oil immersion
Reflected light
Field dimensions = 0.10x0.10 mm



CHAPTER 4

Preparation of Polished Sections, Thin Sections, and Particle Mounts

Methods of sample preparation for the microscopical investigation of clinker and cement are essentially the classic geologic techniques of optical mineralogy and petrography, with minor variations. In this chapter the use of diamond-rimmed cutoff saws and various grinding and polishing equipment is given principal emphasis in the production of polished sections, thin sections, and polished thin sections. Figure 4-1 illus-

trates the principal types of sample preparations. Table 4-1 gives the recommended techniques for various kinds of materials to be examined. This chapter summarizes sample preparation procedures for clinker and cement studies using the so-called “petrographic” microscope with transmitted polarized light, the so-called “metallographic” microscope with reflected light, and the scanning electron microscope (SEM).

Table 4-1. Recommended Methods of Microscopical Examination

	THIN SECTION Transmitted Light	POLISHED SECTION Reflected Light	POWDER MOUNTS Transmitted Light
<u>Clinker and Cement</u>			
Porosity	++	++	0
Alkali Sulfate	0	++	0
Periclase	0	++	0
Free Lime	0	++	++(epezite)*
Tricalcium Aluminate	0	++	0
Alkali Aluminate	+	++	+
Ferrite	+	++	+
Alite	++	++	++*
Belite	++	++	++*
Metallic Iron	+	++	++(magnetic)
Calcium Sulfates	+		++
Portlandite	++	++	++
<u>Raw Feed**</u>	++	0	+
<u>Quarry Rocks**</u>	++	0	+
<u>Pozzolans</u>	++	++	++

0 Not recommended.

+ Recommended, but somewhat difficult, requires more training.

++ Recommended, relatively easy.

Note: A well-made polished, ultra-thin section, allowing the combination of transmitted- and reflected-light observations, sometimes simultaneously, is probably the best method for all phases, particularly for fly ash, quarry rocks, and clinkers.

* KOH-sugar treated sample

** Optional staining for mineral identifications

The importance of a well-prepared surface should not be underestimated. The author strongly believes that efforts to produce a high-quality polished section or thin section are rewarded by the relative lack of artifacts which can possibly lead the investigator to incorrect interpretations. Phase identifications free of doubt are worth the extra few minutes of preparation time.

Methods making use of epoxy resins, resulting in polished sections in only a few minutes, are discussed first, followed by details of impregnation and encapsulation. Equipment and techniques for grinding and polishing, including thin-section procedures, are described. The use of Hyrax™, a synthetic resin with an index of refraction of 1.70, is discussed, followed by a description of a recommended method for refractive-index determination of particles mounted on a thin film of epoxy.

Methods of raw feed examination utilizing powder mounts and thin sections are discussed in detail in Chapter 10.

NOTE: Many of the chemicals used in sample preparation and examination are toxic and adequate ventilation is an absolute requirement, as are other common laboratory safety precautions.

BASIC STEPS FOR RAPID POLISHED SECTION PREPARATION

The procedure described here is an outline of recommended steps, not to be taken as unalterable, in the production of polished sections of whole clinkers or a sieved fraction of crushed clinkers. The recommended procedure involves the use of epoxy resin, a rotating-wheel grinder/polisher and a tabletop saw. An elapsed time of less than 30 minutes is typical for the proposed procedure by which a virtually flawless polished section is produced. Following are the basic recommended steps:

1. Vacuum impregnate the clinker fragments or whole clinkers with epoxy resin.
 - a. Encapsulate in labeled polyethylene cups, or
 - b. Mount small whole clinkers (or a selected sieved fraction of crushed clinkers) on a cleaned, labeled, glass microscope slide (46x24 mm), see Fig. 4-1.
2. Cure in an oven or slide warmer at approximately 45°C.
3. Cut with the small tabletop saw or grind the base of the encapsulation to expose the particles.
4. Grind the exposed surface with the grinder/polisher using No. 320 adhesive-backed, silicon-carbide paper for approximately two to three minutes.
5. Grind on No. 600, adhesive-backed, silicon-carbide paper for approximately two to three minutes.

6. Gently coarse polish the mount on Texmet™ (a low-nap chemotextile polishing cloth) with 6- μ m diamond for approximately four minutes.
7. Final polish on Texmet™ or equivalent with 0.3- μ m alumina (or 0.25- μ m diamond, or a mixture of the two) for roughly four minutes. Examine the section microscopically and repolish if grinding pits are observed.
8. Clean the polished section with a forceful isopropyl alcohol spray and dry with forced warm air (an electric hair dryer).

Propylene glycol is used as the grinding and polishing liquid in all steps. Recent tests by the writer, upon the suggestion of Paul Lehoux (Lafarge) and Wase Ahmed (Buehler), indicate the superior quali-



Figure 4-1. Modes of sample preparation: (1) single clinker, impregnated with epoxy resin, cut, and polished; (2) crushed clinker fragments, encapsulated and impregnated with epoxy, cut, and polished; (3) whole clinkers impregnated with epoxy and mounted on a thin film of epoxy on a glass microscope slide, cut and polished; (4) millimeter-size crushed clinkers, embedded in epoxy, ground, and polished; (5) cement, size graded by sedimentation in an alcohol-mineral spirits mixture in a glass vial, dried, impregnated with epoxy, cut, and polished; (6) drilled holes in an epoxy plug, filled individually with cement (a) extracted with a potassium hydroxide-sugar solution, (b) extracted with maleic acid, and (c) unextracted—the plug has been cut and polished; (7) thin section of whole clinkers; section thickness is approximately 22 μ m; (8) crushed clinker, 45- to 75- μ m fraction, in Hyrax, for determination of the kiln parameters with the Ono Method. Scale divisions in mm. (S#A7094)

ties of food-grade mineral oil, the type used in “baby oil,” as an excellent, low-viscosity, non-toxic liquid for a grinding vehicle and saw-blade coolant. Slight reaction of “baby oil” and mineral oil with the silicates precludes its use in polishing, unless the reaction (etching) is seen to be helpful. Recent results with a “hydraulic line” oil, apparently a food-grade mineral oil designated as “Mobil DTE® FM 32,” are quite promising. This oil can economically substitute for propylene glycol and other liquids in sawing and grinding (but not polishing).

Pressure on the section surface during grinding is one kilogram. Excessive pressure causes too much topographic relief on the section surface, requiring a long time in the polishing step. Care should be taken not to allow drying of the polished surface prior to the last step because grinding and polishing debris is difficult to remove, even with a sonic cleaner. Contamination of a polishing cloth can quickly ruin a polished section, sometimes requiring the worker to return to the grinding steps. Therefore, between each of the grinding and polishing steps, the section is washed with isopropyl alcohol.

ENCAPSULATION, IMPREGNATION, AND PARTICLE MOUNTING

Many materials (clinkers, metals, rocks, minerals, and so on) require impregnation or encapsulation or both in order to prepare them properly for sectioning. If they are friable, or even slightly crumbly, impregnation is mandatory to produce a high-quality section. Several resins are suitable for both impregnation and encapsulation (see Table 11-2).

The epoxy-resin procedures described here are intended for single polished sections and polished thin sections of selected sieve fractions of whole or fragmented clinkers, rocks, bricks, ceramics, concrete, and many other materials. The desirable properties of an epoxy-encapsulating and -impregnating medium are:

1. Insolubility of the hardened epoxy in acetone, xylene, alcohol, or other similar solvents.
2. Hardness sufficient to promote the development of a relatively flat surface during grinding and to minimize the development of particle relief during polishing.
3. Quick setting, within a few hours at most, with neither inordinate heat generation nor excessive shrinkage. Some epoxies and other cements, such as cyanoacrylate ester (Super Glue™), which harden in only a few minutes, are recommended in circumstances where quick answers are needed.
4. Low viscosity for maximum penetration of the specimens. Xylene and toluene can be used as a thinner at a concentration of not more than 25 percent by mass of resin, but these liquids also soften the epoxy and lengthen the curing time. Filling as many of the pores as possible with epoxy is desirable in order to reduce retention of grinding and polishing debris and of cleaning liquids that can interfere with stains and etches. Low viscosity resin is a suitable medium for producing a size-graded cement or raw feed sample, using a centrifuge to effect the particle separation and segregation in a glass or polystyrene test tube (Campbell, 1986).
5. Wetting characteristics that produce a tight bond on the particles, improving edge retention of the particles during grinding and polishing.

Encapsulation and Impregnation

The procedure utilizing epoxy resins to encapsulate and impregnate a wide range of materials in the petrographic laboratory is as follows:

1. Immerse the whole clinker or a sieved fraction representing several clinkers in the freshly mixed epoxy+hardener in a small, labeled polyethylene cup (approximately 10-mL capacity and 25-mm diameter), or other suitable labeled container, coated with a thin film of silicone mold release. A small file-card label, inscribed with India ink, can be placed on the inside of the cup before the sample and epoxy are added. If a thin section is to be made and determination of its thickness is necessary, quartz grains (50 to 100 mesh) with a known constant birefringence of 0.009 may be added to the mix in this step. Thin-section thickness can, therefore, be calculated. The inclusion of quartz increases the time required for sawing, grinding, and polishing due to the mineral's hardness (7 on Mohs' scale).
2. Place the polyethylene container with its contents in a vacuum container and evacuate for a few minutes. Epoxy will bubble under vacuum and, if the container is too full, will overflow. Periodically breaking the vacuum will reduce the bubbling tendency. Slowly release the vacuum, allowing atmospheric pressure to force the resin into the sample.
3. Epoxy hardening time ranges from 10 minutes at 105°C up to several hours at room temperature. Temperatures above 75°C or several hours on the slide warmer cause significant strain birefringence in the epoxy, thereby reducing its

optical usefulness in transmitted light. Strain is minimized by curing at room temperature. For polished sections, epoxy strain is normally not important. Waiting time for the epoxy to harden is almost never a problem because, normally, several clinker projects are concurrently underway and in various stages of completion.

Prout (letter, 1984) recommends the use of Quickmount™ (see Table 11-2) which hardens in 25 to 30 minutes. Clinkers are placed in bottomless brass cups on a glass plate covered with a petroleum jelly, such as Vaseline™, and the Quickmount is added.

To speed the sample encapsulation/impregnation step using a slide warmer or hot plate, the technique described by Chromy (1992a) is helpful. A sample cup, the bottom of which was covered with 1.0 to 2.0 mm-diameter clinkers or crushed clinker particles, was heated to approximately 80°C. Freshly mixed low-viscosity epoxy resin was poured over the clinker particles and allowed to harden, requiring from 5 to 10 minutes. The encapsulation was then sawn to expose the clinker sections or, better, the bottom side was ground with a coarse grit (180 to 320) to quickly expose the particles.

For encapsulation cups, the present writer has occasionally used 20 to 25 mm-tall cylinders made from sections of a copper or brass pipe and some of the relatively heat-resistant polyvinylchloride plastics, both reusable. The interiors of these containers are coated with silicone stopcock grease as a bond breaker. A glass microscope slide, also coated with silicone stopcock grease, supports the cylinder and the pair are placed on the slide warmer or hot plate; the epoxy resin is introduced as described above.

SAWING, GRINDING, AND POLISHING

The wide variety of available sawing, grinding, and polishing equipment, and the necessity for economically producing a high-quality polished section, result in several options in building a compact, relatively maintenance-free and inexpensive system for sample preparation.

Isomet™ and Minimet™ Method

Preparation of high-quality polished sections or polished thin sections requires expertise and patience. A tabletop saw (the Isomet™) and a small polishing device (the Minimet™) have greatly improved the polishing of encapsulated clinkers and single thin sections. The method of preparing polished sections and polished thin sections described here is relatively

quick and, in the long run, economical, especially if several sections are examined in the course of microscopical investigations. Although not as fast as grinding and polishing with a horizontal rotary wheel, the major advantage of the Isomet-Minimet method is that the instruments are busy cutting, grinding, and polishing while the microscopist is elsewhere, returning frequently to keep the project progressing. In addition, the Minimet™ is useful in polished section electron microprobe studies. The Isomet-Minimet procedure is as follows:

1. The sample is impregnated and encapsulated with epoxy resin as previously described.
2. The encapsulation is placed in the proper chuck attached to the Isomet™ saw, which slowly cuts the sample as it is lowered by gravity onto a slowly moving, thin, diamond-rimmed blade. The blade edge passes through propylene glycol (or “baby oil”) in the coolant container. Sawing time normally takes 5 to 10 minutes, after which the saw automatically stops. A 127-mm-diameter blade with 45-mm flanges is recommended.
3. At this point, the Minimet™ is used for grinding and polishing. A 4.75-mm-diameter hole is drilled into the center of the top of the encapsulation into which the arm of the Minimet™ is placed. Prout (letter, 1984) recommends the use of a carbide-tipped bit. The bottom of this hole must be 5.6 to 6.4 mm from the surface to be polished. A sample alignment fixture (also supplied by Buehler Ltd.) aids in drilling the hole to the standard depth. Using a moderate load of one half to one kilogram on the encapsulation, the freshly cut surface is ground successively with propylene glycol on No. 320 and No. 600, adhesive-backed, silicon-carbide papers mounted on glass platens within plastic bowls placed on the Minimet™. A moderate Minimet™ arm speed is used. Recent models of the Minimet™ do not require hole-drilling because the sample is held in a “caged” holder. Approximately 6 to 10 minutes for grinding each paper is normally sufficient, after which the sample is thoroughly cleaned with isopropyl alcohol in a sonic cleaner or with a spray bottle. Using a figure-eight motion, the sample is finely ground by hand on a glass plate with 5-μm alumina in isopropyl alcohol, polishing oil, or propylene glycol for approximately three minutes. Again, the sample is thoroughly cleaned in alcohol.
4. At the same speed and load settings, an adequate polish is produced in approximately 6 to 10 minutes as the sample moves in an irregular manner on the adhesive-backed Texmet™ on

which a few drops of propylene glycol (or polishing oil) and 0.3- μm alumina have been placed. The sample is removed and thoroughly cleaned as previously described. If, after microscopical inspection, the polished surface still shows grinding pits, repeat the polishing step. Diamond paste can be applied to Texmet™ along with the alumina.

5. The final polish (optional) is produced in approximately 6 to 10 minutes with the Minimet™, using liberal amounts of 0.05- μm alumina on Texmet™ with a few drops of propylene glycol or polishing oil, using the same speed and load settings. Care must be taken, if using isopropyl alcohol as the vehicle, to prevent drying of the cloth during polishing. For easy recognition of periclase, relief is enhanced by using Microcloth™ or equivalent and 0.05- μm alumina. Diamond grinding and polishing compounds quickly produce a superb surface and are advisable especially when use of the microprobe is anticipated.
6. After thoroughly cleaning the specimen first with a sonic device then with an alcohol spray, and drying with forced warm air, the polished section can be examined in reflected light. An etched surface may be necessary for study with a scanning electron microscope and microprobe.

Use of the Horizontal Rotary Grinder/Polisher

The versatility of this instrument is clear from the fact that its rotating wheel is removable and interchangeable with other wheels on which a variety of adhesive-backed grinding papers and polishing cloths can be attached. Consequently, with a single instrument and several interchangeable wheels, the entire grinding and polishing process can be accomplished. Or three instruments are used with several interchangeable wheels: one for coarse grinding, another for fine grinding, and a third (with variable speed) only for polishing. Interchangeable wheels on which polishing cloths and polishing compounds have been placed are kept in large zip-lock plastic bags between periods of use in order to minimize contamination. This is particularly important when diamond is used as the polishing compound. Having more than one instrument lessens the chances for contamination by decreasing the handling of wheels. A section can be routinely ground, polished, and sonically cleaned in approximately 10 minutes.

Assuming that the sample has been impregnated and encapsulated in epoxy resin as previously described and that the mount has been cut with the

Isomet™ or other suitable saw, the encapsulation is ready for grinding and polishing as follows:

1. Grind the saw-cut surface by hand for at least three minutes on a rotating wheel with an adhesive-backed, No. 320-grit, silicon-carbide paper. Wheels and discs with embedded diamonds are also available and highly recommended because they significantly shorten the grinding steps. Propylene glycol or polishing oil are used as vehicles in all grinding and polishing.

While the encapsulation is in contact with the grinding paper, using a moderate pressure (1 kg) move the mount clockwise (opposite the direction of the revolution of the wheel). Periodically rotate the encapsulation between the fingers to promote uniform abrasion. The wheel rotates at approximately 350 revolutions per minute. To minimize relief on the section surface, use only a moderate pressure on the wheel during grinding and polishing. Excessive relief is very difficult to “polish out” and it makes the observation of alkali sulfate troublesome.

2. After cleaning the fresh, coarsely ground surface with a forceful isopropyl alcohol spray, apply a No. 600 grit, silicon-carbide, adhesive-backed paper to the grinding wheel and grind the specimen surface for at least three minutes. Be certain to clean the encapsulation and hands thoroughly between the grinding steps. Contamination can quickly ruin all previous work and is quite probable with a less than careful technique. A forceful alcohol spray is moderately successful for cleaning, but a sonic cleaner followed by the isopropyl alcohol spray appears best.
3. After thorough cleaning, coarse polish the sample for at least four minutes on Texmet™ to which 6- μm diamond paste has been applied.

If the clinker is hard and dense, encapsulation, impregnation, and sawing are not absolutely necessary. A flat surface can be produced by applying the clinker to a coarse grinding paper (No. 240 grit or coarser) on a rotating wheel, followed by the required grinding and polishing steps.

4. Final polishing of the clinker by hand requires diligence, patience, and practice to produce a high-quality finish, but it can be done in only a few minutes. The edge of the section surface should be beveled (rounded) by abrading it against a fine steel file or a coarse abrasive paper attached to a rotary wheel to remove sharp corners or edges that might tear the polishing cloth.

Using a thick slurry of 0.3- μm alumina on Texmet™ (or equivalent polishing cloth) with polishing oil or propylene glycol as a vehicle,

polish the sample on the rotating horizontal wheel. A moderate pressure on the sample against the Texmet™ with a circular motion opposite to the rotation of the wheel facilitates the production of a mirror finish in approximately three minutes.

5. An additional polishing step (optional) is accomplished in roughly two minutes with 0.05- μm alumina on Texmet™, followed for one minute on Microcloth™, which, because of the slight nap of the latter, will produce a minor relief and can be helpful in identifying periclase.

After cleaning the polished surface with isopropyl alcohol in the sonic cleaner, the section is dried with forced warm air and is ready for study in reflected light. Effects of stains and etches can be removed by repolishing the section with 0.03- μm alumina and Texmet™. Suitably polished and etched surfaces can be examined with a scanning electron microscope.

Drafting linen, washed to remove the starch, can be successfully used as a polishing cloth with SnO_2 or other polishing compounds. Diamond pastes or aerosol sprays are applicable in all the grinding and polishing steps and are highly recommended. In addition, Kraft wrapping paper with 0.25- μm diamond paste on the polishing wheel produces an excellent low-relief surface, particularly valuable for detection of alkali sulfate.

Preparation of a low-relief polished-section surface with Kraft wrapping paper is easily done by “forming” water-saturated paper over the polishing wheel, placing a rubber band around the sides to hold the paper in place, and allowing the assemblage to dry on the slide warmer or in a low-temperature ($<50^\circ\text{C}$) oven. For application on the Minimet™ the paper is formed over the glass platen in the polishing bowl. If desired, a water slurry containing diamond or alumina powders can be allowed to dry on the paper, thus facilitating the polishing with the diamond paste (0.25 μm) added later. Liquids, such as propylene glycol or polishing oils, are not used on the papers during polishing.

Resin-bonded diamond discs placed on a flat tabletop function quite well for rapid hand grinding of a saw-cut surface of epoxy-encapsulated clinkers preparatory to polishing (Hoodmaker, personal communication, 1985). A few drops of propylene glycol are used as the grinding and polishing liquid. The diamond discs are cleaned with soap and water.

Harris's Technique

A quick technique using Duro Super Glue™ (containing a cyanoacrylate ester), or equivalent, has been described by Roy Harris (1984) of The Monarch Cement Company, Humboldt, Kansas. With Harris's method

the -0.59-mm to +75- μm mesh clinker fraction is polished on a glass microscope slide, the entire procedure typically requiring less than 40 minutes. Harris's technique, designed for rapid analysis, is as follows:

1. On a cleaned, labeled, petrographic glass slide sprinkle a liberal amount of crushed clinker and add a few drops of Super Glue™, or equivalent.
2. Place the slide on the slide warmer for 5 minutes at 105°C .
3. With a slide holder designed for use with the Minimet™, the mounted material is ground by hand with 5.0- μm alumina on a glass plate. Isopropyl alcohol or polishing oil is used as the vehicle.
4. After cleaning the slide, slide holder, and hands, the final polish is accomplished with the Minimet™ with 0.3- μm alumina and polishing oil or propylene glycol on Texmet™.

This writer has had excellent results using techniques somewhat similar to those of Harris (1984) for producing polished sections of small whole clinkers (pea size), crushed clinkers (1 to 2 mm), or cements. The technique, using epoxy instead of Super Glue™, is as follows:

1. Place 15 to 20 small clinkers or clinker fragments in freshly mixed epoxy resin with hardener and vacuum impregnate.
2. Remove the clinkers from epoxy with forceps and place them on a clean, labeled, petrographic glass slide.
3. Put the slide in an oven (or on a slide warmer) set at 50°C . The epoxy that flows from the clinkers during heating is sufficient for bonding the clinkers to the glass.
4. Withdraw the slide from the oven and allow the slide to cool for a minute or two. If any epoxy has hardened on the bottomside of the glass, scrape it off with a single-edged razor blade. The slide, with clinkers firmly mounted, is now ready for cutting on the tabletop saw, or grinding, after which full cross sections of the clinkers will be exposed. Cutting time is approximately three minutes. Grind the saw-cut surface with No. 320 and 600 silicon-carbide papers on the rotary grinder. Using the slide holder, grind the sample on a glass plate with 5- μm alumina.
5. Polishing the mounted clinkers can be accomplished in as short a time as three minutes on the rotary polisher or four to eight minutes with the Minimet™, using 0.3- μm alumina on Texmet™ and isopropyl alcohol or propylene glycol. The writer prefers to

use propylene glycol (or polishing oil) with the Minimet™ because evaporation is slow and the Minimet™ can be largely left unattended.

Between polishing steps, the mount and slide holder should be cleaned with a forceful isopropyl alcohol spray. The hands may be washed with soap and water. Before examination, the polished section should be cleaned in a sonic cleaner with isopropyl alcohol, followed by a brief rinse with an alcohol spray.

Up to 30 samples of cement, embedded in epoxy and polished on the same glass slide (50x75 mm), have been simultaneously etched and studied.

THIN SECTIONS

Routine clinker investigations normally do not involve thin sections. However, for some aspects of clinker research and for many raw material studies, thin sections are invaluable.

A clinker thin section can be made from the polished epoxy encapsulation after the latter has been studied in reflected light and mounted on a glass microscope slide with epoxy resin. The thin-section top surface may also be polished and, therefore, the section can be studied with both transmitted and reflected light, each of which has distinct advantages. Thin sections on the order of 15- to 20- μm thick can be easily made, using a diamond-rimmed cutoff saw, diamond grinding equipment, a glass plate, and polishing wheels. At a thickness of approximately 15 μm the problem of crystal overlap is minimal. Examination in transmitted light allows measurement of optical properties, such as birefringence, and observation of pleochroism; reflected-light examination at higher magnification (particularly with oil immersion) permits study of the interstitial materials and hardness relief. Doubtful phase identifications with reflected light may be resolved with transmitted light. By using a multichambered container, selected size fractions of the clinker, cement, and raw feed can be combined in a single encapsulation. The procedure for making thin sections, requiring a worktime of approximately 15 to 30 minutes, is as follows:

1. The previously ground (or polished) surface of the encapsulation is mounted on a cleaned, labeled, petrographic slide (standard size, 46x24 mm) with a small amount of epoxy. The writer has found that by smearing and striking off a few successive droplets of epoxy with the glass microscope slide, the epoxy fills virtually all the voids on the section surface and thereby promotes a firm bond. A weight of approximately

100 grams, such as a lead fishing sinker or a 25.4-mm diameter hexagonal steel nut, weighing approximately 125 grams, can be placed on top of the mount during hardening of the epoxy to maintain a uniform epoxy thickness between the polished surface and the glass slide. The top surface of the slide warmer should be protected from epoxy with aluminum foil, waxed paper, or, better, a 4 mil polyethylene sheet. Epoxy that overflows the slide and hardens on the bottom of the slide must be carefully removed with a single-edged razor blade after hardening. Curing time at 40-50°C on the slide warmer may range from 2 to 5 hours, depending on the type of epoxy. Some epoxies are rapidly cured with ultraviolet light and work quite well.

2. After the epoxy has hardened, the excess mount is removed by sawing on the tabletop saw or a thin-section cutoff saw or similar device (for example, the Buehler PETRO-THIN™) so that a wafer with a thickness of approximately 0.5 mm remains on the glass slide.
3. The wafer is then slowly and gently reduced to approximately 30 μm on the diamond cup wheel of the oil-cooled thin-section grinder or other similar equipment. Grinding time is approximately five minutes. If a mechanical thin-section grinder is not available and time is not a problem, the wafer thickness can be reduced by hand, using a Buehler thin-section holder (Buehler catalog No. 30-8005) and a sequence of coarse-to-fine, adhesive-backed, silicon-carbide papers or, preferably, diamond discs on a horizontal rotating wheel. Propylene glycol as the vehicle ("baby oil") and a speed of approximately 200 to 350 revolutions per minute are recommended. Rather than using the thin section grinder for the entire grinding step, less damage to the thin section results when thickness reduction from 30 to 20 μm is accomplished with silicon-carbide papers on the rotary wheel, or with loose No. 600 grit silicon-carbide powder on a glass plate. Finally, gentle hand grinding with a 5- μm alumina for a few minutes with alcohol or propylene glycol on a glass plate brings the section to the proper thickness, which for portland cement clinker is approximately 15 to 20 μm . Raw feed thin sections and "half" sections are described in chapter 10. Half sections can be made by lapping (grinding) the upper parts of particles embedded in epoxy resin on a glass microscope slide. The preparation technique is far less time-consuming than that for a normal thin section, the latter requiring a planar cross section of both the upper and lower portions

of most of the particles. The half section provides virtually the same information. After extraction of the clinker matrix phases with a KOH-sugar solution, for example, alite and belite microstructure can be examined with both transmitted and reflected light (sometimes simultaneously) on a grain-by-grain basis in a polished half section. The use of half sections is particularly well-suited for the examination of raw material powders, and therefore, step-by-step details of the method are given at the end of Chapter 10.

4. Using Texmet™ with liberal amounts of 0.3- μm alumina, a few drops of alcohol, propylene glycol, or polishing oil and a slide holder, the thin section is polished on the rotating wheel at a medium speed and moderate pressure. Circular movement of the slide opposite to the direction of rotation of the polishing wheel is recommended. This polishing step requires approximately three to five minutes. Although this step is not intended to reduce thickness, with extended application some reduction in thickness does occur. The Minimet™ can also be used to polish thin sections. With a moderate speed and load, using 0.3- μm alumina, Texmet™, and propylene glycol or polishing oil, the Minimet™ can be left largely unattended during the polishing. Clean the slide thoroughly.
5. An optional final polish is accomplished with 0.05- μm alumina or Microcloth™ in three to five minutes on the rotary wheel. Diamond paste is recommended for thin sections that are to be studied with the scanning electron microscope and the microprobe. The section should be an optimum thickness of approximately 15 to 20 μm , at which the interference colors in cross-polarized light are low first-order gray for quartz and alite and first-order whitish gray to yellowish white for belite. At thicknesses less than 20 μm , damage to the quartz becomes progressively more significant. However, significant clinker damage with these techniques does not occur in most cases until a thickness of approximately 10 μm is reached. For many crystals the damage occurs in the form of cleavage cracks which are sometimes helpful for phase identification.
6. The thin section is then cleaned with isopropyl alcohol in a sonic cleaner, followed by a forceful spray of isopropyl alcohol, then dried with warm air. The section is ready for staining, etching, and examination in reflected light. For work in transmitted light, the cover glass is loose-mounted temporarily with refractive-index oil ($n = 1.71$). Thus, the cover glass can be removed and the slide cleaned with isopropyl alcohol when necessary to examine the section again in reflected light. Effects of most

stains and etches can be removed by repolishing the section with 0.3- μm alumina on Texmet™, but occasionally one has to regrind the surface to ensure against misinterpretations promoted by superimposed effects of some etches. Recently developed vibratory polishing devices appear to produce trouble-free, perfectly polished sections with very little handling by the technician. Preparation of multiple samples simultaneously has been detailed by Ahmed (1991). Also, the use of a steel-mesh pad (Bueler's Ultra-Plan™) for production of a flat section surface prior to polishing, and very important for good thin sections, is described by Ahmed (1996). New equipment and methods of sample preparation are described by Ahmed (1997).

The writer has found that by extending the time of the coarse polishing step with 6- μm diamond on Texmet™ or Ultra-Plan™, an intentionally wedged section that thins to zero thickness on one side and is approximately 20 μm on the other side can be produced. Although subsequent polishing thins the section somewhat, it usually is not detrimental. A wedged polished thin section is actually advantageous for (1) determination of phase birefringence on the thick side and (2) examination of interstitial microstructure in transmitted light on the relatively thin side.

Ultrathin sections for light microscopy and SEM-EDXA or microprobe work can be made by using an epoxy disc that has been polished on both sides instead of a glass microscope slide. An epoxy-encapsulated and polished section of clinker is attached to the disc with epoxy. A wafer is cut, followed by grinding and polishing to a thickness of approximately 10 μm .

A light application of an acrylic spray protects the thin section during storage and can be removed with xylene, trichlorethylene, or isopropyl alcohol. Preferably, a cover glass is mounted in epoxy resin (without hardener). The cover glass can be removed by sliding it off with the fingers until the resin hardens in a few weeks or months. The residual liquid resin is readily removed by a stream of toluene or acetone.

Polished mounts and polished thin sections are prepared commercially by several companies (Table 11-3). Waiting time may range from a few days to several weeks. For clinker thin sections, the microscopist must specify the required thickness and that nonaqueous media must be used in cutting, grinding, polishing, and cleaning.

TECHNIQUES WITH HYRAX™ AND MELTMOUNT™

Properly cured Hyrax™ has an index of refraction of approximately 1.70, which is very close to most clinker

phases. Therefore, when used as a mounting medium for a clinker thin section and its cover glass, or for whole particle mounts as in the Ono Method, the high quality of the preparation becomes a permanent feature, changed only by remelting the resin. Unfortunately, Hyrax™ is no longer available from the referenced source in the original edition. Meltmount™ 1.70, marketed by McCrone and Cargille, may be a suitable substitute but has a faint yellow color and tests are required; the addresses have been placed in Table 11-2. The procedures for using Hyrax™ or Meltmount™ as a powder-mounting medium are described below.

1. Place a ceramic-covered, iron-wire triangle on a small, level, electric hotplate under a ventilating hood. Place separately on two corners of the level triangle a cleaned, labeled glass microscope slide (petrographic type, 46x24 mm) and a cleaned cover glass. Bring the temperature of the glass slide and cover glass to approximately 90°C.
2. Place a drop of Hyrax™ (normally shipped diluted with toluene or xylene) on the petrographic slide and add a few grains of the clinker or cement (44- to 75- μ m fraction, for example).
3. Stir the particles briefly with a clean needle to produce a uniform dispersion and allow the mixture to heat until it stops bubbling (evaporation of toluene). The heating time may take up to 20 minutes.
4. Using broad-tipped forceps, place the cover glass on the molten resin by first resting one edge of the cover glass on the slide and slowly lowering the cover glass into position. The excess resin, if present, can be squeezed out by gentle pressure with a pencil eraser.
5. Using broad-tipped forceps, remove the mount to a flat, cool surface and allow the resin to harden (approximately 5 minutes).

PARTICLE MOUNTS ON THIN EPOXY FILM

Particle mounts in which the particles are attached to a thin film of substrate epoxy on a glass microscope slide are quite useful for repeated examination of the same grain with various refractive-index (RI) liquids and for the application of various stains as in raw feed analysis. An epoxy not soluble in acetone or xylene

is required. The technique for making epoxy film-grain mounts is as follows:

1. Cover a clean, labeled, glass microscope slide (46x24 mm) with a puddle of epoxy resin plus hardener.
2. With the edge of another glass slide, strike off the excess epoxy, leaving only a thin film.
3. Sprinkle the mineral grains over the epoxy film, making sure by stereomicroscope or hand-lens examination that only the bottom side of the particles is in contact with the epoxy substrate. Particles ranging from approximately 74 to 149 μ m are recommended for this type of preparation.
4. Cure the mount on the slide warmer at a temperature no higher than 45°C.
5. After the epoxy has hardened, a cover glass can be placed on top of the mount. Liquid of known RI applied to the edge of the cover glass will move under the cover by capillary action and immerse the exposed particles. Some of the nontoxic RI liquids are clove oil ($n = 1.537$ to 1.544), cedarwood oil ($n = 1.515$), and cinnamon oil ($n = 1.605$ to 1.619).
6. Using the Becke line (or other comparative refractive-index techniques) determine whether the particle has an index higher or lower than the RI of the liquid. Wash off the liquid and cover glass with a gentle stream of xylene over a container that can be sealed for safe storage and disposal.
7. Use of a mechanical X-Y stage, which allows measured movements of the slide in mutually perpendicular directions, enables one to relocate the same particle examined previously, but now in a different RI liquid. Repeated examination with different liquids finally identifies one or more of the refractive indices of the particle. For most minerals, additional optical properties (such as color, pleochroism, twinning, cleavage, fracture, and so on) will be helpful in making the mineral identification. With these data, the tables of optical properties given in many standard optical mineralogy texts may be consulted, especially those in Fleischer, Wilcox, and Matzko (1984) and Winchell and Winchell (1964), who emphasize identification by particle methods instead of thin-section techniques.

CHAPTER 5

Microscopic Characteristics of Clinker Phases

Understanding what one observes in powder mount, polished section, or thin section requires an appreciation of not only the cement manufacturing process but also the varied effects of light as it passes through or is reflected from crystals and amorphous materials. Formal training or extensive experience in microscopy is required. For example, when viewing crushed clinker in cross-polarized light in refractive-index oil on a microscope slide or a thin section, one must be aware that the interference colors are dependent mainly on four factors:

1. The natural color of the phase.
2. The thickness of the phase.
3. The birefringence of the phase, if it is anisotropic. Birefringence is the difference in the approximate reciprocals of the light velocities of the fast and slow rays; in other words, the difference in indices of refraction of the fast and slow rays.
4. The crystallographic orientation of the crystal with respect to the planes of polarized light produced by the analyzer and polarizer of the microscope.

Changes in any of these factors produce changes in what one observes on a polarized-light microscope stage.

When examining a polished section or thin section, the viewer must constantly think in three dimensions, not merely in terms of the nearly two-dimensional view seen in the microscope. Dendritic periclase, therefore, should be considered as a three-dimensional, branching, treelike or skeletal crystal, typically growing within a liquid matrix, the surface of the section revealing only part of the tree. Alite, the most abundant phase in portland cement clinker, tends to form a somewhat discontinuous, open, three-dimensional framework of linked and stacked crystals,

outside of which most of the other phases, including pores, are developed. Belite crystals, developed by resorption of alite and attached thereto, are typically described two-dimensionally as “fringes,” the term suggesting that, in three dimensions, the alite crystal actually has a coating of secondary belite. Belite crystals generally do not develop assemblages of attached crystals like alite, except in a tightly packed nest, and even in such nests a small amount of liquid phase almost always divides the crystals.

Therefore, any cross section of typical clinker displays (1) the more or less loosely tied framework of alite crystals, (2) belite that occurs as single crystals and as concentrations, and (3) a matrix of aluminate and ferrite formed as the molten liquid cools and crystallizes. Microscopical observations clearly suggest aluminate (C_3A) crystallizes after the ferrite, the latter forming a prismatic crystal mesh, the holes of which are partially filled with aluminate. Ferrite can be seen within aluminate and, extremely rarely, *vice versa*. The matrix commonly contains secondary belite and shows effects of reaction with alite. Voids remain in areas not filled by the liquid, forming sites for crystallization of alkali sulfates on the cavity walls. Thus, the typical clinker is a somewhat porous mass of interlocking crystals, a truly glassless crystalline mosaic. Recent studies of the sequence of crystal development in the production of portland cement clinker can be found in papers by Imlach and Hofmänner (1974), Moore (1976), Ono (1981, 1995), Chromy (1974, 1982), and Maki (1982, 1995).

Much of the descriptive information regarding clinker phases is based on early work by LeChatelier (1883), Törnebohm (1897), and Rankin and Wright (1915), each of which is summarized in Bogue's classic text of 1947, *The Chemistry of Portland Cement*. The following optical descriptions of clinker phases have been taken for the most part from publications by Insley (1936), Taylor (1964), and Gille and others (1965).

Other published descriptions of clinker phases are found in the works of Ono, Kawamura, and Soda (1968); Hofmänner (1973); Sansoni and Zybelle (1974); Chromy and Carin (1980/81); Maki (1973, 1974, 1982); and Maki and Kato (1982).

The use of a universal stage on the microscope, permitting orientation of a crystal in virtually any crystallographic direction while viewing the grain in transmitted polarized light, enabled Oberste-Padtberg and Clooth (1986) to describe some of the optical characteristics of alite and belite in oil-well cements. More frequent use of this technique, in the present writer's opinion, is sorely needed to build our understanding of clinker phase characteristics. The data are far more objective and precise, and, undoubtedly, can be used to evaluate burning conditions.

Clinker acid insoluble residues are virtually unstudied microscopically. Without doubt, light and electron microscopy, coupled with x-ray diffraction, can probably provide additional data relating to burning conditions.

Interpretations of clinker phases in terms of burning conditions are listed in Chapter 7, and discussed to a limited extent below.

ALITE

Alite is a solid-solution series of trigonal, monoclinic, and triclinic modifications of impure tricalcium silicate, which is generally termed C_3S in the cement industry. Substitution of magnesium and aluminum for silicon causes triclinic pseudotrigonal forms to change to monoclinic pseudotrigonal forms; other substitutions may involve iron and sodium. Alite may include up to approximately 4 percent impurity (Ghosh, 1983). It comprises 40 to 70 percent of normal portland cement clinker. Its density is 3.13 to 3.22 Mg/m³.

Crystals are idiomorphous, vitreous, compact, lath, tabletlike, or equant, usually six-sided in cross section depending on the angle of cut, commonly perfect hexagons. Crystal forms are typically combinations of two rhombohedra (Ono, Kawamura, and Soda, 1968) or pyramids (Maki, Haba, and Takahashi, 1983), terminated by basal pinacoids. Normal crystal sizes range from 25 to 65 μm . Alite hardness is approximately 5 on Mohs' scale. Alite crystallizes between 1200°C and 1450°C from the melt. Its refractive indices are 1.716 to 1.720 for n_x and 1.722 to 1.724 for n_z , and birefringence is 0.005, ranging from 0.002 to 0.010 as a function of ionic substitution (Ono, Kawamura, and Soda, 1968). Boikova (1980) indicated that alite birefringence ranges from 0.005 to 0.008 and that pure tricalcium silicate birefringence is 0.003. Average birefringence in thin section is bimodal, 0.0044 and 0.0022 (Fundal, 1982).

Crystals are colorless to slightly colored in transmitted light; interference color in grains or thin sections of 20- to 30- μm thickness is low, first-order gray; the phase is length slow. Alite crystals reflect gray but etch brown-blue-red-green-yellow with nital (1% nitric acid in isopropyl alcohol). Nital etch color is, to some extent, a function of length of etch time, temperature, and reactivity of the crystal. Sections parallel to c show least the effect of etch (Ono, 1980d).

In transmitted cross-polarized light, alite crystals show wavy to straight extinction. X , the direction of the acute bisectrix, is perpendicular to the horizontal section that shows a regular hexagon, threefold symmetry, and low interference colors; X is parallel to the length of the section showing an elongate hexagonal shape. The negative $2V$ is 20° to 60°. Alite crystals rarely show polysynthetic twinning. Twinning is 5 to 10 percent on rhombohedral faces and up to 50 percent on the basal pinacoid faces (Ono, 1980d). Alite commonly exhibits poor basal cleavage or parting (perpendicular to the threefold symmetry axis). Crystals may contain round earlier-formed belite and matrix inclusions, and exhibit belite coatings, the latter as a product of alite resorption into the matrix. Crystal zonation is common. Concerning zoned alite crystals, Ono (1996) stated that in poorly burned clinker the ratio of the core area to the whole area of the crystal is large. In well burned clinkers, the ratio of the marginal zone of the crystal to the core may be more than 50 percent, up to 80 percent. Furthermore, in well burned clinker, the outer zone (called the "rim layer") is relatively thick (1 to 2 microns) in areas rich in interstitial materials.

The high-temperature polymorph is ditrigonal scalenohedral, uniaxial negative, with a $2V$ of 0° to 20°; X is parallel to c . Birefringence may reach 0.010 in clinkers rich in sodium, potassium, sulfur, and magnesium. Simple twins are common on basal pinacoid (0001) and rhombohedron; twinning on the basal pinacoid is evident in cross-polarized light after inversion of alite to triclinic polymorph. Twinning on the rhombohedron appears as a hexagonal cross section with a diagonal twin plane that, when inclined to plane of section, results in undulatory extinction.

The medium-temperature polymorph is monoclinic and biaxial negative; X is parallel to c (trigonal), Y is parallel to a (trigonal), and Z is perpendicular to a (trigonal), with the latter two relationships less firmly established. The $2V$ is 20° to 60°. In horizontal sections, alite may show irregular patches of threefold cyclic twins formed in the trigonal to monoclinic inversion; uniform extinction occurs in vertical sections.

Triclinic alite, the low-temperature polymorph, is biaxial negative. The $2V$ ranges from 20° to 60°, with X

inclined to *c* (trigonal) at an angle ranging from 0° to 15°. Obscure extinction occurs in horizontal sections. Indistinct bands parallel to *c* are pseudopolysynthetic twins formed in monoclinic to triclinic inversion; basal pinacoid twins are observed in discontinuous bands.

Some of the optical characteristics of alite polymorphs and their correlative changes with differential thermal analysis (DTA) and X-ray diffraction (XRD) analysis have been the subjects of reports by Maki and Kato (1982) and Chromy and Carin (1980/81).

Maki, Morikoshi, and Takahashi (1985) and Maki (1984) have described two modes of alite growth, unstable and stable. Unstable growth is indicated by relatively large amounts of entrapped interstitial crystals, gases, free lime, and belite, and by morphological irregularity. Stable growth is indicated by a scarcity of entrapped materials and a trend toward crystal faceting. The monoclinic M_1 alite variety was thought to be a primary type (formed by nucleation from the melt) with or without inclusions; the monoclinic M_3 variety was said to be a product of recrystallization, the rate of which being dependent on crystal size and temperature. Combined in the highly variable clinkering environment, the stable and unstable growth modes produce a wide variety of crystalline textures of alite. Preparation of the raw mix, the minor chemical components, precalcination, the heating rate, and the maximum firing temperature were suggested as the controlling factors in alite nucleation and growth from the liquid matrix (Maki, 1986).

In 1994 Maki summarized much of his work on portland cement clinker, adding some details on alite. Alite was said to be produced by crystallization from the liquid and, according to kinetics and growth environments, two modes of growth, stable and unstable, as described above, were defined. Alite from stable growth is characterized by scarce inclusions, low impurity concentrations (aluminum and iron), M_3 dominant, regular faceted morphology, and low defect concentration. Alite representing unstable growth conditions has abundant inclusions, high impurity concentrations, M_1 dominating, an irregular morphology, and high defect concentration. In the industrial clinkering process, both types of alite are seen commonly in the same crystal—an earlier formed, irregular M_1 core over which zoned, well faceted crystal growth is developed. Rapid crystallization of the matrix, according to Maki (1994), occurs with a significant volume reduction, resulting in the development of large tensile stresses, forming many microcracks within alite crystals.

Maki, Masaki, and Suzuki (1997), adding to previously published information on the fine textures of clinker, described the microscopical differences during nodulization in a moving mass of clinkers of various

sizes, including nodules larger than 15 mm. Nodulization begins when the dense interior of clinkers is formed early, at high heating rates, on and near the surface of the moving load which is enriched with K_2O , SO_3 , and coarse-grain components of the raw mix. Alite in the nodule interior is M_1 ; in the nodule exterior M_3 overgrows M_1 . Belite nests in the interior and uniformly scattered belite in the exterior portions of the nodule were said to support the idea of coarse quartz. Dust components, containing abundant single alite and belite crystals, represent weakly-sintered surface layers of nodules. The exterior parts of large clinkers were said to have formed inside the moving load under lower heating rates and firing temperatures. The present writer has usually interpreted the scarcity of belite nests in the nodule periphery as being due to extended time at high temperature, thus facilitating elemental absorption and diffusion where sufficient liquid matrix is available in the porous outer portions of the nodule.

Optical, x-ray diffraction, and compositional data (EPMA) for alite crystals were recently gathered by Katayama and Sato (1997) who studied laboratory and commercial NSP- and Lepol-kiln clinkers. From powder-mount, thin-section, and polished-section analyses of alite, using a universal stage where necessary, the indices of refraction, birefringence, 2V, zoning, crystal size, composition, and crystallographic parameters by XRD were compared within and among various sizes of clinker nodules. In discussing the compositional changes in commercial clinker, Katayama and Sato stated, "There are striking similarities between the smaller clinker nodules and the periphery of coarser clinker nodules. They are quenched and oxidized to show a dark color, and contain zoned alite and well-dispersed grains of transparent belite in the fine-grained matrix of interstitial aluminate and ferrite. In contrast, the interior of the coarser clinker nodules has a brownish color, and contains annealed belite and well-crystallized aluminate and brownish ferrite, along with occasional pore-filling of alkali sulfates. These similarities suggest a similar origin for these portions of clinker."

Alite size was related to bulk clinker SO_3 in the following linear equation:

The median long diameter (*y*) of alite = $45x + 20$, where *x* is the SO_3 (0.09% to 1.10%) in a clinker nodule of a given fraction.

Alite polymorphs "R" and " M_{1b} " were said to represent endmembers of a continuous solid solution series, rather than discontinuous thermal polymorphs " M_1 " and " M_3 " of Maki and Chromy (1978).

Sylla (1993), regarding belite borders around alite observed in a laboratory study, said that "the formation of borders is attributable not so much to the precooling of the clinker, but primarily depends on the

clinker composition and specifically the composition of the matrix. As the C_3A content of the matrix increased, the belite borders at the alite grain boundaries became markedly wider, especially with rapid precooling. With slower precooling, on the other hand, they did not grow larger, but instead became detached from the alite grain boundaries and united to form irregularly shaped belite crystals." Preferential growth of secondary belite from alite into the adjacent C_3A suggests the possibility that ferrite, an earlier crystallization, forms an impenetrable barrier. The C_3A , having a relatively longer time in the molten state, forms no barrier to secondary belite growth. Hence, secondary belite is normally well developed when the adjacent matrix phase is C_3A .

Rivera, Odler, and Abdul-Maula (1987) indicate that the rates of alite and belite formation and the temperatures at which these phases form (above the temperature of liquid development) are distinctly accelerated with increasing iron content.

Additional discussion of alite is presented in Chapter 6.

BELITE

Belite is a solid-solution series of trigonal, orthorhombic, and monoclinic varieties of impure dicalcium silicate, normally termed C_2S in the cement industry. Polymorphs of dicalcium silicate are called alpha, alpha prime, beta, and gamma, of which the alpha-prime and beta forms are said to compose approximately 10 to 30 percent of most portland cement clinker. Substitutions may be magnesium, potassium, sodium, barium, chromium, aluminum, manganese, phosphorus, iron, or sulfur. Impurities may approximate as much as 6 percent (Ghosh, 1983). Belite grains are idiomorphous, vitreous, and normally rounded, with a marked multidirectional lamellar structure, in part due to twinning (Yamaguchi and Takagi, 1968). Hardness is 4 to 5 on Mohs' scale. Belite is colorless, pale yellow, yellow, amber, or shades of green. Periclase is commonly entrapped. The crystal shows poor prismatic cleavage (parallel to the threefold symmetry axis). Belite crystals reflect gray on an unetched polished surface. The interference color in a thin section of 25- μm thickness is first-order whitish yellow. Birefringence in thin section is 0.0153 (Fundal, 1982). Belite size is 1 to 4 μm below 1300°C, but recrystallizes to 20 to 40 μm with treatment at high temperature (approximately 1500°C). Etch colors are brown to blue in nital, dependent on time in the etchant, temperature, and reactivity of the crystal.

Insley's classification of belite, most of which was proposed in 1936, has become a standard for the industry:

Type I—two or more sets of intersecting lamellae

Type Ia—characterized by discrete particles along traces of intersecting lamellae (Insley and others, 1938)

Type II—one set of parallel lamellae

Type III—no lamellae; overgrowth on Type I

Type I belite, according to Yamaguchi and Ono (1962), normally forms rounded grains with indistinct crystal faces and shows two or more sets of lamellae (alpha and beta) crossing at 60°. Minute polysynthetic twins in the lamellae with high birefringence have twin planes parallel to Z. Lamellae are skeletal, being formed during the alpha to alpha prime inversion. Polysynthetic twins within lamellae are produced during the alpha prime to beta inversion. Variable extinction ranges from uniform to extremely patchy and diffuse. Type Ia was said by Insley to exhibit the effects of unmixing (phase separation) during cooling.

Type II belites are irregular grains with one set of distinct parallel striations (lamellae). Minute polysynthetic twins, (101) lamellae, and parting occur on (100) and (010) with a 10- to 20-degree difference in extinction angle. X is parallel to *a* (approximately), Y is parallel to *b* (approximately), Z is parallel to *c*. Z makes an angle of 10 degrees with *a*, and the acute bisectrix is *c*, the threefold axis. Type II belite is not a common variety in normal clinker but is abundant in kiln coatings (DeLisle, 1979) and low-temperature kiln flushes (Dorn, 1985, personal communication). Parallel striations in Type II belite from the α' - β transformation are polysynthetic twins, observed in clinkers produced at a very low temperature or cooled very slowly (Ono, 1995).

Type III belite, the nonlamellar form, is uncommon in normal plant clinkers and is merely a single crystal with a uniform internal microstructure.

Shaft-kiln clinker typically contains Type III belite formed after conversion from Type I (Ono, 1995).

Belite crystals with an internal microstructure of lamellae arranged in a concentric hexagonal pattern are rare.

Belite with significant amounts of alkalis has indices of refraction as follows: n_x is 1.694 and n_z is 1.702, with a birefringence of 0.008. The 2V is 20°. Alkali belite has been said to show one set of evenly spaced parallel lamellae in polished and nital-etched section but published confirmatory microprobe data are scarce. According to Ono (letter, 1977) alkali belite in normal clinker can be recognized by (1) large crystal size, (2) lack of color, (3) a birefringence of 0.012 to 0.015, (4) sharp, clear striations, (5) coarse sandwich structure of alpha and beta forms, and (6) a surface free of ferrite phases. Alkali belite, $KC_{23}S_{12}$, according to Gutt and Osborne (1970), has a doubtful existence, being merely a point on the KCS- C_2S join in a phase diagram.

Alpha dicalcium silicate forms at approximately 1425°C and melts at 2130°C. It is ditrigonal dipyramidal with an n_x of 1.702 and n_z of 1.712, and a birefringence of 0.010. The 2V is 0°. Density is 3.07 Mg/m³. Alpha dicalcium silicate, rich in sodium oxide, is isotropic (Soda, Mizukami, and Shirasaka, 1968). Coarse alpha belite, crystallized from a feldspar melt reacting with calcium oxide, is colorless and alkali-rich (Ono, 1980c). Chromy (1970) stated that the alpha form is generally not twinned and has a weak birefringence (0.003). Boikova (1980) reported indices of refraction of 1.717 for n_x and 1.720 for n_z . The alpha form can occur between lamellae of beta dicalcium silicate (Regourd and Guinier, 1974).

A new hydraulic cement based on the alpha-belite polymorph, stabilized with alkalies and iron, has been patented by the Portland Cement Association (Fulvio Tang, 1996). The U.S. patent number is 5,509,962.

Alpha prime dicalcium silicate is derived from alpha by phase transformation and crystallizes between 830°C and 1447°C; n_x is 1.718 and is parallel to b ; n_y is 1.717 and is parallel to a ; n_z is 1.732 and is parallel to c ; birefringence is 0.019; and (+)2V is 30°. Alpha prime, according to Chromy (1970), has a birefringence of 0.013. Alpha prime_LC₂S is orthorhombic and can be stabilized by potassium, sodium, and phosphorus. Alpha prime_MC₂S is monoclinic, stabilized by sodium and phosphorus. Alpha prime_HC₂S is orthorhombic. Some alpha prime C₂S grains show striations of beta phase. Colors range from black, brown, yellow, green to colorless. Density is 3.31 Mg/m³. According to Boikova (1980), n_x is 1.719, and n_z is 1.732, with one, two, or three directions of lamellae.

Beta dicalcium silicate is metastable below 670°C and monoclinic, with an n_x of 1.717, an n_y of 1.722, and n_z of 1.736 and parallel to b ; birefringence is 0.019. The (+) 2V is 64° to 69°, with the axial plane (010). The beta form exhibits very close polysynthetic twinning (Chromy, 1970). It comprises most of belite in clinker. Cleavage is poor on (100) and (010). Colors range from colorless to yellow or brown. Density is 3.28 Mg/m³. Boikova (1980) reported a typical yellow color and spotty surface (not striated).

Gamma dicalcium silicate forms at 830°C and is orthorhombic with an n_x of 1.642 and parallel to a , an n_y of 1.645 and parallel to c , and an n_z of 1.654 and parallel to b ; birefringence is 0.012. The (-)2V is 60° with the axial plane (001). Cleavage is parallel to (010). Faint yellow to colorless crystals are common. Crystals are prismatic and may be polysynthetically twinned (Wieja and Wieja, 1980). Density is 2.97 Mg/m³. A splintery fracture and microstructure are common.

The polymorphous transformation of beta_H to gamma belite that accompanies the phenomenon of

self-pulverization (dusting) at 500°C, as well as detailed techniques for using the microscope for analysis of the gamma form, were presented by Wieja and Wieja (1980). These authors state that gamma calcium orthosilicate with 10 percent Fe₂SiO₄ in solid solution has n_x equal to 1.653 and n_y equal to 1.677. Optical properties of aluminates in self-pulverizing materials, as well as ferrites, were also described.

Maki and others (1995) investigated the conversion mechanism of quartz to belite, starting with limestone, clay, and laboratory chemicals, heating to 1400°C, and quenching rapidly. With the diffusion of alkalies and lime, the quartz changed to cristobalite surficially, then to a liquid rich in SiO₂. With increase in lime-silica ratio from the outside, lath-shaped wollastonite was formed, and subsequently belite. With further increase in lime, the quartz and wollastonite eventually disappeared and the belite clusters developed.

Three stages were recognized by Maki, based largely on the composition of the liquids, the abundance of impurities (alkalies and magnesia), and the various crystals formed in relation to their locations with respect to the original position of the quartz. In the final stage, as the outer layer of belite underwent Ostwald ripening (grain enlargement), alumina and iron increased and alkalies decreased in the outer crystals; the inner crystals were relatively enriched in alkalies, leading to their higher reactivity to the etchants. The belite clusters were seen to be approximately twice as large as the original quartz grains, thus neighboring quartz grains within a distance of twice the sum of their radii form coalescent belite clusters. The results of this investigation were said to support the notion of an acidic liquid from fine-grained quartz in the raw mix, reacting with a basic liquid developed from free lime clusters to precipitate alite.

Chromy (1974) studied the phase changes leading to clinker minerals in a laboratory equipped with differential thermal analysis, a high-temperature x-ray chamber, and a heating-stage microscope. He described the quartz-to-belite transition with the development of cristobalite, wollastonite, and liquid droplets and, at a higher temperature, the precipitation of alite from a liquid surrounding the earlier-formed belite which, to a major extent, dissolves. This equipment is precisely the type that makes the intimate "microreactions" between the phases *visible* during clinkering, and, in the present writer's opinion, we need much more of these kinds of studies.

Maki (1994) stated that belite contains six sets of twinned lamellae. Polymorphic varieties formed as a function of temperature with the alpha polymorph prevailing when the mix was quenched above a temperature of 1280°C. Slowly cooled belite, showing

Inversion Texture of Type I Belite (Ono, 1975)

Skeleton Structure

The cross striations of Type I belite have been called polysynthetic twinning. However, this structure is not polysynthetic twinning but a skeleton structure, consisting of beta and alpha forms of belite.

In the clinker-burning process, at the low temperatures of about 1100°C to 1400°C, belite is a minute crystal of alpha prime form, and through the alpha prime to alpha inversion, belite recrystallizes into a big crystal of alpha, absorbing impurities from the melt. The alpha form is a round and plain crystal without striations. Through the cooling process, thin lamellae of alpha prime appear in the round crystal of alpha. Gradually the lamellae increase and extend all over the crystal, and finally the belite crystal is cooled to room temperature. If the clinker is cooled quickly, plenty of alpha remains in the spaces between the lamellae. The lamellae of alpha prime usually invert to beta, keeping the outer shape of the earlier lamellae. With an electron microscope, a fine polysynthetic twinning corresponding to the alpha prime to beta inversion can be observed. However, the inversion texture is usually too fine to be observed by optical microscopy.

Color of Type I Belite

The alpha form contains plenty of impurities at high temperatures. The solubility of elements into the al-

pha-prime form in solid solution is very small, less than 1 percent. Therefore, through the alpha to alpha-prime inversion in cooling, the impurities separate into a colloidal state in the grain of belite, and belite changes color from light yellow to amber, according to the cooling rate. If the clinker is cooled quickly, belite is colorless or light yellow. If the clinker is cooled extremely slowly, belite is amber, and minute dispersions can be observed.

Birefringence of Type I Belite

If the lamellar structure is coarse, and the lamellae stand perpendicular to the plane of the section, the lamellae of beta and alpha can be observed distinctly without overlap, and their birefringence can be measured separately. Usually the two phases are overlapped and light passes through both of them, thus the birefringence is measured as the sum of the retardations. The birefringence of alpha is very weak and in proportion to the content of beta.

Inversion Texture of Type II Belite

If the clinker is burned below the temperature of alpha prime inversion, and belite is cooled from the temperature region of alpha prime, belite has only the alpha prime to beta inversion texture. This texture is observed as one set of parallel striations, which is polysynthetic twinning and parting on (100) and (010) after the crystal axes of the alpha prime. Rarely occurring are polysynthetic twins on (110), (011), and (0 $\bar{1}1$).

lamellar extension, eventually developed a surrounding set of small satellite belite crystals formed by partial melting and detachment of individual lamellae of the original belite grain.

Polymorphic transformations in belite have been related to cooling rates in a recent study by Fukuda, Maki, and Ito (1997). These authors stated that rapidly cooled belites have α and α' polymorphs, whereas slowly cooled belite is mainly the β polymorph, the latter crystal commonly showing "remelting" relationships with the parent grain. The rate of the remelting reaction was said to be dependent on temperature and the wetability of the α' -phase lamellae by the exsolved liquid, determined by the kinds of impurities and Al/Fe ratio in the parent α polymorph.

Comments on Belite Classification and Polymorphic Varieties

Type I belite crystals according to Insley (1936) were generally considered characteristic of alpha dicalcium

silicate. Insley also observed that twinning in dicalcium silicate is indicated by interpenetrating sets of parallel bands with extinction inclined in opposite directions in adjacent bands. Type II crystals were described as having a single set of polysynthetically twinned bands that are clearly depicted in his Fig. 10 (Insley, 1936). Type III crystals are untwinned, irregular grains, sometimes as overgrowths on Types I or II and commonly with veinlets or cracks. Insley's Fig. 12 shows belite grains that appear to be internally divided so as to produce relatively large areas of untwinned individuals.

Ono (1975) stated that the structure of Type I belite is skeletal instead of polysynthetically twinned. Thus, confusion, and perhaps some disagreement, in the literature exists as to the description and origin of the microstructure of Types I and II belites. The above pullout presents Ono's argument (1975), with only slight editing, in support of a largely skeletal interpretation of belite and a brief statement of polymorph origins.

Manufacturing aspects of belite doped with barium sulfate (BaSO_4), calcium tribasic phosphate [$\text{Ca}_3(\text{PO}_4)_3\text{OH}$],

or vanadium oxide (V_2O_5) as energy conservation measures are discussed by Matkovic and others (1981). This paper includes well-illustrated microscopical descriptions of polymorphic belite transformations by Chromy who, using a hot stage on the microscope, observed the belite changes as they occurred during heating and cooling. These data were correlated with results from DTA, XRD, and scanning electron microscope examinations and generally indicate a sequence of polymorphs similar to that described by Ono (1975).

Groves (1982) demonstrated optically resolvable twins in alpha prime dicalcium silicate, which, upon transformation to beta, developed a single set of planes. Alpha dicalcium silicate, formed at a somewhat higher temperature, had twin lamellae with widths on the order of 2000 angstroms (beyond the range of resolution by light microscopy) visible only with the transmission electron microscope; however, the groups of twin lamellae, termed "domains," were observed with a light microscope.

Oberste-Padtberg (1986) described an unusual belite in a Class G oil-well cement that exhibited a tendency to false set. The belite was said to be idiomorphic, optically positive, with a 2V of more than 60 degrees, occurring as clear platy crystals with no undulatory extinction, and extremely high concentrations of alumina and iron oxide. The present writer has never seen this type of belite and its conditions of formation appear to be largely unreported.

Application of modern microscopical equipment, such as the transmission electron microscope, to the problem of belite microstructure appears to be a promising field of research and may, as Groves (1982) stated, provide data on belite twinning types relating to the temperature at which the belite formed.

Insley's (1936) morphological classification of belite into Type I, II, and III is particularly valuable because it is not confused with genetic or polymorphic restrictions. Even though Insley discussed polymorphic, compositional, and temperature variations, the morphological classification was apparently meant to be primarily observational with interpretation as a derivative. With progress in defining the relationships between polymorphic varieties of belite (alpha, alpha prime, and so on) and their common forms, we may eventually understand the rather complex genesis of the phases. For now, in the author's opinion, the nomenclature should remain descriptive.

A classification of belite, based on *internal* microstructure, is proposed by the present writer.

- Type A—belite crystals with typical multidirectional lamellae (Photograph 7-14),
- Type B—crystals with a finely microcrystalline interior in which the original lamellar structure

has been obliterated (recrystallization) and replaced by a myriad of tiny polygonal crystals with diameters usually less than a micron (Photograph 7-63), and

- Type C—crystals containing a mixture of residual lamellae and microcrystallinity (Photograph 7-64) as described for Type B.

One could subdivide Type C into two categories on the basis of whether (1) the residual lamellae or (2) the polygonal microcrystals dominate on an areal (volumetric) basis. The proposed classification is purely observational and has no genetic connotations attached, at least by definition. Consequently, it remains to be seen if Type B, for example, can be related to reducing conditions or possibly to cooling rate, both of which have implications regarding crystal stability and, presumably, hydraulic reactivity. Research is needed on the causes and effects of belite recrystallization.

Based on the *external* features (crystal shape and surface texture) belite can also be classified. For example, one could delineate:

- Type D belite with a smooth exterior as seen in reflected light at magnifications up to 600X,
- Type E crystals with lamellar extensions (the so-called "ragged" or "sawtoothed" structure), and
- Type F belites with a ring of smaller satellite belite crystals formed by lamellar extension and detachment (Maki's remelted variety, 1994).

The classification can be extended to "amoeboid," "dendritic," or "dotlike" types, but these terms are self-descriptive and need for alphabetic designations appears unnecessary. Thus one might symbolize a belite grain as Type AE, meaning that it has normal lamellae and they extend into the matrix; or Type CF, indicating a complex internal structure and satellite crystals, etc. Designations of polymorph variety in the writer's classification are not intended, but polymorph variety and abundance are of major significance.

Microscopical appearances of belite polymorphs (alpha, alpha prime, beta, and gamma) have been described by Chromy and Carin (1980/81). These authors illustrated nonlamellar, alpha belite and stated that the transformation of alpha to alpha-prime_H dicalcium silicate is manifested by the growth of six sets of alpha-prime lamellae, the speed and completeness of the transformation being a function of the alkali concentration in the melt.

Geis and Knöfel (1986), in a laboratory-produced belite-rich cement (56% belite), state that alpha belite may be visible as light-gray reflecting lamellae with the alpha prime polymorph in clinkers with Na_2O contents of approximately 1.5%. A similar occurrence, but less distinct, was observed in clinkers with K_2O of

1.5%. The alpha form in either case was barely detectable in the unextracted samples.

Clinkers with abundant belite (as high as 80%), in relation to sulfate content, among other variables, were described by Geis and Knöfel (1988). Type II belite (parallel lamellae) increased in percentage with sulfate; the beta polymorph was the only variety detected by XRD. The alpha form, however, was observed microscopically in rapidly cooled clinkers and said to have a light-gray reflectivity observed after water etching. The matrix of these clinkers became increasingly finely crystalline with increase in sulfate.

Relatively high mortar-cube strengths at 28 days have been correlated with alpha-belite percentage, according to Soda, Mizukami, and Shirasaka (1968). Tomita, Hayashi, and Nagase (1970) have shown that the percentage of alpha belite and the temperature at which quenching occurred have a strong effect on 28-day mortar strength. Certain alkali contents and the abundance of alpha belite (which was shown to be stabilized by potassium oxide, sodium oxide, or both) were correlated with relatively high mortar strengths by Ono, Hidaka, and Shirasaka in 1969.

Ono's method of concentration of belite for XRD and estimation of alpha content is as follows (letter, 1981):

1. Wash 300 grams of clinker or cement with alcohol by suspension and decantation techniques. Several suspensions and decantations are necessary in order to concentrate the 20- to 60- μ m particles.
2. Pass the dried sample through a magnetic separator with a forward inclination of 10° to 20° and a side tilt of $\pm 5^\circ$ in order to separate ferrite from belite. Repeat four to five times.
3. Methylene iodide and benzene are mixed to a density of 3.20 Mg / m³, combined with the fraction produced in Step 2, and centrifuged three to four times. After each centrifuging the floating material (largely alite) is taken away. A 0.2- to 0.3-g separation of belite can be obtained.
4. XRD of the heavy concentrate shows strong peaks for beta belite and weak peaks for alpha. The alpha percentage is estimated from the intensity of 32.95° to 33.00° 2 θ , Cu-k_{alpha} radiation. Alpha prime gives a strong peak at 33.26° to 33.28° 2 θ .

This procedure, in the present writer's opinion, may be improved with a KOH-sugar extraction to concentrate the silicates and eliminate the need for magnetic separation.

Takashima (1958) introduced the salicylic acid-methanol (SAM) method to remove silicates and concentrate aluminate and ferrite. The method calls for

20 g of salicylic acid in 300 mL methanol at room temperature, dissolution of 10 g of crushed clinker at cement fineness for 2 hours, followed by filtering, washing with methanol, and drying at 90°C. For complete removal of the alite, leaving the maximum belite, Taylor (1990) recommends salicylic acid at 5 times the C₃S by the Bogue calculation.

Takashima (1972) describes progressive dissolution of alite and beta belite with an accompanying ease of detection of alpha by XRD using methyl-ethyl-ketone (MEK) and salicylic acid. Alpha belite was most easily detected by XRD when a 1.0-g cement sample was combined with 3.0 g of salicylic acid and 100 mL MEK. Details of the test are given in his article.

Also using XRD techniques, Regourd (1979) stated that in slowly cooled industrial clinker alpha belite was not detected, but in rapidly cooled, air-quenched clinker, alpha belite amounted to 3.0 percent.

Hirano and others (1991) combined microscopy and x-ray diffraction to evaluate alpha and beta belite polymorphs. After treatment with a KOH-sugar solution to remove the matrix, a heavy liquid (d=3.22) was used to separate alite from belite. Alpha C₂S was possibly detected microscopically and with x-ray diffraction.

Daimon and others (1992), using chemical and heavy-liquid methods of phase separation and concentration, described alite and belite microstructure, elucidating the detection of the alpha polymorph of belite with microscopy and x-ray diffraction. Lamellae in belite showing no transmission of cross-polarized light during stage rotation were suggested to be the alpha form. The x-ray diffractogram shoulders at 2 theta of 33° and 46.6° were said to clearly indicate the presence of alpha.

Additional discussion of belite is given in Chapter 6.

TRICALCIUM ALUMINATE

Isometric, orthorhombic, tetragonal, and monoclinic forms of tricalcium aluminate (Ca₃Al₂O₆) with a melting point of approximately 1542°C are termed C₃A in the cement industry. Tricalcium aluminate normally consists of uniform, small, xenomorphous to rectangular crystals (1 to 60 μ m) in low-alkali or alkali-free clinker. C₃A may comprise as much as 18 percent in ordinary clinker. Crystals show poor cleavage parallel to (001), conchoidal fracture, and a hardness of 6. Tricalcium aluminate is normally isotropic in cross-polarized light, colorless (in white cement) to tan and brown in transmitted light in ordinary portland cement, with an index of refraction of 1.710. It reflects gray on unetched polished surfaces and etches blue to

blue-gray in distilled water (preferably warmed to 40°C) and potassium hydroxide. Tricalcium aluminate may be a solid solution with iron, magnesium, silicon, sodium, and potassium. Impurities may approximate up to 10 percent (Ghosh, 1983). It typically fills interstices between crystals of C_4AF and C_2S , and therefore probably crystallized later. Density is 3.04 Mg/m^3 . The existence of monoclinic tricalcium aluminate in commercial clinker has been questioned by Regourd and Guinier (1974).

Aluminate crystal sizes as a function of rotary versus grate coolers, and kiln-outlet versus cooler-outlet sampling locations, were investigated by Sylla and Steinbach (1988). These authors concluded that better cement properties were derived from quickly cooled clinkers, preferably those leaving the kiln at a temperature just above the solidification point of the liquid and cooled as rapidly as possible. Finely microcrystalline matrix (relatively small C_3A) was correlated with rapid cooling, as was the absence of surficial degradation of alite crystals to belite. Clinker particles over 20 and less than 2.0 mm were screened out because of their nonrepresentative character with regard to cooling. Crushed clinker particles, 2 to 4 mm, were studied. Cements made from clinkers taken at the kiln outlet, with few exceptions, produced higher compressive strengths, but set more slowly than those sampled at the cooler outlet. Relatively coarsely crystalline matrix produced a more rapidly setting cement. The matrix of clinkers taken from the kiln outlet at a temperature of 1370°C and cooled with compressed air was said to be “virtually a glassy mode,” but that cooled from a temperature of 1320°C was well differentiated.

ALKALI ALUMINATE

Alkali aluminate is an orthorhombic and monoclinic solid solution series of $NaCa_4Al_3O_9$, NC_8A_3 , and possibly C_3A , with partial substitution of sodium by potassium. It occurs as idiomorphous tablets, laths, and stavelike prismatic forms. It is biaxial with n_x equal to 1.702, n_z equal to 1.710, and a birefringence of 0.008. The $(-2V)$ is 0° to 35° . Alkali aluminate is length slow, colorless to dark in thin section, and, in polished section, turns blue with water and potassium hydroxide, as does C_3A . Orthorhombic (low sodium oxide) experimental phases may be twinned on (110), (010), (100), and (001) with oblique extinction. An experimental monoclinic form (high sodium oxide) shows crossed grids of fine lamellar twins on (100) and (010), wavy extinction, and a $2V$ of 64° to 67° (Maki, 1973). Alkali aluminate may also show microgranular (nonprismatic) habit with isotropic cores surrounded by twinned forms with higher birefringence.

Alkali aluminate crystals clearly entrap alite and some belite, thus the aluminate crystals form later than some of the silicates, but this is not a new conclusion. Alkali aluminate rarely includes crystals of ferrite and appears to interrupt the continuity of ferrite, suggesting that the alkali aluminate crystallized first.

Ono (1995) stated that dendritic non-cubic C_3A crystallized first, in accord with a phase diagram, when laboratory reagents were burned under conditions of rapid heating and cooling. Ordinary clinker, containing an excess of C_3S , crystallized in the following sequence: C_3S , C_2S (small amount), C_4AF , C_3A - C_6A_2F .

FERRITE

An orthorhombic solid solution series of $Ca_4Fe_4O_{10}$ to $Ca_4FeAl_3O_{10}$, ferrite is prismatic and pleochroic with an n_x of 1.98 (olive green), an n_y of 2.05 (olive green), and an n_z of 2.08 (almost opaque). The birefringence is 0.010 and $(-2V)$ is moderate. X equals b , Y equals c , and Z equals a . Crystal color is normally brown to yellow; elongation is positive and the phase is pleochroic with the Z direction showing the strongest brown absorption. Ferrite reflects dull to bright on polished surfaces, hazy yellow for ferrite containing a relatively high percentage of reduced iron. It displays a distinct cleavage on (101) and can show twinning with (101) as the composition plane. Crystals are commonly tabular on (010) but can be idiomorphous interstitial filling; ferrite can also be prismatic, dendritic, or massive to fibrous. It typically forms a mesh in which the C_3A crystallizes. Ferrite may comprise almost all the matrix in sulfate-resisting and oil-well cement clinkers. Polishing hardness is greater than alite and belite but less than periclase. Its index of refraction is lowered by 0.02 by magnesium oxide in solid solution. Impurities can reach 13 percent (Ghosh, 1983). Slowly cooled crystals have a blade form, crystals formed under a moderate cooling rate are prismatic, and quickly cooled crystals are dendritic. Density is 3.77 Mg/m^3 .

Reducing conditions and their microscopical effects have received much attention recently and, because the effects largely involve iron and ferrite, the subject is discussed here.

Reducing conditions, high consumption of coal, and overburning, according to Goswami and Panda (1986), cause large clinkers (25-125 mm) to have less alite, more C_3A , large anhedral alite, large belite, alite and belite decomposition, higher water demand, reduced setting time, and lower mortar strength, compared to small clinkers.

With regard to the observation of brown-centered clinkers, Pennell (1986) stated, “We have observed that brown-cored clinker results from burning in a CO_2

atmosphere at typical burning temperatures of 1400° to 1450°C or at high temperatures of 1500° to 1550°C in a highly oxidizing atmosphere under conditions such that semi-liquefaction and resultant vitrification of the clinker occurs, for whatever reason, so that air cannot penetrate this vitrified mass upon exiting the burning zone.” Brown-centered clinkers were produced in a laboratory furnace with a temperature of 1525°C.

Summarizing much of the previous work on reducing conditions and providing additional microscopical observations with light and electron microscopy, Centurione (1991) showed that reducing conditions affected the composition of the ferrite, increased the content of C_3A , and reduced the stability of alite, the latter illustrated by secondary belite and iron, termed exsolution, developing within the alite crystals. Reducing conditions produced a more rapid set, but decreased later reactivity, leading to lower strengths and attack on the refractories in the burning zone.

Uchikawa and others (1992) defined chemical differences in alite composition as a function of burning environment, showing that alite in gray clinker from oxidizing conditions has an average Al_2O_3/Fe_2O_3 ratio of 1.56, whereas that in brown clinker from reducing conditions has a value of 1.34. Belite gave ratios of approximately 1.87 and 1.64 for oxidizing and reducing conditions, respectively. Data were gathered with the electron microprobe on polished sections.

Ichikawa, Imai, and Komukai (1992) showed that oxidation in ferrite produced a color change from yellowish brown to blackish gray during substitution of magnesium for aluminum and ferric iron. Increases in silica/magnesia ratio in ferrite were said to reduce oxygen vacancies and therefore prevent color change.

The subjects of reducing conditions and their effects on clinker color were reviewed by Johansen and Jakobsen in 1993. These authors, studying the microscopical and chemical features of the brown cores and dark-colored peripheral regions of industrial clinkers, in comparison to the bulk analyses, concluded that clinkers with brown cores are to be expected during normal stable kiln operation. Ferrous iron (FeO) “is present in the light colored as well as the corresponding dark parts of the largest clinker nodules. The light coloring of the interior parts is caused by the transparent orange colored ferrite phase. Both clinker samples (exterior and interior) have higher alkali and sulfate contents than the sample representing the average clinker. The presence of these sulfates is not to be expected if the samples have been subjected to reducing conditions. The presence of FeO is due to the thermodynamic effect of the high temperatures in the burning zone.”

Bhatty (1995) stated that alkali sulfates are decomposed in reducing conditions. Strongly oxidizing con-

ditions and low burning zone temperature promote retention of more sulfur in clinker than in kilns with reducing conditions and high burning zone temperature.

Scrivener and Taylor (1995) concluded that clinkers with “light-colors are associated with decreased oxidation of Fe^{2+} to Fe^{3+} during cooling, which tends to occur in large nodules high in belite and low in interstitial material.” Reducing conditions were said to be capable of producing the yellow color, the latter not necessarily indicating the former. Scrivener and Taylor relate the crystal structure of ferrite to that of perovskite ($CaTiO_3$) in which replacement of some of the Fe^{3+} with a small portion of Fe^{2+} results in loss of extrinsic semiconduction and a change from dark color to brown.

Thus, in the present writer’s opinion, crystal chemistry modifications, resulting from iron lattice position or valence change, appear to create the optical (visual) effects we see in ferrite and nodule colors. Indeed, crystal structure, as always, determines what is observed in microscopy, and in many other fields of analysis.

FREE LIME

Free lime, isometric calcium oxide (calcia), occurs as colorless, rounded, idiomorphous grains, singly, in clusters, or as inclusions in aluminates or alite. Its index of refraction is 1.833 and hardness is 3 to 4. Free CaO comprises approximately 1.0 percent in ordinary portland cement. Free lime has perfect cubic cleavage; reflects brightly with light yellow to cream color, tarnishes to iridescent calcium hydroxide in room humidity; and etches rapidly with water. Its density is 3.32 Mg/m^3 . Free lime is indicated by White’s test (Lea, 1970): to a finely powdered cement or clinker on a microscope slide, add a drop of solution mixed with 5 g phenol in 5 mL nitrobenzene, to which two drops of water are added. If free lime is present, long radiating needles of calcium phenate form in less than 10 minutes, and calcium hydroxide forms in 20 minutes or longer.

In clinkers and cements, expansive hydration of free lime produces popcorn or cauliflowerlike crystals of calcium hydroxide, called epezite, surrounding the original particle of free lime (see Brown and Swayze, 1938). Formation of epezite via air slaking normally causes clinker disintegration.

Epezite was further described and discussed by Olek and Diamond (1991) who noted that hydration of reagent-grade CaO produced portlandite instead of the strange crystals of epezite. D-spacing data from XRD could not be gathered on the epezite due to masking by other clinker phases. Incidentally, the calcium hydroxide crystals that form from the KOH-sugar extraction technique appear to be epezite, there-

fore, simple heavy-liquid separation with a centrifuge should provide an abundance of material for characterization by several methods.

PERICLASE

Periclase is isometric magnesium oxide (magnesia) occurring as small, colorless, triangular, octahedral, rectangular, or round grains with diameters up to 30 μm or as dendritic crystals. Periclase can be interstitial or intragranular; crystal clusters are common. Periclase abundance may range up to 6 to 7 percent in some clinkers. The index of refraction is 1.736. Crystals show cubic cleavage and have a hardness of 5.5 to 6, resulting in a high relief on polished surfaces. Periclase is colorless and reflects brightly with pinkish light gray. It is not affected by usual etch media. Density is 3.58 Mg/m^3 .

Total MgO content in clinker is normally maintained at less than 2.0% to avoid expansion in the autoclave test. Belite containing periclase (at an early stage of crystallization) indicates coarse grains of MgO-bearing silicates, such as diopside, pyroxene, and hornblende in the raw feed. Dendritic periclase occurs in slowly cooled clinkers from large kilns (200 t/hr) and is hardly observed in clinkers from small kilns (20 t/hr), according to Ono (1995).

Microscopical details of dolomitic raw materials and the resulting clinkers were described by Dreizler (1988) in relation to national MgO limits in cements, soundness, and the availability of suitable limestone deposits. Soundness of periclase-rich cement was said to notably improve with decrease in free lime (0.10 percent in the case study presented).

Periclase occurs as inclusions within alite and belite (particularly in some tightly packed nests), clearly indicating that at least some periclase, formed early in the heating portion of the temperature curve, was trapped in the silicates. Large euhedral to subhedral periclase crystals left over from the calcination of dolomite may be retained as such and merely coexist in the aluminoferrite liquid. Periclase of the dendritic variety appears to crystallize from the liquid, and, in many cases, is subsequently coated with belite, perhaps beginning as early as the liquid is formed and sufficient MgO is available; small euhedral periclase crystals may also form from the matrix during cooling, even in clinkers having only 0.3% MgO (Hawkins, 1995, letter).

Periclase, free lime, or coarsely crystalline C_3A (slowly cooled), or any combination thereof, have been shown to be responsible for excessive autoclave expansion (Gonnerman, Lerch, and Whiteside, 1953).

Gebauer (1988) has convincingly shown the lack of expansive effects of periclase in 4-year-old, outdoor-stored concretes, concluding that the ASTM test for

cement expansion in the autoclave is “irrelevant”, and that the test and standard cement specifications regarding MgO levels actually hinder the industry, making an uneconomical use of cement resources. The present writer, after many hundreds of petrographic studies of field concrete, has never interpreted a cause of failure on the basis of cement periclase; the evidence for periclase expansion (associated microcracking) was not observed.

ALKALI SULFATES

Sodium and potassium sulfates occur in various crystal forms of the hexagonal and orthorhombic systems. These phases typically are found as spotty void fillings and deposits on alite crystals and void surfaces in clinker, even in cracks in alite crystals (Gouda, 1980). The sulfur can be derived from raw materials, but mainly the fuels. Concentration may occur in periods of kiln upset. Alkali sulfates make up only a few percent in clinker but have important effects. Alkali sulfates in polished sections have low reflectivity, are dissolved by most etching media, and turn dark with hydrofluoric acid; some alkali sulfates are said to be characteristically surrounded by a halo of unetched clinker (Pollitt and Brown, 1968). Alkali sulfates can be observed in a powder mount beneath a cover glass as floating particles in oil with an RI of 1.715. In thin section and transmitted light, alkali sulfate varieties can rarely be distinguished, occurring in many cases as transparent, irregular, multiphase masses of intergrown crystals that can be more easily seen on a very finely polished section. Optical properties determined on small particles in refractive-index oils will help to identify the phases. A potassium permanganate and barium chloride stain for sulfates (Poole and Thomas, 1975) has been found moderately successful for detection of alkali sulfates in clinker powder (see “Examination of Stained Powders” in Chapter 3).

The effects of alkali sulfate appear to be primarily in early hydration reactions, owing to the very high solubility of these phases. According to Nawa and Eguchi (1988), viscosity of paste made with cement from a high alkali sulfate clinker was significantly decreased with concentration of naphthalene superplasticizer. Paste made with a low alkali-sulfate clinker, the cement containing anhydrite and a lignosulfonate water reducer, showed false set. These results led Nawa and Eguchi to conclude that alkali sulfate exerts a remarkable effect on paste rheology.

For details of the extraction procedures for alkali sulfate from clinker, x-ray diffraction analysis, and specific chemical requirements for the formation of these phases, see Gartner and Tang (1987).

Relationships of alkali sulfate to delayed ettringite formation (DEF) and reported expansion therefrom are “unlikely,” according to Miller and Tang (1996).

For most studies, XRD remains a dependable and rapid mode of analysis for establishing the varieties of sulfate phases. However, their locations, crystal sizes, and, to some extent, their abundances are best described by microscopy. Some of the alkali-sulfate phases are listed below:

Arcanite (K_2SO_4) is orthorhombic with an n_x of 1.49, an n_y of 1.49, and an n_z of 1.50; colorless; void-filling or rarely dendritic; and has a density of 2.67 Mg/m³. It inverts to a uniaxial phase at roughly 650°C.

Calcium langbeinite ($K_2SO_4 \cdot 2CaSO_4$) has an n_o of 1.52, an n_e of 1.53, and a birefringence of 0.010. It undergoes a phase change in K_2SO_4 leading to characteristic cracking (Bye, 1983). Calcium langbeinite is biaxial and relatively dark in reflected light. It is said to control setting in mineralized high-alite cement (Moir, 1982).

Aphthitalite [$(K_2Na)_2SO_4$] is hexagonal with tabular crystals showing marked trigonal development. Crystals can form bladed aggregates. Cleavages are fair on the rhombohedron and poor on the basal pinacoid. Hardness is 3 and density is 2.7 Mg/m³. Crystals are uniaxial positive with an n_o of 1.491, an n_e of 1.499, and a birefringence of 0.008 for K: Na = 2.46:1; n_o is 1.487, n_e is 1.492, and the birefringence is 0.005 for K: Na = 1:1.5. The birefringence increases slightly with increase in the tenor of potassium. Continuity from $Na_2K_8(SO_4)_5$ to K_2SO_4 is improbable (Winchell and Winchell, 1964). Aphthitalite can have a small optic angle and is colorless unless stained by iron oxide.

Syngenite [$K_2Ca(SO_4)_2 \cdot H_2O$] is monoclinic with a beta of 104°5'. Crystals typically develop as (100) tablets or prisms. Twinning is common on (100). Syngenite shows perfect (110) and (100) and distinct (010) cleavages. Hardness is 2.5 and density is 2.6 Mg/m³. The angle of X with c is -2°17', $Z = b$, (-) $2V = 28°18'$, $r < v$ is very strong; n_x is 1.5010, n_y is 1.5166, n_z is 1.5176, and the birefringence is 0.0166. Crystals are colorless or white. Syngenite occurs in silo-stored portland cement and is reported to be responsible for pack set and some problems of flowability.

MISCELLANEOUS PHASES

Calcite ($CaCO_3$) is a hexagonal mineral with perfect rhombohedral cleavage (three directions not at right angles); parting and rhombohedral twinning are common; hardness is 3. Crystals are uniaxial negative with an n_o of 1.654, n_e of 1.485, and a birefringence of 0.169. Calcite is normally colorless and has many forms and habits (anhedral to euhedral crystals, columnar, coarse

to very finely microcrystalline, sugary, layered, and so on). Density is 2.71 Mg/m³. Calcite can occur in clinker as a carbonated hydration product. Calcite can be identified with certain stains and thereby distinguished from dolomite [$(Ca,Mg)(CO_3)_2$], a very similar mineral. **Gypsum ($CaSO_4 \cdot 2H_2O$)** is monoclinic with one perfect cleavage and two good cleavages, the latter intersecting at 66°. Hardness is 2. Gypsum is biaxial positive; n_x is 1.521, n_y is 1.523, n_z is 1.530, and birefringence is 0.009. Gypsum is white to colorless. It loses three-fourths of its water at about 120°C resulting in an n_o of 1.50 and an n_e of 1.56. Gypsum recrystallizes by directed stress or temperatures above approximately 100°C but may retain its original outward form of the particle. Gypsum may be fibrous, platy, or massive. Particles in cement typically show a complex internal microcrystalline character. Density is 2.32 Mg/m³. Gypsum has a blue dispersion “stain” when mounted in oil with an RI of 1.528 (Green, 1984). Application of distilled water at 40°C to a polished section imparts a dark coloration to gypsum particles in cement samples.

Plaster ($2CaSO_4 \cdot H_2O$) is hexagonal with needlelike crystals exhibiting six-sided prisms. It is uniaxial positive; n_o is 1.558, n_e is 1.586, and birefringence is 0.028. Plaster is colorless and the density is 2.7 Mg/m³. Other phases with this composition exhibit slightly different optical properties (see Winchell and Winchell, 1964). Plaster also occurs pseudomorphically after gypsum, retaining the internal microcrystalline character of gypsum as described here. Green (1984) reports a variable RI, usually approximately 1.54, and a relatively high porosity, thus making invisibility difficult in refractive-index oils. Particles composed of gypsum in the interior and plaster in the exterior, and vice versa, have been seen by the writer. Partial re-hydration of plaster or dehydration of gypsum may be commonplace.

Anhydrite ($CaSO_4$) is orthorhombic with crystals showing a varied habit: equant grains or tablets developed on (010), (100), or (001), or elongated parallel to a or c . Cleavages are perfect on (010), very good on (100), and distinct on (001). Polysynthetic twinning is common and may be in two directions. Hardness is 3 to 3.5; density is 2.98 Mg/m³. Anhydrite is soluble in hydrochloric acid. The melting point is 1450°C. X is parallel to b , Z is parallel to c , and the (+) $2V$ is 43°. Dispersion is $r < v$ (weak). The n_x is 1.5698, n_y is 1.5754, n_z is 1.6136, and the birefringence is 0.0438. Crystals are biaxial positive. Anhydrite is generally colorless in transmitted light; thick crystals may be bluish or violet with X colorless to pale yellow or rose, Y pale violet or rose, and Z violet.

Calcium sulfate inverts at 1195°C to alpha anhydrite, which is monoclinic with lamellar twinning like plagioclase and has an n_x of 1.50, n_z of 1.56, and birefringence of 0.060. Beta anhydrite is obtained by heating

anhydrite above 170°C. It is stable to 500°C. It is probably orthorhombic and is pseudohexagonal; density is 2.85 Mg/m³. Z is c , (+)2 E is approximately 45°, n_x is 1.562 ± 0.003 , n_z is 1.595, and birefringence is 0.013. A third phase (gamma anhydrite) has been called soluble “anhydrite” since it is much more soluble in water than ordinary anhydrite. It is made by dehydrating $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ at about 30°C. Crystals are hexagonal basal plates. Density is 2.55 to 2.61 Mg/m³. It is uniaxial positive with n_o of 1.56, n_e of 1.50, and birefringence of 0.060. This phase takes up water readily in contact with moist air. It varies markedly in properties with variations as a function of temperature. For example, at 100°C it has an n_x of 1.547 and n_z of 1.570; at 150°C it has an n_x of 1.499, n_z of 1.544; and at 450°C to 550°C it is isotropic with an n of 1.500 (Winchell and Winchell, 1964).

Quartz (SiO₂) is trigonal trapezohedral, typically seen as equant to somewhat shardlike particles with a conchoidal fracture and virtually no cleavage. It is colorless to cloudy, with a hardness of 7. Quartz is uniaxial positive, with an n_o of 1.542, an n_e of 1.551, and a birefringence of 0.009. Its density is 2.65 Mg/m³.

Fly ash is composed of tiny spherical and ellipsoidal beads and bubbles of glass, typically containing other phases. Other common constituents are irregular carbon particles, hematite, magnetite, tridymite, cristobalite, quartz, mullite, and spinel. It may contain small amounts of belite, aluminate, and free lime. The RI of the glass is 1.50 to 1.63.

Glass of variable composition fills voids in extremely rapidly cooled clinker. It forms equant to highly irregular masses and is normally isotropic unless strained. Glass may comprise up to 20 percent of abnormal portland cement clinker. Regourd and Guinier (1974) state that glass may form “a few percent” in clinker. Glass may occur as a dark-green variety, developed as a uniform groundmass between large belite crystals, and has been called gehlenite glass with a composition of approximately C_2AS . Gehlenite glass has an n of 1.638 and a density of 2.884 Mg/m³. Glass has never been identified by the writer in normal portland cement clinker. Ceramic glasses have a very wide range of refractive index.

Potassium iron sulfide (KFeS₂) is very soft and shows a bright reflection pleochroism of gray-yellow, greenish gray, and copper red.

Calcium sulfide (CaS) is isometric but resembles ferrite. It commonly forms colorless spherical or dendritic crystals, is strongly reflecting, and rapidly etches with dimethyl ammonium citrate. It has an RI of 2.137 and perfect cubic cleavage. Hardness is 4 and density is 2.6 Mg/m³.

Wustite (FeO) is isometric, black and nearly opaque at an FeO content of 80 percent. Wustite is opaque (bottle green) with an n of 2.12 at 78 percent FeO, with the remainder MgO. Wustite reflects gray-white with a

tint of brown, with brighter reflectivity than ferrite. It is dendritic, has poor cleavage, and its density is 5.5 Mg/m³.

Potassium oxide (K₂O) was described by Fundal (1988), using the SEM and EDXA, as free hygroscopic masses. After polishing, droplets rich in K₂O formed on polished sections of high-alkali clinkers, coming out of the matrix and developing around voids. Crystallization of K₂CO₃ mixed with Al₂(OH)₃ was observed on the section surface. The present writer has also observed droplets forming around voids on a polished section surface, but always believed them to be artifacts from exuded residual grinding or washing liquids (propylene glycol, various petroleum oils, isopropyl alcohol, none of which are presumed to be completely anhydrous), and are probably contaminated with numerous “impurities” derived from the clinker polishing and grinding debris.

Metallic iron (Fe) is isometric and occurs as steel-gray to iron-black magnetic masses normally in droplet form with a strong white reflectance. It has distinct cubic cleavage, with a hardness of 4 and a density of 7.87 Mg/m³. It seems to always be impure.

Graphite (C) is hexagonal; it is black and opaque with a moderately bright, strongly pleochroic reflectance. Cleavage is parallel to (0001) and perfect, forming thin basal lamellae. Hardness is 1 to 2; stalk to strip-shape. Density is 2.1 to 2.3 Mg/m³.

Coke (C) forms irregular to round particles of medium reflectivity with a yellowish hue and marked reflection pleochroism of yellowish white to dark gray.

Gehlenite (2CaO·Al₂O₃·SiO₂) is tetragonal; crystals are uniaxial negative with an n_e of 1.658 and n_o of 1.669. It has short prisms or tablets, often with a square outline and distinct basal cleavage (Insley and Fréchette, 1955). Extinction is parallel to crystal edges. Crystals are colorless and may be zoned and twinned. Gehlenite is revealed in high alumina cement clinker with 2% ammonium chloride plus a 2% dibasic sodium orthophosphate solution with an etch time of three to five minutes at 100°C. Hardness is 5 to 6 and density is 3.07 Mg/m³.

Spurrite (2Ca₂SiO₄·CaCO₃) is possibly monoclinic, with distinct (001) and poor (110) cleavages at 79° and multiple twinning. Hardness is 5. It is uniaxial negative with an n_x of 1.64, n_y of 1.674, n_z of 1.679 and birefringence of 0.039. The 2V is 40°. Density is 3.014 Mg/m³ (Amafuji and Tsumagari, 1968).

Double salt (3Ca₂SiO₄·2CaSO₄) has an n_o of 1.628, an n_e of 1.636, a birefringence of 0.008, and a large 2V (Ono, Amafuji, and Okumura, 1966).

Calcium sulfosilicate (2Ca₂SiO₄·CaSO₄), a form of spurrite, is orthorhombic, with irregular to prismatic

crystals; n_x is 1.630 and n_z is 1.640 (Sundius and Peterson, 1960), or n_x is 1.632, n_y is 1.638, and n_z is 1.640, with a $(-)$ 2V of 60° , according to Pryce (1972). The material is made from calcite and silica and has RI of 1.635 and a low birefringence according to Gutt and Smith (1966). Trojer and Warbenowa (1977) reported RI's for the solid-solution series $2\text{Ca}_2\text{SiO}_4 \cdot \text{CaSO}_4 - 2\text{Ca}_2\text{SiO}_4 \cdot \text{CaCrO}_4$, indicating an increase in RI's and birefringence with chromium content. The mineral etches similar to belite in HF vapor, showing elongated prisms with cusp-shaped ends, typically set in a groundmass of calcium sulfate or calcium langbeinite, or both.

CHAPTER 6

Ono's Method— History, Explanation, and Practice

HISTORY OF ONO'S THEORIES OF KILN CONTROL THROUGH MICROSCOPY

Yoshio Ono's major contribution to cement production technology has been largely through the use of transmitted, polarized-light microscopy as one of the methods of quality control. Ono brought transmitted, polarized-light microscopy from the research laboratory virtually onto the kiln floor where, in combination with data from other tests and instruments, the kiln could be controlled and the cement quality enhanced. This brief history of Ono's work in clinker and cement microscopy clearly illustrates the applicability of both reflected- and transmitted-light microscopy to day-to-day cement production. Indeed, polished sections are given major emphasis in Ono's most recent publication (1995). Although some workers have criticized Ono's kiln interpretations as being "oversimplified," his contributions to the field have been seminal, to say the least.

In the 1995 publication, Ono summarized much of his work in clinker microscopy, giving emphasis to the events taking place as clinkers develop in the kiln, the effects of ammonium chloride and nital etches as they relate to the degree of clinker burning, contrasting poorly burned and well burned clinkers, and describing the intimate relations of microchemistry to phase development. Among the many contributions in this publication are the 195 color photomicrographic plates, all polished sections of excellent quality. Ono's observations and interpretations are far too numerous to be listed in the present book, however, some have been inserted in their relevant locations in the text.

Naito and Ono in 1953 reported the relationships between three size fractions of raw feed (greater than 30 μm , 20 to 30 μm , and 10 to 20 μm) and their burnabilities, concluding that (1) coarse quartz increased the difficulty of burning and (2) a few percent alkalis and magnesia as mineralizers greatly improved sintering. Microscopically it was shown that

with the same raw mix burned for 20 minutes, Type II belite with a single set of parallel lamellae characterized a clinker burned at 1380°C, and Type I belite with several sets of multidirectional lamellae formed at a temperature of 1430°C.

Ono described the polymorphs of dicalcium silicate with transmitted-light microscopy and X-ray diffraction (XRD) in 1953, confirming the occurrence of alpha-prime, beta, and gamma forms.

In 1954 Ono discussed changes in the specific gravities of C_2S and C_3S as functions of magnesium, potassium, and sodium oxides and pointed out the inhomogeneity of C_2S , saying that the grain consisted of minute, highly birefringent laminae and isotropic substances in a skeleton structure. Ono stated that the specific gravity and refractive index of the birefringent lamella in belite seemed to be higher than those of the isotropic substances (later said to be the alpha polymorph).

A major contribution came when Ono (1957) published a microscopical study of the formation of portland cement clinker, tracing the changes of phase chemistry and crystal morphology as functions of raw material fineness, mixing, and heating rate. He concluded with a prophetic statement that the microscopical information might be useful in the control of clinker manufacture.

In 1962 Yamaguchi and Ono published a detailed microscopical and XRD analysis of belite, describing and defining the crystallographic orientations of various lamellar structures. The structures were said to be a result of three sets of skeleton crystals and six sets of lamellae, the combination of these forming a pseudohexagonal, orthorhombic crystal. Twinning produced during the alpha prime to beta inversion was observed with a scanning electron microscope. Yamaguchi and Ono stated that (1) during polymorphic inversions from alpha to alpha prime to beta, the crystal axes remain parallel and (2) the typical multidirectional

rectional lamellar structure is formed during the alpha to alpha prime inversion. A belite grain with only one set of striations (Insley's Type II belite) was reported to show cleavage parallel to one set of conjugate planes of polysynthetic twins.

Ono's doctoral thesis (1963), the most exhaustive study of alite and belite known to the present writer, was concerned with many of the microscopic aspects of phase transformation during production of portland cement clinker. Among his many findings was the fact that alite grows larger with increasing particle size of quartz in the raw feed.

Ono, Kawamura, and Fujimura in 1964 described the sequence of reactions that occur during sintering of powders of calcite, clay, siliceous rock, and copper slag (an iron-bearing glass) through chemistry, XRD, and transmitted-light microscopy.

Research results on the effects of alpha-belite on mortar strength, published by Yamaguchi, Ono, Kawamura, and Soda in 1963, led to a definitive paper in 1965 (Ono and Soda) correlating the crystallographic relationships of alite and belite with the strength of mortar. In the latter paper, polymorphic varieties of belite and morphologic changes in alite were related precisely to the following parameters of the burning condition: rate of heating, maximum temperature, length of time at high temperature, and rate of cooling. These parameters, empirically studied, resulted in an equation giving a prediction of 28-day mortar-cube strength. Ono and Soda showed, with microscopy and XRD of selected magnetic and density separations of clinker powders, that the highest mortar-cube strengths were achieved with clinkers enriched in relatively clear, alpha belite.

Also in 1965, Ono, Uno, and Kanai reported data on five laboratory-made polymorphs of tricalcium silicate that persisted at room temperature. These authors described monoclinic, triclinic, and rhombohedral forms of alite.

Ono and Soda (1967) demonstrated that, when finely ground raw mix is burned for a long time in the temperature range of 1200°C to 1300°C, coarse granules of 100- to 200- μ m sizes are produced in a powdery, porous clinker. In addition, the mineralogic changes in raw material were observed as it progressed from white (unburned) to pink, yellow, brown, and gray, with the temperature increasing to 1500°C.

Ferrite microscopy was the subject of a paper in 1967 by Ono and Shimota. Various crystallographic and optical properties of ferrite were described as a function of the aluminum to (aluminum + iron) ratio, the alumina modulus, in laboratory-produced clinkers.

In 1968 Ono and Shimota published a paper concerning the microscopic textures of ferrite in the systems

$C_6A_2F-C_3A$ and $C_2F-C_2A_6F-MgO$ with laboratory-made clinkers. They related ferrite crystal morphology and optics to cooling rates, showing that in slowly cooled clinker, ferrite occurs as fernlike crystals and in quickly cooled clinker the crystals resemble bamboo leaves.

Ono (1995) stated that a portion of the melt can "flow away" from certain parts of a clinker, leaving an irregular cavity and concentrating nearby. The present writer has seen belite lamellae extended into an adjacent void, suggesting the likelihood of melt migration.

Perhaps the most influential paper by Ono was coauthored with Kawamura and Soda in 1968 and presented at the Fifth International Symposium on Chemistry of Cement in Tokyo. This contribution summarized optical properties of polymorphic varieties of alite and belite, showing the correlations between transmitted-light microscopy of these phases and burning conditions. Emphasis was placed on cooling rates to get optimum hydration characteristics from belite. For ordinary and rapid-hardening portland cement, a cooling rate of 17°C to 20°C per minute to a temperature of 1200°C was considered optimum. This paper, probably more than any previous paper, brought international attention to Japanese methods and theories of kiln control through transmitted-light microscopy.

The effects of sodium, potassium, and magnesium oxides on the strength of mortar were investigated by Ono, Hidaka, and Shirasaka (1969) and optimum percentages were established. These authors concluded that mortar compressive strength was related to abundances of alpha and alpha-prime belite.

Alite crystal chemistry was discussed in a paper by Ono (1974) in which he described changes in the atomic structure of alite in response to such variables as solid solution, exsolution, thermal vibration, states of disorder, inversion, and partial decomposition.

Ono's method and theory of kiln control were introduced to the Western world by Mau (1975). In that same year Ono conducted a seminar for North American cement-company personnel in Hawaii, where he taught the details of his theories and method of kiln control with powder-mount microscopy. The dissemination of Ono's technique to the Western world was largely due to this seminar. Since that time Ono's theories and method of clinker interpretation have been subjects of research in laboratories of many North American cement companies, the Portland Cement Association, and in Europe. Mau (1979) reported on the routine application of the Ono technique in Hawaii and strongly supported Ono's Method and theories, stressing their use to control burning temperature.

At the 1980 meeting of the International Cement Microscopy Association (ICMA) in Dallas, Texas,

U.S.A., and at the General Technical Committee meeting of the Portland Cement Association (PCA) at about the same time in Skokie, Illinois, U.S.A., Ono presented a paper (1980d) summarizing relationships between crystal size of alite and heating rate, showing that large alite can be produced by slow heating and not by burning at high temperature for long periods. In addition, Ono stated that, as a substitute for alite birefringence to determine maximum burning temperature, one could use the “etching degree” of alite, by which he meant the rapidity of color change and depth of etch of alite crystals on a polished surface. As a substitute for belite color to estimate the cooling rate, Ono recommended observation of belite crystal surface roughness in etched polished section.

Ono presented the following multilinear regressive equation (among several other similar equations), which gives a prediction of 28-day mortar-cube strength:

$$\begin{aligned} \text{28-day mortar-cube strength in lbs/in.}^2 = & 415 + 1163(\text{HM}) - 205(\text{FL}) \\ & - 0.005(\text{BL}) + 0.375(7\text{d}) \\ & + 89(\text{AS}) + 200(\text{AB}) + 74(\text{BS}) \\ & + 237(\text{BC}) \end{aligned} \quad (\text{Eq. 1})$$

where

HM = hydraulic modulus
 FL = free lime percent
 BL = Blaine specific surface
 7d = 7-day mortar-cube strength
 AS = alite size
 AB = alite birefringence
 BS = belite size
 BC = belite color

The microscopical parameters (AS, AB, BS, and BC) are given Ono's arbitrary numerical values of: excellent (4), good (3), average (2), and poor (1) as seen in Table 6-1. This paper was also published in the Onoda Cement Company Journal of Research (Ono, 1980b).

Ono (1980c) indicated that differences in cements with Blaines of 300, 330, 360, and 400 m²/kg could be easily detected by microscopical examination. Free-lime abundances of 0.5, 0.7, 1.0, and 1.5 percent were also said to be microscopically discernible, as well as hydration films on cement particles and flower petal or cauliflowerlike crystals of calcium hydroxide. Ono microscopically described the progressive sequence of clinker particle characteristics resulting from repeated grinding of clinker in a porcelain mortar and pestle, and sieving with a 150-mesh sieve, and related these data to clinker grindability. This paper also gives a brief history of Ono's professional career upon graduation from Tokyo University in 1950.

In 1981 Ono published an article tracing the microscopic changes of raw feed constituents along the length of a cement kiln, describing the phase changes in terms of temperature and raw feed position in the kiln. In addition, Ono described the characteristics of clinkers in response to different flame lengths and burning conditions. He presented the following multiregressional equations for the prediction of 28-day mortar-cube strength from microscopical data:

$$\begin{aligned} \text{28-day strength in kg/cm}^2 = & 253 + 6.4(\text{AS}) + 21.9(\text{AB}) \\ & + 4.0(\text{BS}) + 21.5(\text{BC}) \end{aligned} \quad (\text{Eq. 2})$$

$$\begin{aligned} \text{in lbs/in.}^2 = & 3422 + 86(\text{AS}) + 296(\text{AB}) \\ & + 54(\text{BS}) + 290(\text{BC}) \end{aligned} \quad (\text{Eq. 3})$$

where AS = alite size, AB = alite birefringence, BS = belite size, and BC = belite color, stated in the arbitrary numerical scale given previously. A standard deviation of 1.69 MPa (230 psi) was indicated for this strength prediction in Ono's presentation at the PCA and ICMA (1980d). See page 53 for an updated equation.

The crystal lattice constants of alite (*a,b,c*) and unit cell volume (*V*), determined by XRD, were studied in relation to alite double refraction (Ono, 1984). Alite with high double refraction was characterized by long *a* and short *b* and *c*, *V* was decreased, and (*a/b*)² was large. Laboratory-prepared alite, burned at high temperature for a long time, had a small *V*, large (*a/b*)², and a high double refraction. Therefore, XRD can be used in much the same way as the microscope in the quality control of clinker.

To study the formation of clinker and the temperature distribution in a 100-meter, 5000 t/d, NSP-rotary kiln, Ono (1995) sampled the coating and raw material remaining in the kiln for microscopical comparison with laboratory-produced clinker, and devised a computer simulation utilizing parameters in three zones (decarbonation zone, transition zone, and burning zone, the latter including the “cooling zone”). The material flow rate in the transition and burning zones is 2m/min; keeping times in these zones are 3.5 and 10 minutes, respectively. Through a range of temperatures from 1000° to 1500°C, the characteristics of CaCO₃ converting to CaO and the morphologies of C₂S and C₃S are described. Retention time above 1450°C is about 5 minutes over a 10-meter distance. Notable among many interesting observations in this summary are (1) the crystallization of new alite crystals (10 to 15 μm) and growth of old alite crystals (30 to 60 μm), at 1400° to 1500°C, and (2) the dissolution and dispersion of belite aggregations, with crystals of C₂S growing to sizes in the range of 20 to 30 μm in the same tempera-

ture range. Consequently the relation of retention time at high temperature to alite crystal size and belite dispersal is clearly revealed. Ono concludes that the physical shock and compression of material during movement down the big NSP kilns facilitates the burning of coarse raw material.

THE ONO METHOD

Ono's method of cement kiln evaluation is based on observations of clinker or cement powder mounted in a liquid medium on a glass microscope slide. A polarized-light microscope (the so-called "petrographic" microscope) is an absolute necessity, and magnifications at approximately 400X are recommended. To determine the parameters of the kiln conditions in Ono's method as described in 1995, cement or clinker powder is sieved through a 100- μm screen (approximately U.S. Sieve No. 140), and a powder mount is prepared with a liquid of refractive index in the range of 1.705 to 1.715. The principal value of Ono's technique is that it can be employed by a competent, well-trained microscopist on a small sample of clinker

during production. The rapidly performed test permits a virtually immediate modification of some kiln conditions, thus quickly optimizing some of the most important energy intensive variables that impact so importantly in the manufacturing process. The economic value of the technique is obvious.

The principal kiln conditions and microscopical parameters evaluated by Ono's technique are:

1. Rate of heating (alite size, AS)
2. Burning time at high temperature (belite size, BS)
3. Maximum temperature (alite birefringence, AB)
4. Rate of cooling (belite color, BC)

The above list indicates sole emphasis on silicate characteristics observed in powder mounts. However, as Ono recommends, data from other microscopical techniques, such as polished section and thin section, can be routinely used in a corroborative manner. A schematic temperature-time curve and the relationships between the silicates and burning conditions are given in Figure 6-1 and Table 6-1, respectively.

Table 6-1. Burning Condition and Microscopical Character of Alite and Belite (Ono, 1981)

Burning condition	Hydraulic activity			
	4 Excellent (+)	3 Good (vv)	2 Average (v)	1 Poor (-)
Heating Rate Size of alite (μm)	Quick 15-20	— 20-30	— (25) 30-40	Slow 40-60 (120)
Maximum Temperature Birefringence of alite	High 0.010-0.008	— 0.007-0.006	— 0.006-0.005	Low 0.005-0.002
Burning Time Size of belite (μm)	Long (20) 25-40 (60)	— (15) 20-25	— (10) 15-20	Short 5-10
Cooling Rate Color of belite	Quick Clear (C)	— Faint yellow (FY)	— Yellow (Y)	Slow Amber (A)
Birefringence of belite	0.012	0.015	0.017	0.018
Content of alpha	Abundant (40%)	Medium (20%)	Few (10%)	Nil (0%)

Note: If MgO in clinker is higher than 1.8%, birefringence of alite in the table should be increased by 0.001. If MgO is less than 1.2%, birefringence is decreased by 0.001. Belite crystals with abundant dotlike impurities indicate slow cooling. Ono's numerical designations of 4, 3, 2, and 1 were placed in the table by the present writer.

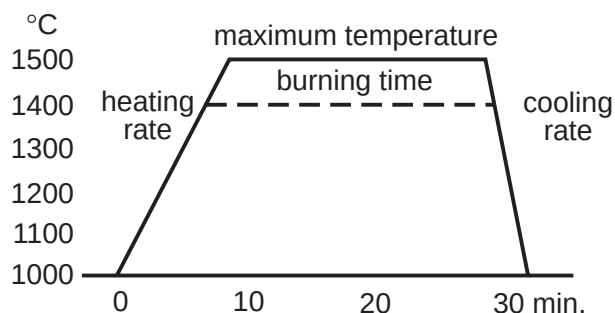


Fig. 6-1. Schematic temperature-time relation of clinker burning (Ono, 1980c).

Ono's method as used by the author may not be precisely the technique used or taught by Ono. Where significant deviations occur, a brief explanation is attempted in the section entitled "Comments on the Ono Method." The technique used by the present author is as follows:

A representative sample of clinker, say approximately 0.5 kg, is crushed to cement fineness, and a small portion is placed on a glass microscope slide with a spatula. After placing the cover glass on the powder, a few drops of oil of known RI (1.715 to 1.720), placed at the edge of the cover glass, are drawn inward by capillary action, thereby immersing the clinker particles. Hyrax™ or Meltmount™ (RI = 1.70) may be used as a permanent media (see Chapter 4). Using a standard petrographic microscope slide (46x24 mm) and cover glasses (of approximately 10x10 mm), up to four powder mounts can be prepared on one slide, thus facilitating comparisons of hourly samples.

A standard polarized-light microscope equipped with a Sénarmont compensator, having magnifications up to 400X, and a rotatable analyzer with a graduated scale are used by the writer. All the observations are made with the use of the upper element of the substage condensing lens on the microscope.

An extraction of the matrix phases with a warm KOH-sugar solution concentrates the silicates for easy determination of alite birefringence and belite color. Details are given in Chapter 11.

Alite Size (AS)

Alite size in the Ono method refers to the most commonly occurring alite crystal *length*. After scanning the powder mount for clinker particles containing whole or nearly whole alite crystals, one measures the lengths of the most commonly occurring crystal sizes, using a calibrated eyepiece scale. "Most commonly occurring" size refers to the modal crystal length. An average of measurements on approximately 10 selected crystals

is recommended. Crystal length, width, and thickness can be measured by crystal rolling in a high-viscosity refractive-index oil, but the procedure is tedious. Alite crystals can easily be measured in reflected light, using a finely polished, suitably etched, cross section of clinker or cement. *Clinker polished sections*, in this writer's opinion, give a better measure of average crystal length because an abundance of clearly cross-sectioned crystals is presented to the viewer for examination. Crystals chosen for size measurement in powder mounts and thin sections are generally *not* those chosen for birefringence determination.

Alite size (according to Ono) depends on burning rate and crystallization rate. Quick-burning by a short flame produces small crystals formed (a) at low temperature by direct contact of CaO and C₂S, and (b) at high temperature; both developments are relatively rapid. Slow-burning in a long flame produces large alite crystals; the rate of crystallization is generally slow, except during the initial stages. Crystal enlargement by cannibalism is also slow and negligible in slow-burning.

Burning too near the discharge end of the kiln, where the temperature change is 1400°C to 1000°C, also produces small alite, and the clinker is usually poorly burned. Alite sizes of less than 15 μm in a 1000 tons-per-day kiln can be indicative of poor burning; a 20-μm alite size is typical of poor burning in a 4000 tons-per-day kiln (Ono, 1980c). A well burned clinker (f-CaO ≤ 0.6%) does not have alite crystals under 20 μm (Ono, 1995).

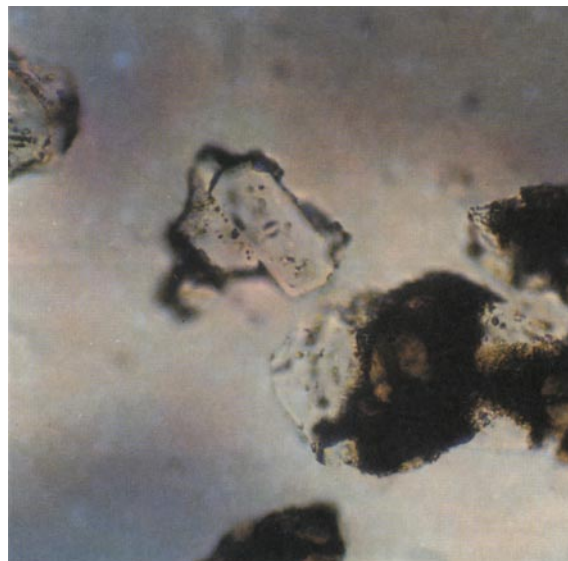
The convexities and concavities on the surface of alite are formed during the last stage of crystal growth during cooling. The roughness of the crystal surface has been observed in several relationships: well burned clinker by a long flame, a well mixed assemblage of alite and belite, alite close to free lime, large crystals of alite and belite in areas rich in matrix, and, areas where the matrix is coarsely crystalline, the ferrite is prismatic, and C₃A is well etched (Ono, 1995).

Ono (1995) characterized the alite in raw (poorly) burned clinker in relation to the occurrence of the alite (1) next to free lime and (2) next to a belite nest. Where alite is next to a free lime cluster, the alite is small, isolated and dispersed, separated from free lime, contains a large amount of melt, is strongly etched, and is heterogeneous and zoned. Alite next to a belite nest is relatively large, connected and welded, touching the belite, contains a small amount of melt, is weakly etched, and is homogeneous and flat (not zoned).

PHOTOMICROGRAPHS ILLUSTRATING ONO'S METHOD

Photograph 6-1 Ono's method for apparent birefringence of alite in powder mount. Crystal length-to-width ratio = approximately 2:1. Ono measures particle width. Other observers, the present writer included, measure crystal width. (S#A6616)

Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm

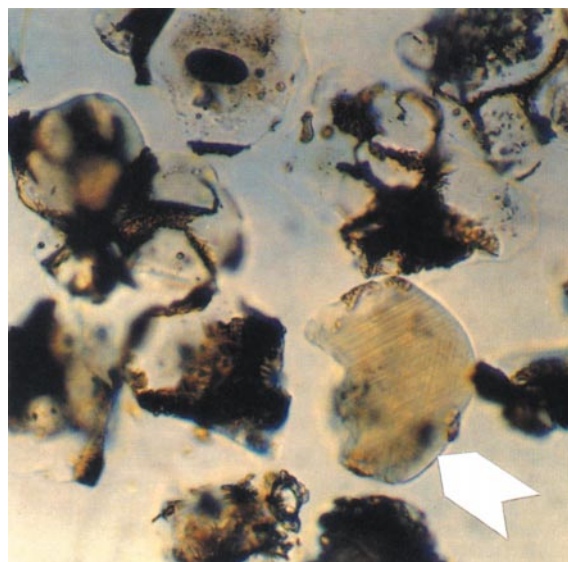


Photograph 6-2 Same as Photograph 6-1 but in cross polars and 45° from the extinction position. (S#A6617)



Photograph 6-3 Crushed clinker in refractive-index oil showing large, clear to pale yellow, round belite (arrow) with typical internal cross lamellae. Moderately high maximum temperature, long burning time, slow heating rate, quickly cooled. Dry-process kiln with flash calciner, 5000 tons/day. (S#A6618)

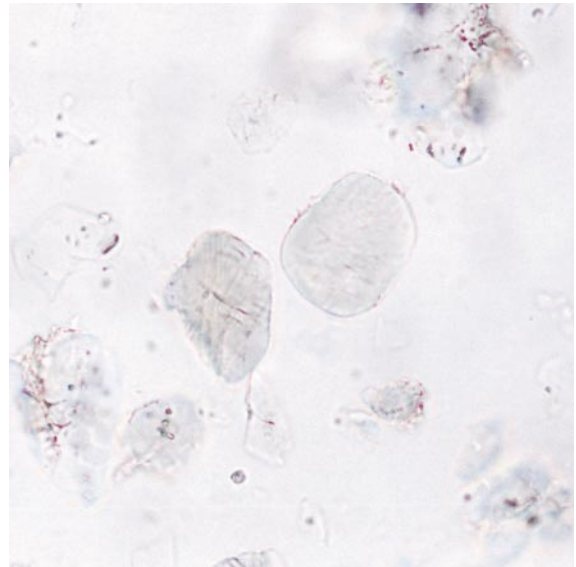
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS ILLUSTRATING ONO'S METHOD (CONTINUED)

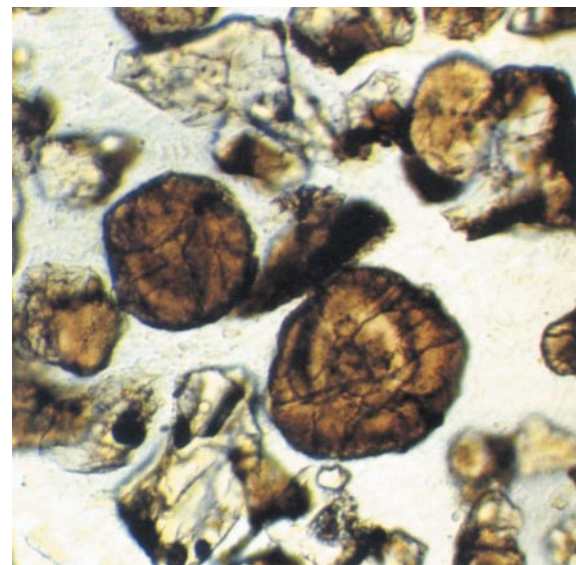
Photograph 6-4 Clear to faint yellow, round belite crystals in powder mount (44- to 75- μm fraction). Fast to moderately fast cooling. Coal- and coke-fired, dry-process kiln, 45 MPa. (S#A6619)

Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



Photograph 6-5 Amber belite crystals in 44- to 75- μm fraction of crushed clinker. Low maximum temperature, long burning time, slow heating rate, moderately slow to slow cooling. Coal-fired, wet-process kiln. (S#A6620)

Powder mount
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



Alite Birefringence (AB)

The term “birefringence” refers to the difference in indices of refraction ($n_2 - n_1$) of relatively slow and fast light rays, respectively, as they pass through an optically anisotropic material, which divides the incoming light into two refracted rays traveling in slightly different directions at different velocities. The birefringence (B) of an anisotropic substance is a constant and dependent on the velocities of light vibrating along certain crystallographic directions. Therefore, if the observed light is not vibrating along these specified directions, the maximum value of B will not be measured, and the maximum temperature not correctly interpreted.

Retardation (Δ) is the distance that the slow light ray lags behind the fast ray and is directly related to crystal birefringence and thickness. In other words,

$$\begin{aligned} \text{Retardation, } \Delta &= (\text{Birefringence, } B) \times (\text{thickness, } t) \\ \text{or } \Delta &= (B)(t) = (n_2 - n_1)(t) \\ \text{and, therefore, } B &= \Delta / t \end{aligned} \quad (\text{Eq. 4})$$

Thus the problem, in practice, becomes the measurement of Δ and t . Delta can be measured with the use of a Sénarmont compensator. The Sénarmont compensator is a crystallographically oriented, thin mica plate designed to produce light path differences of more or less than a quarter wavelength. The fast and slow light velocity directions in the compensator are parallel to those of the analyzer and polarizer of the microscope. It is commonly used for determination of retardations of materials of low birefringence such as alite. Use of the upper swing-out element of the substage condensor intensifies the light and facilitates observation of alite crystals and determination of belite color. With the Sénarmont compensator inserted in the accessory slot over an alite crystal viewed in cross-polarized light, linearly polarized light is produced just below the analyzer. The phase difference (Δ) of this light can be reduced to zero by a measured rotation (θ) of the analyzer. Monochromatic light is required and, therefore, a green filter (wavelength = 546 nanometers) is used.

To measure alite birefringence using a Sénarmont compensator and the upper element of the substage condensor, Ono recommends the following steps:

1. Select a relatively bright alite crystal (appearing white to yellowish white to bright gray in cross-polarized light), having length to width dimensions of roughly 2:1 and, preferably, attached to other clinker phases on at least three sides so that a whole crystal can be examined (Photographs 6-1 and 6-2).

2. Measure and record the crystal width (W) in μm using the calibrated, graduated eyepiece scale.
3. In cross-polarized light, rotate the stage 45° from crystal extinction (darkness) as illustrated in Photograph 6-2. For crystals that exhibit a strongly wavy (undulatory) extinction, birefringence data may be questionable. Therefore, crystals with uniform or nearly uniform extinction are sought.
4. Insert the Sénarmont compensator, properly oriented so that the darkness of the background results in cross-polarized light. Place a green filter in the path of the incoming light. The green filter facilitates observation of the alite crystal compensation point determined in the next step.
5. Rotate the analyzer (upper polarizing element) to crystal darkness (compensation); read the angle of rotation, theta (θ), indicated on the graduated analyzer scale; and record. If the crystal darkens from edge to center (inward movement), the light interference is said to be “subtractive.” If the crystal darkens from center to edge (outward movement), the light interference is said to be “additive.” In the latter case, the angle of rotation is more than 90° and is subtracted from 180° to give θ . The calculation of birefringence, using θ , is as follows:

Retardation (Δ) is a direct function of theta (θ) and the light wavelength lambda (λ) passing through the filter and is expressed

$$\Delta = \frac{\lambda \theta}{180} \quad (\text{Eq. 5})$$

where λ = wavelength in μm

θ = angle of analyzer rotation.

As previously seen,

$$B = \Delta / t$$

and consequently,

$$B = \frac{\lambda \theta}{180} / t \quad (\text{Eq. 6})$$

Assuming that the interference is subtractive, the following equation is used to calculate birefringence:

$$B = \frac{\Delta}{t} = \frac{(\theta)546}{180(0.75)(W)1000} \quad (\text{Eq. 7})$$

where θ = angle of analyzer rotation

546 = wavelength of green filter in nanometers, which is divided by 1000 to convert to micrometers

and W = crystal width in micrometers.

The equation, therefore, reduces to:

$$B = \frac{\theta}{W} (0.004044) \quad (\text{Eq. 8})$$

This formula has been found by the author to produce an apparent birefringence which, more often than not, easily fits with what is thought to be the correct interpretation of kiln conditions or what has been determined in the laboratory. However, Ono has stated that 0.75 times the particle width (instead of crystal width) is the best approximation of t (Ono, 1981). The ratio of vertical thickness to horizontal width of the particles on the slide is statistically 0.75, according to Ono. Alite birefringence is determined on *particles* with thicknesses ranging from 30 to 60 μm and horizontal dimensions of 40 to 80 μm , corresponding approximately to the same order of magnitude as the alite and belite crystal sizes, which, along with the belite color, are determined on the same slide in 10 to 15 minutes. Ono, however, recommends that a combination of polished sections and powder mounts is the preferred method of examination, as does the present writer. This topic will be discussed later in this section.

If true crystal thickness is required, the crystal may be rolled in refractive-index oil to the proper measurable position by tapping the cover glass with a pencil point while observing the particle motion. A high-viscosity liquid such as marine varnish ($n = 1.63$) facilitates the technique of crystal rolling and measurement.

The Babinet compensator, rather than the Sénarmont, is preferred by some microscopists. The Babinet compensator fits into a specifically built slot above the objective of the microscope and is comprised of two precisely cut, crystallographically oriented wedges of quartz. A crystal is set 45° from extinction in cross-polarized light and the 546-nanometer filter is placed on the light source. As the sliding portion of the compensator is slipped into the optical path, the crystal being examined will slowly darken as light compensation occurs. If the crystal is in the subtractive position, the thinnest part will darken first, followed by darkening of the center. The compensator reading lens is inserted, focused, and a scale, observed on the cross-hairs, is read and recorded as "X."

The formula for calculating retardation, Δ , with the Babinet compensator is:

$$\Delta = a_{\lambda 546} (X - b) \quad (\text{Eq. 9})$$

where a and b are constants determined by the compensator manufacturer and normally given in two wavelengths (λ): 546.1 or 589.3 nanometers.

The thickness, X , is determined by rolling the crystal, or it can be approximated by other techniques as previously described. Alite birefringence is calculated as follows:

$$\text{Birefringence, } B = \Delta / t \quad (100) \quad (\text{Eq. 10})$$

A third method of determining alite birefringence requires a refined appreciation for the various colors of alite as seen in cross-polarized light and also the use of a third-order red accessory plate (gypsum). The Michel Lévy Color Chart, which is a required part of this technique, can be found in almost all optical mineralogy textbooks and is included in the back of the present publication. The Chart graphically displays the relationships between interference color, retardation, thickness, and birefringence. The procedure utilizing alite interference color, a gypsum accessory plate, and the Michel Lévy Color Chart is as follows:

1. Select a bright alite crystal (one that exhibits the maximum interference color in cross-polarized light) and rotate the microscope stage so that the crystal is at its extinction position (dark).
2. Insert the gypsum accessory plate (wavelength = 530 nanometers). The interference color of the alite crystal will be first-order red (530 nanometers), as seen on the Chart.
3. Rotate the stage 45° to the left of the extinction position, and match the yellow interference color of the crystal observed in the microscope to the same shade of yellow on the Chart. Mark the position of color identity on the Chart. Rotate the stage 45° to the right of extinction, observe the blue-green crystal color, find it on the Chart, and mark the location.
4. Measure the distance between the color identity points on the Chart and divide by 2.
5. Measure the crystal thickness (μm) by rolling the crystal, or estimate the thickness by determining the crystal width and multiplying by 0.75.
6. On the side of the Chart labeled "Thickness," find the line corresponding to the value determined in Step 5. From the left end of the line, measure the distance finally determined in Step 4. Project a line diagonally to the upper right and read the graphically determined birefringence at the top of the chart.

One of the principal problems with this method of determining birefringence is the variance in color interpretation between workers and even within a single observer. With practice, however, this technique is quite fast and correlates well with methods using other accessory plates. One can easily distin-

guish relatively high and low birefringences in powder mount without charts or calculations after becoming familiar with the optical characteristics of alite. Obviously, this requires frequent practice and an unbiased observation, as does all reliable microscopy.

Alite birefringence observed in clinker is a function of burning temperature and crystal modifications. High temperature, trigonal (R) alite has a birefringence of 0.007 to 0.010. The disordered monoclinic variety (M_1), retaining some of the R form, and the M_3 form (Maki and Chromy, 1978) have birefringences of 0.005 to 0.007. An ordered M_1 form has a birefringence of 0.004 to 0.005. The triclinic form (T_2) has a birefringence less than 0.004.

The birefringence of alite is also a function of where it forms in a clinker nodule. Small alite crystals near a nest of free lime have low birefringence. Large or medium crystals near a belite nest have high birefringence. Isolated crystals blown around in the high-temperature burning zone have very high birefringence (Ono, 1980c).

Belite Size (BS)

This parameter is the average of the longest diameters of approximately 10 crystals. Typical belite crystals are seen in Photographs 6-3 through 6-5. In selecting the crystals for measurement one should look for crystals representing the most commonly occurring crystal size. Belite size, in the writer's opinion, is best determined with polished, etched sections or thin sections.

At a temperature of approximately 1100°C to 1200°C alpha-prime belite forms as small crystals; at about 1400°C the crystals change to alpha and exhibit considerable growth. Crystal size of belite, therefore, is primarily dependent on the time maintained above 1400°C—the burning time.

Belite Color (BC)

Perhaps the most important of the four parameters, belite color is estimated using an arbitrary numerical scale: Amber (1), Yellow (2), Pale Yellow (3), and Clear (4). Crystals with abundant dotlike inclusions (from exsolution) are given a ranking of 1. One should examine approximately 10 belite crystals which are not coated with interstitial phases, noting the most commonly occurring color. Rowe (letter, 1985) recommends observation of belite color in a powder mount made with the minus 100-mesh (0.149 mm) fraction. Use the upper swing-out element of the substage condensor to intensify the light.

As in the estimation of alite birefringence, one should eliminate the extremely large and the very

small crystals. A thin section is particularly advantageous in estimating belite color because the observed belite crystal is a cross section and, therefore, uncomplicated by attached ferrite. The observer should not be unduly influenced by extremes in the range of colors observed. Examination of "true" color and crystal surfaces of silicates is facilitated by a study of samples from which the matrix phases have been extracted with a potassium hydroxide and sugar solution (Hawkins, 1982). See Chapter 11 for details of this extraction. Belite colors are illustrated in Photographs 6-3, 6-4, and 6-5.

Belite in the alpha form can contain up to 2 percent alumina, 2 percent iron oxide, and 3 percent sodium oxide, but only traces of these oxides in the alpha-prime form. The amounts of these impurities, therefore, are functions of the cooling rate. As cooling and exsolution occur, belite changes from clear to faint yellow, to yellow and amber, depending on the rate of temperature decline concentrating impurities adjacent to the lamellae (Ono, 1995). Slowly cooled, rotary kiln clinker produces belite, the center of which is Type I changing to Type Ia with dotted and cross striations, while the rim of Type I changes to Type III, and the round surface and spherical aspects of high-temperature alpha remain (Ono, 1995). Very slow cooling results in dispersed dotlike impurities in otherwise clear belite. Belite colors observed in transmitted light have been generally correlated with data from reflected-light examination of polished sections (Ono, 1981).

Kawamura and Mizukami (1969), while investigating the relation between raw feed containing various particle sizes and different Blaines of quartz and feldspar, described belite rings. Ono (1995) stated that belite rings with diameters of 300- to 600- μ m develop from coarse silicates (quartz, feldspar, and shale), forming large Type I crystals (40 to 60 μ m) which are colorless even in slowly cooled clinkers.

Use of Ono's Table to Interpret Kiln Conditions and Formula to Predict 28-day Mortar-Cube Strength

Each of the four parameters for the kiln conditions given in Table 6-1 (heating rate, maximum temperature, time at maximum temperature, and cooling rate) is given numerical ranking of 4, 3, 2, or 1, according to the data determined by microscopy. Consequently, the predicted 28-day mortar-cube strength can be calculated with Ono's equation (1995), which is slightly different from his previously published equation and apparently replaces the table of 28-day strengths used earlier (1981). Ono's latest equation (1995), stated in standard units, is:

$$F(28d) = 25.309 + 0.513AS + 2.027AB + 0.334BS + 2.179BC \text{ MPa} \quad (\text{Eq. 11})$$

(standard deviation = 1.67 MPa for the strength range 29.42 to 44.13 MPa)

For example, assume the following data: alite size (AS) 50 μm (slow heating rate), alite birefringence (AB) 0.0085 (high maximum temperature), belite size (BS) 30 μm (long time at maximum temperature), and belite color (BC) is pale yellow (moderately fast cooling). Therefore, the numerical rankings for these parameters are 1, 4, 4, and 3, respectively. Thus, $F(28d)$ is calculated:

$$\begin{aligned} F(28d) &= 25.309 + 0.513(1) + 2.027(4) + 0.334(4) + 2.179(3) \\ &= 41.18 \text{ MPa} \end{aligned}$$

Free-lime contents of 1 to 2 percent may result in 28-day mortar strengths less than the predicted value (Ono, 1980c). In addition, Ono states that the alite birefringence value should be increased by 0.001 in the table if the magnesium oxide content of the clinker is greater than 1.8 percent; the table value should be decreased by 0.001 if the magnesium oxide is less than 1.2 percent. A negative correction factor of 0.001 is also recommended by Ono if the sulfate (SO_3) content is greater than 1.25 percent.

In a letter response to questions about clinker quality, burning conditions, and prediction of strength, Ono (1980) made the following statements:

1. The effect of alite and free lime percentages and Blaine on the 28-day strength is small and correction is usually unnecessary.
2. Poorly burned clinker frequently contains many small belite clusters. If the raw mix contains coarse quartz grains, belite clusters appear even in well-burned clinker, and the alite size has a wide range.
3. Alkalies increase 7-day strength, but the effect on 28-day strength is small. Osbaeck (1979) said that alkalies decrease 28-day strength.
4. Grindability of quickly cooled clinker is good. Amber belite is ground at the last stage. J.M. Butt (1974) stated that good grindability of quickly cooled clinker is due to plenty of micropores in the interstitial phase.
5. A section of alite parallel to the trigonal plane (001) is weakly etched compared with a section of another direction in a twinned crystal. In a zoned crystal, a zone with higher birefringence is strongly etched compared to a zone with lower birefringence. If polishing and etching techniques are proper, etching degree is an excellent index of hydraulic activity of alite.

Ono stated (letter, 1977) that an alite birefringence slightly higher than 0.007 could be written 0.007⁺ and ranked as “good”; a birefringence slightly lower than 0.008 may be written as 0.008⁻ and ranked as “excellent.”

Ono readily admits that the powder-mount parameters used to interpret burning conditions are merely expedients and that they provide data in which variations reflect *relative* changes in kiln conditions. Herein lies, perhaps, the salient point of the Ono method: If the method can be used to determine correctly the *relative* changes in the individual variables (maximum temperature, burning time, rate of heating, and rate of cooling), then the use of the method can be rewarding because immediate changes in some of the major energy-related production processes can be made. That the parameters are somewhat imprecise or that their application is not as rigorous as one might want should not detract from the essential purpose of the method: detecting relative changes in kiln conditions.

Successful application of Ono's theories and techniques in routine clinker production and in kiln start-up operations is recorded by Prout (1979) with powder mounts and polished sections providing essential data. Prout strongly asserts that application of the Ono technique should be more “qualitative than quantitative” and that the data should be interpreted *relatively* for optimum benefit (Prout, oral communication, 1984). Furthermore, Prout used the predicted strength as an “Index Number” for relative comparison, a procedure with which the present writer is in complete agreement.

Using a somewhat different approach, Knöfel (1989) reliably predicted the 28-day mortar strength with a simple formula containing microscopically determined percentages of alite, belite, aluminate, and ferrite. The equation is: $F_{28} = 3(\text{alite}) + 2(\text{belite}) + \text{aluminate} - \text{ferrite}$. F_{28} is termed the “characteristic strength.” The equation is designed for use *within a cement plant* where production conditions over the period of investigation are virtually identical.

A bivariate linear equation, containing factors such as phase percentages, crystal sizes, morphology and cluster indexes, for predicting the 28-day mortar strength was presented by Sinha, Rao, and Akhouri (1991). The standard deviation was said to be 17.9 kg/cm², agreeing closely with the actual strength.

A paper by Takagi and Kawashima (1980) shows the effects of various kiln conditions on alite, belite, and interstitial phases. These authors present a clinker “Character Index,” a collection of parameters which, when plotted against compressive strength at 28 days, forms a sigmoidal curve. The Ono parameters figure significantly in the formulation of the Character Index, as seen in the following list of phase characteristics:

1. Alite—crystal size, optics, zoning, fringing, habit, crystal form;
2. Belite—crystal size, optics, morphology and texture, recrystallization, “gelappster,” exclusion of impurity;
3. Interstitial—crystal size and optics.

Kiln variables with which some of the phase characteristics are correlated are kiln speed, coating of burning zone, burning zone temperature, flame length, burning zone length, temperature gradient, cooling rate, and atmosphere.

The Ono parameters were found to be the dominant variables (above chemical composition, including the normal moduli and porosity) in an experiment to explain problems of grindability (Kawamura and others, 1982). These authors gave the following equation to predict the Blaine surface area (BL) with the Ono method, stating the microscopical factors in the arbitrary scale of 4, 3, 2, and 1 as given previously:

$$BL = 1513 + 171AS + 167AB + 417BS - 153BC \quad (\text{Eq. 12})$$

correlation coefficient = 0.840
standard deviation = 97 cm²/g
n = 30

where AS = alite size

AB = alite birefringence

BS = belite size

BC = belite color

Large belite nests were shown to be indicative of poor grindability, even though the same clinker may have relatively high porosity. Clusters of belite crystals remained undivided even at the final grinding stage.

Using alite birefringence and belite size, Ueda and Suzuki (1985) were able to monitor the variable calorific value of coals and make adjustments in the kiln conditions to maintain clinker quality.

The results of microscopy by the Ono method are considered an important part of the data base in a computerized multivariate analysis conducted routinely for cement quality control in plants of the Onoda Cement Company in Japan (Aizawa, 1985). Microscopical data are said to be helpful in making frequent adjustments in kiln parameters, clinker silo operation, and adjustment of cement fineness. The continually updated analysis involves the following process variables: burning zone temperature, kiln outlet clinker temperature, secondary air temperature, extraction air temperature, kiln rotation torque, nitrous oxide, percent clinker passing the 5-mm screen, and liter weight. In some Japanese cement plants, clinkers are recycled until the microscopical targets have been met, according to Uchikawa (1992).

Application of the Ono Method to the evaluation of kiln conditions in relation to cement hydration processes and types of added sulfate (natural gypsum, beta hemihydrate, and anhydrite II) is the subject of a paper by Uchikawa and others (1984). These authors showed that the “burning degree,” defined as an exponential mathematical function of maximum temperature (T), critical temperature $T_o = 1250^\circ\text{C}$, and the retention time (time required to keep the clinker above T_o), corresponds closely to the amount of free lime, liter weight, and microscopical data. The highest 28-day mortar-cube compressive strength (43.1 MPa) was obtained with cement made from the well-burned clinker and gypsum. Well-burned and poorly burned clinker were characterized by the following factors:

	Well burned	Poorly burned
Liter weight (kg/L)	1.25	1.10
Free lime (%)	0.17	1.64
Alite size (μm)	40.00	20.00
Alite birefringence	0.007	0.004
Belite size (μm)	30.00	10.00
Belite birefringence	0.012	0.018

Ono (1991) listed some of the characteristics of poorly burned clinker: free lime greater than 4.5%, tightly packed large free-lime nests, belite nests with a surrounding of small alites, high porosity, a loose framework of free lime and alkali aluminate, and a flow pattern of matrix into the free-lime nest. Well-burned clinker was said to contain small free lime and octahedral periclase from dolomite and coarse aluminate and ferrite, resulting from equilibrium crystallization.

Personal correspondence from Ono (1979) listed some of his preliminary conclusions relating grindability, burning conditions, and clinker microstructure:

1. Clinkers with high Hydraulic Modulus (HM), defined as $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$, are softer and more easily ground. (No precise values of HM were given.)
2. The fine powder fraction of clinker is rich in alite fragments. The coarse fraction is rich in agglomerates of small brown belite and agglomerates of minute alite crystals combined with dark interstitial phase.
3. Well-burned clinker with a high VW, volume weight, is difficult in coarse grinding (getting it to pass the 1-2 mm sieve), but soft in fine grinding (<88 microns). VW is the weight of clinker nodules, 5-10 mm diameter, in a liter container. Optimum VW is approximately 1.35 kg/L.
4. High VW clinker is deficient in large pores, larger than 1 μm (usually 50 to 500 μm), and rich in minute

pores (less than 1 micron), actually approximately 0.1 mm. The volume of minute pores is intimately connected to grindability into a fine powder. The minute pores seem to be gaps between the dendritic structure of the interstitial phase.

The volume weight (VW) of clinker, according to Ono (1995), is [1.43 (1-porosity)]. VW for ordinary clinker is 1.20 to 1.25 kg/L, and porosity is 0.13 to 0.16 cc/cc.

Ono (1995) listed clinker characteristics in relation to burning degree, stating that well-burned clinker has volume weights from 1.30 to 1.37 kg/L, and porosities of 0.04 to 0.07 cc/cc. Furthermore, well-burned clinker is characterized with alite crystals ranging from 30 to 40 μm , perhaps up to 60 μm , and dispersed belites from 20 to 40 μm . In contrast, poorly burned clinkers have volume weights of approximately 1.0 kg/L and porosities of 0.25 to 0.35 cc/cc. Poorly burned clinker generally has a wide range of alite crystal sizes (15 to 60 μm , averaging 30 to 40). In such clinkers belite aggregations occur in hollow spheres (bubbles) with diameters ranging from 200 to 400 μm , also in compact clusters. Belite crystal sizes in poorly burned clinker were also said to range from 10 to 30 μm .

ADDITIONAL COMMENTS ON THE ONO METHOD AND RECENT RESEARCH

Alite Birefringence

According to Ono, Kawamura, and Soda (1968), alite birefringence is a function of maximum temperature in the kiln load: the higher the temperature, the larger the birefringence. Birefringence in Ono's method is measured on alite crystals in clinker particles mounted in RI oil and observed in transmitted, polarized light.

To date, more than 1500 alite birefringences have been determined on crystals in thin section by the present writer, using clinkers embedded with quartz in epoxy resin. Some of these results have been presented in a microscopical comparison of North American and foreign clinkers (Campbell, 1979). The known birefringence of quartz (0.009) was used to calculate the thickness of the section. No correction was made for differential hardness relief on the thin-section surfaces. Average alite birefringence determined by the thin-section method is 0.0044, with a standard deviation of 0.00099. Maximum and minimum values are approximately 0.0083 and 0.0022, respectively. A discrimination among and within zoned crystals was not made. Powder-mount determinations of birefringences, using Equation 8 and clinkers from the same samples studied in thin section, resulted in an average birefrin-

gence of 0.0078, standard deviation of 0.0016, and maximum and minimum values of 0.0104 and 0.0034, respectively.

It is clear that the Ono formula (Eq. 7) gives an *apparent* birefringence and, perhaps, should be indicated "B*" (read "Bstar"). Ono is in agreement with this suggestion (1981). Nevertheless, although one does not determine the true birefringence with Ono's method, the data can be validly interpreted to indicate relative changes in maximum burning temperature, interpretations which can be corroborated by other microscopical data. The apparent birefringence as an indicator of maximum temperature is being used by many microscopists in Asian and North American cement plants.

One of the principal difficulties in the determination of apparent birefringence by powder mount is finding proper crystals, those with relatively bright interference colors and length to width ratios of approximately two. Extreme difficulty in satisfying the ratio requirement may, in itself, be indicative of burning conditions such that the desired crystal development was inhibited.

Pennell (1987) discussed the differences between alite birefringences determined with thin sections (the present author's data) and powder mounts, illustrating the fact that the latter determination was not accurate, but concluding that the values may be "tolerable" for correlation purposes.

The problem of measurement of crystal thickness (t) for the determination of alite birefringence in powder mounts has been the subject of much discussion. Prout (oral communication, 1984) finds that the thickness can be approximated by the equation $(\text{length} + \text{width})/2$, giving a reasonable apparent birefringence.

The factor of 0.75 in the denominator of Eq. 7 for alite birefringence was statistically derived to account for deviations between true and observed birefringences of an alite crystal in which the "X" vibration direction is not exactly parallel to the microscope stage and the "Y" and "Z" directions are not precisely known. In order to minimize this deviation, which lessens the birefringence, a crystal-thickness-to-particle-width ratio of 3/4 is assumed (Ono, letter, 1978). The clinker particle, in this case, was illustrated to contain only part of an alite crystal.

Phillips (1971, p. 101) stated, "Loose fragments consistently lie on their broad side, and it is safe to assume that fragment thickness is slightly less than the narrow dimension that he can see and measure."

Preliminary data from optical techniques with powder mounts to determine apparent maximum and minimum indices of refraction of alite, using an RI oil of 1.72 and its dispersion curves, were discussed by Stark (1980). Stark found a birefringence range of 0.0030 to

0.0065 with this technique, compared to a range of 0.0030 to 0.010 by the "standard" Ono procedure in which the factor 0.75W is used; Ono-method values for birefringence were consistently higher.

A different interpretation of alite has been given by Fundal (1982), who stated that alite crystals are twinned individuals of a lower symmetry which imitate a higher symmetry (a mimetic relationship). The monoclinic form of alite was said to have an index of refraction of 1.72 and a birefringence of approximately 0.0050. Triclinic alite was reported to be polysynthetically twinned in a fused clinker and have a birefringence of 0.0020. Alite birefringence, however, exhibits two average values in Fundal's Table 1 (1982): 0.0043 (monoclinic) and 0.0023 (trigonal and possibly triclinic). In fused clinker the monoclinic form was observed zonally in thin section on the interior triclinic form. The zoning relationship was not revealed by polished section etches with HF-vapor or 4 percent HNO_3 in ethanol. Trigonal alite was seen associated with void deposits of alkali sulfate.

Consequently, Fundal (1982) reports results contradictory to Ono's theory of kiln interpretation, namely, that:

1. Determination of alite birefringence in powder mount is subject to an error of approximately 0.0006 and that a "petrographers rule" of crystal width being equal to $4/3$ crystal thickness is not valid as a short cut.
2. Alite birefringence determined in thin section, using quartz as an internal thickness standard, is a suitable method. However, a correlation with burning temperature was not evident.

Fundal (1982) measured crystal length (L) as an approximation of thickness (t). Fundal's alite birefringences are, therefore, quite similar to true birefringence because the denominator (L) in the birefringence equation is relatively large. Fundal (F.L. Smidth report, Jan. 2, 1978) stated that the variations in D/L , where D = crystal thickness, account for the variations in alite birefringence by Ono's technique, and that small, flat crystals give high birefringences using the Ono formula. A "form factor" was said to represent the birefringence determined by Ono's method. Statistically treated data concerning crystal dimensions and birefringence are greatly needed.

In response to Fundal (1982), Lee (1983) pointed out the bimodality of alite birefringence determined by Maki and Kato (1982), who demonstrated relationships with magnesium oxide content in the crystal. Lee restated the conclusion by Maki and Kato that the M_1 (monoclinic) phase appears pseudotrigonal in an X-ray powder-diffraction pattern. Lee believed that Fundal's comparison of alite compositional and optical data with a tectosilicate solid-solution series, such as plagioclase feldspar, or with a nesosilicate series, such as olivine and monticellite, did not suffice to explain the variation in alite birefringence.

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Nagashima, Asakura, and Uda (1983) have shown with laboratory experiments that the M_1 variety of alite precipitated from the melt is always observed at the maximum burning temperature but it is converted to M_3 with longer holding time. Slow burning results in the M_3 variety even though the holding time is long (up to two hours). These authors also suggested that (1) alite birefringence reaches a maximum in a shorter time when the burning temperature is higher and the raw mix finer, (2) alite impurities decrease with an increase in the maximum temperature, and (3) correlations between alite birefringence and magnesium oxide content do not exist and a high content of impurities is not essential for making M_3 stable at ambient temperature.

Asakura, Uda, and Kawabata (1984) classified alite into four varieties according to birefringence and texture determined by microscopical examination of plant clinkers: (1) coarsely crystalline alite (M_1 variety) with a birefringence of 0.003, possibly formed in slow burning; (2) zoned crystals with round, dusty M_1 cores that have low birefringence (0.003) and M_3 rims characterized by fine inclusions and relatively high birefringence (0.005), the round M_1 cores thought to exhibit the effects of possible remelting with M_3 precipitating from the melt on the original crystal; (3) dusty M_3 alite, with a birefringence of 0.004 to 0.005, interpreted to result from the second variety (described above) by successive addition of heat; and (4) euhedral, prismatic crystals with a birefringence of 0.006 and without fine inclusions, said to be a possible result of rapid heating.

Chen, Conjeaud, and Lehoux (1985) estimated burning zone temperatures with three techniques: by burnability studies of the raw mix, by electron-microprobe analysis of alite in clinker, and by birefringence of alite. The latter method was said to be the least accurate, due possibly to clinker magnesium oxide and sulfate contents, kinetics of alite crystallization from a melt, raw mix particle size, and variable calcination rates.

Nagashima and others (1988) in a laboratory study clarified some of the kiln conditions for the M_1 and M_3 varieties of alite. The M_3 variety, formed by rapid burning, is characterized by fine crystal size, and prismatic, euhedral, clear crystals with few inclusions. The M_1 variety, formed by relatively slow burning or under a low temperature, is typically coarse. With prolonged holding time M_1 changes to M_3 with high birefringence and numerous fine inclusions, giving the crystal a dusty appearance. M_3 was shown to have a slower hydration at 3 days but at later ages develops a relatively dense paste and higher strength than M_1 at water-cement ratio of 0.5.

In a series of laboratory experiments, Maki and others (1995) described a very fast first stage and relatively slow second stage of alite crystallization controlled by diffusion of CaO from the interstitial liquid. Nucleation rate is high at first, forming many small crystals, then as CaO supersaturation in the liquid decreases, crystal growth was dominant, developing crystals by deposition on the basal pinacoid. With a relatively slow heating rate ($10^{\circ}\text{C}/\text{min}$), both nucleation and growth continued slowly, forming well-faceted, relatively stable M_3 alite.

In a series of plant experiments with burning zone temperatures of approximately 1315° , 1530° , and 1600°C , Marchiset and others (1990) found an increasing silicate size and decreasing alite birefringence with increasing temperature. The greater amount of magnesium in the alite at relatively low burning temperature, producing more M_3 than M_1 , was given as the reason for the increase in birefringence. These authors demonstrated that a relatively low burning-zone temperature (1315°C) produced a comparatively reactive clinker, resulting in an increase in the quantity of ions in solution when mixed with water, and an early precipitation of ettringite. Furthermore, the quantity of gypsum necessary to accelerate hydration was less than that required for clinker burned at a high temperature (1600°C) which was said to render the C_3A less reactive.

Mor and Perez (1994) presented a critical evaluation of Ono's method (powder mount only) using laboratory heating stages, concluding that the alite size and alite birefringence did not correlate. Correlation was said to be much better with regard to belite size and color. The correspondence between laboratory and industrial kiln microscopy was seriously questioned and differences in environmental conditions, mainly atmospheric composition, were alleged to be responsible.

Finally, because the measurement of apparent birefringence is fraught with so much controversy and the Method seems to lack standardization, the present writer proposes that alite crystals for determination of B^* have a length-to-width ratio of approximately 2 to 1, with crystal widths in the range of 15 to 25 μm , and silicate crystal size measurements be made in the polished section. One does not have to use transmitted polarized light, however, to interpret maximum temperature. Ono stated (1980d) that the "etching degree" of alite could also be used instead of alite birefringence to interpret maximum temperature. "Etching degree" is covered in Chapter 3.

Alite Size

Suzukawa, Kono, and Fukunaga (1964), in a laboratory study with an electric furnace, studied the effects of

high-temperature burning at 1500° to 1700°C and burning times ranging from 0.5 to 60 minutes. The content of alite increased and belite decreased with increasing burning temperature; alite crystal size distribution curves were Gaussian for the clinker burned at 1600° and 1700°C , but skewed toward the finer sizes for clinker burned at 1500° .

Alite crystal size, according to Fundal (1982), is primarily a function of raw mix coarseness: large raw mix particles promote crystallization of large alite crystals because of relatively large compositional gradients developed during burning. Crystal size, therefore, increases with the increasing temperature normally necessary to sinter the hard-to-burn coarse raw feeds. Crystal volume measurements $(\pi/6)(L^2W)$ where L and W represent crystal dimensions. Fundal found that the larger the crystal volume, the poorer the burnability.

Lee (1983) stated that kiln variables such as feed granulometry, feed composition, fuel characteristics, and alkali sulfur circulation are more or less fixed in a normal kiln. Therefore, alite size reflects the heating rate, as Ono has maintained in many papers.

Bruggemann (1988), using the linear traverse technique for phase abundance, demonstrated that small, lattice-defective, alite crystals produced in kilns with steep temperature profiles and short residence times improve grindability and cement quality. Ono's method, utilizing only a few crystals in a powder mount, was said to "give doubtful results."

Older and Maula (1986), in a laboratory study, concluded that variations in heating rate, burning temperature, duration of burning at maximum temperature, and cooling rate produced only small but distinct variations in alite size; of these, burning temperature had the most noticeable effect. Cement hydration was accelerated with increasing burning temperature, but after one day was little affected by other burning variables.

Asaga and others (1989) stated that a slow heating rate produced larger crystals of alite and that burning temperature had no effect on size. Belite grew large when the interval at high temperatures was long. Annealed clinker produced small alite and changed the belite diffraction pattern. These researchers also demonstrated rapid early hydration of small alite, followed by a slowdown, and relatively rapid hydration of large belite crystals. Annealed alite and ferrite were said to hydrate rapidly at first, also followed by a slowdown.

Scheubel (1988) found that the alite chord length could be used to construct a cumulative crystal size curve, the data from which were used to evaluate heating rates and retention times in various kiln systems. High-quality clinkers were said to have uniform granulometry, small silicate crystals, and easy grindability.

Extremely coarsely crystalline clinkers were produced by a melting process described by Khadilkar and others (1992). Raw mixes with 4 to 6 mm particle sizes were burned at temperatures of 1700° to 1800°C in an induction furnace and cooled in compressed air or quenched in water. The molten metal that formed had to be extracted with a magnet before grinding the cement. Alite and belite crystal sizes were said to be relatively large by many times in the air-cooled samples compared to the water-quenched materials. The matrix in the air-cooled clinker was described as a “eutectic mixture of finer alite and aluminate.” Compressive strength at 7 days (Blaine = 320 m²/kg) reached as much as 320 kg/cm² (31.4 MPa). Later strengths were not reported.

The microscopy of two clinkers produced within 10 seconds by electron beam radiation at 1.2 MEV was described by Handoo and others (1992). Alite and belite appear well formed, with crystal sizes of 10 to 16 µm. Mortar strength at 28 days was said to be 470 kg/cm² (46.1 MPa).

The relationship of silicate percentage and crystal size to SO₃ is described by Strunge, Knöfel, and Dreizler (1990) who state that with increasing SO₃ in the clinker, alite content decreased and belite increased, the matrix remaining without substantial changes. With increasing SO₃ content from 0% to 2.6%, alite crystal sizes become larger by a factor of three, the crystals having an increasing idiomorphic form. Nucleation of alite decreases with additional SO₃ due to reductions in liquid phase viscosity and, perhaps, the stabilization of belite. Alkali sulfate in the clinker was said to retard setting, while sulfate within the silicates accelerates setting. The depth and detail of these investigations are too great to be summarized here, and the reader is urged to study this reference further. These data clearly illustrate that alite crystal size is not simply a function of burning rate and raw feed coarseness.

Bruggemann and Bentrup (1990) studied 27 portland cement clinker samples microscopically and with laboratory prepared cements attempted to determine the correlations with prism strengths at ages of 2, 7, and 28 days, at three Blaine finenesses: 2800, 3800, and 4800 cm²/g. Increasing cement strength with small alite crystal size was found to be statistically significant if the cements were grouped according to soluble alkalis. Strength prediction reliability was improved if (1) the ratio of alite content determined microscopically to the C₃S content calculated with the Bogue equation and (2) the ratio of the calculated C₃S content to the average chord length of the alite were used.

Continuing with the investigation of silicate crystal characteristics, Uchida, Shirasaka, and Hirao (1991), in a laboratory study of three raw meals, varied burn-

ing rate, maximum temperature, retention time, and cooling temperature and measured the clinker silicate parameters by the Ono Method. The size of alite changed from 60 to 30 µm as the burning rate increased from 10° to 40°C/min. Birefringence of alite changed from 0.002 to 0.008 as maximum temperature climbed from 1450° to 1600°C. Size of belite increased from 5 to 40 µm as retention time extended from 5 to 30 minutes. Belite color changed from amber to clear as the cooling temperature increased from 1100° to 1500°C. Using pore-size definitions of less than 1 µm, 1 to 20 µm, and greater than 20 µm, and calculating the pore volumes represented in each of these categories, it was shown that as burning conditions improved, the ratio of the less than 1-µm void volume to the other volumes (except total pore volume) increased.

Ikeda and Ichikawa (1992) in a laboratory study showed that heating rates from 33° to 55°C/min resulted in instability of alite crystal growth, and produced larger crystals with morphological irregularity and formation of zonal structures with sulfate at 1.87%. Relatively minor changes occurred with potassium oxide at 1.34%. With increasing heating rates, alite crystal growth became unstable, resulting in larger crystals, morphological irregularity, and formation of zonal structures. The crystal size of alite was said “to not vary monotonously with heating rates.” These authors correlate increasing heating rate, SO₃, and P₂O₅ with increasing alite crystal size.

Centurione and Tonhi (1995) in a laboratory study stated that increases in burning temperature or residence time resulted in larger alite; alite crystal length-to-width ratio increased with heating rate.

A partial least-square regression analysis was applied by Svinning and Bremseth (1993) on alite crystal size and various process parameters, showing that alite size accounted for only approximately 40% of the total variance and that an increase in the >60-µm crystals occurred with decreasing secondary air temperature measured in the cooler. Statistical analyses of this type, in the present writer’s opinion, are greatly needed in our industry to decipher relative importance of the many kinds of measurements.

Wolter (1985) correlated modern kiln characteristics (length, diameter, speed, firing, rotational speed, degree of calcination, and thermal profiles) with properties of the clinkers (silicate crystal size, clinker granulometry, grindability), showing that great differences exist in clinker characteristics. The relatively high-quality clinker was said to be produced in kilns in which the maximum temperature of the feed material is no hotter than 1420°C and the length of time required for passage through the “transition and burning zones” is short, leading to clinkers with small silicate crystals,

uniform clinker gradation, and ease of grinding. A short preheater kiln with a length to diameter ratio of 10 to 1, a 95% calcination prior to the transition zone, and a maximum of 65% tertiary air was described as the recommended kiln system.

Maas and Kupper (1994) described a series of burnability experiments in a horizontal “gradient” rotary furnace in which variable (but controlled) heating and cooling rates up to 200°C per minute were routinely utilized; a cooling rate of 400°C per minute from a material temperature of 1450° to 900°C was also studied with this furnace. Among the many findings reported are: (1) With rapid heating a more rapid conversion to belite occurred than with slow heating. (2) After the start of liquid phase formation and the initial alite development there was a continuous decrease in belite content, regardless of the heating rate. (3) The delayed appearance of alite in the less reactive raw meal was conspicuous. (4) Alite formed as a melt precipitate. (5) With a burning temperature of 150°C above the temperature of the onset of alite formation, all materials needed a residence time of 25 to 30 minutes to achieve maximum alite development. A burning temperature of about 250°C above the temperature at which alite formation starts reduced the necessary residence time for maximum alite development by about 15 to 20 minutes. (6) Silicate crystals became coarser as the residence time required at sintering temperature increased; therefore, when optimizing a burning process, efforts must be made to produce crystals which are as small as possible. (7) The heating rate of the material to sintering temperature had no great influence on the sizes of the silicates. (8) The more rapid the heating rate, the smaller the free lime crystallite size.

Belite Color

The color of belite crystals, according to Ono, is dependent on their contained impurities and the degree to which the impurities are exsolved as the crystal cools. Slow cooling permits time for exsolution to occur and a relatively dark (amber-colored) crystal results. In a cement, one commonly observes a wide range of belite colors, extending from clear to amber and probably representing a range of cooling rates or crystal compositions (and other kiln variations). Therefore, a modal color, that is, one representing the most frequently occurring color, is given principal importance. If belite clusters(nests) comprise a large portion of the observed belite, then their color is given the most weight in a determination of cooling rate. As discussed later, abundant large belite nests are detrimental to clinker quality and their effect may lessen that of an excellent cooling rate. In a thin section, it is not unusual to find a wide

range of belite color in different belite nests in a single clinker nodule, the color differences being due to local “micro” variations in raw feed chemistry (Ono, letter, 1980). Belite color has been said to be the most important of the Ono parameters (Dorn, oral communication, 1980).

Belite colors in cements with 28-day mortar strengths greater than 48 MPa and cements with strengths less than 38 MPa were studied by Campbell (1994b). The belite color data gave only gross trends and weak correlations with strength, suggesting, as expected, that many other cement factors such as alite and belite size, alite birefringence, number and sizes of belite nest fragments, crystal chemistry, fineness, etc., also exert strong controls on the 28-day strength. Positively sloping regression lines relating clear and pale yellow crystals, occurring singly and in nests, and negatively sloping lines relating yellow and amber crystals, including those with abundant dotlike impurities, also occurring singly and in nests, are evident. Higher correlation coefficients appear likely from a within-plant study where the production variables are not as disparate as those represented in the samples just discussed and strength data, perhaps, should be restricted to the gain beyond 14 days.

Certain “observational problems” can skew belite color data and complicate the interpretation of cooling rate, and the following comments are reproduced almost verbatim from Campbell (1994b):

1. It is well known in mineralogy that many minerals may be strongly colored in hand specimen but colorless when viewed as small particles under the petrographic microscope (e.g., microcline, fluorite, quartz, dolomite, calcite). With a smaller particle size, such as the 10- to 15- μ m fraction of the cement or crushed clinker, one might find a tendency to judge a crystal fragment color to be clear when actually the color of the original whole crystal was pale yellow. The natural color of belite crystals in plane-polarized light, somewhat like interference colors in cross-polarized light, are functions of crystal thickness and the degree to which the crystal has been allowed to exsolve its impurities, most of which are retained within the particle. Large wedge-shaped fragments of single belite crystals tend to be clearer and always have lower interference color on the thin side of the particle than on the thick side. In the present research the relative thick side was chosen as the color indicator. A “daylight-blue” filter, constant light intensity and aperture setting are standard.

For nests that survive the KOH-sugar treatment, a common situation in the author’s method

of extraction, the problem of crystal color is not as easily resolved. Small round belite crystals are commonly clear (in anyone's definition), but when stacked in a nest like a handful of marbles, the clear color may appear tinted because of tiny masses of ferrite or other phases buried deeply in the nest between the belite crystals and thus protected from the KOH-sugar solution, or due to Becke line effects. When grinding the clinker in a mortar and pestle, all of the chosen subsample must pass the 75- μm screen, if one wants to determine the number of belite nest fragments and their crystal colors. When counting nested crystals along a line of traverse, one must consider each crystal (nested or single) and make the best judgment possible. Separate recording of nested versus single crystals may be helpful in some studies. Colorless belite crystals, in many cases, are seen to have lamellar extensions in transmitted light as whole grains and in polished thin sections. To the present writer, this indicates slow to moderately slow cooling.

Tiny belite crystals formed as a surficial decomposition of the alite during slow cooling have always been clear in the writer's observations; secondary belite (formed out of the matrix during cooling) is also clear, perhaps because these crystals have little to exsolve. Research is needed on this point. Amoeboid crystals are rarely colored; dendritic crystals have never been observed to be colored in the writer's experience. Ono's belite color interpretation seems most applicable to "properly" formed crystals.

2. "Boundary-line colors" refers to colors falling between the major categories of clear, pale yellow, yellow, and amber. In other words, pale yellow to one observer is obviously yellow to another, even when each person is being as objective as possible. The problem is not unique to cement microscopists. An attempt at a photographic belite color standard is presented in this book.
3. The "color" one observes is not altogether a product of exsolution, but also of crystal microstructure. Changes in light-ray velocity and direction (refraction and double refraction) when passing through materials of nearly identical refractive index (belite lamellae, for example) commonly produce faint bands of color or light intensity as the waves interfere. These effects can be linear, that is, occurring along the boundaries of adjacent lamellae, easily visible in thin wedge fragments, or more complexly formed by intersecting lamellae. The Becke line itself may have a yellowish color in liquid with a refractive index of 1.715 or Hyrax™

(1.70), and care should be taken not to confuse it with crystal color. The level of focus should be such that the Becke line is just outside the belite crystal for color determination. Even the Becke line around alite can give the crystal a faint yellowish color as the focus is raised or lowered.

4. Certain cations such as chromium, manganese, and, perhaps, aluminum from refractory bricks and other sources can produce a range of green and yellow variations in belite. These causes of coloration do not appear to be related to cooling rate, however, much research remains. The absence of yellow and amber belite in some slowly cooled white cement clinker suggests that iron is the primary colorant in other portland cements. Various cations from petroleum-derived waste fuels may also color certain phases in the clinker.

A brief report discussing the microscopy of one of the ICMA Exchange Program clinker samples was published by the present writer in 1994. The disparities between Bogue phase percentage calculations and microscopy, vagaries in alite birefringence, and problems in belite color judgement suggest a need for standardized sizes for silicate crystals for the cooling rate and maximum temperature interpretations.

Fundal (1982) also presented a different interpretation of belite stating that, like alite, belite seems to be mimetic, occurring in the trigonal system and transforming during cooling to an orthorhombic (alpha-prime form), twinned symmetrically and pseudohexagonally around the gamma optical vector. Index of refraction was said to vary little from 1.72, with a birefringence of 0.015 for both synthetic (laboratory) and industrial clinker. Fundal pointed out the common occurrence of different belite crystal colors in the same nest and, using the ratio of clear to brown crystals, concluded that the method based on color was useless for kiln control. The ratio was said to be possibly influenced by decrepitation and rebuilding of nodules during burning and by different types of raw mix. Clear crystals were thought to be produced by crystallization from the melt, and nests were produced from quartz, feldspar, low-lime marl, schist, diopside, hornblende, and other types of particles.

Colorless belite, according to Lee (1983), can occur as very small inclusions in alite and contains very little impurity. Large-crystal, ringlike belite nests (from coarse alkali feldspar) are also colorless because of iron-oxide deficiency. These occurrences of belite, therefore, do not reflect the cooling rate. Consequently, *Ono (1978) recommends color observation of roughly 20- μm belite crystals in order to judge the cooling rate.*

If the cement or clinker contains belite only as fringes (coatings) on alite crystals, then the use of

belite color and size in Ono's method appears virtually impossible because of the scarcity of observable belite in powder mount. The other parameters, alite size and birefringence, however, remain and can be utilized.

Using microprobe techniques in a laboratory study, Ikabata, Honda, and Yoshida (1988) described some of the positive effects of rapid cooling rates, beginning at a temperature of approximately 1350°C, concluding, among other things, that belite containing approximately 0.7% to 0.8% alkali is best for 28- to 91-day strength development. Annealing the clinker clearly resulted in "discharging" alkalies and other impurities.

Systematic studies relating the effects of slow heating and cooling in vertical shaft kilns (VSK) in terms of the "Ono parameters," or related observations, are scarce. Raina and Janakiraman (1993) described the microscopical characteristics of VSK clinkers produced from overlimed, underlimed, and optimally limed raw feed with varying fineness and retention time. Abundant free lime was produced in both the underlimed and overlimed materials. The underlimed clinker had a Bogue C_2S of 33.2%; microscopically it was 42%.

Relatively small alite (15 to 18 μm) characterized the overlimed mix, which also had a very low liter weight (950 g/L) and 6.8% free lime; percent alite and crystal size increased with increasing temperature and retention time. Increasing fineness of the interground coke was related to the absence of evidence for reducing conditions (yellow nodules and metallic iron). Increasing the burning zone temperature to 1450°C inhibited the production of gamma belite.

A multiregressional equation predicting the 28-day mortar cube strength was presented by Rao, Akhouri, and Sinha (1992), the data coming from rotary and vertical shaft kiln clinkers. The prediction has a standard deviation of 17.9 kg/cm², utilizing alite and belite percentages and average crystal sizes.

Detailed microscopical characteristics of clinkers from vertical shaft kilns, compared to laboratory burns, are presented by Ahluwalia and Raina (1992). Alite and belite crystal sizes in plant clinkers averaged approximately 21 and 19 μm , respectively, possibly accounting for high mortar strengths (44.8 MPa at 28 days).

CHAPTER 7

Microscopical Interpretation of Clinkers

Alite and belite, which comprise most of portland cement clinker, have a close genetic relationship and, as evident in the previous chapter, are not easily separated for microscopical discussion. Alite crystals, for the most part, quickly nucleate and grow within the melt, exhibiting dissolution, recrystallization, and decomposition, the latter to belite (Maki, 1982, and Maki, Morikoshi, and Takahashi, 1985). Belite can form during the heating stage as well as in the cooling stage of the burning process. Thus, the microstructures that one may observe in the silicates reflect a rather complex genetic history. The matrix is an intimate, finely microcrystalline intergrowth of aluminate and ferrite which formed during the very early cooling stage above 1300°C (Bye, 1983).

Consequently, instead of a chapter organization based primarily on genetic sequence (see Hofmänner, 1973; Chromy, 1974; Butt and Timashev, 1974; Ono, 1981, 1995; Chromy, 1982; and Gartner, 1985), the observations and interpretations in this chapter are listed first with some of the relatively large-scale features of clinkers and then, for the most part, according to phase abundance. Rather than in a lengthy narrative survey of interpretive details of clinker phases, stated by various authors in many published papers, the information is presented in tabular form. Table 7-1 presents, in a double column, a list of (a) clearly recorded observations on the left and (b) verbatim published interpretations, associations, or correlations on the right. This survey is not a critical review.

Seldom does a single observation of a particular microscopic feature provide sufficient evidence to warrant a widely applicable interpretation. Most interpretations given herein represent conclusions drawn

from reported observations of clinkers made by many authors in laboratory experiments and in cement plants. The author of each observation and interpretation is indicated, although it is very difficult in many cases to establish historical originality. The reader should be aware that such a listing of observations and interpretations taken out of context from the referenced publications can be misleading, and that general application of the interpretation could be risky.

Unfortunately, some interpretations stated by different authors in the table are contradictory and the reader is left to his or her experience to determine the correct statement. Additionally, some observations may have more than one correct interpretation, that is, multiple causes. Some of the stated correlations may not be cause and effect relationships. Furthermore, some of the referenced work appears less than systematic. Such problems point out the need for research, and, indeed, it is hoped that the contents of this publication serve to stimulate scientific cement research, particularly quantitative microscopy with a statistical approach, using techniques that group and characterize the sets of observations and genetic conditions.

The photographs in this section are illustrations of clinkers examined and interpreted by this writer, with emphasis on the use of Ono's interpretive table (Table 6-1). It is important to note that individual photographs may not depict all the microscopic features normally associated with the stated interpretation of kiln conditions, the interpretation having been drawn from the results of several techniques of examination and study of several clinkers in the sample. Designations such as 42.8 MPa in the photomicrograph captions indicate reported 28-day mortar-cube strength.

Table 7-1. Microscopical Interpretation of Clinkers

General Features of Clinkers	
Observations	Interpretations
Evenly distributed phases; idiomorphic alite; rounded belite; finely differentiated matrix; scarce, small, free-lime crystals	Optimized manufacturing conditions: "correct" chemical composition of raw feed, well mixed, no particles too coarse, satisfactory maintenance of sintering and cooling temperatures (Hofmänner, 1973)
Even distribution of silicates	Ideal clinker structure, good production conditions (Fundal, 1980)
Increase in alite content and crystal size, increasing difficulty in burning, reduction in cement strength	Relative increase in lime saturation factor (Long, 1982b)
Increase in silicate abundance, decrease in liquid, higher temperature required for combination of feed ingredients, decrease in alite size	Relatively higher silica ratio (Long, 1982b)
Very heterogeneous clinkers as seen in degree of burning, size, and distribution of minerals	Wet process, introduction of precipitator dust after chain system (Hawthorne, Richey, and Demoulian, 1981)
Clinker shape: (a) single grains, (b) lumpy	(a) rotary kiln, (b) shaft kiln (Gille and others, 1965)
Edges of alite damaged, notched and pitted belite, dark intermediate material with low reflectivity	Typical clinker from large kilns (5x185m) (Kolenova, 1974)
Prismatic alite; round belite; light-colored, highly reflective intermediate material; dark prismatic aluminate	Typical clinker from small kiln (4.5x170m) (Kolenova, 1974)
Nodule size greater than 25-mm diameter	Requires longer burning time or higher burning temperature (Heilmann, 1952)
Increasing clinker size	Higher burning temperatures and larger amount of liquid phase; more time for nodulation (Eby, 1985)
Chains of silicates	Bridging reaction between constituents, and between burning zone and cooler inlet; easily eroded, producing dust (Fundal, 1980)
Large pores, wide bridges, and large solid areas	Dry process (Krämer, 1960)
Numerous small pores, narrow bridges, crescent-shaped voids	Pelletized raw mix (Krämer, 1960)
Pores with wide range of sizes, shape, and distribution; abrupt size changes in adjacent pores; small bridges	Wet process (Krämer, 1960)
Increasing roundness of pores, decrease in porosity; higher ferrite and belite content at expense of aluminate and alite; decrease in melt viscosity, increase in grinding time	Increasing MnO content (Knöfel, Strunge, and Bambauer, 1983)
Extremely dense structure, large alite	Kiln wall (Fundal, 1980)
Dense clinker structure, closed pore system	Densification at temperature below melt formation (Fundal, 1980)
High clinker porosity	Low degree of burning (Gille and others, 1965)
Highly porous clinker, open pores, 50-90 μ m alite	Sandy raw meal (Fundal, 1980)
Compact clinker with spherical, closed pores; 10-20 μ m alite	Marl-type raw mix (Fundal, 1980)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

General Features of Clinkers	
Observations	Interpretations
Large pores, nontwinned belite, large alites	High SO ₃ (Tsuboi and Ogawa, 1972)
Rough pore surfaces	Low temperature burning (Tsuboi and Ogawa, 1972)
Very porous clinker consisting of small bright grains with rounded edges	Underburned clinker (Törnebohm, 1897)
Porous, alite-rich, lumpy clinker, some with dense centers; dusty clinker, ring and "stalagmite" formation in kiln and cooler; large alite crystals; sparkling luster of clinker; lowered cement strength	Excessive hard burning (Long, 1982a)
Friable clinkers surrounded by a deposit of alite crystals alone	Very hard burning of high silica ratio materials (Pollitt, 1980)
Clinker nodules of varying composition	Inadequate blending of feed or segregation in kiln (Long, 1982a)
Clinker inhomogeneity	Lower reactivity of ash, too short retention time at clinkering temperature, high ash content, lump coal for precalcining carbon-rich fly ash as a raw material, waste-derived fuels containing graphite (Sprung, 1985)
Nests	Excessive particle size in raw mix (greater than 0.1 mm) (Gille and others, 1965)
Streaks and spots in clinker	Nonhomogeneity of raw mix, segregation of dust in air ducts during transfer to silo or in kiln (Gille and others, 1965)
Spots in clinker	Local increase of individual components of raw material; low burning degree (temperature too low or burning time too short); low lime content (Gille and others, 1965)
Overall crystal size	Function of temperature, time, and chemical composition of surrounding material; absorbed nests and prior nonhomogeneities (Gille and others, 1965)
Large crystals	High temperature, long burning time, surrounding material is low lime (belite) (Gille and others, 1965)
Large crystal cements	Unsatisfied charges on broken crystal surfaces resulting in agglomerations, abnormal setting characteristics, and increased grinding time (Hansen, 1977)
Large segregated silicates, belite nests, poor matrix distribution, high free lime	Long burning zone, maximum temperature below 1500°C, preheater kiln (DeHayes, Grady, and Vidergar, 1986)
Pronounced segregation of silicates and matrix phases, wide alite size range, large crystals, some > 100 µm, high porosity, relic coarse quartz grains	Short residence time, high production rates, roller-mill raw grind, coarsely ground coal precalciner kiln (DeHayes, Grady, and Vidergar, 1986)
Large crystal size and narrow crystal size range	Unfavorable grindability (Tachihata, Kotani, and Jyo, 1981)
Overall increase in crystal size; alite more than belite, which tends toward yellow color	Lowering of feed to speed ratio, thinning clinker bed depth as burning zone moves uphill (Rader, 1985)
Coarsely crystalline clinker	High early strengths, abnormal setting problems (Hansen, 1980)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

General Features of Clinkers	
Observations	Interpretations
Coarsely crystalline clinker with a high degree of hydration per unit specific surface	High compressive strengths (Entin, Nekhoroshev, and Sorochkin, 1980)
Hard, dense clinker, with large alite, plus soft, porous clinker with low alite content	Variable burning, flushing (passage of charge too rapidly through kiln), or excessive feed (Long, 1982a)
Small, poorly formed phases; very high porosity; uneven phase distribution; alite surrounded by large amounts of liquid phase; belite in clusters	Flushing or sintering temperature is too low (Hofmänner, 1973)
Increase in specific crystal surface (surface area of solid particles/volume of solid particles) and reduction in melt volume	Results in an increase in specific pore surface and reduction of power requirement for grinding (Petersen, 1980)
Three zones in clinker: (a) Dense core (b) Intermediate porosity (c) Cokelike	(a) Primary nodules (kiln ring fragments or nodules formed before burning zone) (b) Forms in burning zone (c) Forms between burning zone and cooler due to heavy dust load (Fundal, 1980)
Dense core, high-porosity shell	Agglomeration of dust (less than 1.0 mm) on nodule between burning zone and cooler inlet (Fundal, 1980)
Peripheral zones in clinkers	Differentiation or segregation of melt during liquid stage of groundmass (Gille and others, 1965)
Fine clinker	Soft burning, insufficient liquid phase; extreme hard burning and abrasion of porous shells on clinkers; Mn mineraliser (large alite crystals) (Long, 1984b)
Dusty clinker: high porosity, "breaded" nodules, agglomerated fine particles, alite-rich, large alite crystals, and relatively scarce liquid phase	(a) Decomposition of outer clinker shell and concentration of liquid phase in clinker core (Allegre and Terrier, 1960) (b) Recycling of precipitator dust, reducing zones, lack of Al_2O_3 in raw slurry (Hofmänner, 1973)
Dusty clinker (poor nodulization) and snowmen	(a) Unfavorable temperature distribution (b) Too little melt (c) Too much coarse quartz, lime, slag (d) Heavy alkali circulation resulting in early crystal growth of belite and free lime and large silicate crystal size (Miller, 1980)
Belite nest with dense, thick layer of alite with very porous outermost zones	Typical in dust formation (Fundal, 1980)
Clinker dust with abundant belite clusters	Inferior burnability (Fundal, 1980)
Dusty clinker, coarsely crystalline silicates, low-porosity nodules, poor grindability	Slow temperature rise, higher clinkering temperature, longer time in burning zone and transition zone (Wolter, 1985)
Coal ash shells on clinkers and nests at boundary zones	Nonuniform combustion of fuel and partial reaction on clinker surface; inadequate grinding of coal and distribution (Krämer, 1960)
Clinker color: earth brown to light brown to dark brown to black with greenish brown hue	In order of increasing degree of burning (Gille and others, 1965)

Table 7-1. Microscopical Interpretation of Clinkers (continued)**General Features of Clinkers**

Observations	Interpretations
(a) Reddish brown (b) Dark gray with reddish hue (c) Slate gray	(a) Abundance of Fe ⁺⁺ (b) Fe partly replaced by Mn (c) Normal clinker with Mg in greenish-brown ferrite (Gille and others, 1965)
Gray-black clinker color	Overall oxidizing environment (Long, 1982b)
Yellow-brown clinker colors	Rapid cooling (Long, 1982b)
Gray color of clinker	Burning under oxidizing or neutral conditions; MgO in lattice of aluminoferrite, presence of trivalent iron (Sylla, 1981)
Gray color of clinker	Burned under reducing conditions, cooled in air after removal from kiln at temperature greater than 1250°C (Sylla, 1981)
Brown clinker	Burned under reducing conditions, cooled at approximately 1250°C under reducing conditions, further cooled in air (Sylla, 1981)
Bleached region in clinker	Localized extreme reduction due to partly burned coal deposition (Long, 1982b)
Well-defined yellow band separating gray-black periphery from brownish black core	Reducing environment with reoxidation (Long, 1982b)
Black, oxidized parts of same sample show usual features but with three sets of belite lamellae strictly oriented crystallographically with host alite	Moderate reducing conditions (Woermann, 1960)
Clinker is densely burnt, light brown; ferrite has distinctly lower reflectivity than in normal clinker; calcium and iron sulfides	Reducing conditions (Woermann, 1960)
Disappearance of ferrite phase, iron transformed to metallic state, clinker color changes to white, alite decomposition structures vanish	Extreme reducing conditions (Woermann, 1960)
Brown-centered clinkers, larger alite, lower birefringence	Reducing conditions; longer, cooler flame; reductions in set control and strength (Brugan, 1979)
Spotty, banded coloration	Chemical differences or varying burning conditions (Gille and others, 1965)
Green clinker nodules, chromium-rich green belite, gehlenite matrix	Consumption of refractory brick during production at less than optimum kiln capacity or excessive flame length for rated capacity conditions (Brugan, 1979)
Greenish brown—greenish yellow	Entrapped magnesium (Gille and others, 1965)
Clinker weight (liter)	Varies as a function of total porosity (Gille and others, 1965)
High liter weight	High alite content (Brown, 1948); increased time of burning at high temperature (Hawkins, 1979)
Low liter weight	MgO slightly high, CaO distinctly high; aggregated clinkers (Brown, 1948)
Hydration shells on clinker	Air-exposed piles of clinker with “roofs” of partial hydration (Krämer, 1960).

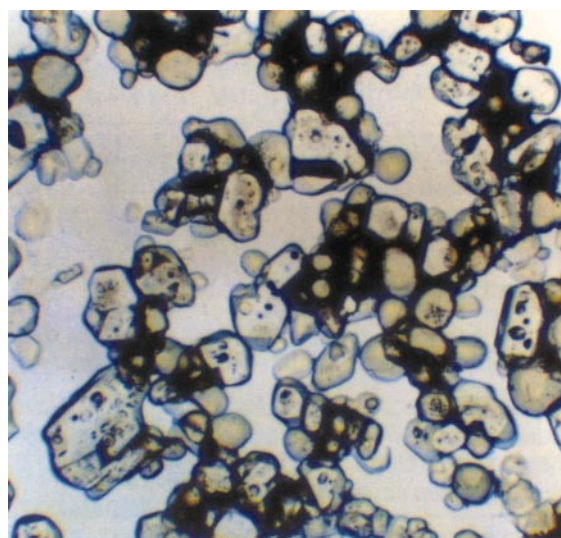
Table 7-1. Microscopical Interpretation of Clinkers (continued)

General Features of Clinkers	
Observations	Interpretations
Green, yellow, and brown clinkers	Addition of Cr^{+3} , Ti^{+4} , and $\text{Fe}^{+3}/\text{Mn}^{+2}$, respectively (Laxmi, Ahluwalia, and Chopra, 1984)
Weathered clinker and low Blaine fineness of cement	Problems in thickening time and free water in oil-well cement (Reeves, Bailey, and McNabb, 1984)

PHOTOMICROGRAPHS OF GENERAL FEATURES OF CLINKERS

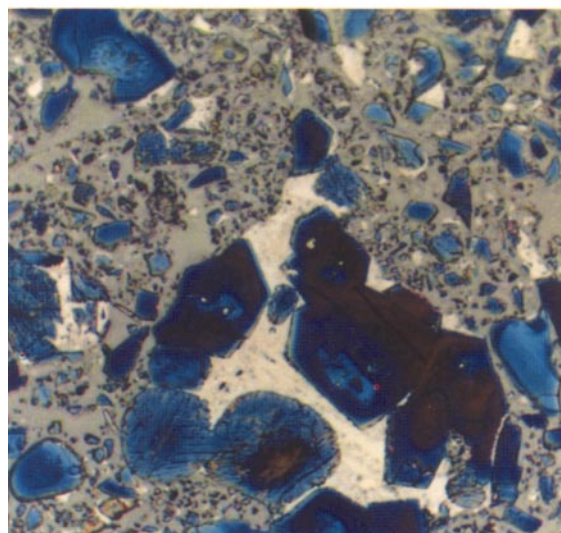
Photograph 7-1 Porous outer zone of clinker, surrounding relatively dense clinker core. Evenly distributed, round, clear belite crystals and angular alite. Pores filled with epoxy. Moderately high maximum temperature, long burning time, slow heating rate, quickly cooled. Dry-process kiln with flash calciner, 5000 tons/day. (S#A6621)

Thin section
Transmitted, plane-polarized light
Field dimensions = 0.53x0.53 mm



Photograph 7-2 Polished section of cement in epoxy, illustrating large multiphase (composite) particles and small, single phase particles, a typical relationship for most portland cements. (S#A6622)

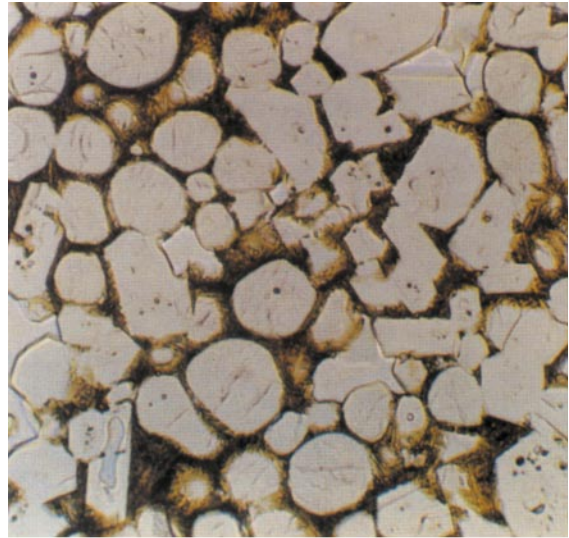
Nital etch
Field dimensions = 0.38x0.38 mm



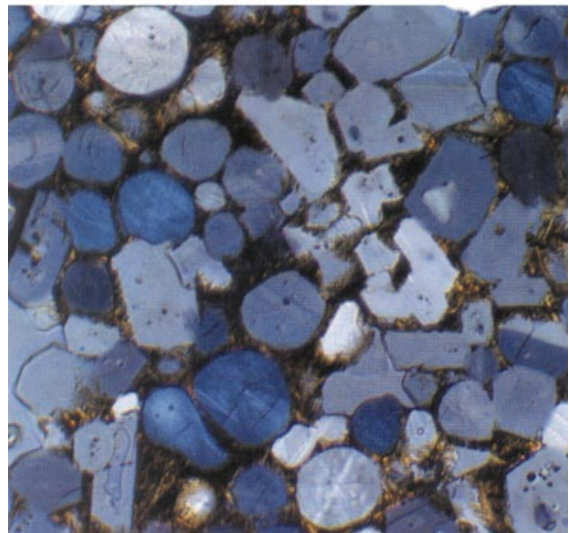
PHOTOMICROGRAPHS OF GENERAL FEATURES OF CLINKERS (CONTINUED)

Photograph 7-3 Uniform silicate distribution in polished clinker thin section showing angular, equant to elongated alite; round, clear belite with typical multidirectional lamellae; and a finely microcrystalline matrix of aluminite (C_3A) and ferrite (C_4AF). (S#A6623)

Transmitted, plane-polarized light
Section thickness = 15 μm
Field dimensions = 0.53x0.53 mm

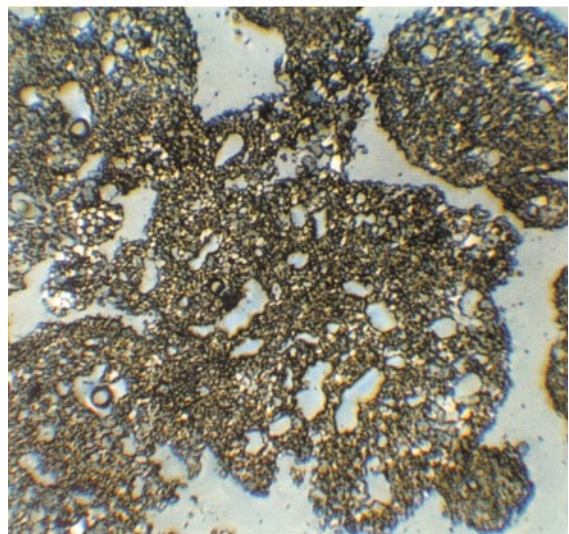


Photograph 7-4 Same field of view as previous photograph. Different shades of gray on silicates indicate different crystallographic orientations in partially cross-polarized light. High maximum temperature, long burning time, slow heating rate, quick cooling, 42 MPa. Dry-process, coal- and coke-fired kiln, 2145 tons/day. (S#A6624)



Photograph 7-5 Clumpy clinker with generally small crystals. Average alite and belite sizes are 24 and 24 μm , respectively. Coal- and coke-fired, wet-process kiln, 1000 tons/day. Moderately high maximum temperature, moderately long burning time, moderately quick heating rate, quickly cooled, 48 MPa, Type III cement. (S#A6625)

Thin section
Partially crossed polars
Field dimensions = 1.9x1.9 mm



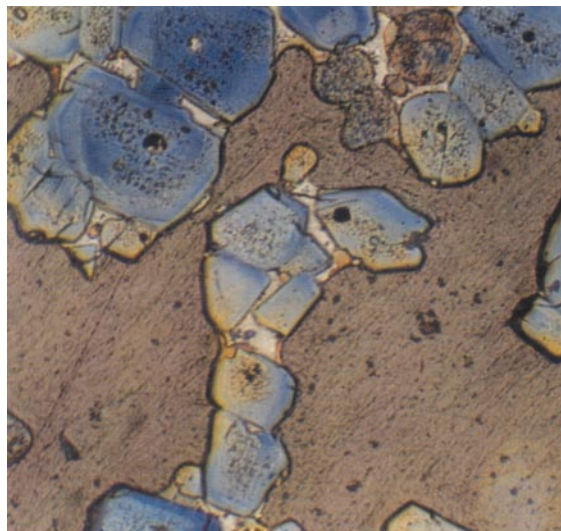
PHOTOMICROGRAPHS OF GENERAL FEATURES OF CLINKERS (CONTINUED)

Photograph 7-6 Extremely porous, sandy clinker showing silicate crystal chains. High maximum temperature, long burning time, slow heating rate, slowly cooled, 35 MPa. Coal-fired, wet-process kiln. (S#A6626)

Polished section

Nital etch

Field dimensions = 0.38x0.38 mm

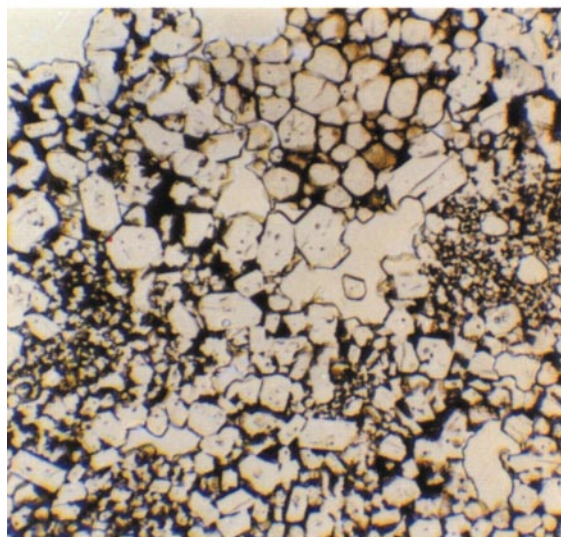


Photograph 7-7 Variation in alite crystal sizes: clusters of small crystals (14 μm), noncluster crystals (38 μm). Round belite crystals in nest in upper center. High maximum temperature, long burning time, moderately slow heating rate, quickly cooled, 42 MPa. Gas-fired, dry-process kiln, 770 tons/day. (S#A6627)

Thin section

Transmitted, plane-polarized light

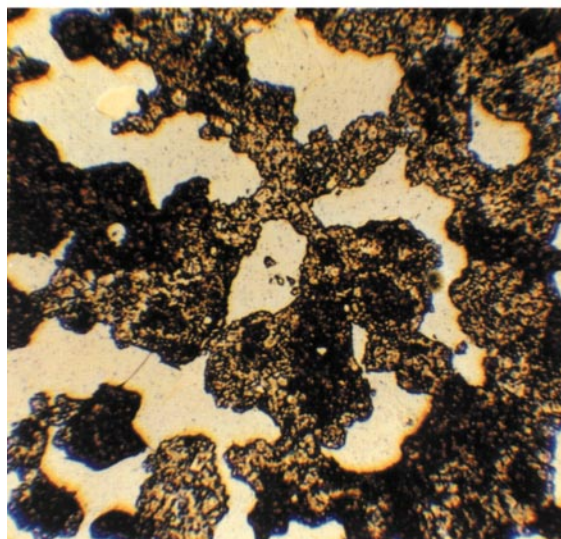
Field dimensions = 0.59x0.59 mm



Photograph 7-8 Inhomogeneous coarse feed resulting in highly porous clinker with extremely nonuniform distribution of silicates. Thin edges of this relatively thick thin section reveal a clear to pale yellow belite color. High maximum temperature, long burning time, moderately slow heating rate, quickly cooled, 42-46 MPa. (S#A6628)

Transmitted, plane-polarized light

Field dimensions = 1.9x1.9 mm



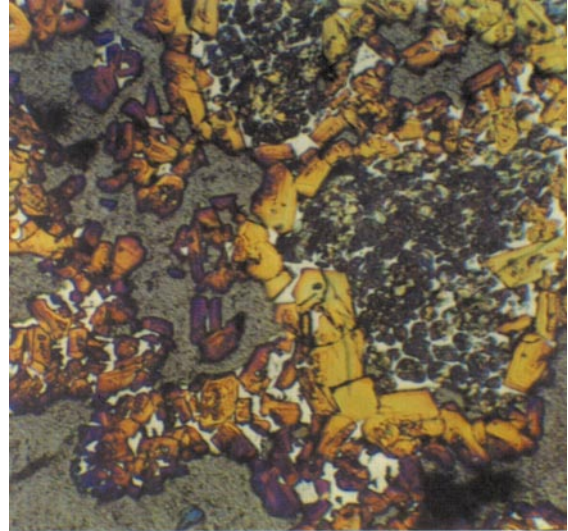
PHOTOMICROGRAPHS OF GENERAL FEATURES OF CLINKERS (CONTINUED)

Photograph 7-9 Porous heterogeneous clinker showing nests of dark, round belite surrounded by relatively large alite crystals. Insufficient liquid phase. Very sandy raw mix with abundant metasiltstone. High maximum temperature, moderately short burning time, slow heating rate, moderately slow cooling rate. Gas-fired, dry-process kiln, 3000 tons/day. (S#A6629)

Polished section

Nital etch

Field dimensions = 0.53x0.53 mm

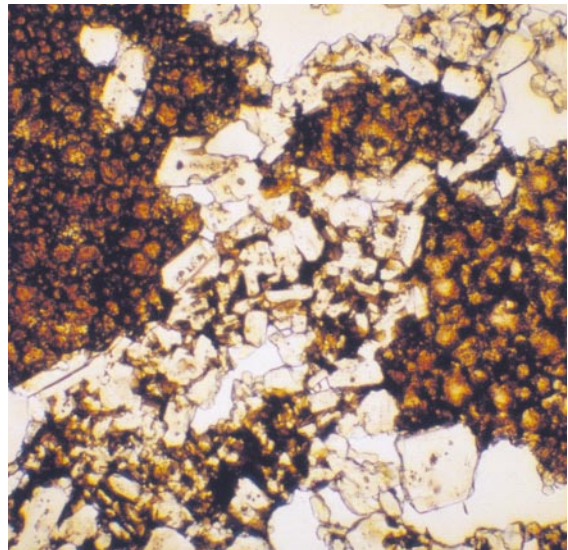


Photograph 7-10 Amber to yellow belite in large, sharply bounded nests and clear, angular alite crystals with a wide range of sizes and nonuniform distribution. Insufficient liquid phase. Feed contains abundant coarse metasiltstone particles. Estimated free lime = 1.5% to 2.5%. Gas-fired, dry-process kiln. High maximum temperature, moderately short burning time, slow heating rate, moderately slow cooling. (S#A6630)

Thin section

Transmitted, plane-polarized light

Field dimensions = 0.60x0.60 mm

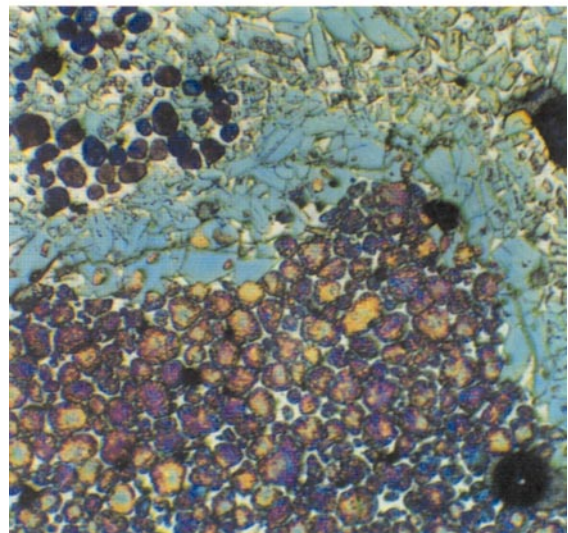


Photograph 7-11 Extremely heterogeneous clinker containing large concentrations of loosely packed yellow-amber belite and alite with a wide range of crystal sizes and, like the belite, a nonuniform distribution. Free lime is abundant (dark, round crystals). Sandy, silica-rich raw feed with coarse quartz. Gas-fired dry-process kiln, 3000 tons/day. (S#A6631)

Polished section

Nital etch

Field dimensions = 0.53x0.53 mm



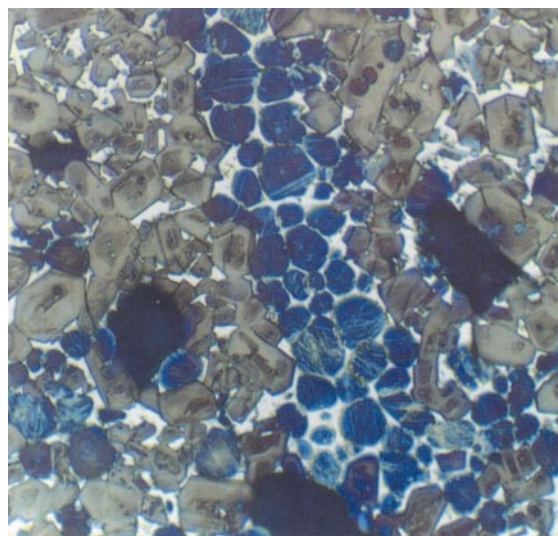
PHOTOMICROGRAPHS OF GENERAL FEATURES OF CLINKERS (CONTINUED)

Photograph 7-12 Streak of belite crystals in sulfate-resisting cement clinker, suggesting nonuniformity in feed. Gas-fired, dry-process kiln, 770 tons/day. (S#A6632)

Polished section

Nital etch

Field dimensions = 0.53x0.53 mm

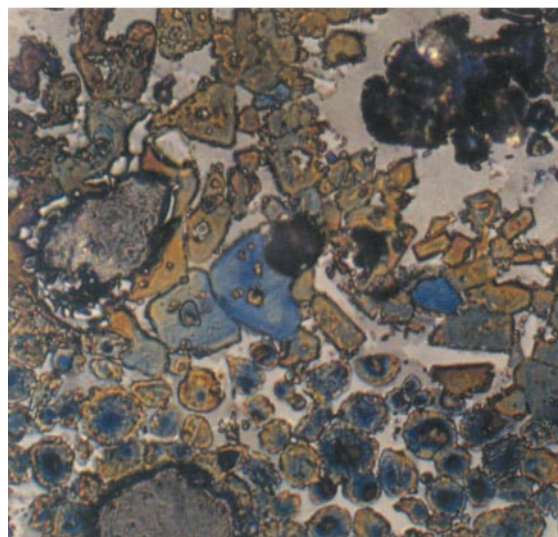


Photograph 7-13 Clinker from vertical shaft kiln, Indian mini-cement plant, in which clinker heterogeneity is the rule. Dark free lime in upper left, anhedral small alite (center) small, round, zoned belite (lower left and bottom). Dull ferrite. Coke breeze as fuel. Reducing conditions. Kiln residence time is approximately 6 hours, 30-40 min in burning zone, 4 hrs in cooling zone. Reported 28-day mortar strength = 54 MPa. (S#A6633)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm



Photograph 7-14 Randomly scattered silicates in well-made clinker. Small, angular, brown alite. Relatively large, round, multicolored Type A belite; well-differentiated matrix of aluminat (C_3A) and ferrite (C_4AF). Moderate porosity not shown. See proposed belite classification on p. 35. (S#A6634)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

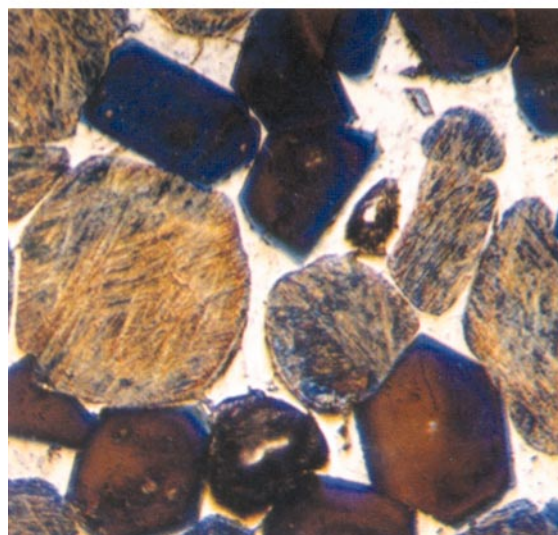


Table 7-1. Microscopical Interpretation of Clinkers (continued)

Alite	
Observations	Interpretations
Increase in alite content, decrease in belite and free lime	Increased nucleation of alite by adding 0.5% C_3S (less than 20 μm) to raw mix (Strunge, Knöfel, and Dreizler, 1985)
Alite abundant, belite scarce, free lime abundant (evenly distributed)	(a) Lime saturation too high (b) Sintering temperature too low (Hofmänner, 1973)
Widely fluctuating C_3S abundance in clinker and dusty kiln conditions	Periodic dumping of silica-rich loads resulting from silica buildups in dry raw feed grinding mill and consequent surges of fine calcite (Dorn, 1980)
Increase in alite percentage and crystal size, decrease in belite percentage, decomposition of C_3A	Increase in burning temperature and time with $T = 1450^\circ C$ to $1750^\circ C$ and time up to 800 seconds (Butt, Timashev, and Starke, 1973)
Alite scarce, belite abundant, free lime absent	Lime saturation too low (Hofmänner, 1973)
Increase in abundance of alite and belite	Increase in TiO_2 content in clinker (Knöfel, 1977)
Pronounced decrease in alite content	Slow cooling under reducing conditions (Sylla, 1981)
Very large alite and belite crystals (averaging or exceeding 100 μm), cubic C_3A , K_2SO_4 , and $CaSO_4$ crystals	Burning with fuel oil containing 2.5 to 3.5% sulfur (Hawthorne, Richey, and Demoulian, 1981)
Extremely large and thick alite (100-200 μm)	Contamination of considerable amounts of Na_2O , K_2O , and SO_3 in clinker (Ono, Hidaka, and Shirasaka, 1969)
Large, thick crystals of alite, developing on rhombohedron faces (01 $\bar{1}$ 2) and (10 $\bar{1}$ 1)	Slow crystallization (Ono, Hidaka, and Shirasaka, 1969)
Large alite with small inclusions of fine ferrite and aluminate crystals; alite is mostly M_1 variety	Result of burning at $1450^\circ C$ (Maki and Goto, 1982)
Stacked alite crystals	High temperature (Gouda, 1980)
Alite crystals, granular, showing strong growth perpendicular to basal pinacoid (0001) due to development of pyramidal faces; solely T_2 variety; concomitant increase in belite size	Recrystallization of alite during retention for 120 min at $1600^\circ C$; melt is low in degree of supersaturation (Maki, Haba, and Takahashi, 1983)
Alite crystals tabular, indicating growth parallel to basal pinacoid; exclusively M_3 variety	Recrystallization of alite during retention for 5 min at $1600^\circ C$; melt is highly supersaturated (Maki, Haba, and Takahashi, 1983)
Xenomorphic crystals	Low temperature (Gouda, 1980)
Large alite	Long flame, slow heating rate (Ono, 1981); coarse limestone or calcite in feed (Akatsu and Monna, 1966); coarse quartz (Ono, 1954); long thickening time in oil-well cements (Reeves, Bailey, and McNabb, 1984)
Large alite	Longer burning time, higher temperature, lime-poor environment in the vicinity of belite; coarse raw mix; and high-viscosity liquid due to alkali or sulfate (Dorn, 1979); extreme hard burning and porous shell on clinker nodule (Long, 1984b)
Relatively large alite crystals, somewhat rounded	Clinker burned under reducing conditions, removed from kiln at $1350^\circ C$, cooled in air (Sylla, 1981)
Increasing size of alite	Coarse raw feed, coarse quartz, increase in firing temperature, decrease in strength (Long, 1983)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Alite	
Observations	Interpretations
Large densely packed alite crystals	Derived from large belite in nests from coarse silica (Long, 1983)
Cannibalistic (fused) alite	Erratic thickening times and unpredictable retarder response (Reeves, Bailey, and McNabb, 1984); reduced activity level (Dorn, 1985)
Relatively large alite crystals, typically corroded; well-differentiated matrix	Clinker burned under oxidizing conditions and cooled to 1250°C in the kiln (Sylla, 1981)
Relatively large alite and belite crystals, narrow range of size variation, lower than average reactivity	Burning with natural gas (Hawthorne, Richey, and Demoulian, 1981)
Large alite crystals	Large quartz grains in raw mix; enhanced M_1 development during prolonged heating; abundant SO_3 (Maki and Goto, 1982); long burning zone relative to flame length (Hansen, letter, 1985)
Large alite in cluster	Derived from belite nest from quartz grains near critical size (44 μm) or higher temperature burning (Fundal, 1980)
Alite cluster, small crystals (10 μm) plus minor f-CaO or belite in same cluster	Marly grain near cement composition (Fundal, 1980)
Coarser alite (average = 50 to 60 μm) with a few large inclusions	Longer coal flame (Krämer, 1960)
Increasing alite size, densification of clinker	Relatively lower alumina ratio (Long, 1982a)
Coarsening of alite and belite	Clinker at highest temperature for too long or sintering temperature is too high (Hofmänner, 1973)
Increase in alite and belite sizes, deformed belite, low alite birefringence	Dusty, oxidizing divergent flame (Campbell and Weiss, 1987)
Amount of small alite decreases, moderate and large size alite increases	Slow burning at medium temperature (Ono, Kawamura, and Soda, 1968; Ono, 1980d)
Large to very large, idiomorphic alite crystals	Correlated with increasing SO_3 content in low-alkali laboratory clinkers; reduced viscosity of melt; strength loss (Dreizler, Strunge, and Knöfel, 1985)
Alite and belite are greater than 30 μm	Irregularities during burning do not influence mortar strength so markedly (Tsuboi and Ogawa, 1972)
Alite and Type I belite greater than 30 μm	High mortar strength at 28 days (Tsuboi and Ogawa, 1972)
Alite more than 20 μm and dense belite nest	Numerous quartz grains greater than 100 μm (Tsuboi and Ogawa, 1972)
Large alite adjacent to belite nest	Reflects composition gradient of belite to alite with very little interstitial phases (Fundal, 1980)
Large alite crystals near belite	Surrounding area low in lime (Gille and others, 1965)
Alites more than 20 μm and euhedral, large Type I belite	Well-fired clinker, high mortar strength (Tsuboi and Ogawa, 1972)
Alite size ranges by factor of two at distance of 100-200 μm	Insufficient diffusion due to low temperature as a result of too brief burning (Tsuboi and Ogawa, 1972)
Alite size decreasing, alite abundance increasing	Increasing burning temperature from 1500°C to 1700°C (Suzukawa, Kono, and Fukunaga, 1964)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Alite	
Observations	Interpretations
Great difference in sizes of alite and belite in individual clinkers	Nonuniform firing: changes in fuel consumption, SO_3 , and alkali circulation (Tsuboi and Ogawa, 1972)
Small alite crystals vs. large crystals	Lime-rich vs. silica-rich regions in clinker (Bye, 1983)
Alite size variation	Absorbed nests or prior nonhomogeneities (Gille and others, 1965)
Alite size decreases	Increasing feed volume through kiln, burner pipe retraction, and increase in primary air (Brugan, 1979)
Decrease in alite crystal size	Increase in feed rate (Jany, 1986)
Coarsely crystalline alite surrounded by finer-grained alite and free lime	Coarse quartz and locally high lime saturation factor converting previous belite nest to alite (Miller, 1980)
Wide variation in alite size, small alite	Nonhomogeneous raw mix; locally high lime saturation factor (Fundal, 1980)
Small grains of alite	Relatively rapid strength gain (Krämer, 1960)
Thin tabletlike crystals	High SiO_2 in mix, iron-rich liquid phase (Gouda, 1980)
Large, platy alite crystals in eutectic matrix of finely crystalline alite and C_{12}A_7 (halogenated)	Fused clinker, quickly cooled from temperature of 1720°C (Maki and others, 1984)
Small, thin crystals of alite, developing on basal pinacoid (0001)	Rapid crystallization (Ono, Kawamura, and Soda, 1968)
Alite size is small, dominance of M_3 variety	Rapid crystallization during 10 minute retention at 1600°C (Maki and Goto, 1982)
Small alite	Short flame, fast heating rate (Ono, 1981); burning zone shorter than flame (Hansen, letter, 1985)
Relatively numerous small alite crystals	K_2O without sulfate and increase in melt viscosity (Strunge, Knöfel, and Dreizler, 1985)
Small alite (average = 20 to 50 μm) containing various inclusions	Short oil flame (Krämer, 1960)
Small alite crystals	Burning of very fine raw feed at low temperature; silica feed particles less than 50 μm (Long, 1982a); short thickening time in oil-well cements (Long, 1984a)
(a) Small alite (15 μm) (b) Moderate alite (15-30 μm) (c) Large alite (30-60 μm)	(a) Fine raw feed or half-burned clinker (b) Well-burned clinker (c) Coarse raw feed (Ono, Kawamura, and Soda, 1968)
70- to 100- μm alite crystal size	Optimal size for greatest effect on cement properties (Okorokov, 1975)
70- to 90- μm alite crystal size; 20- to 70- μm size	Optimal size from chalky raw materials; optimal size from marl+clay (Fataliev, 1965)
20- to 40- μm alite crystal size	Optimum size (Butt and Timashev, 1965)
Alite, thin tablets, may be attached to compact crystals, skeletal overgrowths on older crystals	Excess of SiO_2 in melt (mostly iron-rich); increase in flow media; or very high burning temperature (Gille and others, 1965)
Increase in amount of small alite, decrease in large alite	Rapid burning at high temperature (Ono, Kawamura, and Soda, 1968)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Alite	
Observations	Interpretations
Increase in alite size and idiomorphism	Increasing TiO_2 content in clinker (Knöfel, 1977)
Decreasing alite size, higher burning temperature	Relatively higher alumina ratio (Long, 1982a)
Increase in alite size and idiomorphism	Lowered viscosity of melt resulting from increase in clinker sulfate and degree of sulfatization (sulfate to alkali ratio) (Strunge, Knöfel, and Dreizler, 1985)
Decrease in alite size	Rapid burning, resulting in growth rate of crystals slower than formation of nuclei (Butt, Timashev, and Starke, 1973)
Decrease in range of alite crystal sizes	Increase in burning temperature, decrease in burning time (Butt, Timashev, and Starke, 1973)
Birefringence = 0.004-0.007 in normal alite but reached 0.010	Maximum birefringence in clinker rich in Na_2O , SO_3 , and MgO burned at high temperature (Ono, Kawamura, and Soda, 1968)
Alite with high birefringence	Imperfectly inverted monoclinic form, partially rhombohedral (Ono, 1981). Large, long kilns, high MgO levels, high burning zone temperature (Dorn, personal communication, 1985)
Large alite crystals with high birefringence	High MgO raw meal (4 to 5%), high temperature, long flame (Ono, letter, 1978)
Alite birefringence = 0.005 to 0.006	M_3 form, MgO -rich (Maki and Goto, 1982)
Alite birefringence = 0.003 to 0.005	Hybrid (M_1 and M_3) forms (Maki and Goto, 1982)
Alite birefringence = 0.003	M_1 form, relatively rich in SO_3 (Maki and Goto, 1982)
Alite birefringence = 0.0026	T_2 variety, formed during 120-minute firing (Maki, Haba, and Takahashi, 1983)
Simple twinning in pure C_3S	Develops as a result of rhombohedral to monoclinic transition at approximately 1050°C during cooling (Hofmänner, 1973)
Three-fold cyclic twinning of alite synthesized at high temperature and cooled quickly is coarser than texture of alite formed at low temperature and cooled slowly	Fineness of twinning depends on starting temperature of the quick cooling, which is still in stability region of high-temperature form, and does not depend on maximum temperature or duration of heating (Ono, 1974)
Polysynthetic twinning (very minute) in alite	Triclinic alite due to failure to absorb enough impurities at high temperatures (Ono, 1975)
Polysynthetic twinning in pure C_3S	Develops as a result of monoclinic to triclinic transition at approximately 980°C during cooling (Hofmänner, 1973)
Zoned alite	Varying burning conditions (Gille and others, 1965); low temperature core, high temperature overgrowth (Ono, 1980d and Chromy, 1967); slow heating to high temperature (Ono, Kawamura, and Soda, 1968); cooler to kiln recirculation (Long, 1984b);
Zoned alite with dotlike inclusions	Clinker burned with long flame (Ono, 1981)
Zoned alite with lower B in inner part	Slow burning to a high temperature (Ono, Kawamura, and Soda, 1968)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Alite	
Observations	Interpretations
Zoned alite, normally M_3 over M_1 , boundaries marked by liquid inclusions	Crystallization over wide range of temperatures; slow heating rate (Maki and Goto, 1982)
Alite crystals with small liquid inclusions (intergrowth of fine ferrite and aluminite)	Precipitation of alite at 1450°C during 30-min firing (Maki and Goto, 1982)
Reversed zoning (M_1 overgrows M_3)	Quick precipitation of alite from melt (Maki and Goto, 1982)
Zones in alite broaden toward nearby belite nests	Calcium and silica abundant in nest area (Ono, Kawamura, and Soda, 1968)
Alite with spindle or lancelike bands	Monoclinic to triclinic inversion (Gille and others, 1965); T_2 twinning (Maki, Haba, and Takahashi, 1983)
Decomposed alite shows blurred dark spots in thin section	Moderately reducing conditions (Woermann, 1960)
Alite interiors diffusely reflecting ("soiled")	Very slow cooling (Tsuboi and Ogawa, 1972)
Diffusely reflecting alite, appearing unstable and black	Decline in 28-day mortar strength by 1% to more than 5% (Tsuboi and Ogawa, 1972)
Idiomorphous alite	Relatively rapid cooling (Knöfel, Strunge, and Bambauer, 1983)
Idiomorphous alite, glassy matrix	Clinker burned under reducing or oxidizing conditions, removed from kiln at temperature greater than 1250°C and quenched in water (Sylla, 1981)
Straight-sided crystals of alite and belite; continuous, uniform interstitial glass	Extremely rapid cooling (quenching) (Brown, 1948)
Cokelike clinker, rounded alite (more than 100 μm) and amoebalike alite	Increasing SO_3 (Tsuboi and Ogawa, 1972)
Emerald-green alite, yellow-green belite	Presence of chromium (Bozhenov and Kholopova, 1974)
Brownish alite, blue belite	Manganese (Bozhenov and Kholopova, 1974)
Brown alite	Coarse iron ore or iron fragments in raw mix (Ono, 1975)
Bright yellow alite, brown belite	Cobalt (Bozhenov and Kholopova, 1974)
Decomposition of alite	Long annealing time or repeated heat treatment at lower temperatures, approximately 1200°C (Ghosh, 1983)
Surficial deterioration of alite, amoeboid ragged belite, dendritic and "lake" periclase, loss of alumina brick	Overburning from delayed petroleum coke, producing longer burning zone (Jefferson and Kruse, 1987)
Decomposition of alite to belite and free lime; abnormally large belite and alite	Slow cooling in kiln (Hofmänner, 1973)
Decomposition of alite into belite, free lime, ferrite, and iron sulfide pseudomorphous after alite; myrmekitic intergrowth	Reducing conditions (Woermann, 1960)
Pseudomorphic crystals after primary alite contain fine inclusions or margins of ferrite, belite, and free lime	Moderate reduction, and introduction of iron into alite lattice resulting in instability and decomposition (Woermann, 1960)
Relatively wide and more numerous belite borders on alite which shows lamellar structure, the latter well-developed upon withdrawal from kiln at temperatures lower than 1200°C	Clinker burned under reducing conditions, removed from kiln at 1200°C, air cooled. Similar texture when removed at 1150°C and quenched in water (Sylla, 1981)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Alite	
Observations	Interpretations
Irregular alite with wide border of belite, well-differentiated matrix of large crystals, metallic iron in aluminoferrite	Clinker burned at 1450°C for 1 hour, cooled to 1200°C in kiln (Sylla, 1981)
Decomposition of alite to secondary belite and free lime; decrease in compressive strength; possible abnormal expansion	Reducing conditions, coarse coal particles falling into raw mix (Hawthorne, Richey, and Demoulian, 1981)
Decomposition of alite varied between 10% to 85%; exceptions in low-Fe or no-Fe clinker	Lab experiment with reducing conditions, slow cooling (5°C per min, 90 min from 1450°C to 1000°C) (Woermann, 1960)
Intimate mixture of belite and dicalcium ferrite on alite lattice planes; free-lime crystals with inclusions of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$	Low temperature re-oxidation (Long, 1982b)
Belite fringes on alite (degradation of alite to belite + free lime)	Maintenance of clinker at 1200°C, and slow cooling of clinkers with high alumina ratio, accentuated in reducing environment (Long, 1982b); increased thickening time for oil-well cements (Long, 1984a); and initial viscosity increase in oil-well cement slurry (Reeves, Bailey, and McNabb, 1984)
Decomposition of alite to belite and free lime	Presence of bivalent iron (Hofmänner, 1973)
Alite decomposition into secondary belite	Overburning (Dorn, 1979)
Corroded crystals of alite	Slow cooling (Gille and others, 1965)
Belite coating alite	Pseudomorphic resorption of alite from lime-poor melt; slow cooling (Gille and others, 1965)
Belitized alite surfaces	Slow cooling (Tsuboi and Ogawa, 1972)
Alite decomposed into CaO and C_2S ; corrosion of alite	Tempering (Krämer, 1960)
Serrated alite	High $\text{Al}_2\text{O}_3/\text{FeO}$, especially when alkalies are abundant (Brown, 1948)
Alites greater than 20 μm , with belite fringes	Strength decreases about 1% (Tsuboi and Ogawa, 1972)
Mortar strength with average size of alite less than 10 μm	Strength decreases usually more than 5% (Tsuboi and Ogawa, 1972)
Compressive strength is 10% higher for 20- μm alites than 10- μm alites, and 10% lower than 30- μm crystals	28-day strength variation with alite size (Tsuboi and Ogawa, 1972)
Increase in triclinic alite, increase in gamma belite; strength not well-developed	Reducing conditions (Uchikawa, 1992)
Alite with ultra-fine particles under 0.5 μm (inclusions)	Excess solid solution (Ono, 1995)

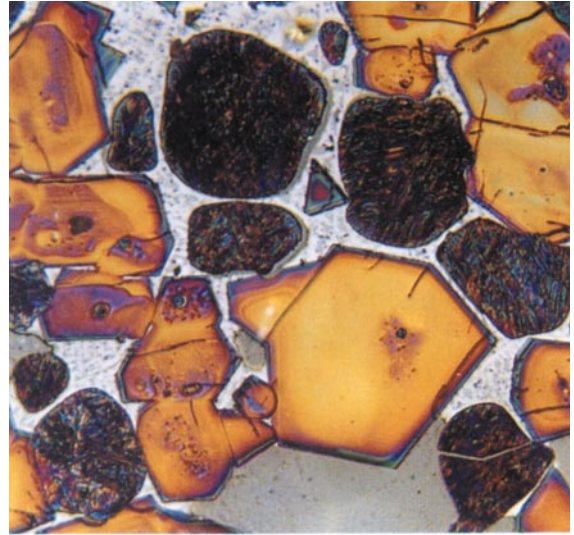
PHOTOMICROGRAPHS OF ALITE

Photograph 7-15 Euhedral to subhedral, zoned, yellowish tan alite; dark, round belite with typical multidirectional lamellae; and a well-differentiated matrix of aluminite (C_3A) and ferrite (C_4AF). Small belite inclusions in alite. Epoxy-filled pore at bottom of photo. Coal-fired kiln, wet-process, 1000 tons/day, 38 MPa; coarse seashell feed (30% greater than 75 μm). (S#A6635)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

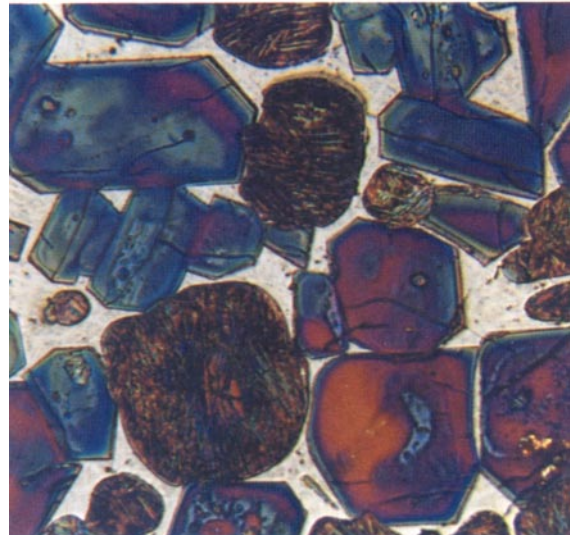


Photograph 7-16 Euhedral blue and reddish brown alite; round, brown belite with multidirectional lamellae; well-differentiated, very finely microcrystalline matrix of aluminite and ferrite. Moderately high maximum temperature, long burning time, moderately slow heating rate, moderately rapidly cooled. Coal-fired, wet-process kiln, 1000 tons/day. Clamshell, clay, iron-ore feed. (S#A6636)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

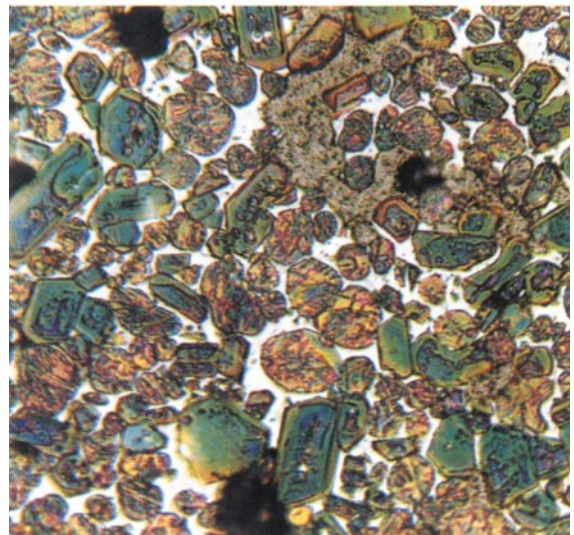


Photograph 7-17 Small, green-yellow angular alite and round multicolored belite showing a wide range of crystal sizes in bright ferrite-rich matrix. Highly reactive silicates. Coal-fired, wet-process kiln, 47-48 MPa. (S#A6637)

Polished section

Nital etch

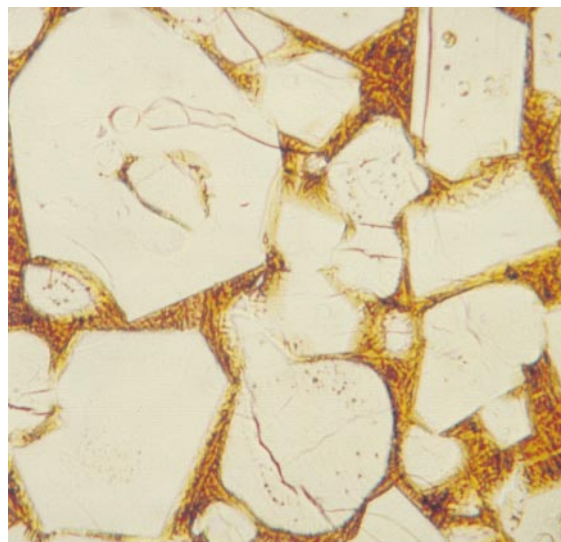
Field dimensions = 0.21x0.21 mm



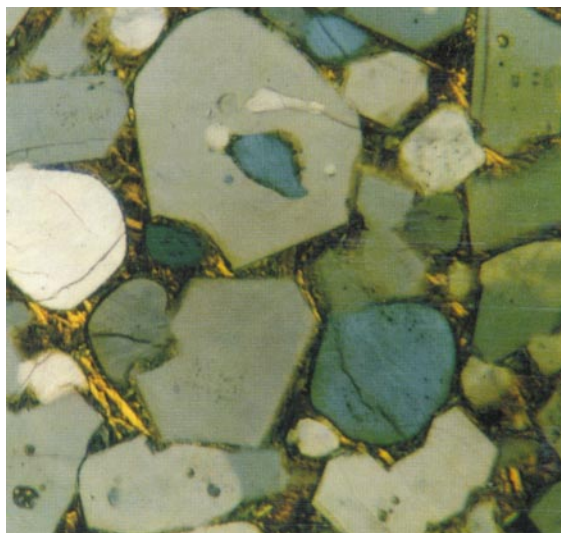
PHOTOMICROGRAPHS OF ALITE (CONTINUED)

Photograph 7-18 Clinker thin section (approximately 15 μm thick) showing relatively large angular alite; smaller, round belite; and normal ferrite with its short slender intersecting crystals, between which the aluminates occur (not visible at this magnification). (S#A6638)

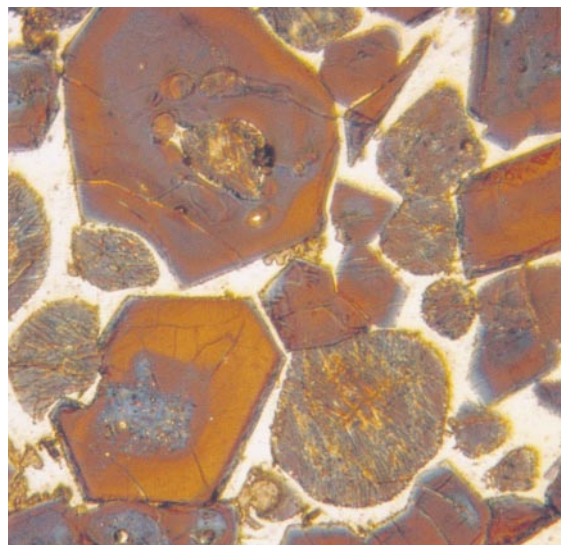
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



Photograph 7-19 Same field of view as previous photograph except in partially crossed polars. Various interference colors due, in large part, to different crystallographic orientations. (S#A6639)



Photograph 7-20 Same field as previous photograph but with reflected light and nital etch. Euhedral, brown alite; round belite with multidirectional lamellae; well-differentiated matrix (almost invisible in the photograph). High maximum temperature, long burning time, slow heating rate, quickly cooled. Coal-fired, dry-process kiln, 2000 tons/day. (S#A6640)



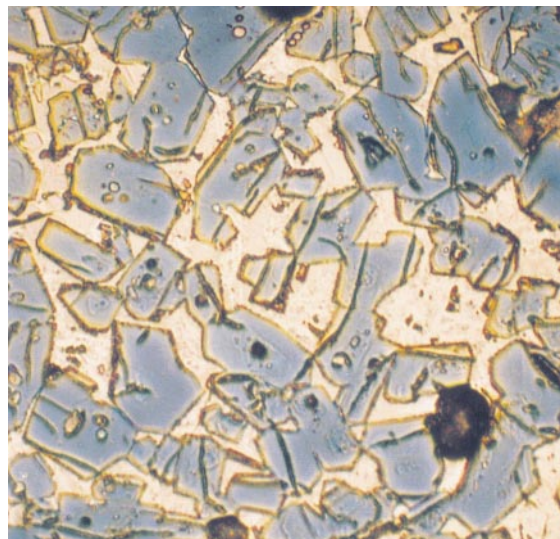
PHOTOMICROGRAPHS OF ALITE (CONTINUED)

Photograph 7-21 Blue, subhedral alite crystals with very narrow belite fringe (almost the only belite in the clinker) and matrix of gray aluminate and dull ferrite. Average alite size is approximately 26 μm . Coal-fired, dry-process kiln, 550 tons/day. (S#A6641)

Polished section

Nital etch

Field dimensions = 0.12x0.12 mm

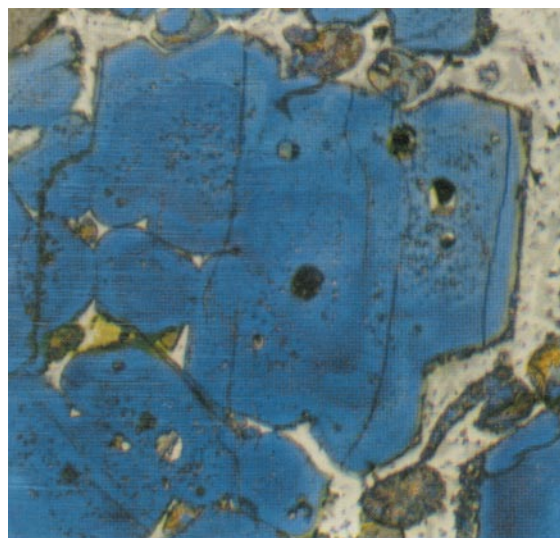


Photograph 7-22 Stacked, blue, cannibalistic, strongly zoned euhedral alite with abundant inclusions. Small, round belite crystals; well-differentiated matrix. Belite coating on alite. High maximum temperature, long burning time, slow heating rate, slowly cooled, 35 MPa. Coal-fired, wet-process kiln. (S#A6642)

Polished section

Nital etch

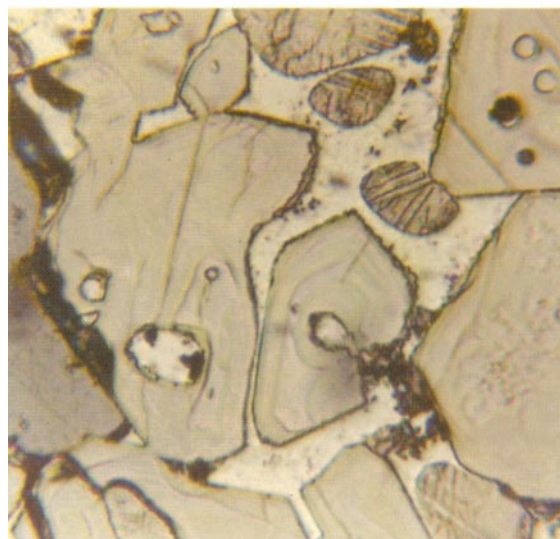
Field dimensions = 0.21x0.21 mm



Photograph 7-23 Marked topographic relief accentuating silicate crystal internal structures. Produced by 10-second nital etch followed by 10-second polish on Texmet™ with 0.05- μm alumina. (S#A6643)

Polished section

Field dimensions = 0.14x0.14 mm



PHOTOMICROGRAPHS OF ALITE (CONTINUED)

Photograph 7-24 Coarsely crystalline silicates from coarse seashell feed. Angular, strongly zoned alite and round, relatively small belite with coarse lamellae. Coal- and coke-fired, semidry process kiln, 1850 tons/day. High maximum temperature, long burning time, slow heating rate, quick to moderately quick cooling, 44 MPa. (S#A6644)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

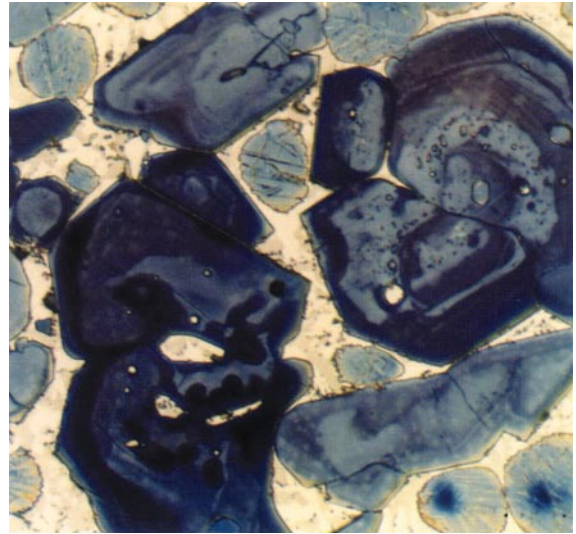


Table 7-1. Microscopical Interpretation of Clinkers (continued)

Belite	
Observations	Interpretations
Large proportion of belite	Low lime saturation factor (Long, 1982a; Fundal, 1980)
Equal alite and belite	Lime saturation factor = approximately 88% (Fundal, 1980)
Belite agglomerations: (a) Sharply outlined clusters (b) Diffuse limited clusters (c) Streaks (d) Spots	Classification of belite agglomerations (Hofmänner, 1973)
Belite nests	Ash shortage, excessive quartz grain size, presence of feldspar and blast furnace slag (Gille and others, 1965)
Nests of belite	Inadequately mixed raw material, decline of mortar strength (Tsuboi and Ogawa, 1972)
Nests of belite	Vestigial quartz grain (Krämer, 1960)
Round, compact belite nests of large, polygonal, well-lamellated crystals	Large quartz or flint, +44 μm (Fundal, 1980)
Pore-centered belite nests with relatively large, densely packed crystals, producing large alite at higher temperature if lime is available	Coarse quartz in feed (Long, 1982a)
Belite nests, possibly with central pore	Low lime inclusions such as quartz splinters, ash droplets (Gille and others, 1965)
Glass core in belite nest, large alite adjacent to belite nest	Residual SiO_2 , a frequent component of insoluble residues (Fundal, 1980)
Glass C_2S in center of belite nests	Quartz grains are large or poorly burned (Tsuboi and Ogawa, 1972)
Closely spaced belite	Large quartz grains in raw mix (Tsuboi and Ogawa, 1972)
Tight belite crystals in nests with sparse liquid phase	Coarse quartz (Miller, 1981; Gille and others, 1965)
Large belite clusters	Unstable ring formation, especially in sulfate-rich clinkers, if no large quartz grains in raw mix (Fundal, 1980); segregation of raw mix (DeLisle, 1979); poor strength development in oil-well cements (Reeves, Bailey, and McNabb, 1984)
Large clusters of belite associated with high contents of free lime	High lime saturation factor (Fundal, 1980)
Large patches of belite; belite nests from coarse quartz	Selective reaction of raw mix components: clay at lower temperature than that for quartz, muscovite, hornblende, and Ca-feldspars resulting in early nodulation (micronodules) and clinker dust with high lime saturation factor (Fundal, 1980)
Subhedral, pseudo-hexagonal, lath shaped alite and belite clusters (subround), some hexagonal belite	Coal ash absorption (Rao and others, 1993)
Rounded belite in dense nests	Intense burning (Tsuboi and Ogawa, 1972)
Belite nests with curved boundaries and very little liquid phase	Concentration of siliceous component (lack of lime) (Hofmänner, 1973)
Large number of belite clusters	Decrease in grindability (Dorn, 1985)
Peripheral annular region of belite and flux-rich material in clinker nodule	Late deposition of coal-ash layers (Long, 1982)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Belite	
Observations	Interpretations
Belite concentrations on the clinker surface, free lime in clinker interior	Coal-ash deposition on already formed clinker nodule; similar effects in coatings and clinker rings (Pollitt, 1980)
Belite nests (loosely packed) with aluminite-rich melt	Coarse aluminosilicate grain, perhaps a feldspar (Miller, 1980)
Amoeboidal clusters of belite (crystal ≥ 30 to $40\ \mu\text{m}$)	Marl or calcitic shale ($35\% \text{CaCO}_3$) with feldspar in a prenodulized raw meal (Fundal, 1980)
Belite clusters rich in liquid phase, relatively small crystals	Coarse shale particles (Long, 1982a)
Decrease in belite nests, increase in liquid phase	Added iron reduces liquid viscosity and promotes reduction of belite nests (Dorn, 1985)
Belite nests rich in melt phase (loosely packed)	Nonquartz argillaceous particles or fuel ash particles (Miller, 1980)
Cluster of belite, dense or tightly packed with very little interstitial material	Concentrations of SiO_2 in the form of large quartz and/or slag (Fundal, 1979)
Irregular clusters (some quite large) of belite containing considerable amounts of interstitial melt	Large, low-lime marl grains (less than $60\% \text{CaCO}_3$) and/or large feldspar grains (Fundal, 1979)
Decrease in belite nests	Increase in amount of clay or shale in mix (Frederick, 1985)
Elimination of belite clusters	Increase in maximum kiln temperature from 1454° to 1516°C (Rowe, 1995)
Belite cluster with small periclase crystals	Large diopside ($\text{CaMgSi}_2\text{O}_6$) grain (Fundal, 1980)
Large areas of belite and flux with high-limed clinker nodules adhering or embedded	Very late deposition of coal ash or insufflation of raw feed (Long, 1982a)
Clinkers with belite and flux-rich cores	Kiln coating fragment (Long, 1982a)
Belite streaks, generally in peripheral areas of small clinker	Local coal ash deposition (Hofmänner, 1973)
Belite coatings on clinkers, heterogeneous clinker	Wet process, raw mix leaves chain system still wet (Hawthorne, Richey, and Demoulian, 1981)
Segregation of belite, digitation, gamma polymorph, exsolution in alite, reduced areas with metallic inclusions and oldhamite (Ca , MnS); variation in phase percentages	Assimilation of high silica and alumina coal ash (Kihara, 1988)
Belite streaks in central areas of large clinkers	Inhomogeneity in raw mix (Hofmänner, 1973)
Large belite clusters, peripheral layers, veins, cores in clinkers, dispersed in aluminite and ferrite	Coal ash deposition (Long, 1983)
Belite streaks	Local inhomogeneities due to sandy raw mix (Fundal, 1980)
(a) Belite streaks (b) Zones of normal composition between belite streak and surface of clinker	(a) Coal-ash contamination on clinker surfaces during burning results in low-lime area and belite (b) Products of low abrasion coated on belite streak (Gille and others, 1965)
Crusts of belite on clinkers; crystals of various sizes	Semi-dry process, coal fuel with 15% to 20% ash, 0.5% to 1.5% sulfur (Hawthorne, Richey, and Demoulian, 1981)
Relatively large belite in clinker fines, small belite in nodules	Comparatively long time in burning zone for clinker fines (Samuel, Rao, and Chopra, 1984)
Large belite with rough exterior surface	Overheating or overburning (Dorn, 1979)
Large belite crystals	Prolonged heating below liquid-formation temperature (Maki and Goto, 1981); coarse quartz or quartzite in feed (Akatsu and Monna, 1966)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Belite	
Observations	Interpretations
Belite size increasing, belite abundance decreasing	Increasing burning temperature from 1500°C to 1700°C (Suzukawa, Kono, and Fukunaga, 1964)
Coarsening of belite, aluminite, and aluminoferrite; irregular belite outline, idiomorphous alite	Clinker burned under oxidizing conditions, cooled to temperatures below 1250°C in the kiln (Sylla, 1981)
Relatively large belite inclusions in alite, large belite crystals (45 µm)	Abundance of coarse quartz in feed; belite and alite became much smaller upon use of finely ground friable silica (Dorn, 1980)
Large, irregularly shaped belite	Very slow cooling (Ono, Kawamura, and Soda, 1968)
Belite is 1-4-µm diameter at 1300°C but grows to 20-40 µm crystals	Recrystallization during burning at high temperature (Ono, Kawamura, and Soda, 1968)
Multidirectional lamellar structure of belite	Formed and coarsened during alpha to alpha prime transition during cooling (Hofmänner, 1973); clinker burned at greater than 1420°C (Ono, 1975)
Increase in proportion of cross laminations in belite crystals	Increase in TiO ₂ content in clinker (Knöfel, 1977)
Amber belite with Type I microstructure (multidirectional lamellae)	Belite kept at "alpha temperature" in kiln coating (Ono, 1981)
Small, round Type II belite	Low burning temperature (Ono, Kawamura, and Soda, 1968)
Sharp, wide lamellae	Distorted beta belite, raw mix rich in Fe ₂ O ₃ and alkalies (Gouda, 1980)
Colorless Type II belite (parallel striations)	Belite held at "alpha-prime temperature" in kiln coating (Ono, 1981); burning below 1420°C (Ono, 1975)
Rounded belite without lamellae, finely intergrown groundmass	Rapidly cooled clinker (Gille and others, 1965)
Belite crystals with no stripes, commonly with rents and cracks	Stress during rapid quenching (Gille and others, 1965)
Nontwinned belite	SO ₃ more than 1% (Tsuboi and Ogawa, 1972)
Structureless belite crystals (uniform reflection)	Extremely rapid quenching, as in lab (Gille and others, 1965)
Polysynthetic twinning in belite	Formed during very slow cooling as a result of alpha prime to beta transition (Hofmänner, 1973)
Belite with polysynthetic twinning	Normal cooling rate (Krämer, 1960)
Ragged belite with dotlike inclusions	Clinker burned with long flame (Ono, 1981)
Ragged crystals of belite	Very slow cooling (Krämer, 1960)
Ragged belite with no degradation of alite	Slow cooling at certain alumina to iron ratios; also affected by alkali content (Long, 1984, unpublished ICMA presentation)
Ragged belite	Alpha to alpha prime inversion in contact with melt and slow cooling (Ono, 1981)
Ragged belite	Slow cooling and resolution (Gille and others, 1965; Midgley, in Taylor, 1964; DeLisle, 1976, 1979)
Belite with lamellar extensions, surficial deterioration of alite to belite, relatively coarse crystalline matrix	Slow in-kiln cooling due to excessive insufflation (Hoodmaker and Franklin, 1995)
Belite overgrowths	Slow cooling (Gille and others, 1965); very slow cooling (Lee, 1982)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Belite	
Observations	Interpretations
Rough belite surface, prominent lamellae, segmented fingerlike sections	Reducing conditions (Dorn, 1979)
Secondary belite, free lime corrosion of alite	Slow cooling (Gille and others, 1965)
Erosion of alite crystals to intimate mixture of belite and free lime pseudomorphic after alite	Slow cooling, temperature at approximately 1200°C for an appreciable time (Long, 1983)
Erosion of alite crystals to form surface belite; pinhead belite in matrix	Slow cooling; alumina ratio above 2.5; up to 10% reduction in 28-day strength (Long, 1983)
Droplike belite in liquid phase; commonly associated with dendritic periclase	Excess SiO ₂ (Hofmänner, 1973)
Secondary belite, free lime, periclase; autoclave problems	Failure of solid fuels (fly ash, carbonaceous shales, coal tailings as part of raw mix) to burn before granulation zone (Hawthorne, Richey, and Demoulian, 1981)
Secondary belite in the matrix	Slow cooling in the temperature range > 1300°C (Scheubel, 1987)
Secondary belite coating on alite	Resorption into liquid phase (Hofmänner, 1973); slow cooling (Midgley, in Taylor, 1964)
Myrmekitical intergrowth of belite in alite, pseudomorphous free lime, and remnants of nondecomposed alite	Decomposition via slow cooling; sometimes accelerated by foreign ions, excess alkalies, embedded Fe ⁺⁺ , and moderate reducing conditions (Gille and others, 1965)
Belite grains with distinct fissility planes	Gamma belite and reducing conditions (Rajczyk, 1990)
Belite laminae on rhombic alite planes, usually three groups intersecting	Reducing conditions in sinter zone (Gille and others, 1965)
Tiny belite inclusions suggestive of lamellae in alite	Deficient air supply in sintering zone (Gille and others, 1965)
Dismembered, finely dendritic crystals of belite	Excess crystallization of belite (Gille and others, 1965)
Belite next to free lime in normally burned clinker	Alkali belite (Gille and others, 1965; DeLisle, 1976)
Irregular belite	Overburning (Prout, 1979)
Overlapping belite	Too much MgO, ZnO, and others that lower viscosity (Tsuboi and Ogawa, 1972)
Wide lamellae on belite, corroded alite, and cooling cracks	Alkali in clinker (Gille and others, 1965)
Large belite crystals, colorless, low birefringence (0.012-0.015), sharp striations, coarse sandwich structure of alpha and beta seen under crossed nicols, crystal surface free from iron phase	Alkali belite (Ono, letter, 1977)
Clear belite ring	Alpha belite, alkali-rich, derived from melted feldspar which reacted with f-CaO (Ono, 1981)
Dendritic belite	High alkali (K-feldspar) in raw mix (Gille and others, 1965); Low primary air volume or pressure, excessive burning-zone temperature, slow cooling rate, high MgO level—approximately 4.5% (Dorn, personal communication, 1985)
Increase in amount of alite, crystals with higher aspect ratio and smaller size, decrease in belite percentage, becoming brain, finger, or leaflike	Fluorine in the presence of SO ₃ in raw mix (Wei and Mingfen, 1988)
Alite containing K ⁺ may tend to decompose	Above a certain potassium percentage alite does not form, but instead belite and free lime (Woermann, 1960)
Clear belite crystals	Quick cooling, no exsolution of impurities (Ono, 1975)

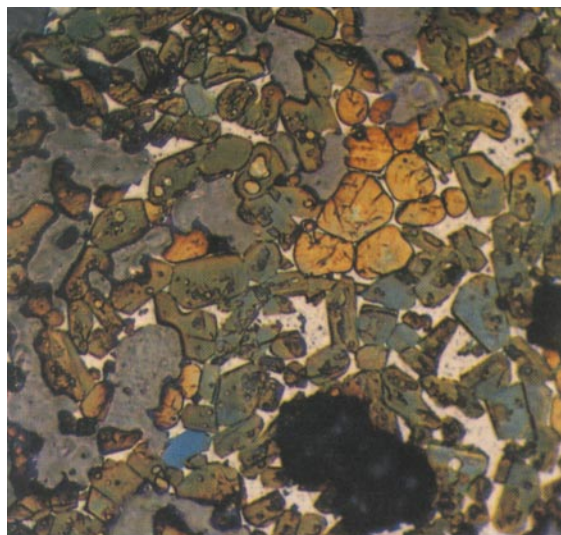
Table 7-1. Microscopical Interpretation of Clinkers (continued)

Belite	
Observations	Interpretations
Pale yellow belite	Medium cooling rate (Ono, 1975)
Yellow nested belite	Coarse quartz, lack of lime diffusion into nest (Dorn, 1985)
Belite crystals of normal type microscopically but with extra XRD reflections	Sodium- or potassium-stabilized belite; alkalies in excess of sulfur (Tang and Gartner, 1986)
Colorless, yellow, brown belite	Alpha percentages are 15% to 30%, 10% to 25%, and 0 to 15%, respectively (Ono, 1981)
Muddy yellow belite	Slow cooling rate (Ono, 1975); relatively hard to grind if nested (Ono, in Dorn, 1985)
Zoned belite with yellow or muddy colors in outer zone	Differences in absorption of impurities produced by alpha prime to alpha transition (Ono, Kawamura, and Soda, 1968)
Belite containing abundant alpha form, alite with high birefringence	High temperature and quick cooling; high strength (Ono, Kawamura, and Soda, 1968)
Scarcity of alpha form in belite	Slow cooling, low strength (Ono, Kawamura, and Soda, 1968)
Dotted, colorless belite (crystals with internal particulate dispersions)	Very slow cooling (Ono, 1981)
Dots of impurities in belite	Extremely slow cooling (Ono, Kawamura, and Soda, 1968)
Cracks and fissures along belite lamellae, partial decomposition of belite crystal	Belite transition from beta to gamma during cooling, due to solid solution with foreign ions; insufficiently rapid cooling (Hofmänner, 1973)
Disintegration due to beta to gamma belite transformation and dusting. Nondusted nodule shows partly idiomorphous alite, belite lamellae in alite; large belite crystals; matrix almost totally aluminate, metallic iron, and fine-grained periclase	4-hour burn in reducing atmosphere, air cooled (Sylla, 1981)
(a) Gamma belite, dusted (b) Grains with rents and cracks	(a) Entrapped Fe ⁺⁺ and reducing conditions; (b) Long-lasting tempering occurs in kiln scale and results in dusting (Gille and others, 1965)
Dusting in samples of same composition in oxidizing and reducing atmosphere	Low lime content, beta to gamma transformation of primary belite (Woermann, 1960)
Dusting	Half-burned clinker at very low temperature; belite cooled from alpha prime form (Ono, Kawamura, and Soda, 1968)
Type I belite, with slight excess MgO or burning under reducing conditions	Strength decrease up to 5% (Tsuboi and Ogawa, 1972)
Large quantity of belite next to free lime	High alkali and sulfate content in mix hinders reaction of belite and free lime to alite in laboratory clinkers (Dreizler, Strunge, and Knöfel, 1985)
Decreasing lamination in belite, increasing stabilization of alpha form	Increasing Na ₂ O content of clinker and low degree of sulfatization (Strunge, Knöfel, and Dreizler, 1985)
Belite inclusions in alite	Relatively large (12 to 13 μ m) in clinker made with quartz sand; 8 μ m in clinker made with sponge-silica (Dorn, 1980); residual original belite (Brown, 1948)

PHOTOMICROGRAPHS OF BELITE

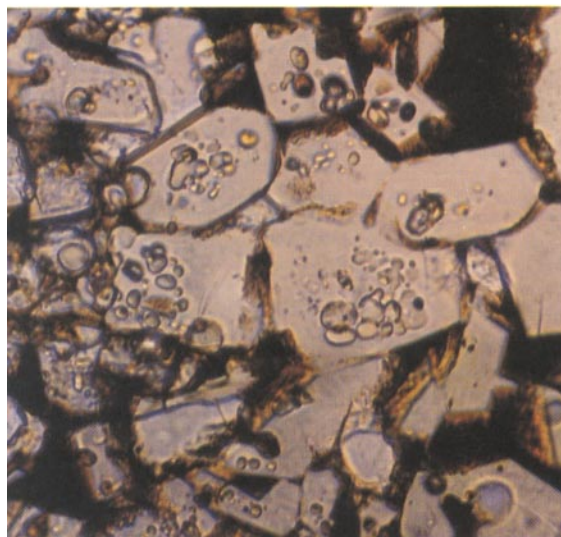
Photograph 7-25 Experimental laboratory burn with raw mix containing marl instead of quartz as a silica source. Resulting belite was well scattered in clinker and, to a minor extent, as nests. 1000°C for 30 min, 1425°C for 10 min. Very rapid temperature change. Average alite size = 20 μm . Clinker courtesy of Joe Garcia, Capitol Cement, San Antonio, Texas. (S#A6645)

Polished section
Nital etch
Field dimensions = 0.53x0.53 mm



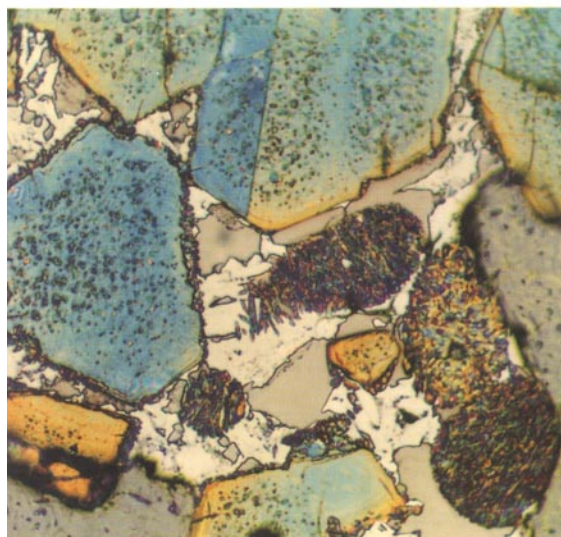
Photograph 7-26 Experimental laboratory burn with raw mix containing quartz (44-75 μm) as a silica source. Average alite crystal size = 44 μm . 1000°C for 30 min, 1425°C for 10 min. Very rapid temperature change. Note abundant free lime inclusions in alite. Clinker courtesy of Joe Garcia, Capitol Cement, San Antonio, Texas. (S#A6646)

Thin section
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



Photograph 7-27 Ragged belite crystals and belite coating on alite, one of which is twinned. Note abundant dotlike impurities in alite. Coarsely crystalline matrix with gray aluminate and relatively bright ferrite. Slowly cooled clinker. (S#A6647)

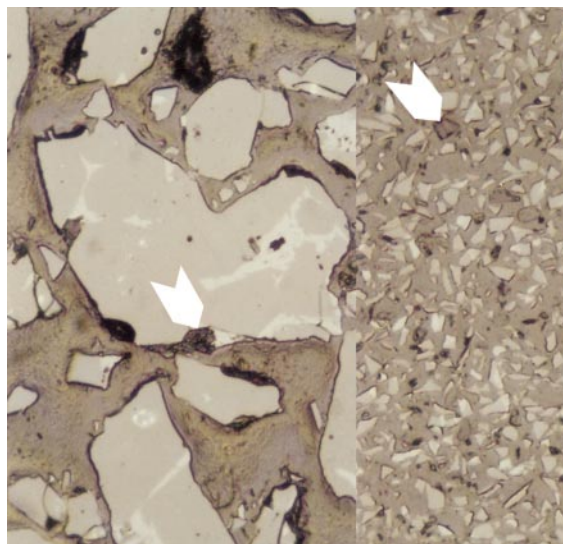
Polished section
Nital on KOH etch
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF BELITE (CONTINUED)

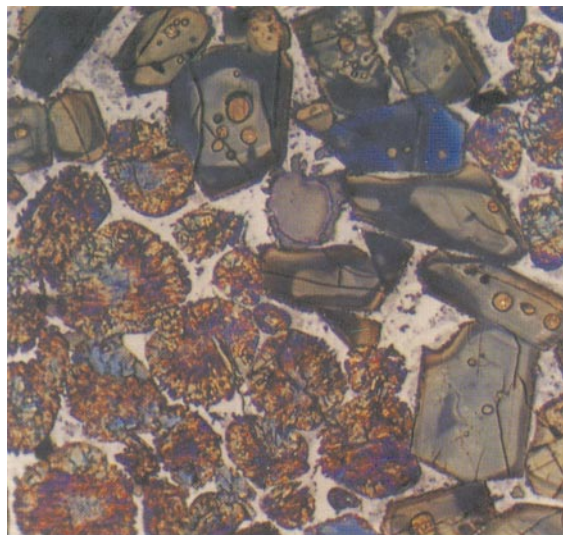
Photograph 7-28 Polished section of cement centrifuged in low-viscosity epoxy to produce a particle size and density gradation. Arrow on coarse particle near the base of the test tube (left) indicates alkali sulfate. Arrow on fine particle near the top of the cement (right) indicates gypsum. See Campbell (1986). (S#A6648)

Reflected light
Field dimensions = 0.21x0.21 mm



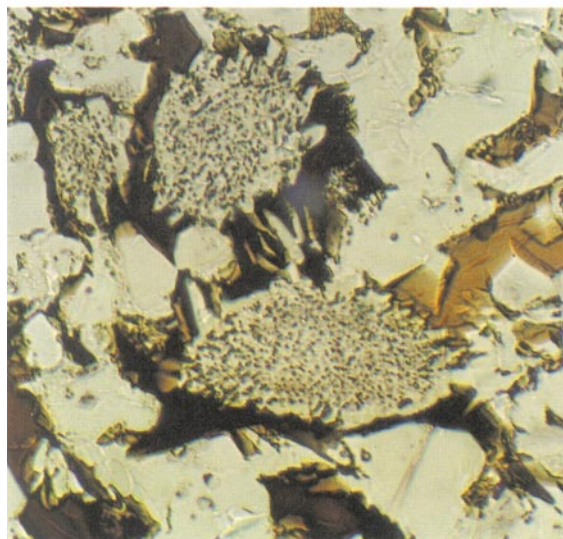
Photograph 7-29 Zoned euhedral to subhedral alite; ragged, round, internally disorganized belite; well-differentiated matrix; and round pore (upper center) with peripheral alkali sulfate. Coal- and coke-fired, dry-process kiln, 900 tons/day. High maximum temperature, moderately long burning time, slow heating rate, slow to moderately slow cooling rate. (S#A6649)

Polished section
Nital etch
Field dimensions = 0.21x0.21 mm



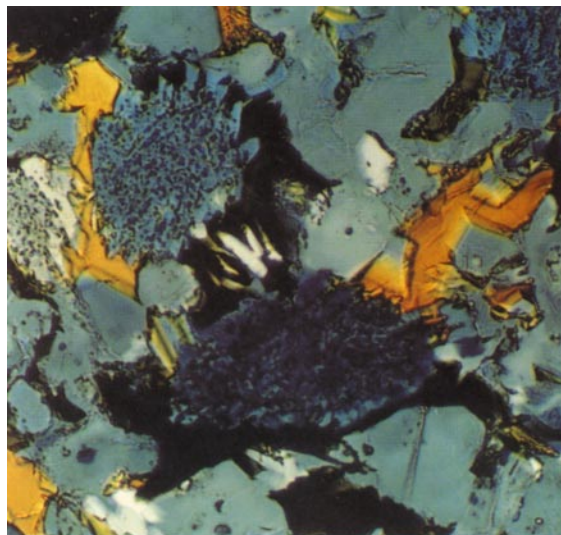
Photograph 7-30 Ragged belite from very slow cooling. Extension of "fingers" into matrix. Note dotlike impurities. Kiln coating. Coal-fired, dry-process kiln, 2350 tons/day. (S#A6650)

Thin section
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm

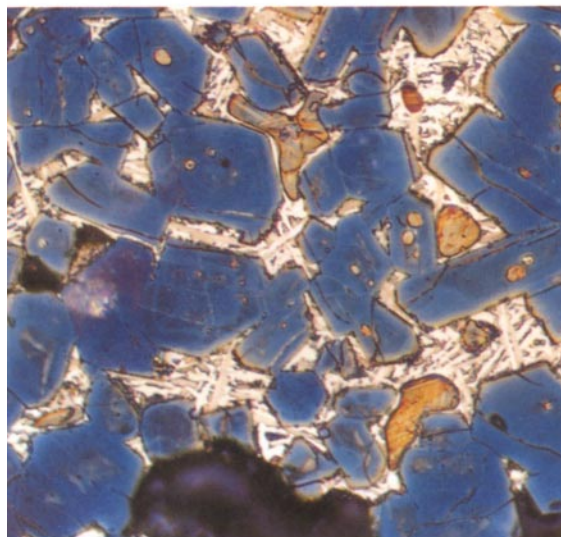


PHOTOMICROGRAPHS OF BELITE (CONTINUED)

Photograph 7-31 Same field of view as previous photograph, but with partially crossed polars, showing highly birefringent and strongly pleochroic ferrite. (S#A6651)

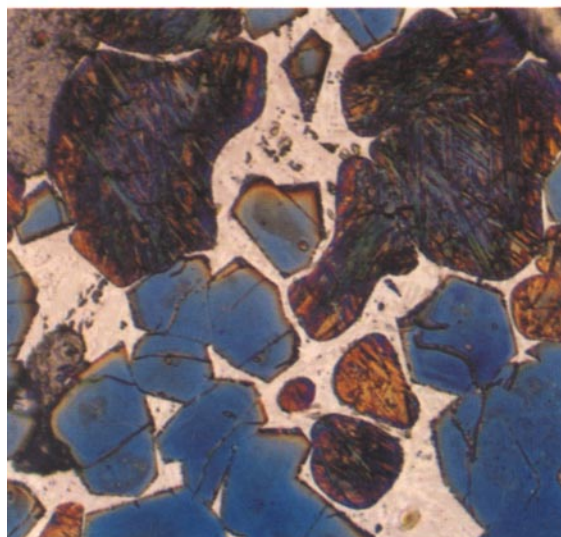


Photograph 7-32 Same clinker sample as above but different nodule, showing relatively small, irregular, brown belite wrapping around blue alite crystals, thought to be typical for clinkers burned at a high temperature for a long time. (S#A6652)



Polished section
KOH followed by nital etch
Field dimensions = 0.21x0.21 mm

Photograph 7-33 Irregular to normally round, brown belite; subhedral, angular, blue alite with cleavage cracks; and matrix of finely microcrystalline aluminite (C_3A) and lath-form ferrite. High maximum temperature, long burning time, slow heating rate, quick cooling, 41-42 MPa. Coal-fired, dry-process kiln, 2750 tons/day. (S#A6653)



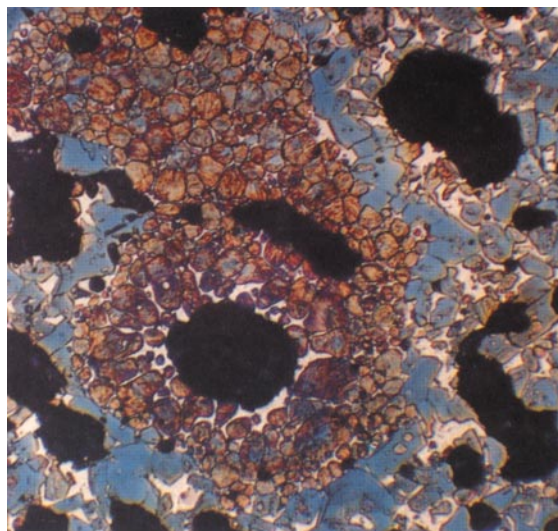
Polished section
Nital etch
Field dimensions = 0.21x0.21 mm

PHOTOMICROGRAPHS OF BELITE (CONTINUED)

Photograph 7-34 Belite crystals comprising sharply delineated nest around pore (black), probably the site of a coarse quartz grain in the feed. Coal- and coke-fired, dry-process kiln. (S#A6654)

Thin section

Field dimensions = 0.53x0.53 mm

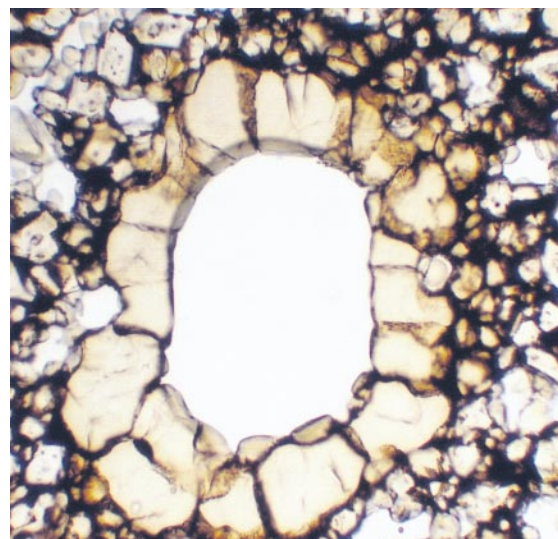


Photograph 7-35 Clear belite ring around central pore formed by silica mobilization during sintering of coarse quartz in feed. (S#A6655)

Thin section

Thickness = approximately 20 μm

Field dimensions = 0.53x0.53 mm

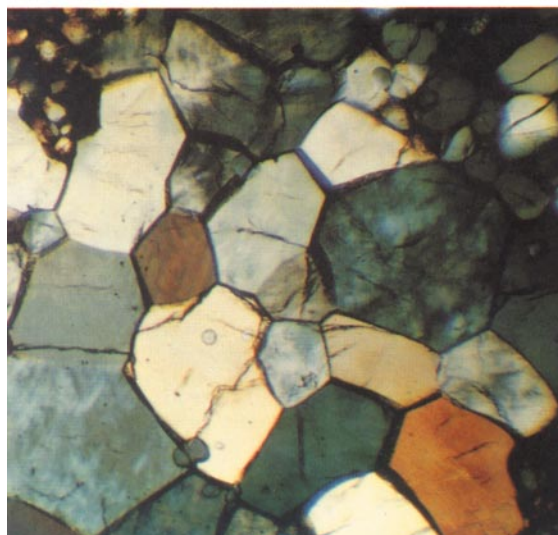


Photograph 7-36 Tightly packed clear belite nest from coarse quartz in raw feed. Crystals exhibit wide range of interference colors due to different crystallographic orientations. Note also the generally mottled pattern within individual crystals, suggesting a somewhat disorganized lamellar structure. (S#A6656)

Thin section

Crossed polars

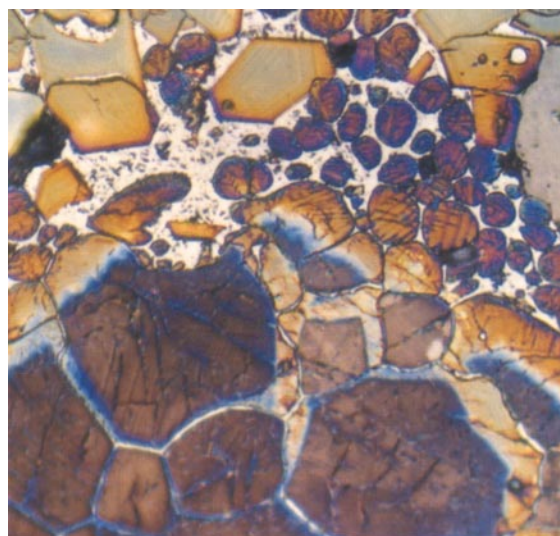
Field dimensions = 0.60x0.60 mm



PHOTOMICROGRAPHS OF BELITE (CONTINUED)

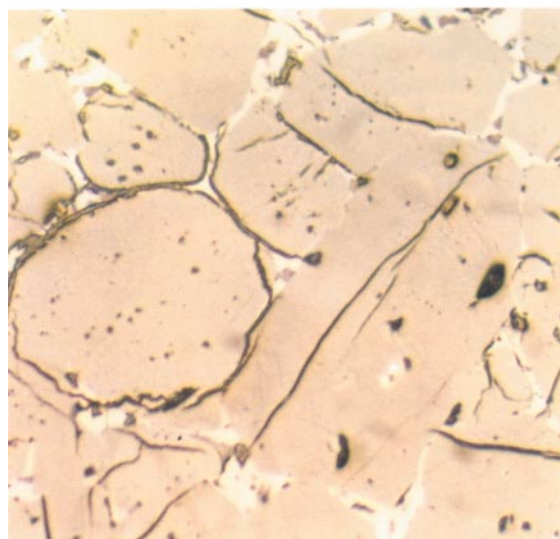
Photograph 7-37 Bimodal belite in laboratory-burned clinker made from a raw feed containing coarse quartz sand. Large nest of tightly packed belite crystals and much smaller crystals showing wide lamellae. Note gradational color response in nital etch of nest. 55% of the alite crystals were said to be greater than 75 μm . Clinker courtesy of Joe Garcia, Capitol Cement, San Antonio, Texas. (S#A6657)

Polished section
Field dimensions = 0.21x0.21 mm



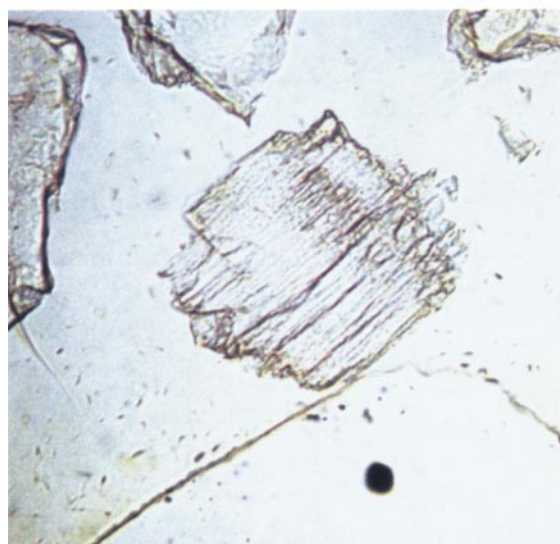
Photograph 7-38 Circumscribing cracks around belite (center left) and linear cleavage in alite. Low liquid phase. Shrinkage cracking during clinker cooling. Epoxy penetrates many of the cracks; therefore, cracking occurred prior to impregnation. Coal-fired, dry-process kiln with flash calciner, 5000 tons/day; moderately high maximum temperature, long burning time, slow heating rate, quickly cooled, 40 MPa. (S#A6658)

Polished section
No etch
Field dimensions = 0.21x0.21 mm



Photograph 7-39 Gamma belite fragment in thin section. Note semisplintery fracture and internal microstructure. (S#A6659)

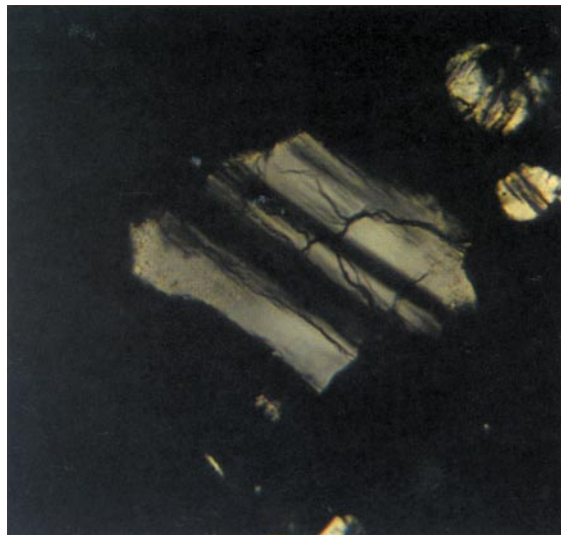
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF BELITE (CONTINUED)

Photograph 7-40 Thin section of gamma belite fragment in cross-polarized light. (S#A6660)

Field dimensions = 0.21x0.21 mm

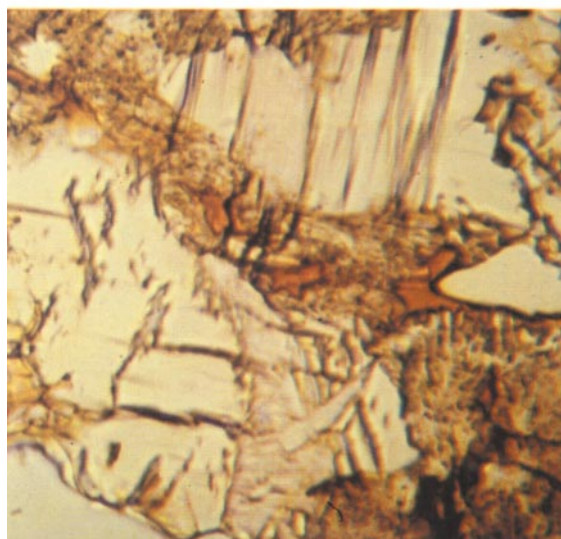


Photograph 7-41 Slowly cooled kiln buildup from the transition zone containing, for the most part, polysynthetically twinned belite (Type II, Insley) in lower left and slightly splintery gamma belite (upper right) in matrix of coarsely microcrystalline ferrite and aluminates. (S#A6661)

Thin section
Crossed polars
Field dimensions = 0.21x0.21 mm



Photograph 7-42 As above but in transmitted, plane-polarized light. (S#A6662)



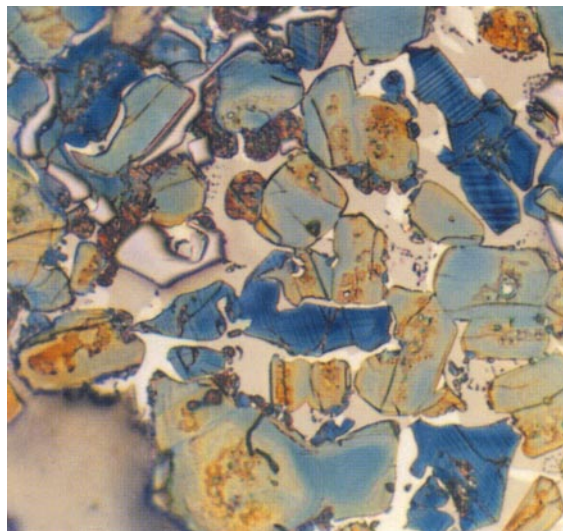
PHOTOMICROGRAPHS OF BELITE (CONTINUED)

Photograph 7-43 Dark blue belite (Type II, Insley) at upper right, subhedral to anhedral alite (pale blue), and pink periclase (center left). Coarsely crystalline matrix. Coal- and coke-fired kiln, wet process, 950 tons/day. Moderately long burning rate, slow heating rate, moderately slow cooling rate. (S#A6663)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

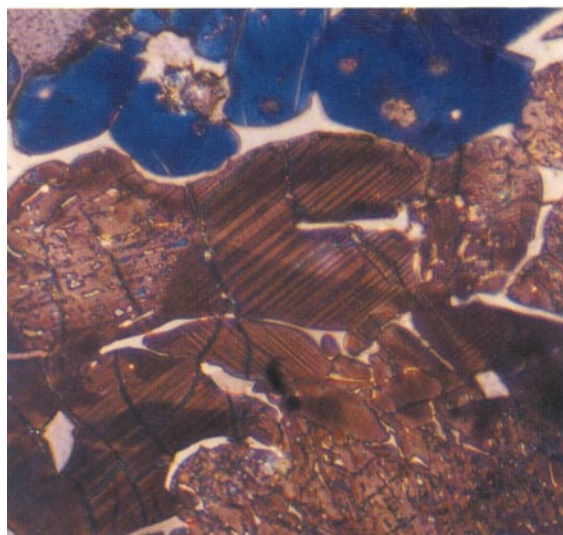


Photograph 7-44 Polysynthetically twinned belite (Type II, Insley) in slowly cooled kiln buildup. (S#A6664)

Polished section

Nital etch

Field dimensions = 0.14x0.14 mm

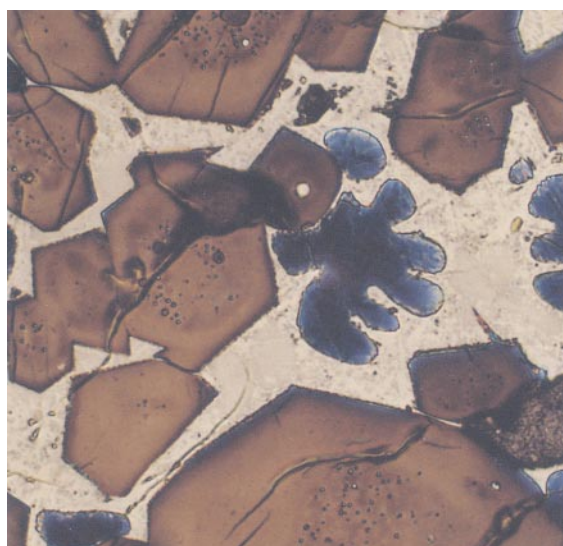


Photograph 7-45 Blue, amoeboid belite in a coarsely crystalline, matrix-rich clinker. Amoeboid belite crystals seem to be most common in clinkers burned at a high temperature. Angular, tan alite. Other clinkers in this section contained alite that produced a blue color. (S#A6665)

Polished section

Nital etch

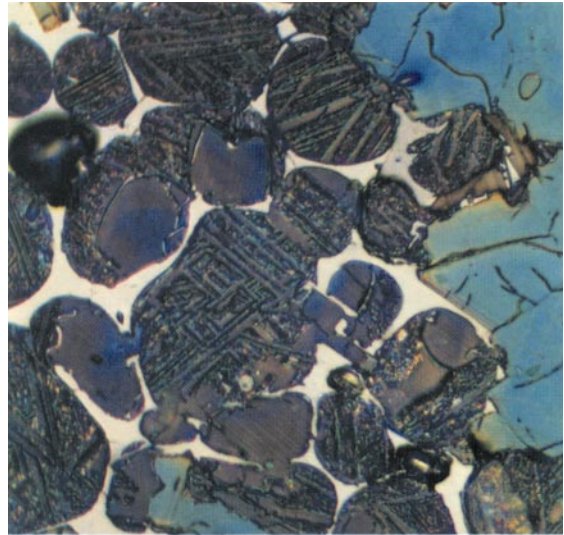
Field dimensions = 0.14x0.14 mm



PHOTOMICROGRAPHS OF BELITE (CONTINUED)

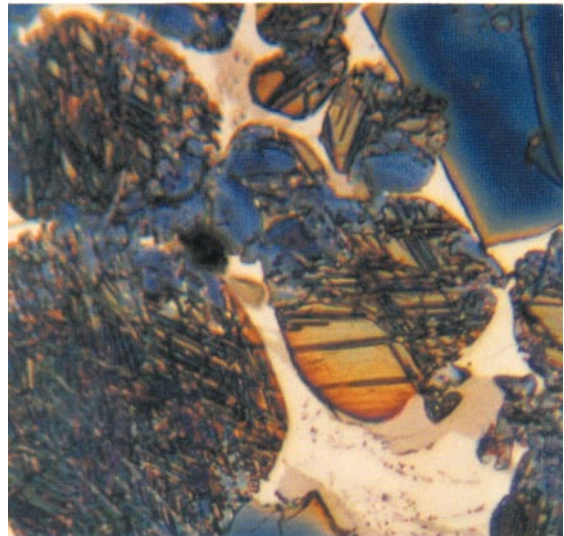
Photograph 7-46 Polished section of coarsely crystalline clinker. Belite crystals exhibit relatively large areas which are either nonlamellar or show a single set of parallel lamellae. Type I belite (Insley) dominates clinker. KOH extraction of matrix and concentration of silicates, followed by XRD analysis indicating 7% to 10% of the belite comprised of alpha form. Brightly reflecting ferrite. Wet-process kiln, 1000 tons/day. High maximum temperature, long burning time, slow heating rate, moderately quick cooling. (S#A6666)

Nital etch
Field dimensions = 0.21x0.21 mm



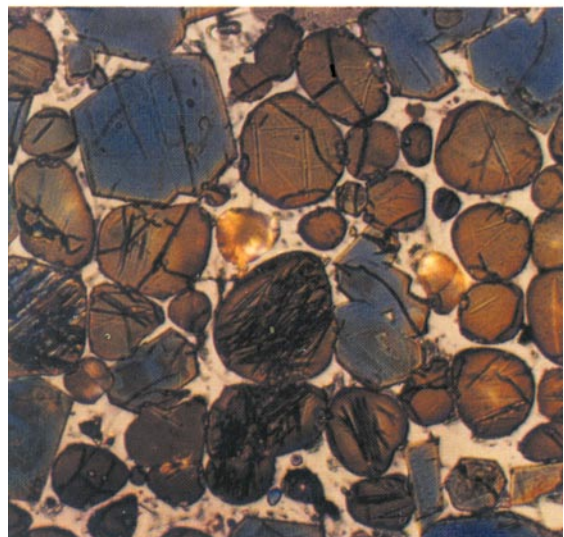
Photograph 7-47 Very coarse, yellow-brown lamellae in belite grain (lower center), perhaps residual from an earlier polymorph. Coal-fired kiln, wet process. High maximum temperature, long burning time, slow heating rate, quickly cooled, 42 MPa. (S#A6667)

Polished section
Nital etch
Field dimensions = 0.13x0.13 mm



Photograph 7-48 Round belite crystals (brown) showing minimal development of lamellae. Coarse feed. Low maximum temperature, moderately long burning time, slow heating rate, moderately slow cooling rate. Dry-process kiln, gas fired, 3000 tons/day. (S#A6668)

Polished section
Nital etch
Field dimensions = 0.38x0.38 mm



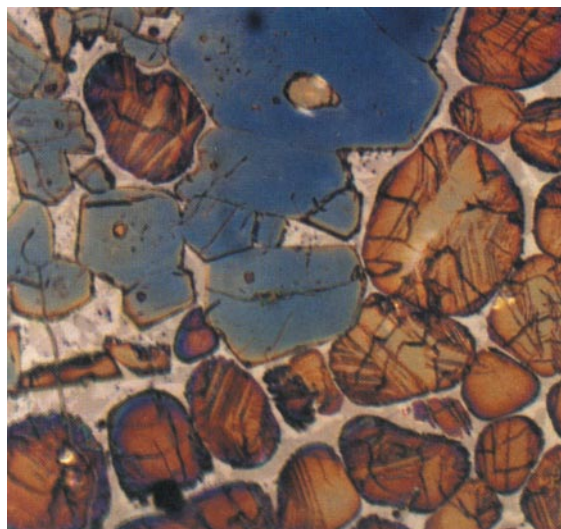
PHOTOMICROGRAPHS OF BELITE (CONTINUED)

Photograph 7-49 Large, joined crystals of blue alite (cannibalistic) and round, brown-tan belite with unusually wide lamellae. Well-differentiated matrix. (S#A6669)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

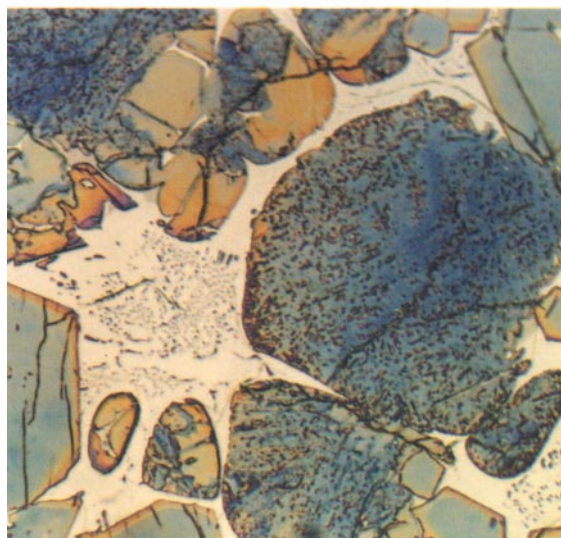


Photograph 7-50 Dense, coarsely crystalline clinker showing large, blue belite crystals (center right) with numerous exsolved dotlike inclusions; tan areas (upper left) of apparently nonlamellar belite; secondary belite dots in ferrite matrix (center left). Coal-fired, wet-process kiln with temperature known to be approximately 1650°C. (S#A6670)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

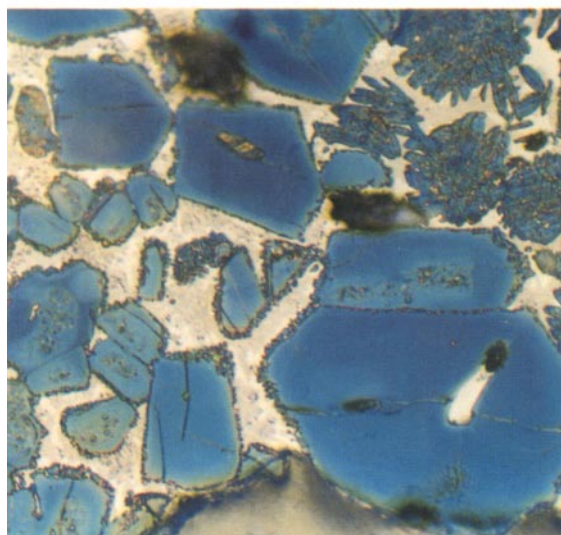


Photograph 7-51 Blue, subhedral alite with well-developed belite coating (fringes); ragged and dismembered round belite (internally somewhat disorganized); and a well-differentiated matrix of aluminate and dull-reflecting ferrite. Moderately high maximum temperature, moderately long burning time, slow heating rate, moderately slow cooling rate; reducing conditions. Coal- and coke-fired wet-process kiln, 950 tons/day. (S#A6671)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm



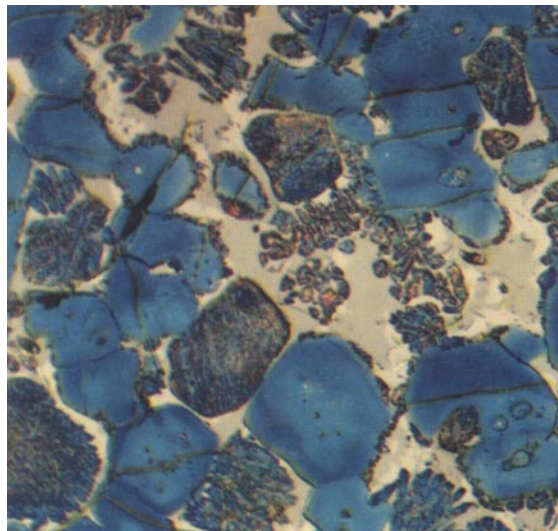
PHOTOMICROGRAPHS OF BELITE (CONTINUED)

Photograph 7-52 Dismembered and dendritic belite, ordinary round belite, and belite coatings on alite. Coarsely crystalline matrix. Gas- and coal-fired clinker from wet-process kiln, 500 tons/day. High maximum temperature, long burning time, slow heating rate, slow cooling. (S#A6672)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

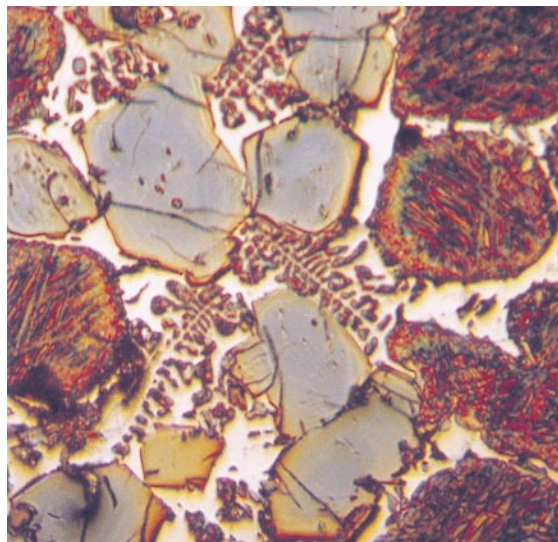


Photograph 7-53 Dendritic belite in ferrite-rich matrix of clinker containing fragments of refractory brick (not shown). Brightly reflecting ferrite in plane-polarized light is unusually pleochroic, suggesting compositional change from refractory brick consumption. (S#A6673)

Polished section

Nital etch

Field dimensions = 0.14x0.14 mm

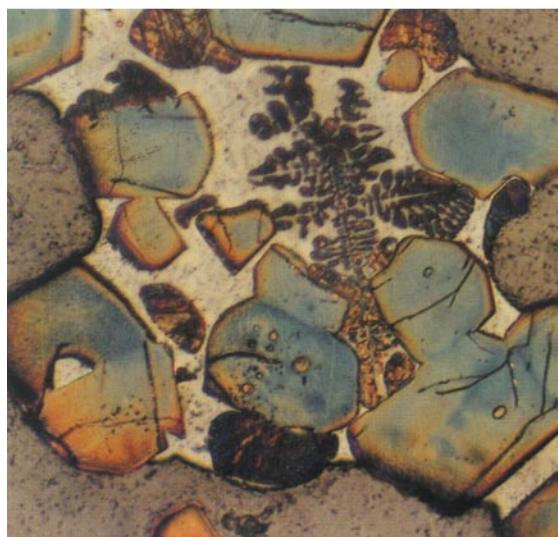


Photograph 7-54 Dendritic belite in coarsely crystalline clinker. Raw feed has almost 38% greater than 45 μm . Moderately high temperature, long burning time, slow heating rate, and quick cooling rate. Coal-fired wet-process kiln; 960 tons/day. (S#A6674)

Polished section

Nital etch

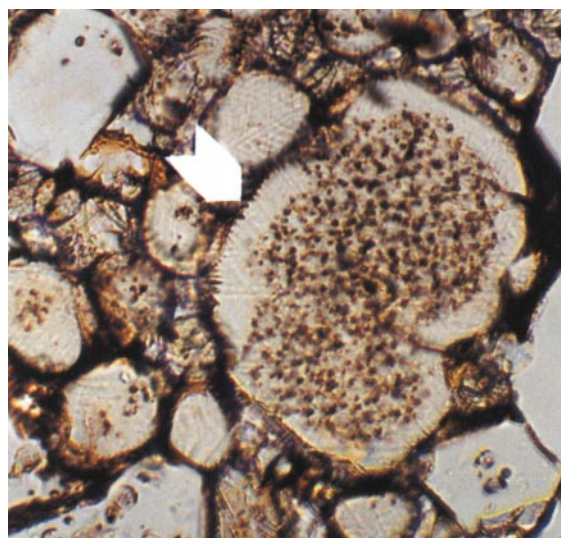
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF BELITE (CONTINUED)

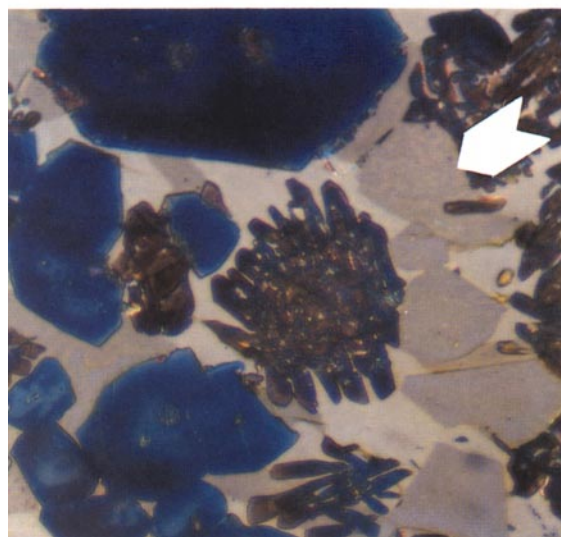
Photograph 7-55 Clinker thin section in Hyrax™ showing dotlike products of exsolution and ragged, inclusion-free overgrowth (arrow) on large belite crystal. Brown-centered clinker. Reducing conditions and slow cooling are suggested. (S#A6675)

Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



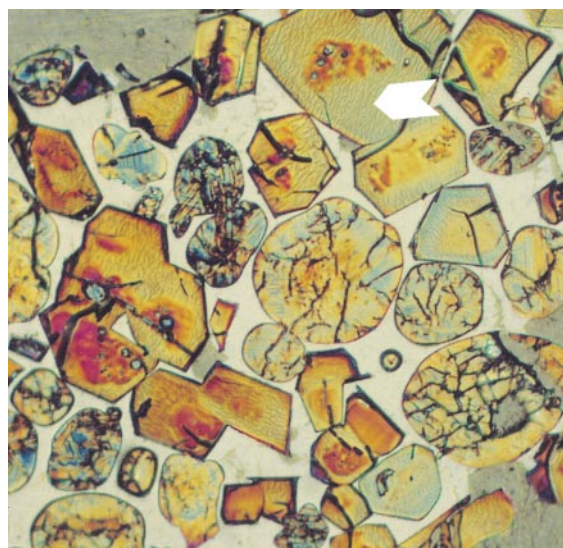
Photograph 7-56 Kiln coating showing belite crystals with Type II “fingers” around relatively disorganized core. Coarsely crystalline matrix containing large periclase crystals (arrow). Slow cooling from alpha-prime belite temperature range. Dry-process kiln, 2350 tons/day. (S#A6676)

Polished section
Nital etch
Field dimensions = 0.14x0.14 mm



Photograph 7-57 Radial cracking in round belite crystals. Subparallel microcracks on a much smaller scale (arrow) from excessive etch time in angular alite crystals. Class G oil-well cement clinker. (S#A6677)

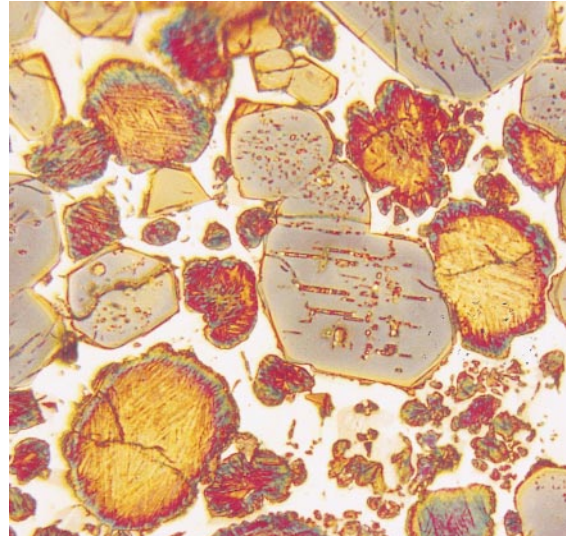
Polished section
Nital etch
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF BELITE (CONTINUED)

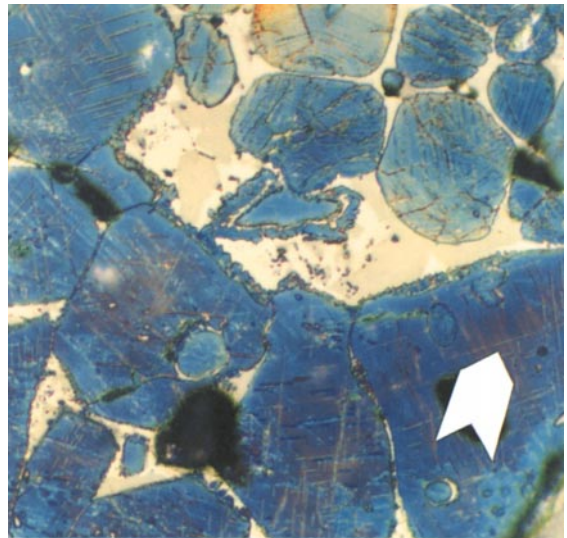
Photograph 7-58 Belite striations in light blue alite. Multicolored, round belite showing typical lamellae, but somewhat scalloped cross section. Small secondary belite in brightly reflecting ferrite matrix. Clinker sample contains remnants of chrome-magnesia refractory brick. (S#A6678)

Polished section
Nital etch
Field dimensions = 0.21x0.21 mm



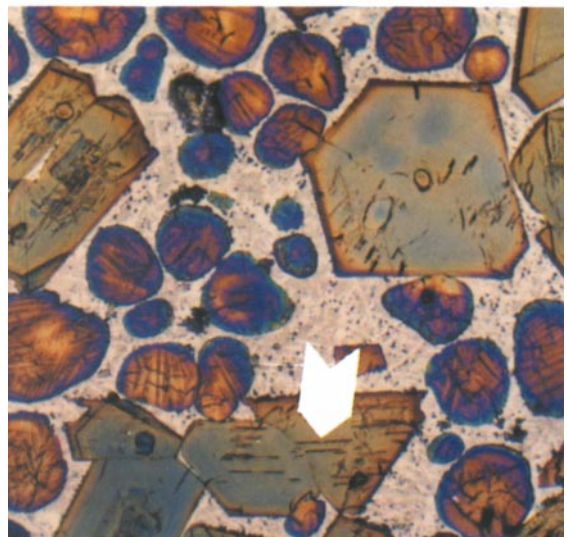
Photograph 7-59 Alite crystals with secondary belite striations (arrow) and belite fringes. Coarsely crystalline matrix of aluminite and dull ferrite. Slow cooling and reducing conditions. (S#A6679)

Polished section
Nital etch
Field dimensions = 0.21x0.21 mm



Photograph 7-60 Coarsely crystalline silicates from coarse seashell feed. Pale olive to tan, angular alite crystals with belite striations (arrow); round, coarsely lamellar belite; and a finely microcrystalline matrix of aluminite and dull ferrite. High maximum temperature, long burning time, slow heating rate, quick to moderately quick cooling, 44 MPa. Coal- and coke-fired, semidry-process kiln, 1850 tons/day. (S#A6680)

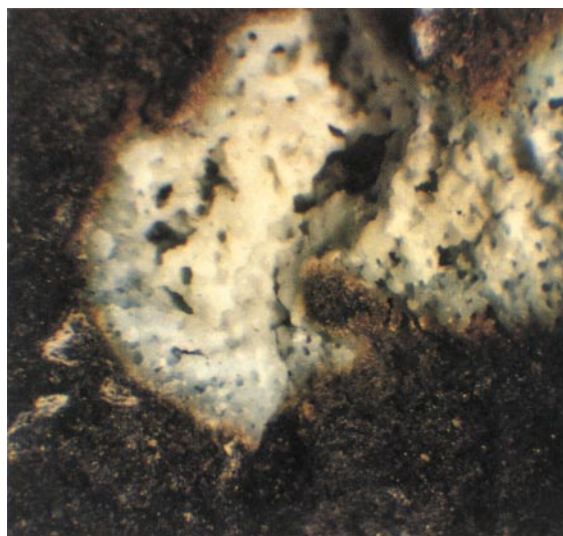
Polished section
Nital etch
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF BELITE (CONTINUED)

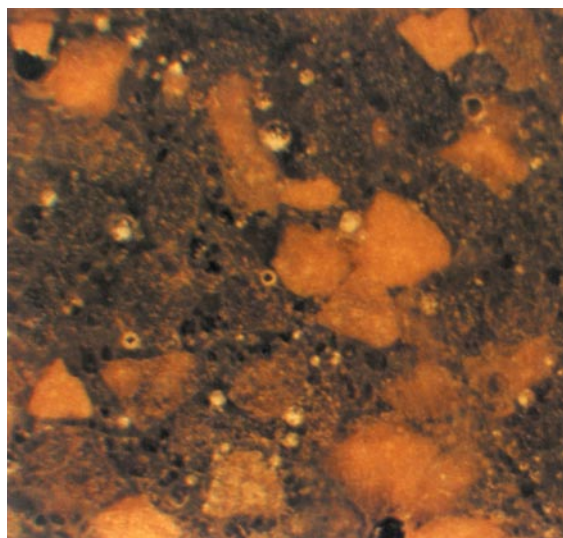
Photograph 7-61 Green belite nest in center of broken clinker. Energy dispersive X-ray analysis (EDXA) indicates calcium, silicon, potassium, and traces of chromium, magnesium, aluminum, sulfur, chlorine, and iron. (S#A6681)

Reflected light, stereomicroscope
Field dimensions = 1.25x1.25 mm



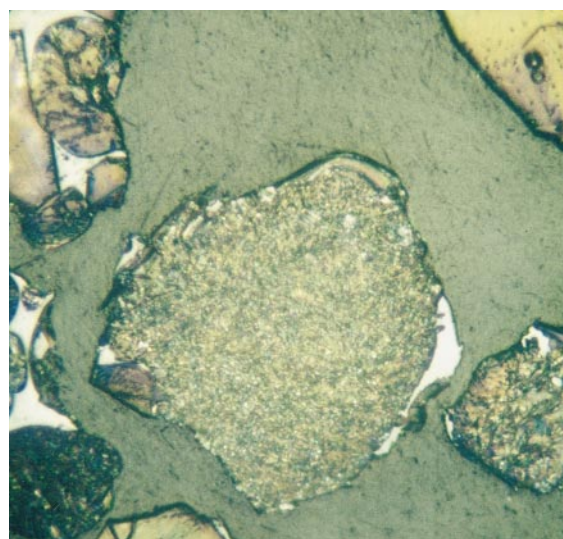
Photograph 7-62 Crushed clinkers with yellowish brown centers, produced in a kiln with a reducing environment. Examination at high magnification reveals belite coatings on alite, dull ferrite reflectivity, and alkali aluminates. (S#A6682)

Polished section
No etch
Field dimensions = 1.2x1.2 mm



Photograph 7-63 Photomicrograph of clinker particle in a Class H oil-well cement, showing recrystallized belite classified by the writer as Type B. Note the finely microcrystalline interior of the crystal and near-total loss of lamellar structure. Lamellar extensions are not a criterion of this belite designation. Possible interpretations of Type B are slow cooling, reducing conditions, or both. (S#67842)

Polished section
Nital etch
Field dimensions = 0.20x0.20 mm



PHOTOMICROGRAPHS OF BELITE (CONTINUED)

Photograph 7-64 Type C belite showing alteration only visible in the outer regions of the grain where the original lamellae have been recrystallized into a finely microcrystalline mosaic. Class H oil-well cement. (S#67843)

Polished section

Nital etch

Field dimensions = 0.12x0.12 mm

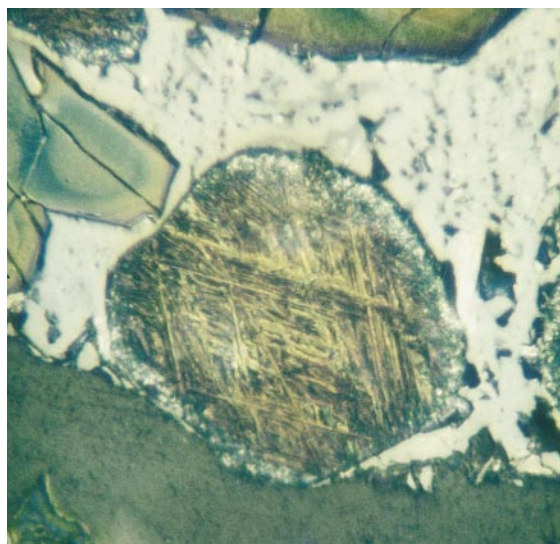


Table 7-1. Microscopical Interpretation of Clinkers (continued)

Matrix	
Observations	Interpretations
Abundant aluminate	High Al_2O_3 to Fe_2O_3 ratio, alumina ratio (Gille and others, 1965)
Abundant aluminate, abundant ferrite	Low Al_2O_3 to Fe_2O_3 ratio, less than 0.7 (Gille and others, 1965)
Plenty of liquid phase	Silica ratio (SR) low (Hofmänner, 1973)
Aluminate greatly dominates liquid phase	High alumina ratio (Long, 1982a); strong reducing conditions (Dorn, personal communication, 1985)
Aluminate greater than ferrite	Alumina ratio high (Hofmänner, 1973)
Ferrite greater than aluminate	Alumina ratio low (Hofmänner, 1973)
Large quantity of liquid phase, high ferrite content	Low silica ratio and alumina ratio (Long, 1982a)
Great relative increase in aluminate content	Cooling under reducing conditions and temperature range between 1000°C and 1200°C (Sylla, 1981)
Small quantity of liquid phase, dusty fine clinker	High silica ratio (Long, 1984b)
Low quantity of melt phases	High silica modulus (Miller, 1980); silica ratio too high (Hofmänner, 1973)
Differentiation of interstitial aluminate and ferrite; alite and belite lose sharp regularity	Equilibrium cooling to complete crystallization through 1250°C (Brown, 1948)
(a) Groundmass structure of large crystals (b) Tight, interlaced structure of small crystals	(a) Extended conditions for development (b) Quenching (Gille and others, 1965)
Coarse structure of aluminate and ferrite; belite fringes on alite	Very slow cooling (Long, 1982a)
Large separated ferrite and aluminate crystals surrounded with normal matrix; brown areas in clinkers	Reducing conditions (Brugan, 1979)
Coarsening of aluminate crystals, aluminoferrite, and belite; increase in aluminate at expense of aluminoferrite	Clinker burned under reducing conditions, removed from kiln at temperature less than 1250°C, slow cooling under reducing conditions (Sylla, 1981)
Aluminate growth at expense of aluminoferrite; additional metallic iron; large, irregularly shaped belite crystals	1-hour burn in reducing atmosphere, cooled to 1050°C in kiln (Sylla, 1981)
Simply bounded, rectangular aluminate and bright ferrite	Slow cooling (Brown, 1948)
Coarsely crystalline liquid phase	Slow cooling (Hofmänner, 1973)
Microcrystalline matrix; two distinct phases: ragged alite (belite coating) and irregular belite; prismatic aluminate	Slow cooling rate (Fundal, 1980)
Large aluminate (C_3A) crystals	Extremely slow cooling; fast-setting cement (Eby, 1985)
Microcrystalline matrix: primary, aluminatelike gray phase; secondary ferritelike white phase, containing third interstitial phase with lower reflectivity, possibly aluminate	Intermediate cooling rate (Fundal, 1980)
Fine structure of aluminate and ferrite	Rapid cooling from high temperature (Long, 1982a)
Finely crystalline liquid phase	Fast cooling (Hofmänner, 1973)
Coarsely crystalline aluminate	Slow cooling and exsolution of lime from silicates; development of $\text{C}_6\text{A}_2\text{F}$ (Vanisko, 1980)
Submicroscopic crystals in matrix; rectilinear alite, sometimes with thin layer of belite; spherical matrix belite	Fast cooling rate (Fundal, 1980)
Increasing C_3A crystal size and number; change in etch color	Clinker drops out of kiln at successively lower temperature from maximum of 1500°C (Hawkins, 1979)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Matrix	
Observations	Interpretations
Cryptocrystalline aluminate, ferrite, and periclase in matrix (seen with SEM)	Very rapid cooling (Hofmänner, 1973)
Rodlike (somewhat dendritic) intergrowth of groundmass phases	Relatively rapidly cooled clinker (Gille and others, 1965)
Separation of matrix phases, ferrite and aluminate, but without typical eutectic intergrowths; content of free lime high; alite coated with thin ferrite seam, then by thick belite cover	Reducing conditions, quenched, lab experiment; melt rich in silica, poor in lime; resorption of belite which was prevented by quick cooling (Woermann, 1960)
Same texture as air-cooled clinker with distinctly recognizable aluminate and aluminoferrite	Clinker burned under oxidizing conditions, removed at temperature of 1250°C and below, and quenched in water (Sylla, 1981)
Mottled interstitial phases	Burning time too short, and temperature too low (Brown, 1948)
Submicroscopic crystalline liquid phase (apparently undifferentiated with microscope)	Laboratory quenching (Hofmänner, 1973)
Xenomorphous, void-filling aluminate	Low alkali clinker (Gille and others, 1965)
Zoned aluminate	Changing chemical environment during crystallization (Hofmänner, 1973)
Nonprismatic dark interstitial	Low mortar strength (Tsuboi and Ogawa, 1972)
Alkali aluminate; alkali-modified belite	Excess alkali over equivalent sulfate (Long, 1983)
Alkali aluminate	Alkalies, mainly sodium, in clinker (Hofmänner, 1973); more pronounced with Na ₂ O-bearing laboratory clinkers than in K ₂ O-bearing clinkers; negative effect on cement properties (Dreizler, Strunge, and Knöfel, 1985)
Idiomorphous laminae or long "staves" (prismatic) aluminate	Alkali aluminate and relatively high-alkali clinker (Gille and others, 1965)
Prismatic C ₃ A (alkali modified)	Reducing conditions (DeLisle, 1979; Rader, 1985)
Alkali-modified lath-shaped aluminate	Slow cooling or reoxidation (Long, 1982b)
Ragged, dark interstitial; dark prismatic phase prominent	Rapid cooling; high alkali clinker (Brown, 1948)
Disappearance of prismatic aluminate; decline of mortar strength	MgO more than 1% (Tsuboi and Ogawa, 1972)
Brown aluminoferrite	Absence of MgO in aluminoferrite, presence of divalent iron (Sylla, 1981)
Dark brown-yellow, strongly pleochroic ferrite	Normal clinker (Gille and others, 1965)
High reflectivity of ferrite, eutectic intergrowth of ferrite and aluminate, no decomposition of alite	Normal, oxidized clinker (Woermann, 1960)
Lower reflectivity of ferrite; aluminate increases; no massive belite seams around alite	Equilibrium through slow cooling under reducing conditions (Woermann, 1960)
Massive ferrite	Quick cooling (Long, 1984a)
Zoned ferrite crystals with earliest formed (inner) zones having different alumina-to-iron ratios	Disequilibrium during crystallization (Glasser, 1979)
Local concentrations of ferrite	Possible coarse mill scale (Long, unpublished ICMA presentation, 1984)

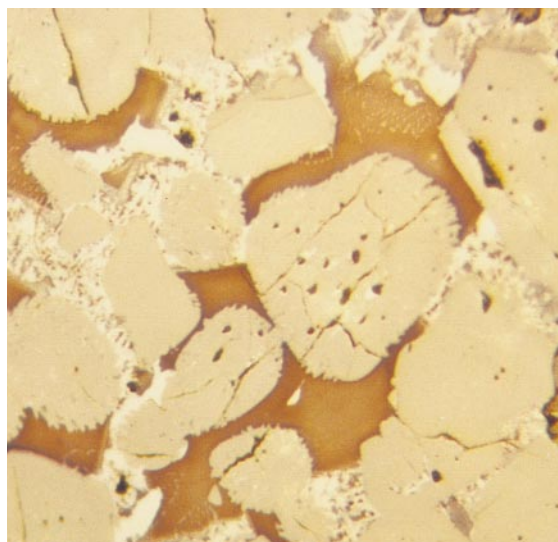
PHOTOMICROGRAPHS ILLUSTRATING THE MATRIX

Photograph 7-65 Brown, coarsely crystalline aluminate in slowly cooled clinker. Belite crystals exhibit short lamellar extensions into matrix. Coarse raw feed. High maximum temperature, long burning time, slow heating rate. Coal-fired, wet-process kiln, 633 tons/day, 41 MPa. (S#A6683)

Polished section

KOH etch

Field dimensions = 0.21x0.21 mm

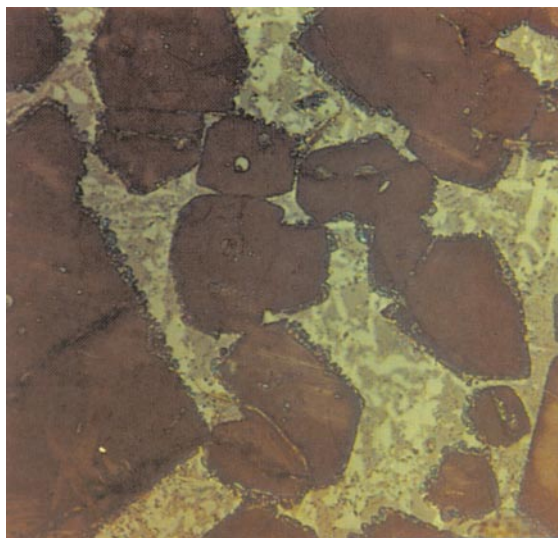


Photograph 7-66 Secondary coating of belite on alite in very dense, coarsely crystalline, matrix-rich clinker. Matrix is well-differentiated gray aluminate and dull-reflecting ferrite. Clinker breaks with subconchoidal fracture. Periclase crystals (not shown) up to 120 μm . High maximum temperature, slow heating rate, reducing conditions. Coal-fired, wet process kiln. (S#A6684)

Polished section

Nital etch

Field dimensions = 0.14x0.14 mm

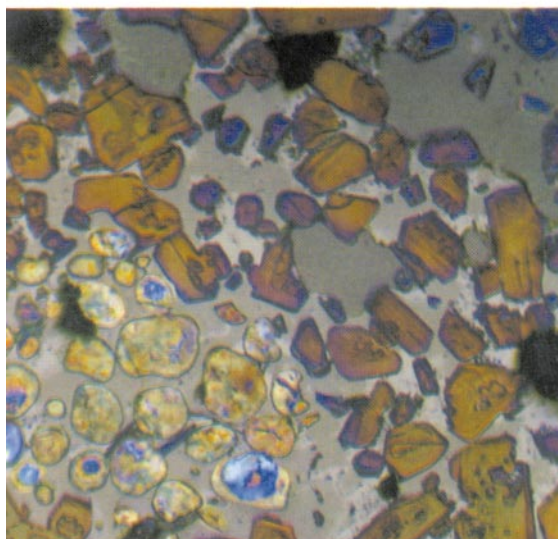


Photograph 7-67 Multicolored, round free lime crystals in aluminate-rich matrix (dull gray) from coarse marl particle. Estimated $\text{C}_3\text{A} = 14\%$ to 18%. Anhedral to subhedral, tan to bluish red alite. High maximum temperature, long burning time, moderately slow heating rate, moderately fast cooling rate, 40 MPa. Coal-fired, dry-process kiln, 1600 tons/day. (S#A6685)

Polished section

Nital etch

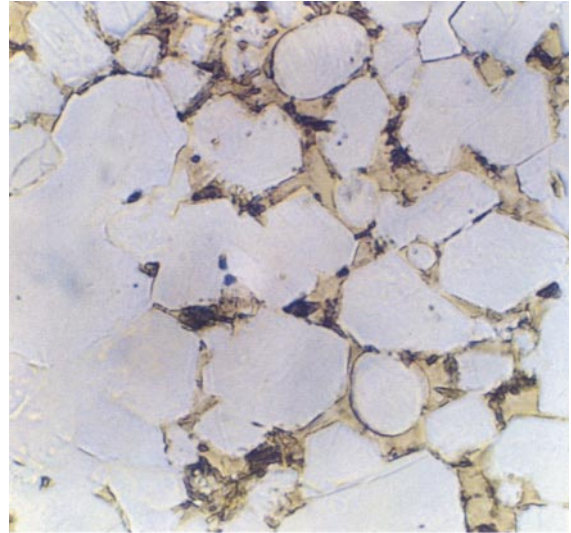
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS ILLUSTRATING THE MATRIX (CONTINUED)

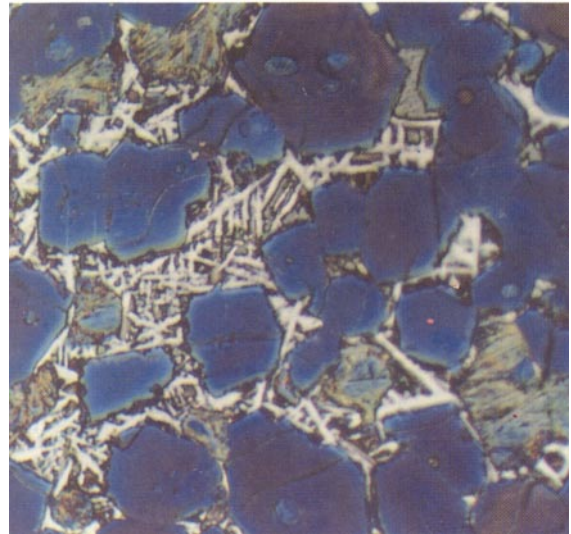
Photograph 7-68 Ultrathin section, approximately 10 μm thick, showing tan to beige aluminite (C_3A) crystals comprising most of the matrix in this clinker. Round belite crystals, angular alite crystals. (S#A6686)

Transmitted, plane-polarized light
Field dimensions = 0.14x0.14 mm



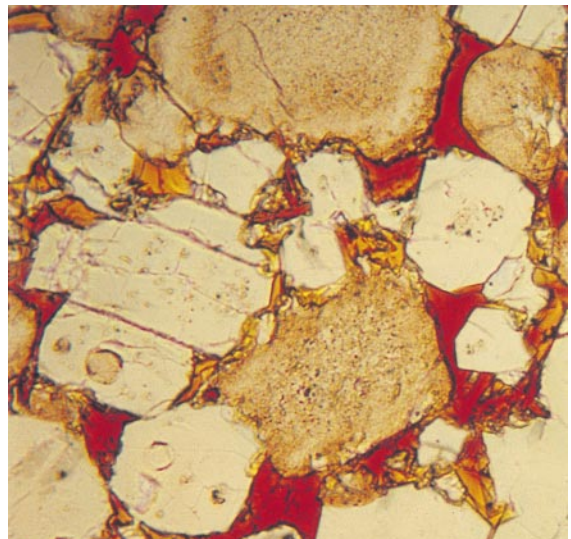
Photograph 7-69 Well-differentiated matrix of bright, lath-form crystals of ferrite between which the aluminite (C_3A) occurs. Small, bluish green belite crystals tend to be irregularly shaped. Gas-fired wet-process kiln, 770 tons/day. High maximum temperature, long burning time, moderately slow heating rate, quickly cooled. (S#A6687)

Polished section
Nital etch
Field dimensions = 0.21x0.21 mm



Photograph 7-70 Strongly pleochroic red ferrite in clinker containing partially consumed chrome-magnesia refractory brick (not shown). Belite with abundant exsolved impurities. Belite crystals in other parts of this clinker nodule are pale green. (S#A6688)

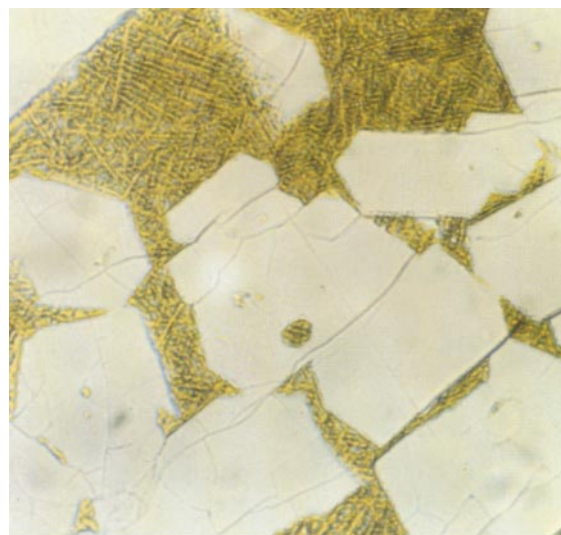
Thin section
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



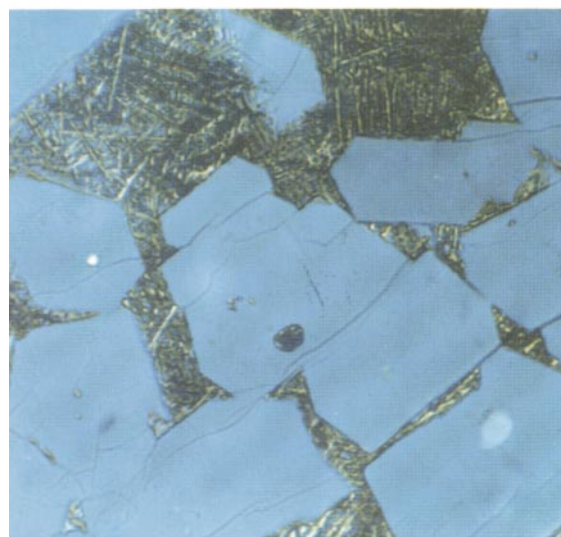
PHOTOMICROGRAPHS ILLUSTRATING THE MATRIX (CONTINUED)

Photograph 7-71 Thin, typical lath-form crystals of ferrite and extremely finely microcrystalline crevice-filling aluminate (C_3A). Clear, angular alite crystals stacked on the basal pinacoid (001). Coal- and coke-fired, semidry-process kiln, 1850 tons/day. High maximum temperature, long burning time, slow heating rate, quick to moderately quick cooling, 44 MPa. (S#A6689)

Ultrathin section
Transmitted, plane-polarized light
Thickness = approximately 10 μm
Field dimensions = 0.21x0.21 mm

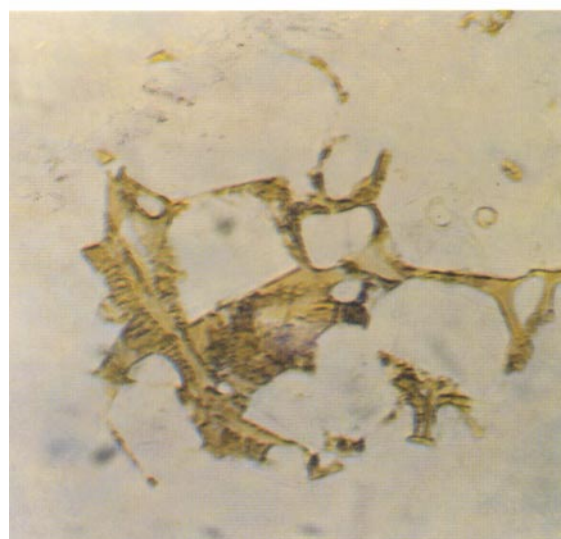


Photograph 7-72 Same field of view as previous photograph but in partially cross polars. Note relatively high interference colors of some ferrite crystals. (S#A6690)



Photograph 7-73 Ultrathin section of clinker showing lengthy alkali aluminate prisms in matrix. Angular alite and clear, round belite. Coarse, alkali-rich feed. Low maximum temperature, long burning time, medium to slow heating rate, quickly cooled; slight reducing conditions. Dry-process kiln, 1440 tons/day. (S#A6691)

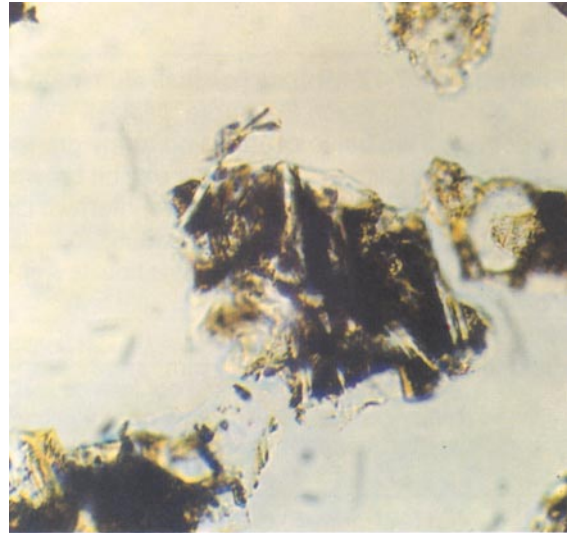
Section thickness approximately 12 μm
Oblique illumination
Transmitted, plane-polarized light
Field dimensions = 0.14x0.14 mm



PHOTOMICROGRAPHS ILLUSTRATING THE MATRIX (CONTINUED)

Photograph 7-74 Prismatic alkali aluminate crystals in crushed clinker powder mount. High maximum temperature, long burning time, slow heating rate, moderately quick to moderately slow cooling rate. Gas- and coal-fired, wet-process kiln, 500 tons/day. (S#A6692)

Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



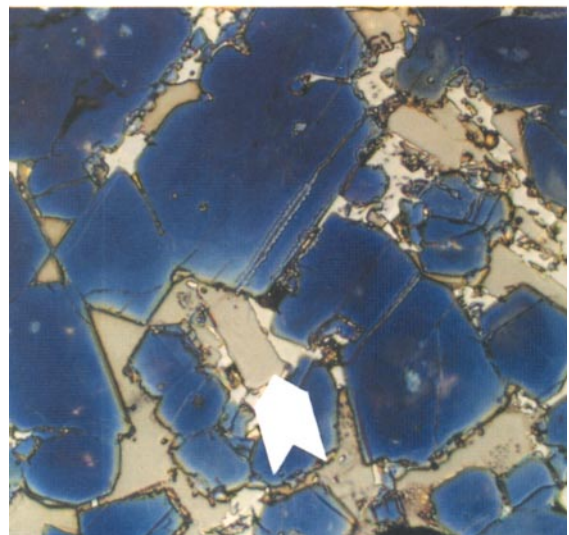
Photograph 7-75 Brown prismatic (alkali-rich) aluminate crystals, some entrapping alite and appearing zoned or twinned along a prism face. Dry-process kiln. (S#A6693)

Polished section
Water etch
Diameter of field = 0.12 mm



Photograph 7-76 Alkali aluminate crystal (arrow) exhibiting typical prismatic form. Brightly reflecting ferrite in the matrix. Blue, subhedral alite crystals. Area shown within brown core of clinker probably represents reducing conditions. Porous shell on clinker contains normal C_3A . Moderately high maximum temperature, long burning time, slow heating rate, moderately quickly cooled. (S#A6694)

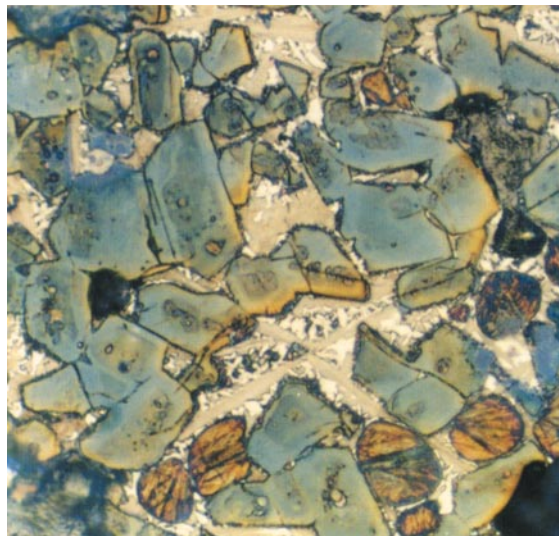
Polished section
Nital over KOH etch
Field dimensions = 0.10x0.10 mm



PHOTOMICROGRAPHS ILLUSTRATING THE MATRIX (CONTINUED)

Photograph 7-77 Prismatic alkali aluminate (light tan) in matrix in which the ferrite displays a dull reflectivity. Thin belite coatings on many greenish blue alite crystals. Clinkers commonly exhibit brown areas. Moderately reducing conditions are inferred. Coal- and coke-fired, dry-process kiln. (S#A6695)

Polished section
Nital on KOH etch
Field dimensions = 0.21x0.21 mm



Photograph 7-78 Dark prismatic alkali aluminate (arrow) in gas- and coal-fired clinker from wet-process kiln. Type C belite. Slightly reducing conditions. High maximum temperature, long burning time, slow heating rate, moderately quick to moderately slow cooling. 500 tons/day. (S#A6696)

Polished section
Nital over water etch
Field dimensions = 0.21x0.21 mm

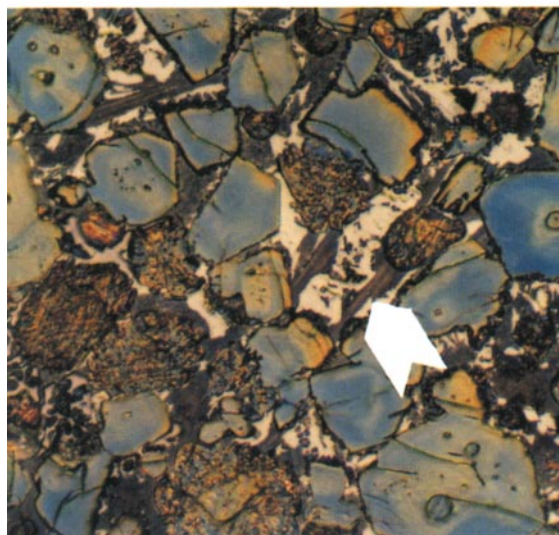


Table 7-1. Microscopical Interpretation of Clinkers (continued)

Free Lime	
Observations	Interpretations
Decrease in free-lime percentage	Correlated with increase in burning temperature (Akatsu and Monna, 1966)
Increase in free-lime percentage	Correlated with increase in particle size of quartzite, slag, and limestone (Akatsu and Monna, 1966)
Free lime as primary phase; belite only as inclusions in alite	High lime saturation factor (Long, 1982a)
Dispersed free lime, low belite content	Overlimed mix, high lime saturation factor (Miller, 1980)
(a) Equal distribution of free lime (b) Local free lime (c) Uniformly distributed free lime in clinker with high porosity	(a) CaO content too high (b) Incomplete absorption of limestone in raw mix (c) Low burning temperature (Gille and others, 1965)
Spherical grains of free lime	High temperature equilibrium (Brown, 1948)
Clusters of free lime	Pieces of raw mix, indicating fineness of grinding and uniformity of raw mix (Brown, 1948)
Differentiated zones of high and low concentrations of CaO	Insufficient homogenization of raw mix (Krämer, 1960)
Irregular distribution of free lime	Inadequate homogenization of large calcite grains in raw mix (Fundal, 1980)
Nodules of CaO, melt-rich nodule, alite dust, belite nodules	Improper nodulation and not raw-meal inhomogeneity (Fundal, 1980)
Clusters of free lime and belite with almost rectilinear boundaries	Large feed particles, limestone and quartz, respectively (Hofmänner, 1973)
Free-lime cluster with sharp boundaries	Calcite particles (Miller, 1980)
Intimate mixture of free lime and belite	Sufficient excess alkali such that belite does not react to form alite (Long, 1983)
Free-lime nests	Local concentration of limestone (Tsuboi and Ogawa, 1972)
Free-lime cluster with open structure and small interstitial alite	Marly grains, > 125 μm (Fundal, 1980)
Dense free-lime clusters	Pure calcite particles (Fundal, 1980)
Free-lime nests	Relics of limestone grains (Krämer, 1960); calcite above critical size of 125 μm (Johansen, 1978); coarse calcite (Long, 1984b)
Free-lime cluster with alite and liquid phase	Concentration of carbonate component (local surplus of lime) (Hofmänner, 1973)
Free-lime nests and belite nests	Quartz above critical size of 44 μm in feed (Johansen, 1978)
Free-lime nests near belite accumulations or many small pores	Low burning degree (Gille and others, 1965)
Nests of free-lime or belite	Coarse limestone, dolomite, or quartz, suggesting insufficient grinding (Gille and others, 1965)
Zones at pores, for example, free lime on pore surface	Reducing conditions; possibly volatilization of silicon as SiO (Gille and others, 1965)

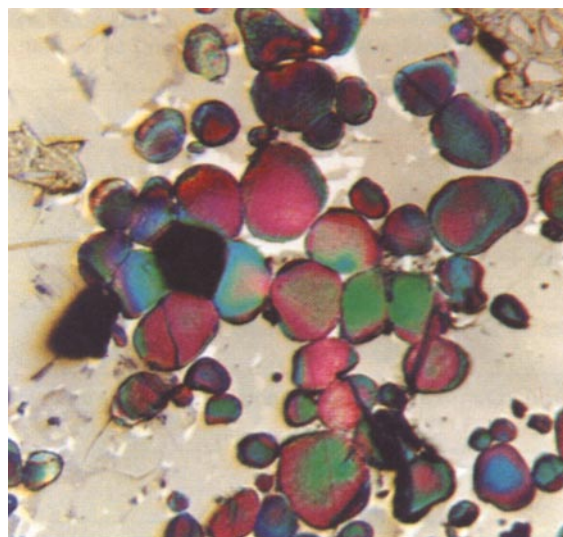
Table 7-1. Microscopical Interpretation of Clinkers (continued)

Free Lime	
Observations	Interpretations
Central clinker region rich in lime, deficient in flux	Occurs in high temperature reoxidation (Long, 1982b)
Hoop-stress cracks around free lime nests	Expansion due to lime hydration, typical for aged clinker (Brugan, 1979)
Popcornlike secondary crystals associated with free lime	Epeizite, a form of calcium hydroxide, originating by air slaking of free lime, leading to clinker disintegration (Brown and Swayze, 1938)
Increase in free lime abundance and crystal size	Addition of alkalies (Radic, 1995)
Weak water-etch response	Dead burned (Hamilton, personal communication, 1998)

PHOTOMICROGRAPHS OF FREE LIME

Photograph 7-79 Free-lime nest colored by water etch in polished section. Chemical analysis gave clinker free-lime value of 2.69%. High maximum temperature, moderately long burning time, moderately slow heating rate, moderately slowly cooled, 31 MPa. Gas-fired, dry-process kiln, 3000 tons/day. (S#A6697)

Field dimensions = 0.21x0.21 mm



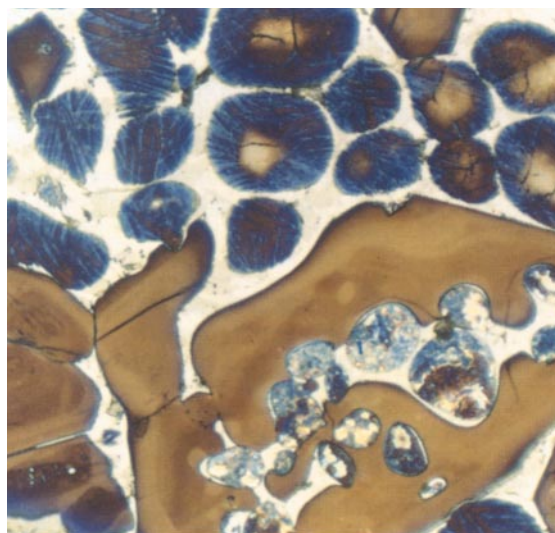
PHOTOMICROGRAPHS OF FREE LIME (CONTINUED)

Photograph 7-80 Strongly zoned, tan alite with free-lime inclusions and round, coarsely lamellar belite with tan cores, the latter believed to have a relatively low calcium-to-silicon ratio. Coarse seashells in feed. Coal- and coke-fired, semiwet-process kiln, 1850 tons/day, 44 MPa. (S#A6698)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

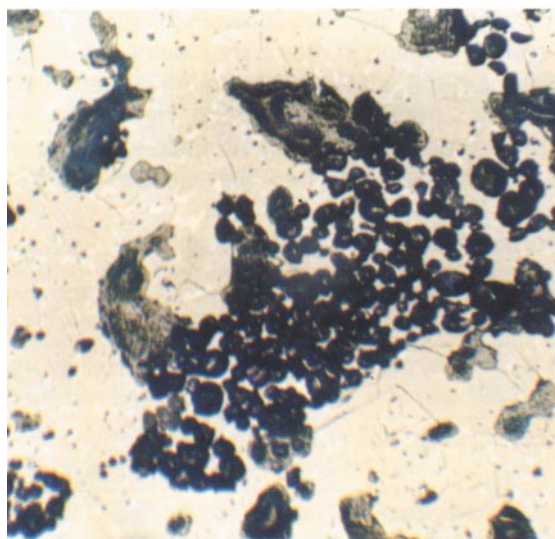


Photograph 7-81 Free-lime nest from coarse calcite particle in raw feed. Very low liquid phase. Coal- and coke-fired, dry-process kiln. Moderately high maximum temperature, long burning time, moderately fast heating rate, quick cooling rate. (S#A6699)

Polished section

Water etch

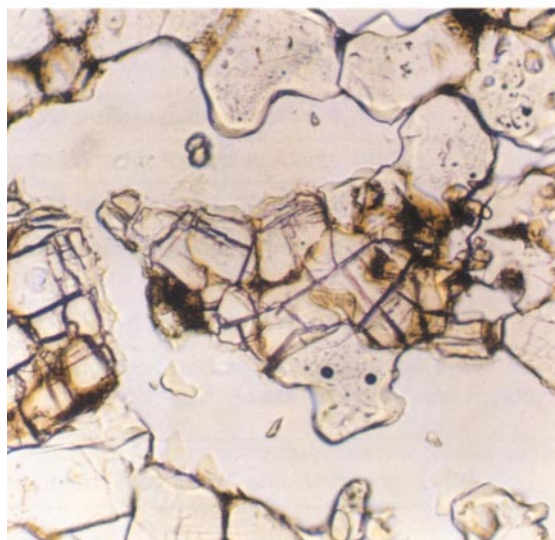
Field dimensions = 0.53x0.53 mm



Photograph 7-82 Free lime in clinker thin section. Crystals exhibit prominent cubic cleavage characteristic of free lime. An abundance of free-lime nests (some showing original limestone particle outline), anhedral alite, and extremely nonuniform distribution of silicates suggests poorly mixed coarse feed. Dry-process kiln, coal fired. (S#A6700)

Transmitted, plane-polarized light

Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF FREE LIME (CONTINUED)

Photograph 7-83 Clear popcornlike crystals of epepite, $\text{Ca}(\text{OH})_2$, floating in refractive-index oil. A product of air slaking of free lime, the 97% change in crystal volume results in clinker disintegration, even in sealed containers. Crushed clinker, 45 to 75 μm . (S#A6701)

Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



Photograph 7-84 Cauliflowerlike crystals of epepite, $\text{Ca}(\text{OH})_2$, floating in refractive-index oil. Note green alite, perhaps related to chromium contamination as a result of refractory consumption. High maximum temperature, long burning time, slow heating rate, and quickly cooled. Coal-fired, wet-process kiln. (S#A6702)

Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm

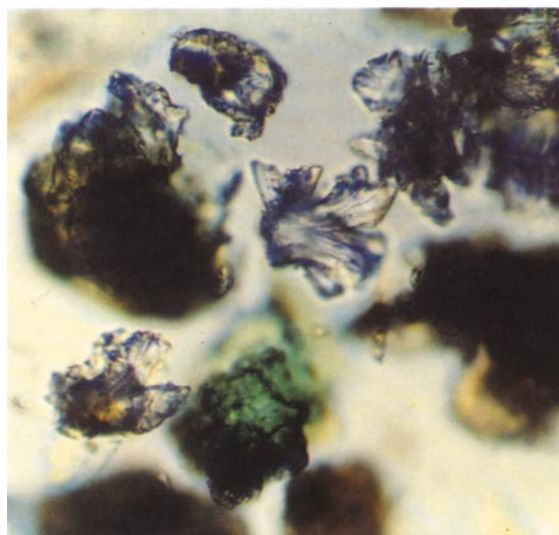


Table 7-1. Microscopical Interpretation of Clinkers (continued)

Periclase	
Observations	Interpretations
Periclase	More Mg^{++} than can be incorporated in lattices of other phases (Hofmänner, 1973); crystallized from melt or residual from raw mix (Brown, 1948); MgO concentration greater than 2% in total clinker or locally (Gille and others, 1965)
Relatively low C_3S content and high periclase; improved crystallinity of C_3A ; unsoundness at MgO of 4.0% with C_3A greater than 7%	Effects of slow cooling in laboratory test. Suggested remedy is to lower alumina modulus and increase fineness of cement (Chopra and others, 1982)
Relatively large periclase in liquid phase; large, clustered, silicate crystals with less defined boundaries; irregularly shaped C_3S ; 8% to 30% drop in 28-day strength	Effects of slow cooling in lab test; similar interpretation for commercial clinkers (Chopra and others, 1982)
Large number of periclase crystals in high MgO clinker	Slow cooling of clinker (Gouda and Bayles, 1981)
Small number of periclase crystals in high MgO clinker; retention of MgO in silicate and interstitial-phase solid solutions	Quick cooling (Gouda and Bayles, 1981)
Large periclase	High temperature and slow cooling (Long, 1982a); slow cooling (Hawkins, 1979)
Periclase departure from perfect octahedral form, developing skeletal, lacy, or large intricate designs	Nonattainment of high temperature equilibrium (Brown, 1948)
Idiomorphic periclase	Slow cooling (Hofmänner, 1973)
Dendritic periclase	Rapid cooling (Hofmänner, 1973); rapid cooling from above 1400°C (Hawkins, 1979)
Dendritic periclase	Relatively fast cooling from temperatures above 1500°C, long dry kiln (DeHayes, Grady, and Vidergar, 1986)
Dendritic periclase associated with belite, also dendritic	Slow cooling from high temperature and coprecipitation of phases (Hawkins and Hayden, 1976)
Periclase resorption into alite	Variations in burning conditions (Gille and others, 1965)
Periclase with high reflectivity and low polishing hardness	Wustite in solid solution with periclase (Woermann, 1960)
Wide areas of secondary periclase and autoclave problems	Coarse coal particles, high MgO raw mix (Hawthorne, Richey, and Demoulain, 1981)
Lime nest with periclase	Dolomite particle (Gille and others, 1965)
Periclase nest with free lime	Coarse dolomitic limestone (Long, 1982a)
Small periclase crystals with free lime	Dolomite grain (Fundal, 1980)
Open cluster of periclase plus free lime nest with interstitial periclase	Large dolomite, depending on local surrounding chemistry (Fundal, 1980)
Large crystals of CaO and MgO	Volume unsoundness (Krämer, 1960)
Crystals of +45 to -63 μm size range	Greater autoclave expansion than that with equal amount of -90 μm periclase (Goswami, Mohanty, and Panda, 1984)
Excessive autoclave expansion	Periclase, free lime, or coarsely crystalline (slowly cooled) C_3A (Gonnerman, Lerch, and Whiteside, 1953)

PHOTOMICROGRAPHS OF PERICLASE

Photograph 7-85 Dendritic periclase forming substrate for belite overgrowth (center left). Alite crystals exhibit facial extensions into matrix of very finely microcrystalline aluminite and ferrite. Slowly cooled from high temperature. (S#A6703)

Polished section

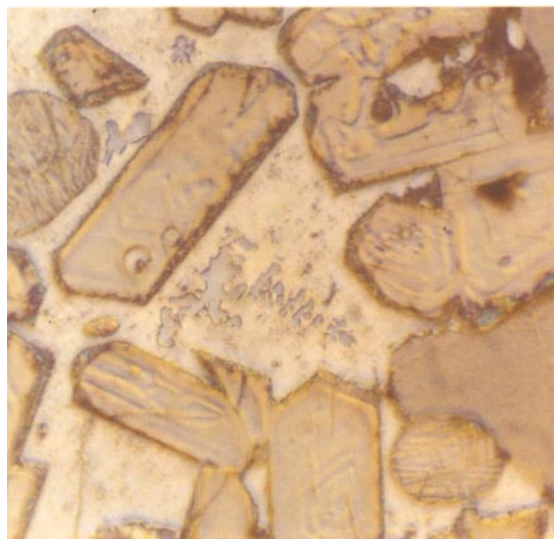
Water etch

Field dimensions = 0.14x0.14 mm



Photograph 7-86 Marked topographic relief produced on polished section by 10-sec nital etch followed by 10-sec application on Texmet™ with 0.05- μ m alumina. Note dendritic periclase (pinkish gray in matrix) and silicate zonation. High maximum temperature, moderately long burning time, slow heating rate, and slow to moderately slow cooling. Coke- and coal-fired, dry-process kiln, 918 tons/day. (S#A6704)

Field dimensions = 0.95x0.95 mm



Photograph 7-87 Ultrathin section showing dendritic periclase within irregular belite crystals (center and upper left). Section thickness is approximately 10 μ m. Coal-fired, wet-process kiln, 444 tons/day. High maximum temperature, long burning time, moderately slow heating rate, and moderately fast cooling rate. (S#A6705)

Transmitted, plane-polarized light

Field dimensions = 0.21x0.21 mm

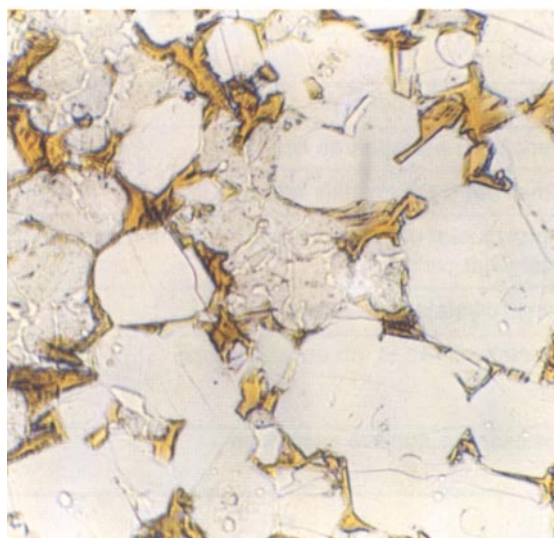


Table 7-1. Microscopical Interpretation of Clinkers (continued)

Miscellaneous	
Observations	Interpretations
Metallic iron	Residual from pyrite cinder (Brown, 1948)
Iron metal	Very strong reducing conditions, lack of air (Gille and others, 1965)
Wustite (FeO)	Clinker rich in iron, very rapid quenching (Gille and others, 1965)
Iron sulfides	Reducing conditions (Gille and others, 1965)
Calcium sulfide	Slight reduction (Gille and others, 1965)
Calcium sulfide dendrites	Reducing atmosphere (Gille and others, 1965)
Dendritic calcium sulfide	Reducing atmosphere (Krämer, 1960)
K, Fe sulfide	Reducing conditions (Gille and others, 1965)
Formation of calcium sulfide and KFeS_2	More extreme reducing conditions (Long, 1982b)
Unburned fuel (coke, graphite)	Reducing conditions, lack of air (Gille and others, 1965)
Alkali sulfates	Increased early mortar-cube strength, decreased late strength (Jons, 1981)
Abundant Ca-K sulfate	Decline in 28-day strength (Sarkar, 1989)
Halo of unetched phases around central sulfate deposit	Characteristic for alkali sulfate deposits in clinkers (Pollitt and Brown, 1968; Long, 1984a)
Deliquescent alkali oxide associated with aluminate phase	Dissociation of alkali sulfates or alkali-calcium sulfates in reducing environment (Long, 1982b)
Calcium langbeinite in interstitial phase	Excess sulfate over equivalent alkalis (Long, 1983)
Anhydrite in laboratory clinker voids, bonded to aluminate and ferrite	Sulfate-rich raw mix with SO_3 greater than 2.3% (Dreizler, Strunge, and Knöfel, 1985)
Glassy spheres containing Si, Ca, K, and Ti in clinker	Wet process, 90% fuel oil and 10% combustible material containing titanium in feed (Hawthorne, Richey, and Demoulian, 1981)
Gehlenite glass	Severe local decrease in CaO (Gille and others, 1965)
Glass in matrix	Impossible to establish microscopically with certainty; very unlikely in normal plant clinker (Hofmänner, 1973)
Fine silica intimately dispersed in limestone (cement rock)	Easily burned, even if as coarse feed (Long, 1982a)
Coarse, very acidic or very basic particles in heterogeneous feed	Generally requires increases in burning temperature (Long, 1982a)
Increases in lime saturation factor, silica ratio, alumina ratio; increase in combinability temperature	Result from burning in reducing environment (Long, 1982a)
Higher burning temperature required for adequate combination; increase in alite crystal size	Coarse raw feed (Long, 1982a)
Increase in silica ratio, decrease in melt volume	Results in decrease in power for grinding, providing that small crystals are produced and that the clinker is not dusty (Petersen, 1980)
Air-setting of cement during storage, poor workability	Alkali-water combination, alkalies developed upon quick cooling of reduced clinker (Long, 1982a)

Table 7-1. Microscopical Interpretation of Clinkers (continued)

Miscellaneous	
Observations	Interpretations
Relatively rapid set of cement	Clinker burned and cooled under reducing conditions; highly reactive, well-crystallized, more abundant C_3A , slowly cooled (Sylla, 1981)
Relatively high 28-day mortar strength	Clinker burned in oxidizing atmosphere (Sylla, 1981)
Decrease in 28-day mortar strength	Excess carbon or sulfide in raw feed; clinker burned and slowly cooled in reducing atmosphere (Sylla, 1981)
Depression of 28-day strength; premature stiffening; loss of workability; cement flowability problems; silo blockages; lighter colored cement	Reducing conditions, slow cooling (Long, 1982b)
Increase in alite and interstitial percentage; decrease in belite percentage	Correlated with decrease in 28-day mortar strength (Akatsu, Monna, and Maeda, 1965)
Increase in free lime and belite percentages; decrease in alite and interstitial percentages; decrease in alite size	Correlated with increase in porosity (Akatsu, Monna, and Maeda, 1965)
High proportion of biogenic material, negligible matrix, small amount of organic substances; compact microstructure	Ideal limestone raw material for high degree of burning (Gotthardt and Wilder, 1981)
Increasing consumption and premature failure of basic brick in burning zone, difficulty in forming coating	Poor raw feed composition and uniformity, resulting in excessive and fluctuating burning temperatures (Chen, Conjeaud, and Lehoux, 1985)
(a) Fast-setting cement, small C_3S crystals, faster cooling rate, potassium as K_2SO_4 (b) Fast-setting cement, higher porosity resulting in higher water demand and changing viscosity (c) Lower initial hydraulic activity and hardness, higher long-term hardness, higher C_2S , and decrease in grindability	(a) Oil-fired cement (b) Gas-fired cement (c) Ash-rich coal (Philipp and others, 1981)

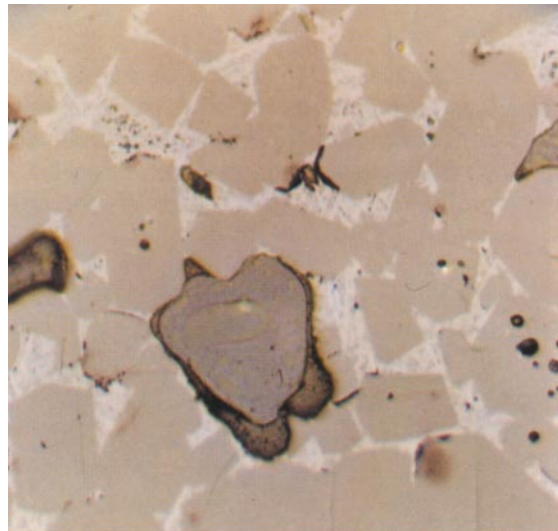
PHOTOMICROGRAPHS OF MISCELLANEOUS PHASES

Photograph 7-88 Dark alkali sulfate deposits on wall of void now filled with epoxy. Coal-fired kiln, wet process. High maximum temperature, long burning time, slow heating rate, quickly cooled, 42 MPa. (S#A6706)

Polished section

No etch

Field dimensions = 0.21x0.21 mm

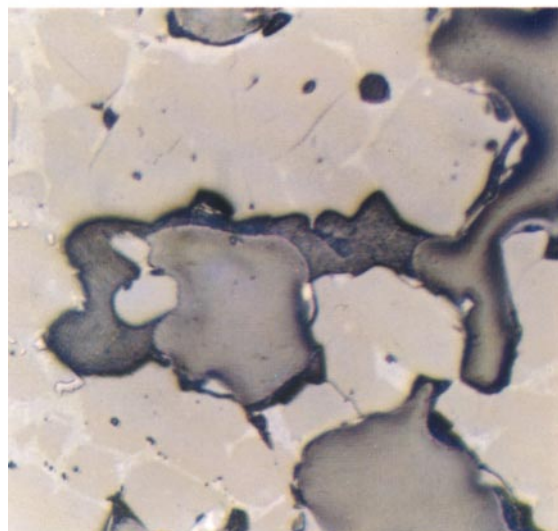


Photograph 7-89 Dark alkali sulfate as pore and channel fillings (center and left center). Remainder of pore is filled with epoxy. XRD analysis indicates arcanite and aphthitalite. Coal- and coke-fired kiln, wet process, 920 tons/day. Moderately high maximum temperature, moderately long burning time, moderately slow heating rate, quickly cooled. (S#A6707)

Polished section

No etch

Field dimensions = 0.21x0.21 mm

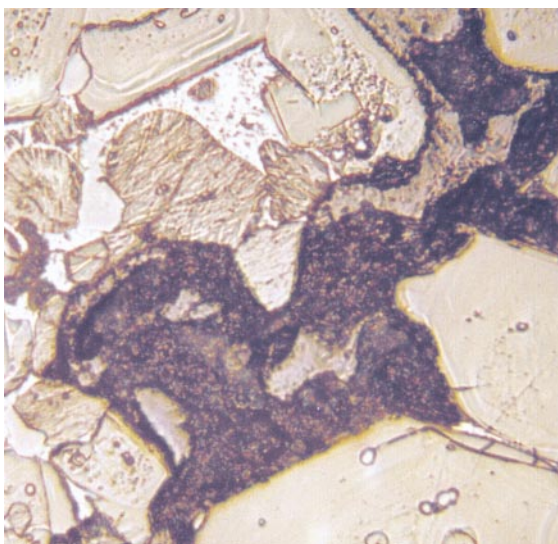


Photograph 7-90 Dark alkali sulfate in clinker void. Prominently zoned alite. Clearly defined lamellae in relatively small, round belite. Low maximum temperature, long burning time, slow heating rate, slow cooling rate, reducing conditions. (S#A6708)

Polished section

Final polish with mixture of 0.05 μm alumina, isopropyl alcohol, and propylene glycol

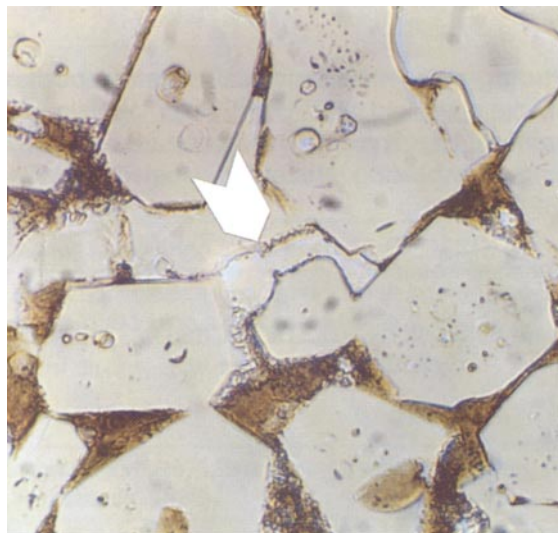
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF MISCELLANEOUS PHASES (CONTINUED)

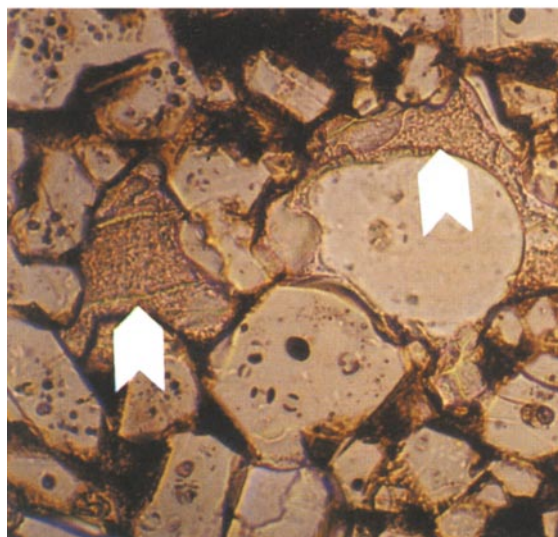
Photograph 7-91 Thin section view of alkali sulfate (arrow) as partial filling of void. High maximum temperature, moderately long burning time, slow heating rate, slow to moderately slow cooling. Four-stage preheater dry-process kiln, coal- and coke-fired, 918 tons/day. (S#A6709)

Transmitted, plane-polarized light
Field dimensions = 0.14x0.14 mm



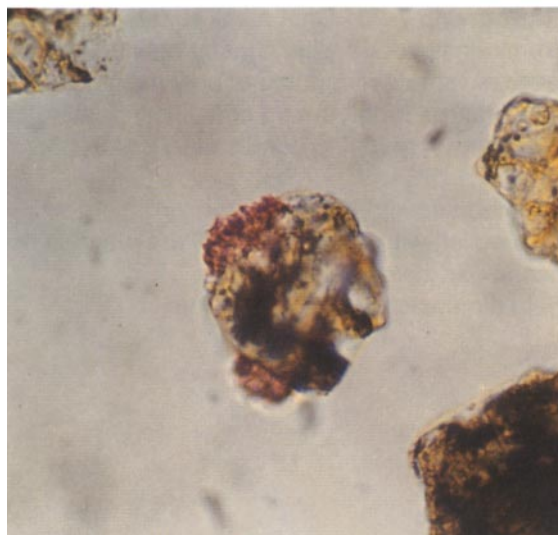
Photograph 7-92 Alkali sulfate deposits (arrow) in clinker voids. Clinker $\text{SO}_3 = 1.12\%$. Moderately high maximum temperature, moderately long burning time, slow heating rate, moderately slow cooling rate, 33 MPa. Coal- and coke-fired, wet-process kiln, 950 tons/day. (S#A6710)

Thin section
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



Photograph 7-93 Alkali sulfate stained purplish red with a $\text{BaCl}_2\text{-KMnO}_4$ solution. (S#A6711)

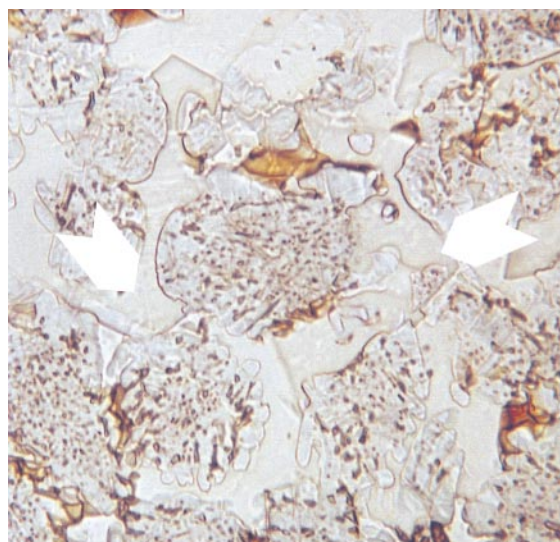
Clinker powder, 45- to 75- μm fraction
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF MISCELLANEOUS PHASES (CONTINUED)

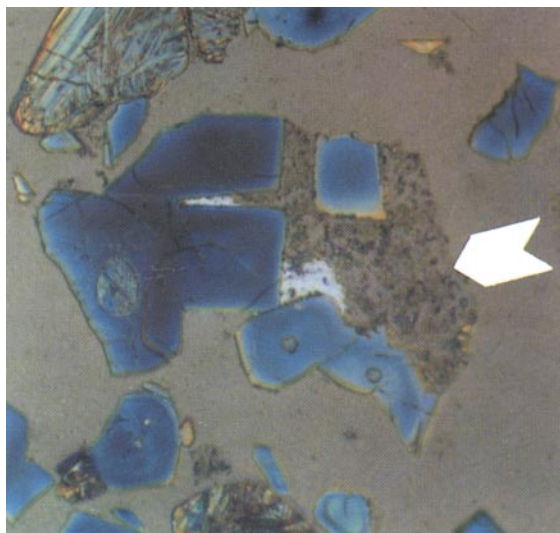
Photograph 7-94 Isotropic glass matrix (arrows) in clinker formed at near-melting temperature. Belite shows prominent lamellar extensions; ferrite is red and strongly pleochroic. Numerous exsolved dots in belite. (S#A6712)

Thin section
Transmitted, plane-polarized light
Field dimensions = 0.21x0.21 mm



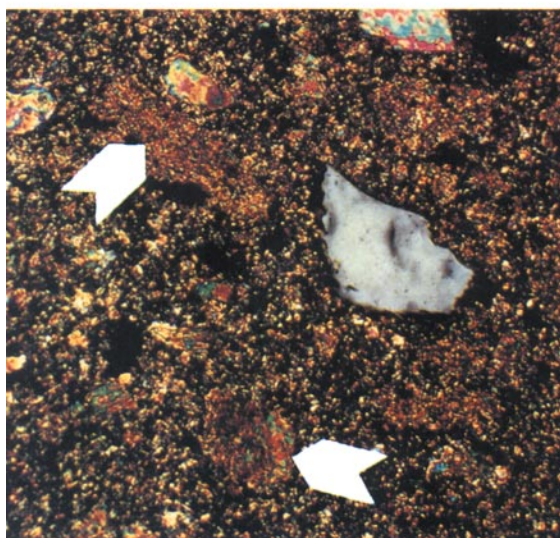
Photograph 7-95 Polished section of clinker particle after KOH-sugar solution extraction, leaving partly crystalline material (arrow) and brightly reflecting residual ferrite (center). (S#A6713)

Nital etch
Field dimensions = 0.21x0.21 mm



Photograph 7-96 Kiln feed in thin section. Multi-colored particles are grains of polycrystalline limestone (calcite). Gray quartz in center. Brown shale particles (also polycrystalline) indicated with arrows. (S#A6714)

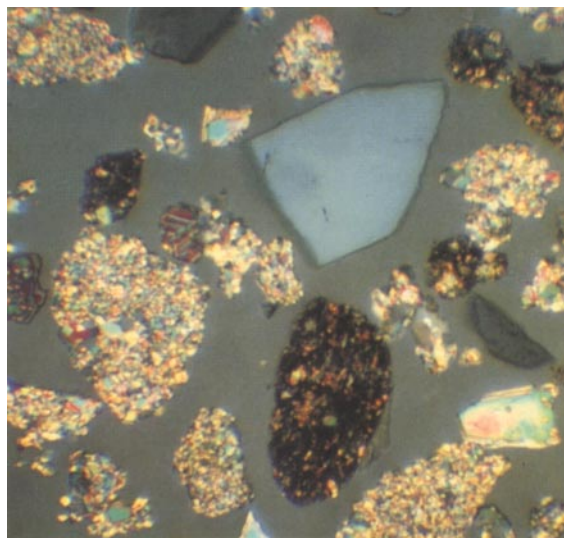
Crossed polars
Field dimensions = 1.9x1.9 mm



PHOTOMICROGRAPHS OF MISCELLANEOUS PHASES (CONTINUED)

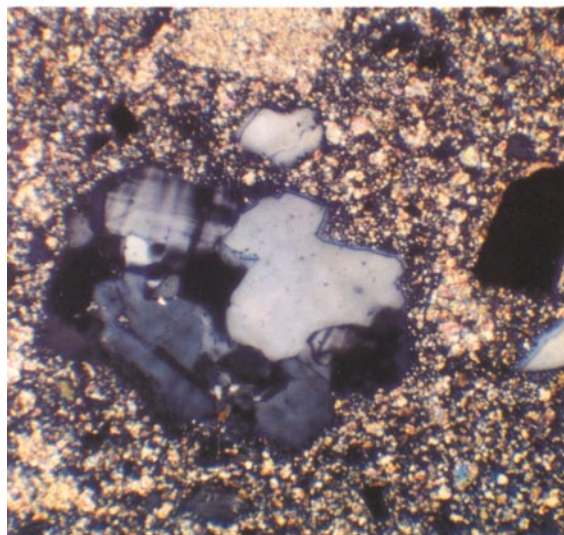
Photograph 7-97 Feed particles in thin section. Gray quartz (upper center), microcrystalline limestone (left center and bottom right), and dark shale (center). (S#A6715)

Partially crossed polars
Field dimensions = 0.60x0.60 mm



Photograph 7-98 Kiln feed containing coarse particles of sandstone in which microcline feldspar (showing grid twinning) is common and presumably a source for potassium in the clinker. Fine particles of limestone comprise most of the feed. (S#A6716)

Thin section
Crossed polars
Field dimensions = 0.53x0.53 mm



CHAPTER 8

Misinterpretations in Clinker Microscopy

After several years of practice in making and studying thin sections and polished sections, one gradually develops an ability to discern quickly the differences between artifacts of preparation technique and properties of the specimen examined. Unfortunately, misidentifications caused by cracks, scratches, holes, pits, and other surface irregularities (as well as interference from residual liquids used in the grinding, polishing, etching, and cleaning) are common in the published literature of clinker microscopy. The writer has found that only with methodical patience, and with the proper equipment, can a perfect polished section or thin section be produced. If the proper procedure is followed the first time, repeated steps in the preparation sequence are rare and, consequently, hours spent trying to interpret a misidentification are few.

Photomicrographs 8-1 through 8-11 illustrate some of these artifacts and will help the beginning clinker microscopist to discriminate actual clinker properties from the effects of sample preparation. Some problems, however, are not easily solved. For example, interference of exuding polishing or cleaning liquids with etching media may lead to "halo" patterns of discolored or unetched crystals around clinker pores and absorbent phases. Poorly understood chemical reactions may create "whiskers" near pores. Polishing vehicles must be chemically "pure" or, at least, the impurities must not react with any of the clinker phases. Ethanol denatured with methanol is not recommended (Prout, letter, 1984). Water is a common deleterious contaminant in isopropyl alcohol used for both a polishing vehicle and cleaning solution. Drying with moist air (as from a house air line) may lead to a patchy pattern of discoloration, some of which could be caused by oil, grease, water, or other impurities. Cracks and gaps between phases typically contain polishing powders or pastes. Scratches are particularly troublesome. A few coarse

particles producing scratches during final polishing will quickly ruin an otherwise perfect section.

One should not, therefore, immediately draw the conclusion that a clinker phase is particularly "reactive" if its freshly polished surface exhibits a slight etch or stain due to impure polishing vehicles or cleaning solutions. Keeping the etchants at constant temperature is recommended to eliminate that persistent question of temperature effects. Etching and staining should be consistently timed.

Use of the hair dryer to warm the surface of a polished section accelerates etching and staining. Therefore, beware of a premature conclusion of high phase reactivity. Delayed etching may inhibit normal coloration and give one a misinterpretation of sluggish phase reactivity.

Microscope light intensity and use of filters should also be employed consistently. Use of a sonic cleaner is also advisable, but, even so, lint from the polishing cloth or concentrations of dried polishing debris may remain in clinker pores. Grinding or polishing powder that dries in clinker pores is almost impossible to remove. Therefore, temporary storage of polished sections in a shallow tray of propylene glycol or other non-reactive liquid between grinding and polishing steps is recommended to keep the section surface from drying.

Finally, make interpretive generalizations based on the dominant (most common) clinker characteristics, always attempting to be quantitative and systematic.

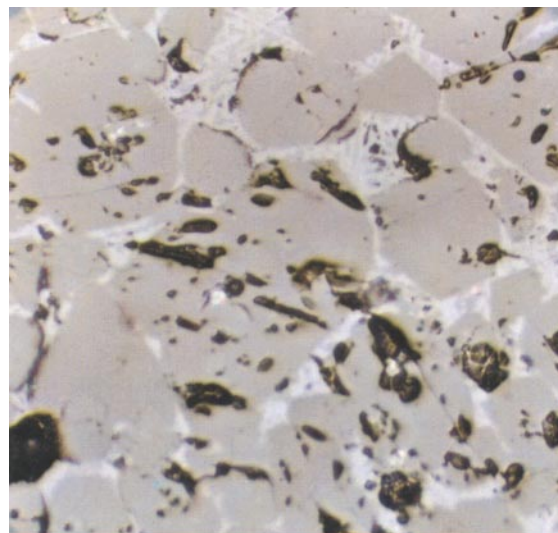
PHOTOMICROGRAPHS OF ARTIFACTS

Photograph 8-1 Grinding pits remaining on hastily polished surface of clinker appear somewhat like dark alkali sulfate. (S#A6717)

Polished section

No etch

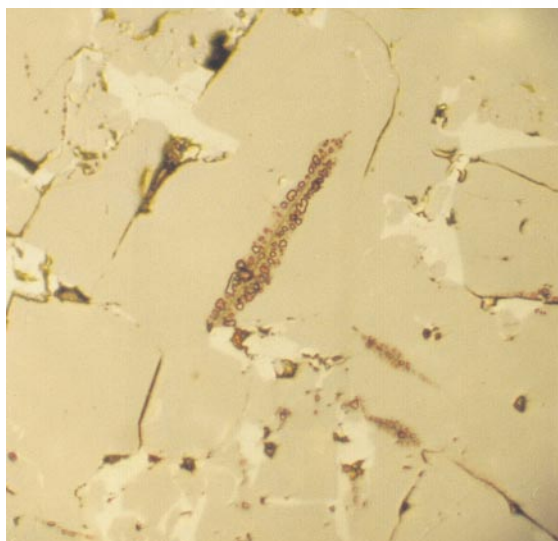
Field dimensions = 0.21x0.21 mm



Photograph 8-2 Exudation of polishing vehicle (propylene glycol) or cleaning medium (isopropyl alcohol) from an alite cleavage on polished section surface. The exudation could be misinterpreted as chemical attack of the alite crystal. (S#A6718)

No etch

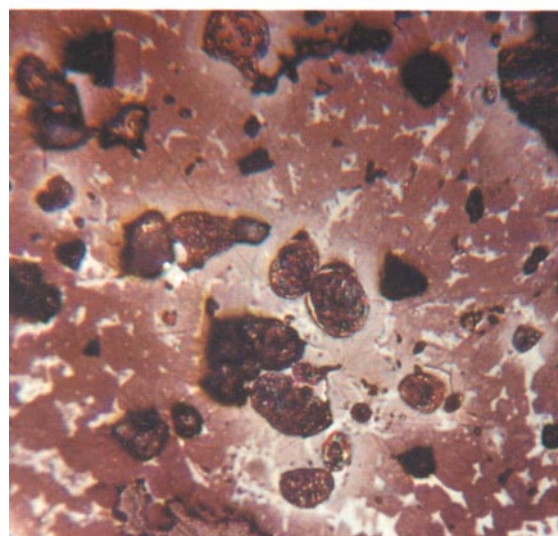
Field dimensions = 0.21x0.21 mm



Photograph 8-3 Etch halo around free lime nest observed after NH_4Cl etch ("H" in text, Chapter 3). The halo may be the result of etch interference by liquid exuding from the porous free lime crystals and nearby pores. (S#A6719)

Polished section

Field dimensions = 0.21x0.21 mm



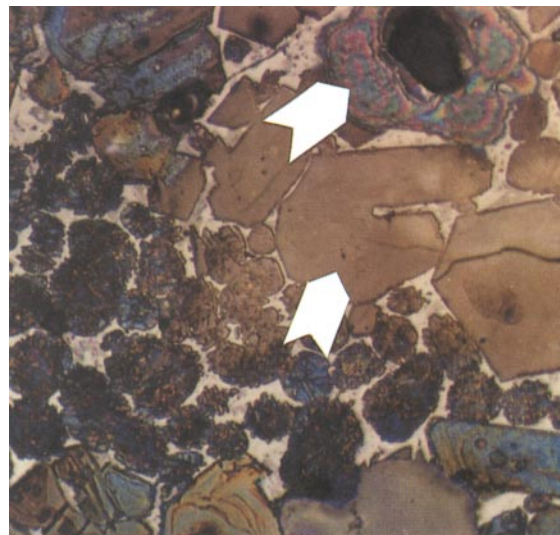
PHOTOMICROGRAPHS OF ARTIFACTS (CONTINUED)

Photograph 8-4 Residual liquid and halo (arrow) from polishing, cleaning, or etching, extending across alite into blue belite nest. (S#A6720)

Polished section

Nital etch

Field dimensions = 0.21x0.21 mm

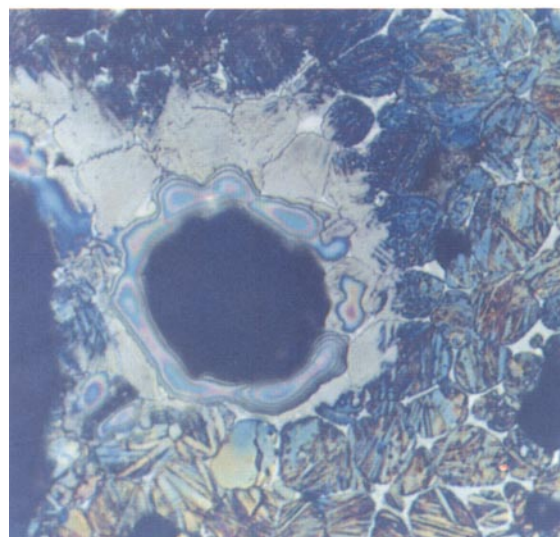


Photograph 8-5 Residual liquid from polishing or cleaning sample and halo of unetched belite surrounding central pore. Liquid could be misinterpreted as free lime. Liquid eventually dried. (S#A6721)

Polished section

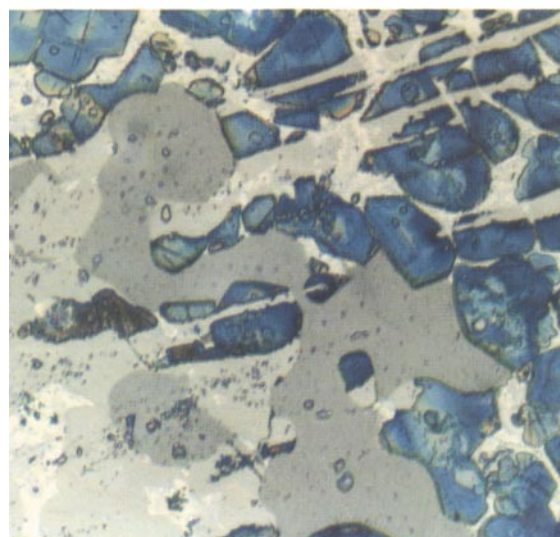
Nital etch

Field dimensions = 0.21x0.21 mm



Photograph 8-6 Nonuniform nital etch on polished section. Cross-cutting stripes and patches in silicates could be misinterpreted as structural variations or aluminate concentrations. (S#A6722)

Field dimensions = 0.21x0.21 mm

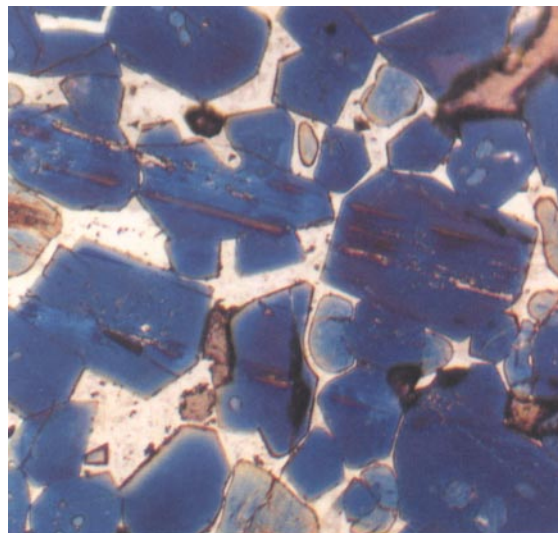


PHOTOMICROGRAPHS OF ARTIFACTS (CONTINUED)

Photograph 8-7 Polished section showing polishing marks, probably shallow scratches, extending across three blue alite crystals. (S#A6723)

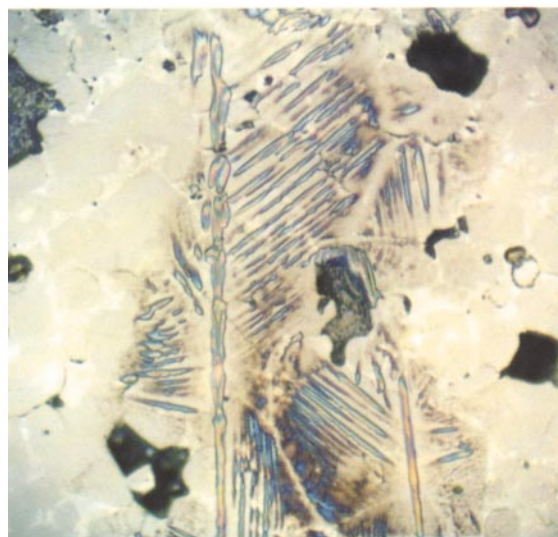
Nital etch

Field dimensions = 0.21x0.21 mm



Photograph 8-8 Unidentified, presumably organic, crystals formed on unetched polished-section surface, perhaps as a result of mixing of propylene glycol, used as a polishing vehicle, and isopropyl alcohol used in cleaning. (S#A6724)

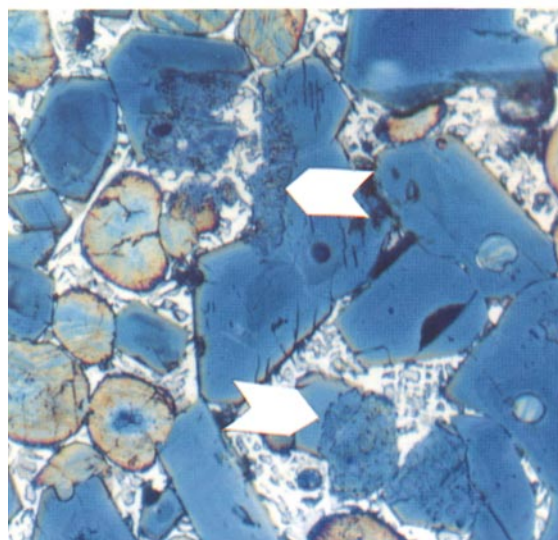
Field dimensions = 0.21x0.21 mm



Photograph 8-9 Residual polishing, cleaning, or etching liquids causing blotchy patterns (arrows) on blue alite crystals. Patterns removed after repolishing and drying before etching. Well-differentiated matrix of aluminite (C_3A) and ferrite is made clearly visible by application of nital over a previous KOH etch. (S#A6725)

Polished section

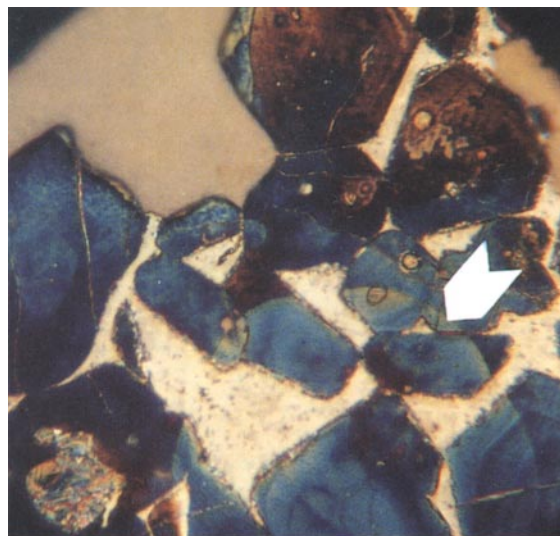
Field dimensions = 0.21x0.21 mm



PHOTOMICROGRAPHS OF ARTIFACTS (CONTINUED)

Photograph 8-10 Interference by residual liquid or air bubble (arrow) on nital-etched, polished clinker surface. Note “ghost” boundary (arrow) transecting several alite crystals but not visible on the matrix. (S#A6726)

Field dimensions = 0.21x0.21 mm

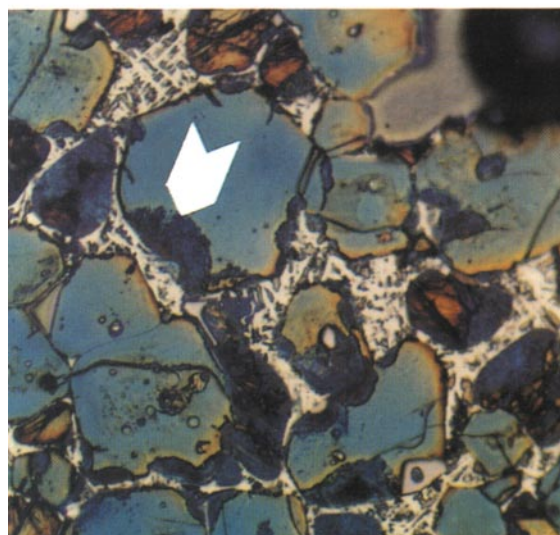


Photograph 8-11 Residual liquid interference with etch, producing dark blobs (arrow) on silicates. (S#A6727)

Polished section

KOH followed by nital etch

Field dimensions = 0.21x0.21 mm



CHAPTER 9

Scanning Electron Microscopy

Although this publication is not designed to portray details of all the various methods and results of microscopical analysis, mention of some of the applications and possible pitfalls of the scanning electron microscope (SEM) and Electron Dispersive X-ray Analysis (EDXA) is appropriate. Most of the SEM and microprobe studies to date have dealt with the general characterization of clinker phases, including their compositional variations. Among the articles describing use of the SEM in analysis of clinker microstructure is the work of Gouda (1979a, 1980) in which the various clinker phases are identified and described in order to interpret the manufacturing process. Other publications in this field are those of Yamaguchi and Takagi (1968); Regourd and Guinier (1974); Skalny, Mander, and Meyerhoff (1975); and Grattan-Bellew, Quinn, and Sereda (1978). The latter publication emphasizes some of the possible problems in SEM analysis, including preparation techniques, surface charging, image distortion, phase abundance, and other factors.

Use of the SEM and EDXA in this book has been primarily for phase identification, photography, and, in some cases, to gain specific compositional information. Much of the time spent with the SEM-EDXA has also been for the purpose of developing sample polishing and etching techniques to facilitate examination. A word of caution is given to workers who examine only fractured clinker surfaces with the SEM: Such surfaces may not present the observer with a representative cross section of the clinker's many phases. Moreover, attention is too often directed to well-formed crystals projecting into clinker voids, which are ideal places to study deposition of alkali sulfates on previously formed crystal surfaces, but are poor localities for analysis of matrix-silicate relationships.

Used properly, the SEM-EDXA allows one to precisely elucidate some of the microstructural and compositional details unseen with other techniques of mi-

croscopy. Routine application of SEM-EDXA to daily production problems is not common. However, a semi-automatic SEM-EDXA system for routine production quality control may not be beyond the realm of possibility and practicality. A computer-controlled method of SEM-EDXA was used by Minnis (1984) to determine the mineralogy of a sandstone thin section, the data expressed in volumetric percentages; the method also provides an approximation of phase grain size and a graphical description of grain locations.

Stutzman (1994) and Stutzman and Odler (1991) illustrated some of the profound implications in application of electron imaging in clinker and concrete analysis, demonstrating the details of microstructures at magnifications having resolutions of approximately 0.2 μm .

Bonen and Diamond (1991) with image analysis comparisons of roller-milled and ball-milled cements illustrated that two major variants in cement performance are phase abundance and phase specific surface, particularly in the finer fractions. Roller mill cements differed from ball mill cements in having fewer very small particles, lower aspect ratios and shape factors, and differences in the content of particles of specific mineralogies. Alite was relatively enriched in the finest fractions of the ball-milled cement.

In a laboratory study of grinding techniques (ball mill vs. roller mill) Chen and Odler (1992) showed that roller mill cements exhibit inferior quality because of higher water demand, resulting from adverse packing characteristics developed during grinding. Microscopically, clear cut differences were observed with regard to particle size, shape, Blaine, and additionally, dry bulk density and flow rates.

Sarkar and Samet (1994), utilizing x-ray diffraction and light and electron microscopy, concluded that an abundance of a potassium-calcium sulfate (from excessive insufflation) and unusually large belite crystals (from long residence times) were responsible for low

late-age strength. And, in another plant, finer grinding of the raw meal to minimize the occurrence of tightly packed belite nests in clinker resulted in an immediate improvement of strength properties of the cement.

The techniques of sample preparation described in the following paragraphs are those used by the author.

Clinker powder mounts for SEM-EDXA study are made by scattering an alcohol-washed, 45- to 75- μm fraction of crushed clinker on a thin film of fresh epoxy resin (plus hardener) on a glass microscope slide. The particles stand above the general level of the epoxy film, and, after the epoxy hardens, can be subjected to repeated examination with different refractive-index oils with cover glasses. Using photographs (or marking the area of interest with India ink) and knowing the orientation of the slide in the SEM-EDXA sample holder, a specific particle can be found again and analyzed. Thus the same particle is examined with light and electron microscopy. Particles are also mounted directly on the stub for SEM study. For relatively precise chemical composition, a suitably

polished section is the preferred surface for EDXA and microprobe. Particles mounted with epoxy on a glass or epoxy slide, followed by polishing only the tops of the particles (half sections), allow one to gather reliable chemical data by these electronic methods in combination with observations with transmitted and reflected light.

Polished thin sections are also examined in transmitted, polarized light and, after etching for 15 to 30 seconds with nital, certain areas are selected and marked with India ink for SEM-EDXA. The thin section is then mounted on silver adhesive tape attached to an aluminum sample holder. Colloidal graphite is painted over the tape and holder, covering all exposed areas except the sample. After drying, the sample is carbon-coated (approximately 10 nanometers thick) in a vacuum evaporator. Elemental analyses are done with the thin section or powder mount at -10 to $+25$ tilt, 15 to 25 keV, timed mode = 100 to 250 seconds. The problem of "smearing" over the polished-section surface is not totally eliminated but appears to be minor. The problem might be resolved by slight ion-beam etching.

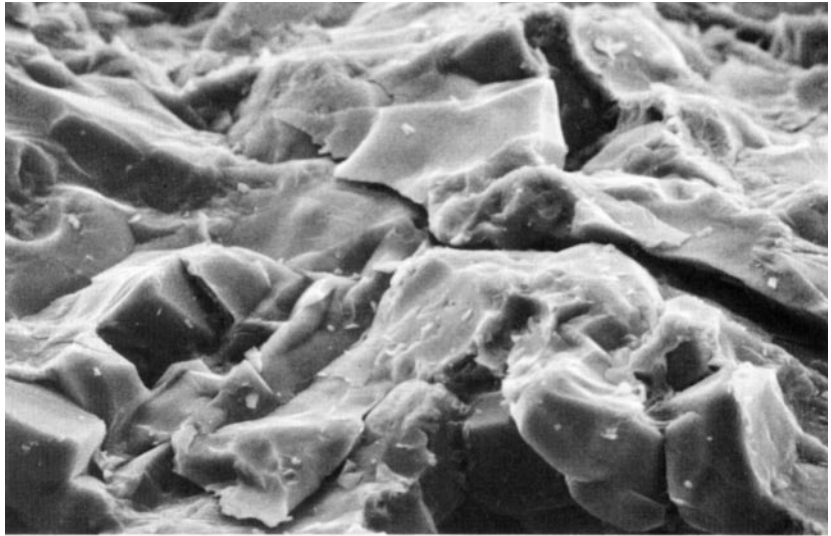
SCANNING ELECTRON MICROSCOPY (SEM)

Photograph 9-1

Semiconchoidal fracture surface of dense, hard-to-grind clinker. (S#A6728)

SEM

Field dimensions = 98 μm x 182 μm

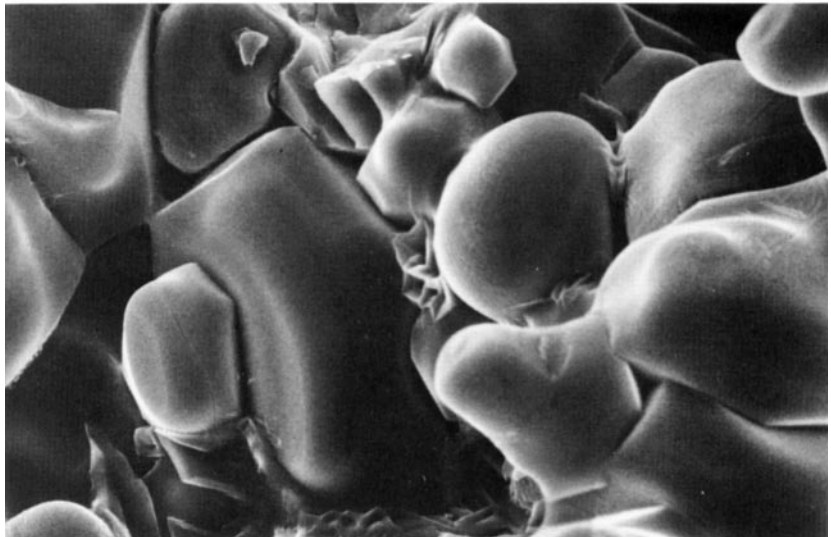


Photograph 9-2 Angular alite and round belite crystals. Boxlike pattern of ferrite crystals in center. Sulfate-resistant cement clinker. (S#A6729)

SEM

Fractured surface

Field dimensions = 86 μm x 131 μm

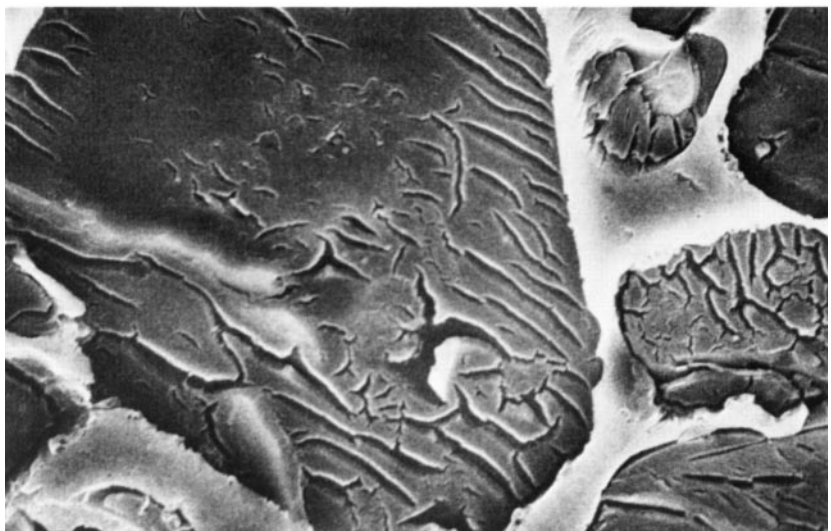


Photograph 9-3 Microcracks (from etching?) in alite crystals in ferrite matrix. (S#A6730)

SEM

Nital-etched polished section

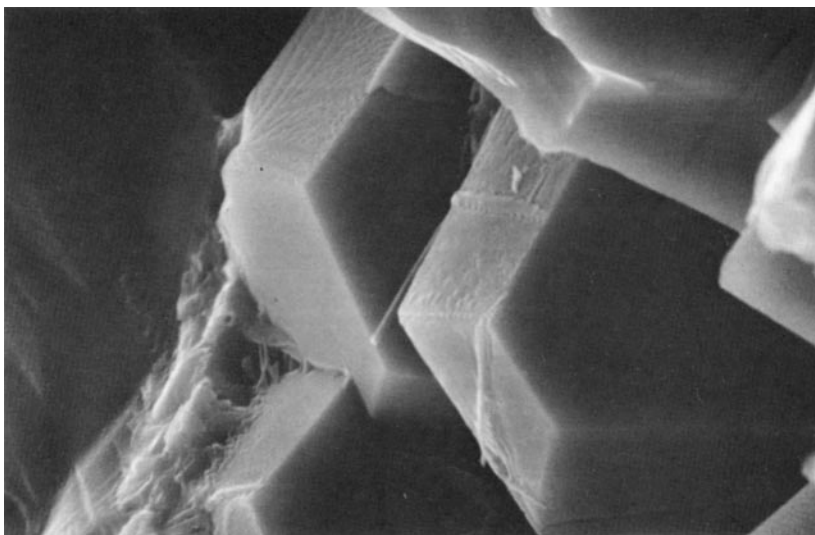
Field dimensions = 46 μm x 70 μm



SCANNING ELECTRON MICROSCOPY (SEM) (CONTINUED)

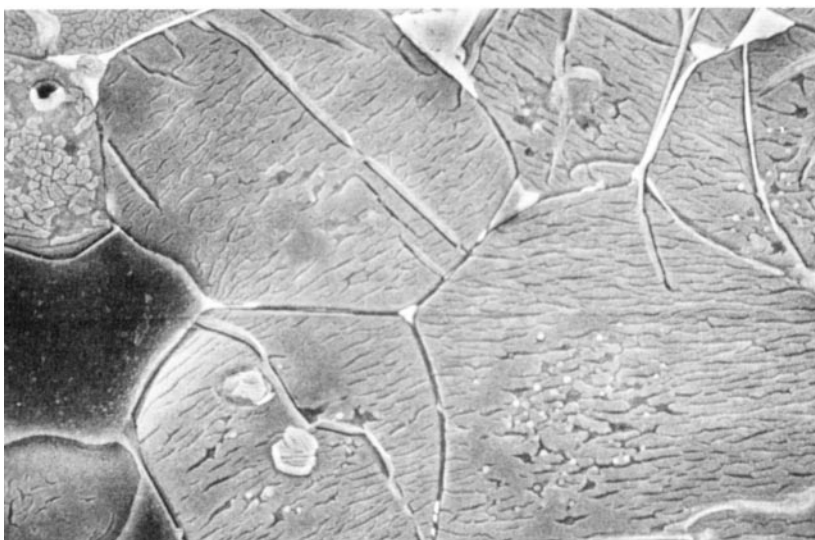
Photograph 9-4 Euhedral alite crystals in clinker void.
(S#A3453)

SEM
Broken surface
Field dimensions = 46 μm x 70 μm



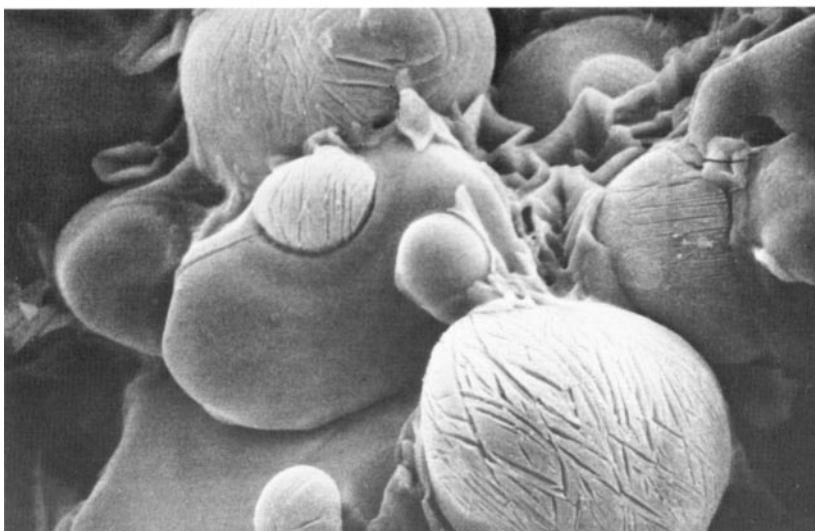
Photograph 9-5 Nital-etched polished clinker section showing tightly packed belite in nest.
(S#A6731)

SEM
Field dimensions = 86 μm x 131 μm



Photograph 9-6 Nital-etched, broken surface of clinker, revealing belite lamellar structure. Note small belite inclusion in alite crystal (left center). (S#A6732)

SEM
Field dimensions = 86 μm x 131 μm

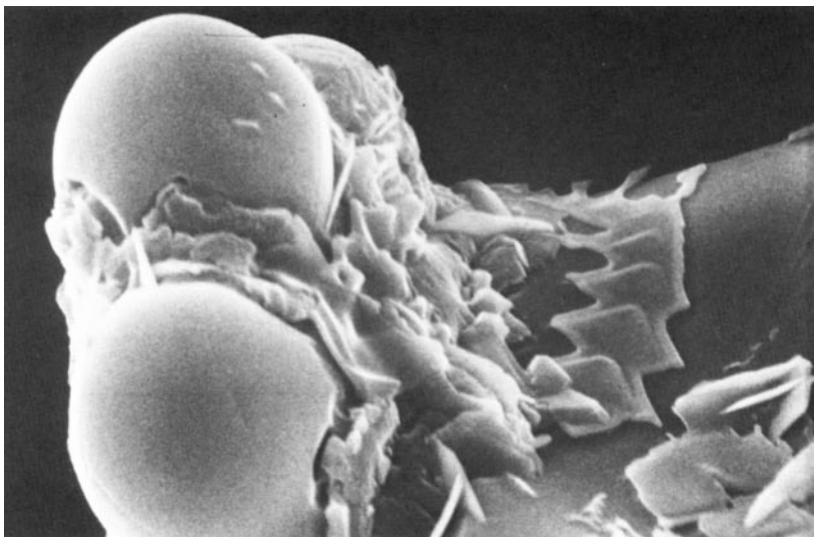


SCANNING ELECTRON MICROSCOPY (SEM) (CONTINUED)

Photograph 9-7 Apparently featureless surfaces of round belite crystals on broken clinker. Light-colored ferrite. (S#A3454)

SEM

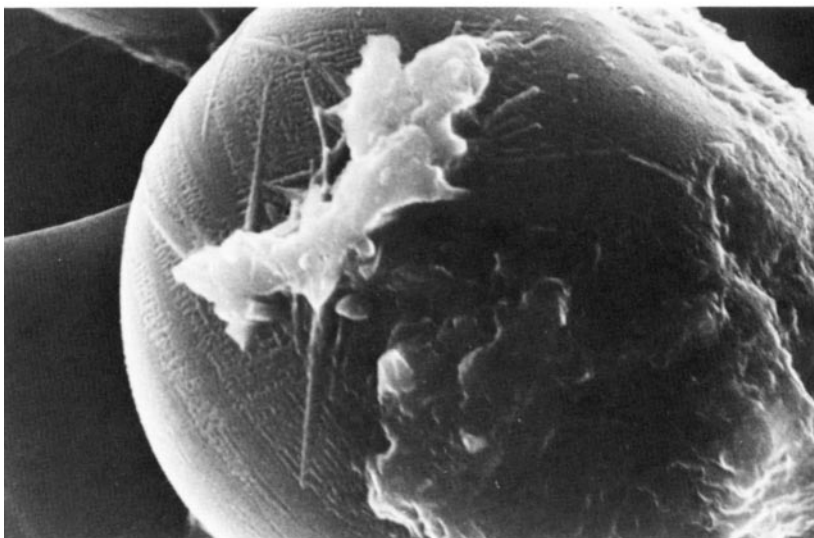
Field dimensions = 18 μm x 28 μm



Photograph 9-8 Belite crystal showing lamellae on outer surface and ferrite deposit (white material). (S#A6733)

SEM

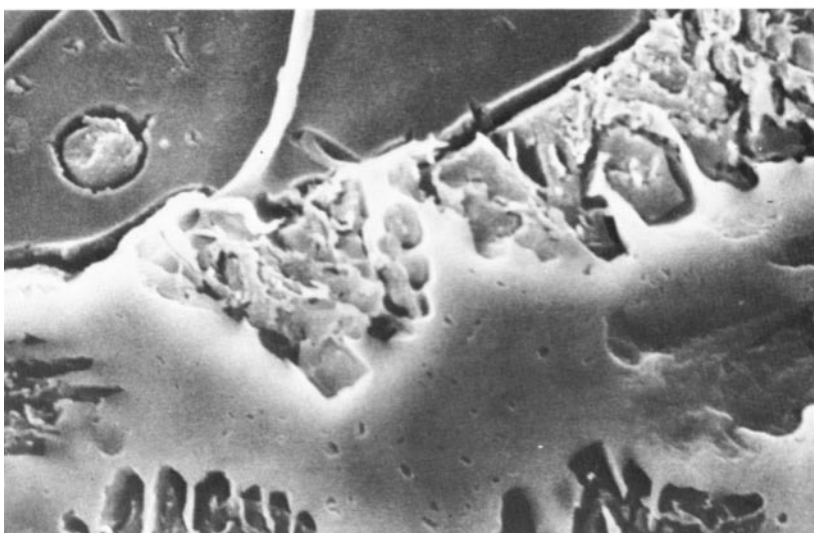
Field dimensions = 18 μm x 28 μm



Photograph 9-9 Nital-etched polished clinker section showing belite fringe on alite (upper half) and lamellar extensions of belite (lower border). (S#A6734)

SEM

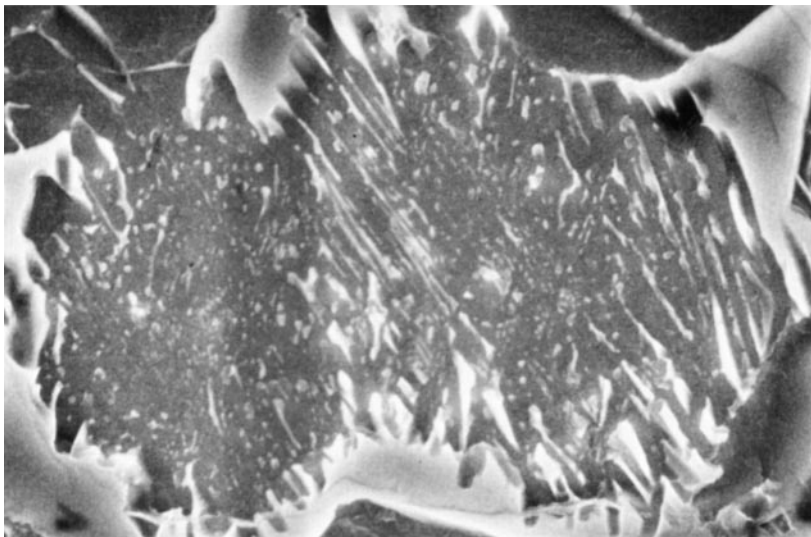
Field dimensions = 30 μm x 46 μm



SCANNING ELECTRON MICROSCOPY (SEM) (CONTINUED)

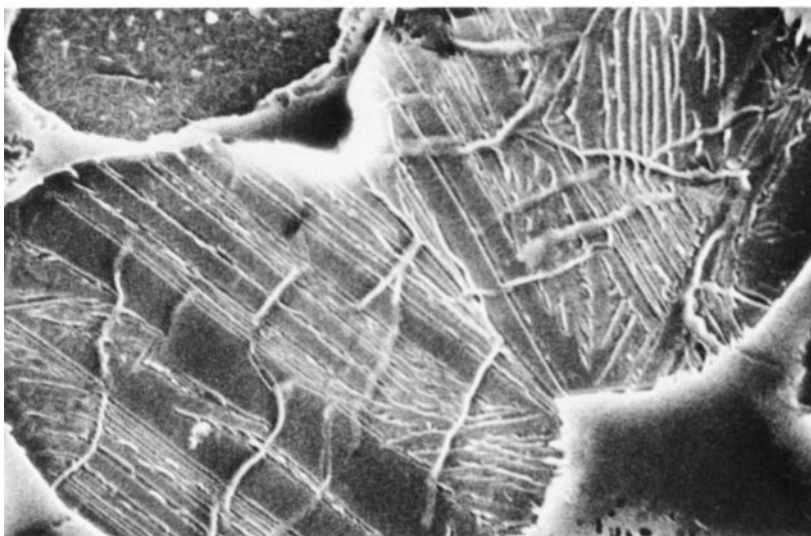
Photograph 9-10 Sulfate-resistant clinker, slowly cooled and ferrite-rich, showing belite lamellae extending into matrix. Gas-fired, wet-process kiln, 830 tons/day. (S#A6735)

SEM
Nital-etched polished section
Field dimensions = 46 μm x 70 μm



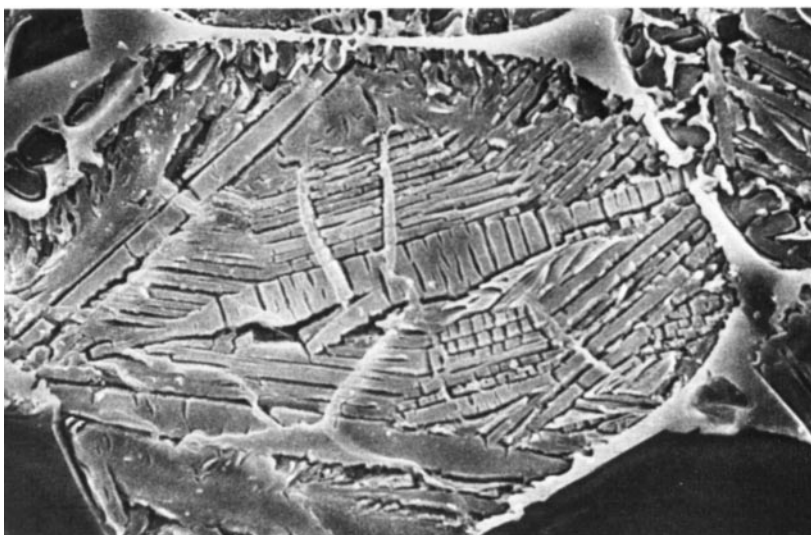
Photograph 9-11 Nital-etched polished section showing well-developed lamellae in belite crystals. (S#A6736)

SEM
Field dimensions = 46 μm x 70 μm



Photograph 9-12 Lamellar structure of belite revealed after nital etch on polished section. (S#A3456)

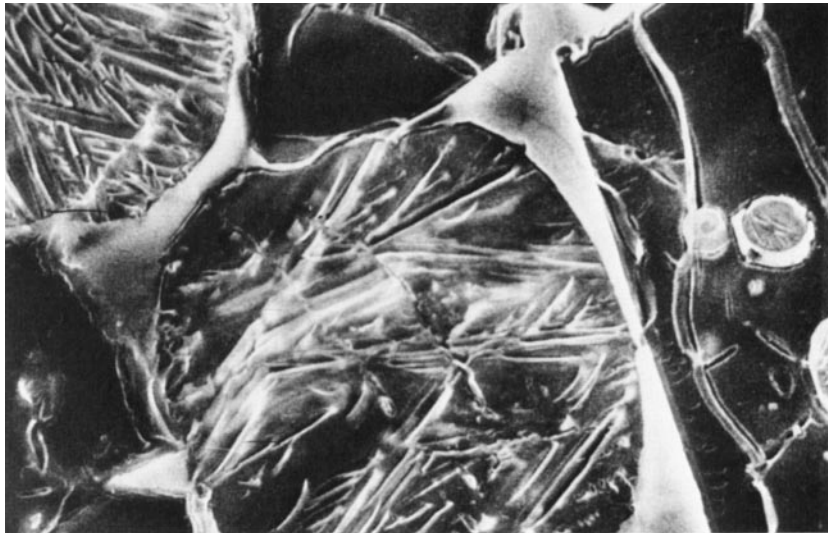
SEM
Field dimensions = 46 μm x 70 μm



SCANNING ELECTRON MICROSCOPY (SEM) (CONTINUED)

Photograph 9-13 Polished section of Class G, oil-well cement clinker showing wide nonlamellar areas in belite crystal. (S#A6737)

SEM
20-sec nital etch
Field dimensions = 30 μm x 46 μm



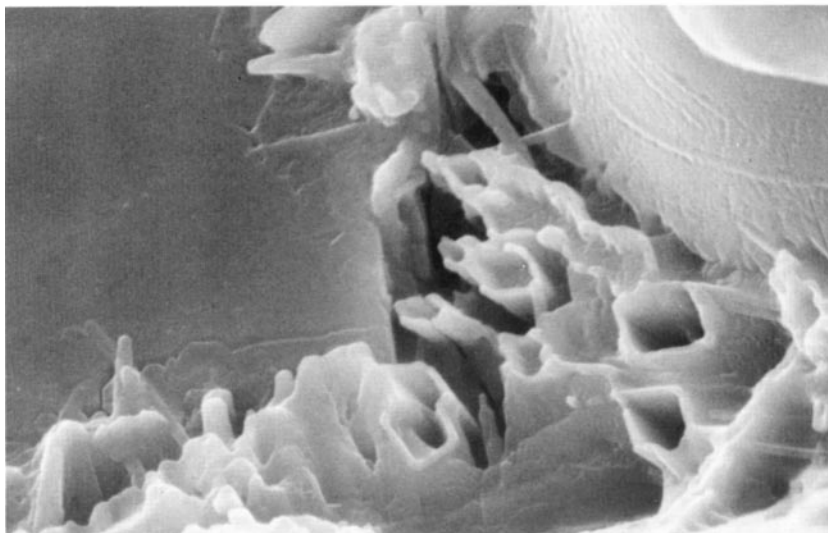
Photograph 9-14 Belite striations (arrow) in alite and belite "footprint" in 10-sec nital-etched clinker polished section. Reducing conditions. (S#A6738)

SEM
Field dimensions = 46 μm x 70 μm



Photograph 9-15 Ferrite-crystal boxwork exposed on broken, nital-etched clinker surface. Voids in boxwork presumably previously occupied by aluminates. Note faintly visible lamellar belite structure in upper right. (S#A6739)

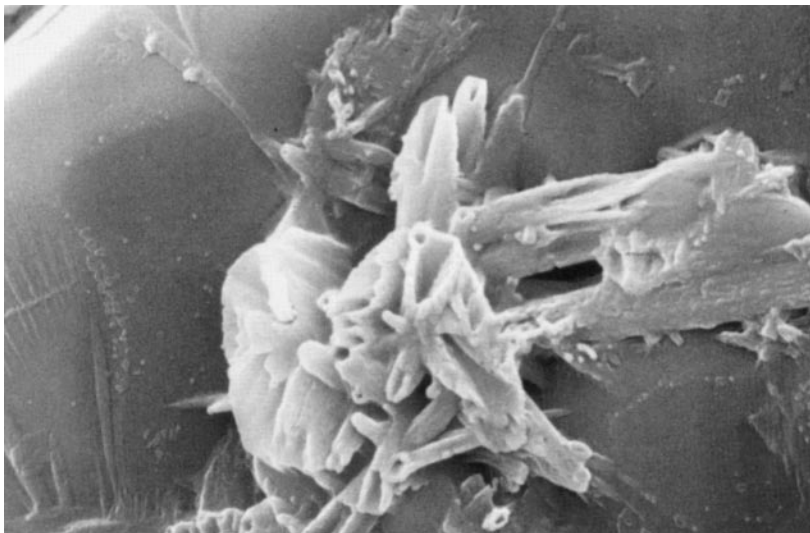
SEM
Field dimensions = 18 μm x 28 μm



SCANNING ELECTRON MICROSCOPY (SEM) (CONTINUED)

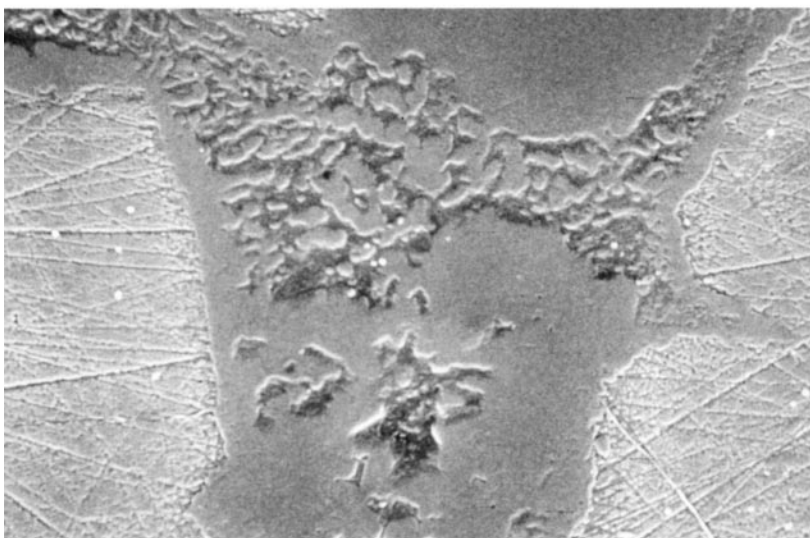
Photograph 9-16 Ferrite crystals showing typical hollow boxwork and lathlike crystal form. (S#A6740)

SEM
Broken surface of clinker
Field dimensions = 18 μm x 28 μm



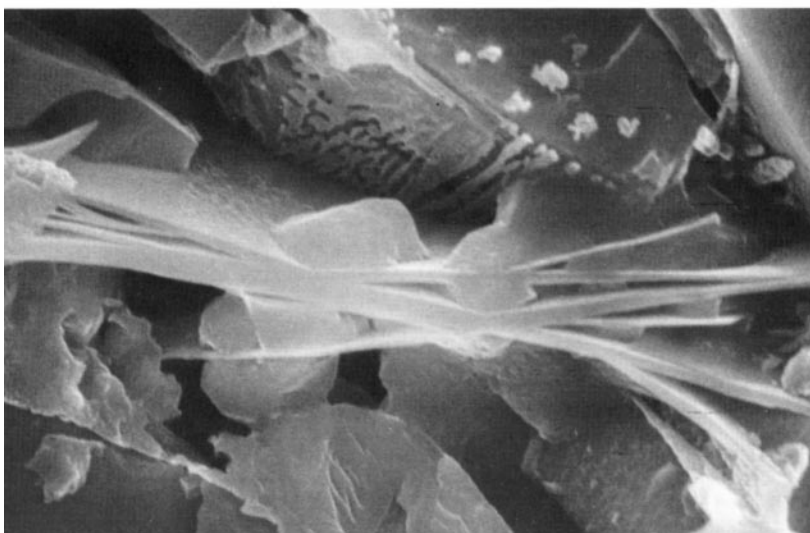
Photograph 9-17 Polished section of clinker, showing effects of 10-sec etch from water applied to Microcloth™, reveals aluminate (highly irregular forms) and ferrite (smooth surface) in sulfate-resistant cement clinker. Scratches on alite crystals. Moderately high maximum temperature, moderately slow heating rate, quickly cooled, 37 MPa. Coal-fired, wet-process kiln, 1300 tons/day. (S#A6741)

SEM
Field dimensions = 30 μm x 46 μm



Photograph 9-18 Alkali aluminate crystals in nital-etched clinker. (S#A3458)

SEM
Broken surface
Field dimensions = 18 μm x 28 μm

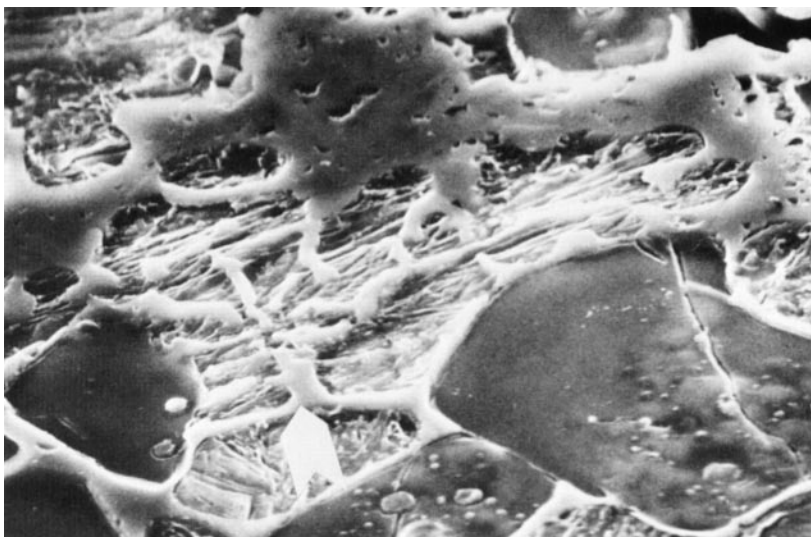


SCANNING ELECTRON MICROSCOPY (SEM) (CONTINUED)

Photograph 9-19 Polished section of clinker with a nital etch (20 seconds) showing a periclase skeleton (arrow) within belite. (S#A6742)

SEM

Field dimensions = 46 μm x 70 μm

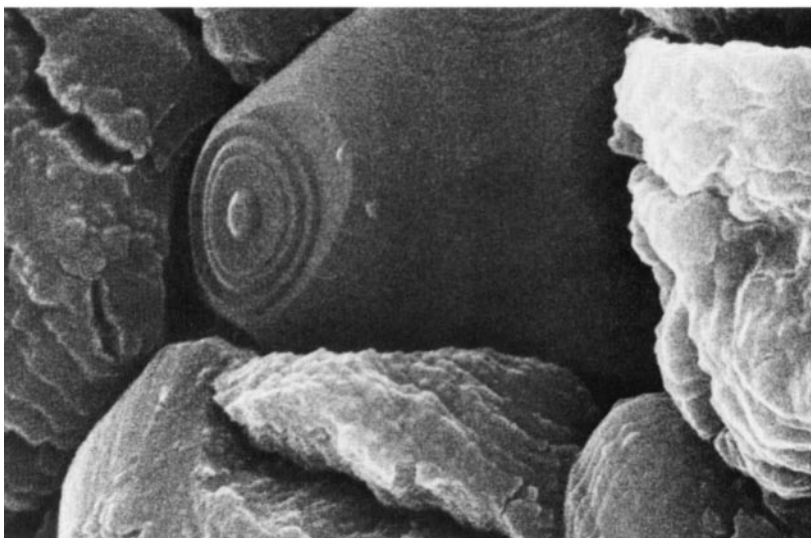


Photograph 9-20 Periclase crystal amidst calcium hydroxide, left and right, the latter resulting from free-lime hydration (air-slaking). (S#A6743)

SEM

Broken clinker surface

Field dimensions = 9 μm x 14 μm

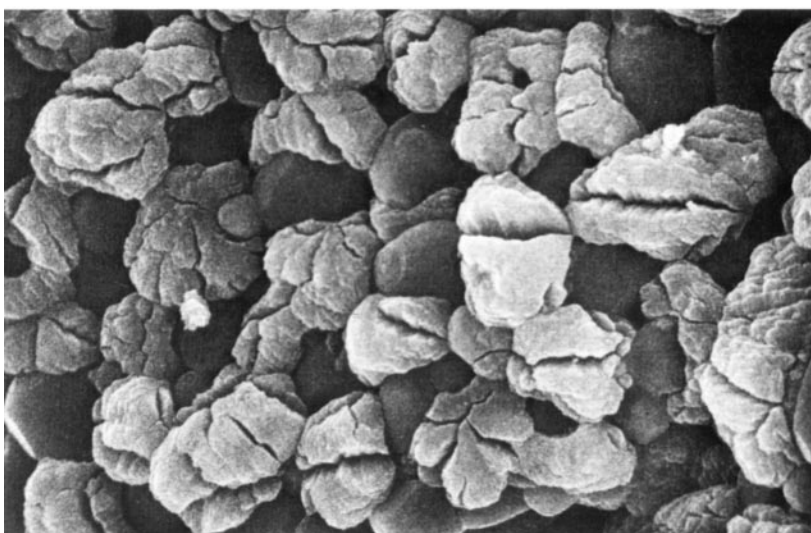


Photograph 9-21
Cauliflowerlike calcium hydroxide crystals (presumably epepizite), from hydration of free lime (air slaking), and round, gray periclase crystals in a nest, suggesting coarse dolomite in the feed. (S#A6744)

SEM

Broken clinker surface

Field dimensions = 46 μm x 70 μm



SCANNING ELECTRON MICROSCOPY (SEM) (CONTINUED)

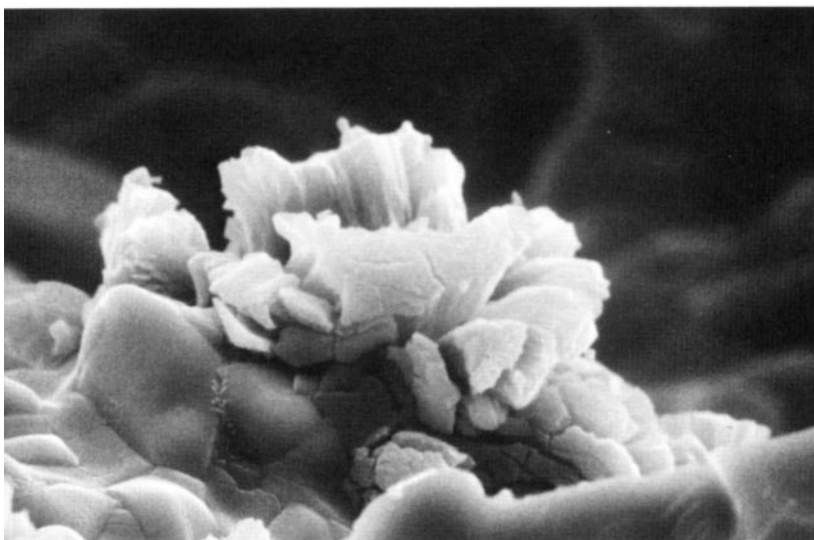
Photograph 9-22 Calcium hydroxide crystals (presumably epepizite) growing on free-lime substrate in clinker. Portlandite crystals in upper center. (S#A6745)

SEM
Broken surface
Field dimensions = 46 μm x 70 μm



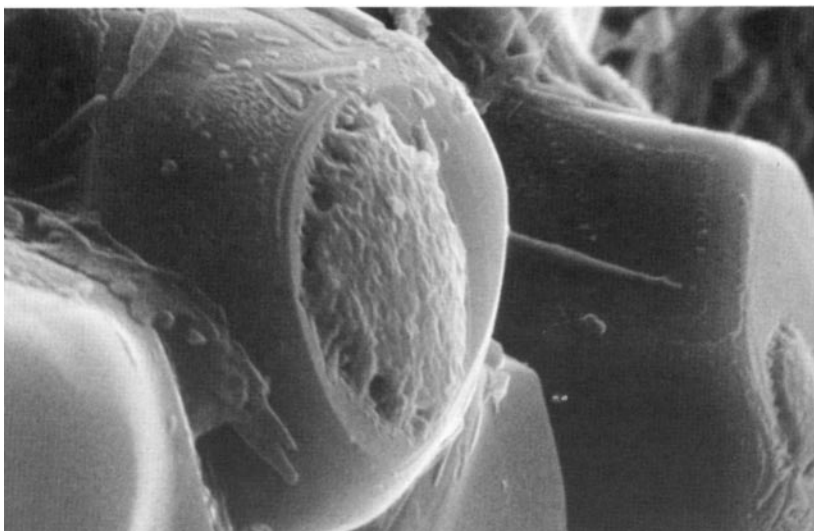
Photograph 9-23 Calcium hydroxide crystals (presumably epepizite) derived from free lime in clinker. Indicative of air slaking. (S#A6746)

SEM
Broken clinker surface
Field dimensions = 46 μm x 70 μm



Photograph 9-24 Round patches of alkali sulfate on alite crystals. (S#A6747)

SEM
Broken clinker surface
Field dimensions = 18 μm x 28 μm

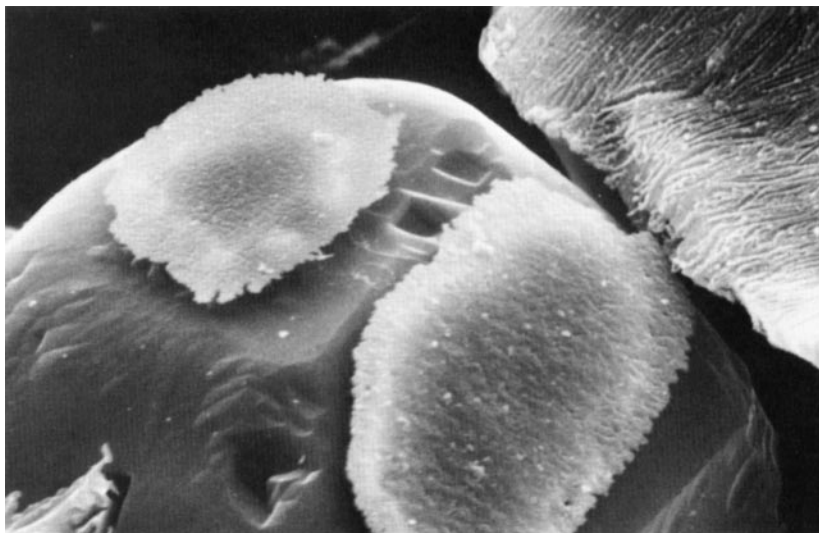


SCANNING ELECTRON MICROSCOPY (SEM) (CONTINUED)

Photograph 9-25 Alite crystal with attached alkali sulfates. Lamellar structure in belite revealed in upper right corner. 30-min maleic acid etch on crushed, sieved clinker. (S#A6748)

SEM

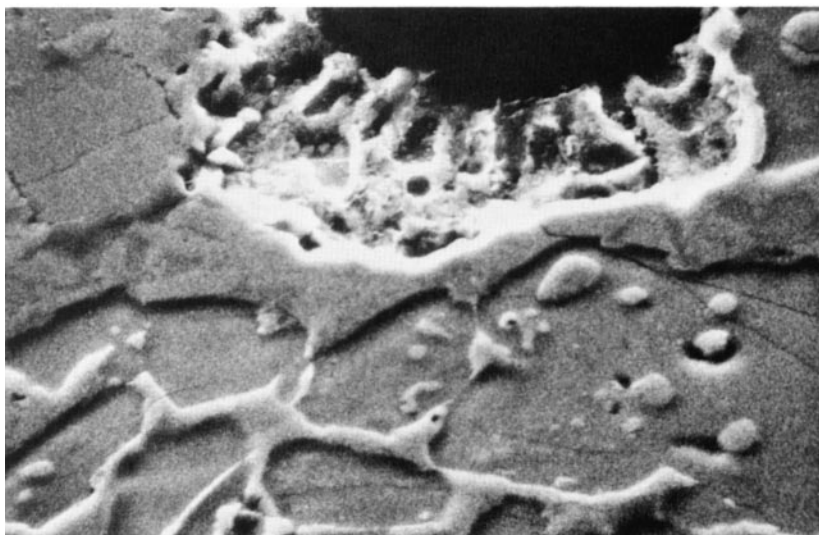
Field dimensions = 30 μm x 46 μm



Photograph 9-26 Alkali-sulfate deposit on void wall in nital-etched clinker polished section. EDXA data (expressed in approximate percentages) on bright ridges: S = 36.0%, K = 38.5, Ca = 25.4, Fe = 0.1; dark pits between ridges: S = 37.8, K = 46.1, Ca = 14.9, Fe = 0.4. (S#A6749)

SEM

Field dimensions = 18 μm x 28 μm



CHAPTER 10

Microscopical Examination of Portland Cement Raw Materials

This chapter is about petrography and petrographic methods as applied to an elementary examination of raw materials, and its purpose is to describe how one performs the examination. A brief review of recent literature given below clearly illustrates the value of petrography to cement raw material investigations, much like it is in ceramic science. The writer strongly believes that routine proficiency in cement quality control with microscopy *begins in the quarry* and continues through the final product, the cement, and even the concrete.

The intricate chemical and physical processes that take place in the burning of portland cement raw feed are much too complicated to be dealt with here. But, as an introduction to these subjects, a brief survey of selected recent literature and a presentation of elementary steps in raw feed examination are offered. This is not to imply that all needed information has been published, for much systematic research remains to be done. Our understanding of clinkering, however, demands an appreciation of exactly what it is that we are burning.

SELECTED LITERATURE REVIEW

The following summary of selected papers represents material published, for the most part, in the last 10 to 20 years. Emphasis is given to studies that suggest correlations of feed and clinker characteristics with kiln conditions, such as rate of heating, time at maximum temperature, maximum temperature, rate of cooling, and burnability. It is virtually impossible to present a clear-cut separation of these subjects in this book, thus one might find discussions of similar topics in several previous chapters. In other words, not all of the information on quartz in relation to belite nests and feed fineness, for example, is gathered in this chapter, and so on. Some of the salient observations and interpretations recorded in the recent literature, relating the

mineralogy and texture of feed and clinker, are listed in the lengthy table making up most of Chapter 7, Microscopical Interpretation of Clinkers.

Akatsu and Hanada (1963) investigated the burnability of "clays" containing various measured percentages of silt- and sand-sized metamorphic and sedimentary rock fragments, feldspar, volcanic rock fragments, ordinary quartz, and chert in 66 samples. Burnability was shown to increase with increasing percentages of metamorphic and sedimentary rock fragments, all polycrystalline rock types.

Miller (1976), building on the work of Akatsu and Ikeda (1971) and those mentioned above, emphasized raw feed homogeneity and uniformity, and listed silica particles in order of decreasing burnability: fine quartz (<44 μm), chert (most burnable), silica gel, vein quartz, and quartzite. Coarse quartz (88 to 149 μm) was said to be less burnable than quartzite. The importance of keeping the siliceous raw feed, particularly the quartz, particle size below approximately 45 μm was shown, decreasing the energy requirement to reduce the level of free lime in clinker. Free lime decreased rapidly as the temperature increased, especially with fine-grained feed.

With the use of Ono's Method and microscopy of raw feed, clinker, cement, gypsum, and kiln dust, coupled with laboratory burns and sieve analysis of the raw feed, Vanisko (1978) demonstrated the deleterious effect of belite nests in development of mortar strength. He showed that coarse quartz was correlated with numerous large belite nests and, when the raw sand was separately and more finely ground, mortar strengths jumped to 41 MPa.

By reducing the coarse fractions of the feed, thereby decreasing the coarse siliceous particle percentages, and adjusting the raw mix chemistry (addition of slag, among other changes) so as to lower the silica modulus, Legate (1987) demonstrated a major improvement

in clinker quality, producing relatively uniform silicate crystal development and distributions, improving strength at less cement fineness.

Pennell (1986) provided an insight to the vastly different microstructures of clinker size fractions produced in a long wet, coal-fired kiln with a very coarse, hard-burning feed containing coral, basalt dust, and silica sand. Pennell pointed out that, because of the grindability of the calcareous materials, the fine fraction of the feed is vastly overlimed, the coarse fraction underlimed. Consequently, a higher residence time or higher temperature, or both, are required to complete combination of the coarser fractions, resulting in densification of the nodule core with attendant close packing and cannibalism of the alite. Alite crystals in the outer porous shell of the clinker are generally larger, and C_3A is larger in the cores.

Illustrating some of the effects of fine-grained raw feeds, mortar strengths of 44.8 MPa with a cement at approximately 400 m²/kg were attained when 8.15% lime kiln dust was added to the raw feed, the burning process in the plant monitored closely with the microscope (Jany, 1986).

Hargave, Venkateswaran, and Chatterjee (1987) stated that whenever the alpha quartz (>45 μ m) exceeds 30% of the insoluble residue on the No. 350 screen, free lime increases. Additional grinding without effectively reducing the oversize quartz did not significantly help in reducing the free lime, the test for which was "White's Test." An equation for predicting the 28-day mortar strength from clinker microscopy data was given, having a correlation coefficient of 0.84 with laboratory-ground cements. Practical means for evaluating the glass content of air-cooled blast furnace slags, a lime source in some raw feeds, were also described by these authors.

Fortune, Johansen, and Fundal (1987) microscopically evaluated the effect of changing the kiln feed fineness from a normal value of 12% retained on the 90- μ m sieve to 5-6%, with reduction in the silica modulus (MS) from 3.0 to 2.4. The results were an improvement in kiln fuel consumption, a much better clinker granulometry, smaller alite, and fewer belite nests.

Burki and Braun (1988) asserted that the clinker structure from laboratory tests is principally determined by raw meal properties and to a lesser extent by the heating rate. Rapid heating was said to increase the alite formation rate, accelerated with a homogeneous raw meal made of a chalky, clayey limestone (cement rock). A coarse microstructure (large voids and large crystals) was produced from coarse meal made largely of monomineralic particles. No influence of the final size of the alite and belite was observed after variations in heating rates.

Alite crystals with a multitude of small belite "spots" were described by du Toit (1988) in a clinker made with "phosphogypsum" as the lime source. The setting time of the relatively finely ground cement made with this clinker was almost twice as long as that made from limestone.

Rao (1988) related the microscopy of three different limestones (all calcium sources for cement clinker) to the microstructure of the corresponding clinkers. The use of limestones with relatively high proportions of coarsely crystalline calcite and quartz was discontinued and a better quality clinker resulted, due largely to feed particle size and compositional improvement.

Norris (1988), illustrating the importance of feed homogeneity, showed that belite nest frequency was reduced 50% when the feed silo was changed to a blending silo, thereby providing a relative improvement in the distribution of silica in the feed.

McKenzie (1989) studied the relationships between feed particle size distributions and the clinker microscopy, showing that coarsely crystalline clinkers generally result from coarse inhomogeneous feeds.

Clinker microstructure as a result of raw feed coarseness was also outlined by Harrison (1989), beginning with an ideal model in which all of the feed particles are on the same scale as the sizes of the crystals produced, a liquid of mixed composition is absorbed into the lime crystals, or, if the lime and silica grains are not in contact, ion transport occurs through the liquid, forming belite and, eventually, alite. Extension of this model to feeds containing coarse silica (flint) and limestone grains results in dense, pore-centered, belite nests from silica grains; from coarse limestone particles either dense belite or lime clusters are derived. Dense belite clusters are formed by inward migration of a lime-silica melt into already lime-rich grains. Dense lime clusters were said to form by inward "collapse" of the lime-rich grain in silica- or melt-deficient areas. With coarse particles of feed, the clinker structure is initially in the form of "micronodules" composed of small crystals of belite, the micronodules linked by narrow bridges of other clinker phases.

Scheubel (1989) characterized the sintering processes of two raw materials, one with silica distributed as clay minerals and the other with coarse quartz. With the former material, the reaction that forms the silicates in the short sintering zone with a steep temperature profile was said to be dependent primarily on the physical parameters of the melt (diffusion constant) and the mean path length for elemental migration. With the raw material containing coarse quartz and burned with a shallow temperature profile, coarsely crystalline belite which had formed

around coarse quartz obstructed further uptake of lime (a conclusion also reached by Chromy [1976]) and inhibited alite crystallization. Therefore, additional sintering time and higher temperatures were required for combination. In the latter case, the result was large alite, belite nests, and free lime. Grindability was promoted by finely crystalline clinkers because of the numerous boundary surfaces (zones of potential weakness). Cements made from finely crystalline clinkers were generally easier to grind and produced higher strengths, particularly evident at 90 days (correlation coefficient of 0.93).

In 1990, Wolter discussed the effects of burning various raw meals in a short kiln (50 meters), stating, "The following parameters can be used for intervening in the system and controlling the processes inside the kiln:

- the kiln speed to control the residence time within the sintering zone,
- the proportion of fuel to be burned in the rotary kiln to suit the degree of precalcining,
- the flame shape and length to control the temperature profile within the sintering zone,
- the amount of excess air, which is also important for flame configuration and heat transfer as well as for the recirculating sulphur systems, although it hardly has any influence on the heat consumption of a precalciner kiln."

In support of these parameters, two quite different raw meals were characterized and compared: (A) homogeneous, readily sintered meal consisting of calcareous marl, high-grade limestone, and iron ore, coarsely ground (18 to 20% retained on the 90-micron sieve) and (B) difficult-to-sinter meal composed of shell sand, clay, pure limestone, iron ore, and bauxite, finely ground (10% retained on the 90-micron screen). Raw Meal A, rapidly heated (short sintering time), produced smaller alite crystals at a moderate sintering temperature. Raw Meal B required a long residence time due to chemical-mineralogical variations and resulting differences in component grindability, primarily in the coarse fraction (the meal said to be finely ground). Wolter stated that these "heterogeneous coarse fractions of the raw meal result in long reaction paths which have to be overcome by diffusion during the sintering reaction . . . a long residence time within the sintering zone is therefore beneficial." Lowering the kiln speed and increasing the sintering temperature were required for adequate combination of ingredients.

Replacement of the silica source with sandstone in a raw feed resulted in a general coarsening of the alite, fusion of alite (cannibalism), development of high peripheral porosity in nodules, increase in alkali

sulfates, and a decrease in mortar strength (Sarkar and Tagnit-Hamou (1991).

Johansen and Kouznetsova (1992) summarized much of the recent thought on many of the relationships between raw feed and kiln reactions, and stated that an inhomogeneous raw feed distribution cannot be burned away. Burning temperature was decreased by 50°C with finely ground raw mixes. These authors also state that the recent contributions in cement production have been innovations in grinding of raw feed, leading to finer-grained, more homogeneous raw meals.

Total replacement of the raw feed silica with rice husk ash (Ghosh, Mohan, and Gandhi, 1992) resulted in more uniformity in the clinker silicate distribution, larger alite and smaller belite crystal sizes, and an approximately 11% higher 28-day strength (41.2 MPa), compared to a standard mix with 7% sand as the silica source.

Shirasaka and others (1993) conducted a laboratory study in which heating rates varied as did the raw feed percentage retained on the 88- μ m sieve with reagent chemicals and three plant feeds. Plant feeds slowly heated at 10°/min from 900° to 1250°C and then 20°/min above 1250°C produced 16% to 24% belite nests when the coarse feed percentage was 15% to 17%. Rapid heating (100°/min to 1250°C and 20°/min above 1250°C) produced lower percentages of belite nests within two of the three plant feeds. Nests characterized by tightly packed crystals were most abundant in the reagent-grade feed with 0% feed particles >88 μ m at all heating rates and in one of the slowly heated plant feeds; the remaining trials produced nests with loosely packed crystals. The highest percentage of belite nests was produced under average heating rates (50°C/min below 1250°C and 20°C/min above 1250°C) with a finer plant feed (only 7.1% >88 μ m) and with reagent grade chemicals (0.0% >88 μ m). The amount of clustered belite was said to be influenced by the tumbling action in the rotary kiln and absent in the laboratory apparatus. Clustered belite in both laboratory and plant clinker decreased with increase in alite percentage.

Zivanovic (1995) presented a description of clinkers made with silica fume, instead of quartz sand, as the primary silica component in the raw feed. The silica fume made up approximately 3.0 percent of the feed. Alite crystal size was reported to be from 50 to 200 μ m and belite grains were said to be rounded and between 50 and 60 μ m. No mention of belite nests was made. The cements made with silica fume or tuff and a particular marl, compared to other cements not made with these materials, did not require as much grinding and produced higher 28-day mortar strengths.

A microcrystalline limestone, as opposed to a limestone made of coarse fossil shells and other calcite particles, was shown to grind differently, producing a raw meal with a relatively uniform and finer particle size distribution, leading to an improved burnability (Sas, 1997).

Dreizler and Schafer (1990) also stated that the concentration of less active quartz in the coarse fraction of the raw material decreases sinterability, increases energy requirements or free lime, and increases development of belite nests. A chemical method of evaluating the burnability of various particle-size fractions of the feed, involving the calculation of the “weighted mean of the lime saturation standard,” along with microscopy of the feeds, was said to be a very cost-effective tool in control of energy consumption and cement quality. For this study, six raw feed size fractions, from <32 to $>200\text{ }\mu\text{m}$, were investigated.

In the present writer’s opinion, this summary of selected papers indicates that a detailed understanding of the raw feed mineralogy-particle size relationship and the effects of the temperature profile in a kiln is absolutely mandatory for continued quality control. These papers, and many others of similar subject matter, demonstrate the practicality of cement plant microscopy. The microscope, perhaps better than any other instrument of analysis, and certainly as a corroborative tool, provides the means for visual appreciation of the cement-making process. But what kind of training is necessary? What are the essential microscopical observations and the “standard” microscopical procedures that one can use to help ensure a quality product? Knowing the microscopical nature of the raw materials is the first step.

RAW MATERIAL EXAMINATION

A chemical analysis alone cannot describe the form, particle size, or mineralogy of the feed. SiO_2 from a chemical analysis does not necessarily mean quartz, nor does Fe_2O_3 necessarily imply hematite. Analysis by X-ray diffraction (XRD) quite accurately records most of the detectable mineralogical varieties and with calibrated standards allows an estimation of abundance. But XRD cannot elucidate the particle form or size, and virtually misses the occurrence of amorphous materials such as glass or poorly crystalline materials such as limonite, $\text{FeO}(\text{OH})$, a major constituent in many iron sources for portland cement. Phases below the detection limit by XRD can easily be seen in the microscope. However, chemical and XRD analyses of each of the raw materials individually, in sieved fractions, and in their blended combination in the feed, are immensely helpful, indeed strongly recommended, for routine

quality control, but are far less applicable to clinker production without microscopy. Microscopy gives visual form to the data from other methods of analysis.

A working knowledge of some of the principles of elementary optical mineralogy is obviously necessary. One should be conversant with the concepts of polarized light transmission through isotropic and anisotropic crystalline solids, birefringence, interference colors, index of refraction, cleavage, fracture, and so on—in short, the appearance of rocks and minerals under the stereomicroscope and the polarized-light microscope. The use of reflected light, as in metallography, is also necessary for the opaque materials. Those trained in geology, ceramics, and material science are normally familiar with these subjects.

Consequently, the purposes of microscopical examination of raw materials are to describe the mineralogy, and to estimate the mineral abundances and particle size variations, all of which bears directly on the ease with which the material combines in the kiln. The importance of microscopy can hardly be overstated.

Petrographic Identification of Raw Feed Constituents

Microscopical examination should start *in the quarry* where samples of each of the varieties of limestone, sandstone, shale, etc., are collected, layer by layer, by a geologist or someone with an adequate knowledge of the quarry. An assumption of the mineralogy of most quarried materials, as well as many of the industrial byproducts, is commonly questionable. Representative portions of each rock variety are sent off, if necessary, for thin sectioning (see partial list of professional companies in Table 11-3). Some of these companies will also stain the thin sections as directed. Another portion of the rock is crushed in the plant laboratory with a mortar and pestle or other suitable crushing device, and sieved to produce a 45- to 75- μm fraction for examination in a powder mount, using, at first, a liquid with a refractive index of approximately 1.542. Samples of nondeposit materials, such as slag, fly ash, bottom ash, rice husk ash, clay catalyst, etc., are examined similarly.

Insoluble residues from a portion of this sieve fraction can be prepared with 20% acetic acid and 20% HCl; the residue is then sieved to retain the $>45\text{-}\mu\text{m}$ material which can then be studied in powder mount, thin section, or both. The difference in the two residues is related to dolomite percentage.

Commercially prepared thin sections (Table 11-3) are studied along with the powder mounts in order to see which features of the “whole rock” can be observed in the powder particles, thus facilitating their

identification in the raw feed. Consequently, for optimum benefit of microscopical examination of portland cement raw materials, each component should be studied separately, followed by examination of the feed, each serving as a "petrographic standard."

Petrographic identification of particles may not be as easy as it might appear and numerous geologic textbooks exist on this subject, most having detailed descriptions of geologic and mineralogic relationships stated in a language neither immediately understood by, nor relevant to, cement laboratory personnel who mainly need to know the microscopical characteristics and the chemical compositions of the materials. To make the problem of identification more difficult, the feed particles represent only a small fraction of the original rock which, on a larger scale, displays geologic features that clearly allow its precise classification in standard petrographic terms. Nevertheless, by far the best geologic reference book on the microscopy of limestone and carbonate sediments is that by Scholle (1978), and for sandstones and shales, Scholle (1979). Color photomicrographs of most of the major rock types are presented in an excellent, highly recommended book by MacKenzie and Adams (1994).

Certain minerals in cement raw materials examined in thin sections or sieved powders can be selectively stained with a wide variety of liquids (Carver, 1971; Hutchison, 1974) and studied with a stereomicroscope and a petrographic microscope. The stains are normally used to augment data from ordinary optical microscopy.

Mineral characteristics in transmitted and reflected light are clearly described in standard optical mineralogy texts (Heinrich, 1965; Kerr, 1977). The optical properties of almost all known minerals, with a concise description of optical theory and technique, are given by Fleischer, Wilcox, and Matzko (1984) who emphasize particle-mount analysis.

However, not all the components of portland cement raw materials are geologic, and descriptions of materials such as ceramic waste, polishing sludge, slag, fly ash, bottom ash, etc., are found sparingly in the industrial literature. A highly valued source of microscopical data on man-made, inorganic crystalline solids is found in the work of Winchell and Winchell (1964), republished by the McCrone Research Institute, Chicago, Illinois.

Published references cannot substitute for personal examination of the raw materials and all raw feed components are subjects for microscopical analysis. For our purposes, the important data in raw materials analysis are mineralogy, microstructure, and chemistry.

Thus to help one identify many of the common raw-feed constituents, a collection of photomicrographs is offered in this chapter. Be aware that geologic varia-

tions are to be expected. Even for petrographers with experience, rapid sight identification of some rocks and minerals is sometimes weak, forcing one to utilize various organic stains, refractive index liquids, and thin sections to define the mineralogy and correctly classify the grain. X-ray diffraction, allowing the precise identification of the mineralogy, is of tremendous value at this stage of an investigation and one should not neglect this exquisite tool.

A pig's eyelash mounted on the end of a wooden shaft is quite useful in manipulating particles under the stereomicroscope. The lash retains its stiffness and very sharp point, facilitating the teasing out of certain particles of raw feed (or clinker) for mounting on microscope slides for further examination, X-ray diffraction, FTIR analysis, light microscopy, or study with the SEM and EDXA. With the tip of the lash, particles in a dry mount can be transferred to a vaseline-coated quartz plate (cut in a specific crystallographic manner to eliminate the effects of glass) for X-ray diffraction or to a fresh epoxy-coated slide for permanent total or partial immersion for determination of refractive index. Crystals with prominent cleavages or faces can be oriented crystallographically with the eyelash and placed on an epoxy substrate, thus facilitating determination of certain refractive indices, enabling phase identification. Particles of 100 to 200 mesh are optimum size for these techniques.

Feed Particle Classification

To circumvent the complex task of deciphering the correct and up-to-date geologic name for a rock, one can usually classify typical raw feed particles microscopically on the basis of internal microstructure as either *monocrystalline*, *polycrystalline*, or *glassy*, identified largely by characteristics visible in transmitted light with a powder mount or thin section. Particles that do not transmit light on the microscope stage are termed "opaque" and for them a polished section and reflected light are required; these particles, likewise, may be either monocrystalline, polycrystalline, or amorphous. Some particles have combinations of two or three types of microstructure and would be classified on the basis of the dominant type volumetrically, their verbal or photographic description bringing out the fact of their complexity.

Nonopaque materials, those that allow the transmission of light, can be optically classified as "isotropic" or "anisotropic." Isotropic materials (e.g., oil, water, epoxy, crystals in the isometric system) transmit light in all directions at the same velocity. Anisotropic materials (e.g., alite, calcite, quartz, all crystals in systems other than the isometric) divide the light into

two waves vibrating in mutually perpendicular planes at different velocities and directions.

Limestone, like sandstone, is a polycrystalline rock comprised of various crystalline phases (mostly calcite). Microcrystalline limestone is composed of tiny interlocking calcite crystals; the rock is also called micrite (pronounced "mick-rite") and, by definition (Folk, 1974), has average calcite crystal size of 1.0 to 5.0 μm . "Microsparite" is a recrystallized limestone with average calcite crystal sizes of 5.0 to 15 μm ; the rock can also be classified as "very finely crystalline" according to an arbitrary scale of crystal size definitions. Limestones normally have various amounts of fossils (fragmented or otherwise), oolites, pieces of previously formed limestone or lime mud, and siliceous "impurities" such as terrigenous sand, silt, and clay, and other constituents. These impurities in some carbonate rocks facilitate their use in the cement industry, particularly marl which, by definition, has 35 to 65% clay, the remainder being mainly calcite (Pettijohn, 1975). Clay minerals within and between calcite crystals in raw feed limestone particles are well-known aids in calcination and sintering of "cement rock" and "lime rock." High porosity and "micropermeability" would also, presumably, promote chemical combination in the kiln.

Sand and sandstone are assemblages of quartz, chert, feldspar, mica, fragments of feldspar-rich igneous, sedimentary, and metamorphic rocks, fossils, clay, and other constituents in various percentages. Sandstones contain cements, normally calcite or quartz, or a clay matrix, that bind the grains together. These rocks, therefore, typically contain a mixture of monocrystalline and polycrystalline particles.

The insoluble residue concentrates the siliceous particles, greatly facilitating their observation. *Monocrystalline* particles are ordinary quartz, feldspar, mica, ferromagnesian minerals, etc.; *polycrystalline* particles are mainly rock fragments, including shale, chert (flint), metaquartzite, siltstone, basalt, and many others. Shale particles typically contain an abundance of clay, fine-grained mica, and tiny grains of quartz and feldspar, calcite, dolomite, mica, and other minerals. Volcanic rock fragments or other fine-grained siliceous igneous and metamorphic rocks, all polycrystalline, commonly contain small crystals of feldspar, magnetite, and ferromagnesian minerals, and are especially abundant in some raw materials taken from streams draining partially igneous mountainous areas. Slag glass, common in the more industrialized areas, is amorphous (not crystalline) for the most part, and is used as an alumina and iron source in some feeds. Amorphous silica is also found in certain opaline-shelled fossils and rice husk ash. Opaque minerals in cement raw materials include

pyrite, magnetite, hematite, and other iron-rich minerals. Magnetic opaque particles can be concentrated with a simple laboratory magnet. Then the particles are placed in epoxy and polished for examination in reflected light. The classification of particles into polycrystalline, monocrystalline, and glassy categories is probably far too broad for normal geologic use but may have a place in cement raw feed investigations.

Because polycrystalline particles are comprised of numerous small crystals within the particle, ready-made weaknesses occur along the crystal boundaries. During sintering, these weaknesses likely promote particle reaction in the kiln and, to some extent, disintegration, thereby opening the microstructure for liquid invasion and chemical combination. Polycrystalline particles composed of small crystals of several minerals, such as a fine-grained schist and argillite, are believed to be more reactive during sintering than quartzite. Many of the naturally occurring alumina and silica sources in feeds are called "clay," but they are often more than that. These polycrystalline rocks are actually siltstones, argillites, and even fine-grained schists; some contain clay and fine-grained mica (extremely finely microcrystalline hydrous aluminosilicates). Belite nests produced from these types of particles tend to have loosely packed crystals. Specific examples of raw feeds and their burning characteristics are discussed below.

After one becomes familiar with the microscopical aspects of the quarry rocks and the raw feed, evaluation of the feed with the use of burnability equations or other routine microscopical procedures can be initiated. Burnability equations help us to organize our thought about the suitability of various raw materials — that is, how easily they combine in the kiln — and can provide a basis for feed comparison and improvement, even though the equations are not used to determine free lime produced in a laboratory test.

Application of F. L. Smidth's Burnability Equations

Fundal (1979) showed that one could consider belite clusters larger than approximately 63 μm or free lime clusters larger than 100 μm as essentially uncombined, if maintained for 30 minutes at 1400°C. Therefore, after determining the *critical mineral-particle sizes* required for combination of various raw mix constituents, Fundal presented a series of burnability equations to predict free lime in laboratory tests (not plant clinker). Research results illustrating the use of these equations have been published by Johansen (1978), Christensen (1979), Miller (1980), and Theisen (1992), the latter providing the following equation:

$$\% \text{Free Lime (1400}^\circ\text{C)} = 0.343(\text{LSF}-93) + 2.74(\text{MS}-2.3) + 0.10C_{125} + 0.83Q_{45} + 0.39A_K \quad (\text{Eq. 13})$$

where

LSF, the lime saturation factor, in percent = $\text{CaO} / (2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3)$

MS, the silica ratio = $\text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$

Q_{45} = percent quartz or flint larger than 45 μm determined in the insoluble residue

C_{125} = percent limestone grains larger than 125 μm

A_K = percent acid insoluble residue larger than 45 μm , other than quartz or flint. If a 20% acetic acid is used, dolomite also remains in the residue and thus can be examined.

To use the F. L. Smidth burnability equation, a lime saturation factor (LSF) of not greater than 100% or less than 88% is stipulated. If the LSF is greater than 100%, the free lime calculated by the Bogue equation must be added, and calculated as follows:

$$\% \text{CaO} = [\text{CaO} (\text{LSF} - 100) / (100 - \text{LOI})] \times 100,$$

where CaO and LOI are determined in percent of the raw meal.

Rock and mineral percentages determined microscopically are expressed as weight percent of whole sample.

To determine C_{125} , assuming a >125- μm sieve fraction of 11%, microscopically count and identify at least 200 particles at approximately 100X magnification in a powder mount made by immersing particles in a refractive index liquid of roughly 1.545. Calculate the percentage of >125 limestone grains. For example, assume 170 grains of 200 are limestone, then $(170/200)(100) = 85\%$. Then $C_{125} = (11)(.85) = 9.35\%$.

To determine Q_{45} , let us assume an acetic-acid insoluble residue >45 μm of 8.3%, and 133 microscopically counted grains out of 200 are quartz (including chert). Therefore, $(130/200)(100) = 65\%$, and 65% of 8.3% = 5.395% = Q_{45} .

A_K , the percentage of insoluble particles other than quartz or flint, is calculated by subtraction: 8.3% - 5.395% = 2.9%.

A_K , the determination of which is necessary in only a few mixes, is said to be largely comprised of feldspar, coarse clay or shale particles, dolomite, iron-rich materials, and slag of calcium aluminosilicate composition, each of which, according to Theisen (letter, 1996), has somewhat different effects on the

burnability. Percentages of these constituents are extremely important in many plants, in the writer's opinion, and should be determined in many detailed burnability or raw feed studies.

Fundal (1996), refining his previously published calculations and summarizing the variable effects of each of the common moduli, presented an updated equation to calculate the free lime (ΔFC) from laboratory testing of the raw feed at 1400°, 1450°, and 1500°C, taking into account some of the variables making up A_K , namely, the percentages of dolomite and flux minerals >45 μm , such as iron oxides, mica, and $\text{Al}(\text{OH})_3$. Fundal's new equation for a 1400°C free lime calculation is:

$$\Delta\text{FC}^{1400} = [112 / (\text{MS} + 0.53)^2] 0.33\Delta\text{MS} + 0.33\Delta\text{LSF} + 0.67\Delta Q_{45} + 0.36\Delta A_K + (k) 0.15\Delta K_{125}$$

where $A_K = A - (Q_{45} + F + D)$, and A is the total insoluble residue from 30% acetic acid, F includes iron oxides, mica, and $\text{Al}(\text{OH})_3$, and D is percent dolomite >45 μm . The interested reader is urged to examine Fundal's calculations and equations for additional details.

Centurione and Kihara (1994) tested the application of F.L. Smidth's burnability equations and methods, including those of Fundal (1979), Theisen (1992), and Miller (1980), in an analysis of 12 samples of raw feed and corresponding clinkers. Centurione and Kihara used an hydrochloric acid digestion method to calculate C_{125} and concluded that coarse quartz (>45 μm) and limestone (>125 μm) should not exceed 2% and 6%, respectively, by weight of sample.

Theisen (1996, letter) stated that although F.L. Smidth has no guidelines for these factors, the files indicated that " Q_{45} is normally <5.0%, C_{125} is <9.0%, and the acid-insoluble residue (>45 μm) is <8.0%." Theisen states further that if the LSF and MS are low, a wide range of coarse grains is acceptable; if both the Q_{45} and C_{125} are high, burnability is generally unsatisfactory. Theisen (1992) characterized a coarse feed as having approximately 14.8% >90 μm and 10.3% >125 μm .

Burnability equations could be modified, perhaps, to include microscopically determined percentages of dolomite >125 μm (termed D_{125}). Thus, C_{125} could be corrected for the coarse dolomite content. Other sieve intervals can, of course, be selected. Percentages of coarse siliceous rock fragments (other than quartzite) larger than 125 microns are also relevant to burnability.

For details concerning the basis of these and other equations, and discussions of specific plant problems, the reader is referred to Fundal (1979), Miller (1980), and Puertas and others (1988), and more recently, du Toit (1996a and 1996b), the latter also using an hydrochloric acid dissolution method to determine C_{125} . Dorn

(1985) provided a simple HCl-based technique for determination of Q_{45} with only 5 grams of raw mix. Some examples of use of these kinds of data follow.

From the southeastern United States, clinker is produced from a raw feed containing microcrystalline limestone, slag, spent petroleum catalyst, bauxite, staurolite, quartz, feldspar, mill scale, and other constituents. Forty five percent of the feed is $>45\text{ }\mu\text{m}$, with 15% $>125\text{ }\mu\text{m}$. $IR_{ACE} = 13.4\%$, $Q_{45} = 6.3\%$, " Q_{125} " = 2.6%, and $C_{125} = 11.0\%$. Surprisingly, a remarkably uniformly distributed, very coarsely crystalline assemblage of silicates with a finely microcrystalline matrix results. The abundant "fluxing" constituents clearly promote silica migration during hard burning.

A reportedly "easily burned" raw feed from the northeastern United States is seen in thin section to be a physical mixture of two kinds of rocks (a two-component feed)—clayey microcrystalline limestone and a fine-grained, calcitic, quartz-mica siltstone (and low-grade schist) containing various amounts of an iron-bearing mineral; ceramic waste, spent catalyst, and other constituents are added. The feed contains 16.5% retained on the 125- μm screen and the $>45\text{-}\mu\text{m}$ acetic-acid insoluble residue is approximately 8.9%; loosely packed belite nests are common (25% of the belite), 75% of the belite is solitary, and the clinker is coarsely crystalline.

Raw feed from the southwestern U.S., said to be unusually easy to burn, contains a clayey microcrystalline limestone and shale. The feed has only 3.2% retained on the 125- μm screen, with 15.2% $>45\text{ }\mu\text{m}$, and has $<1.0\%$ acetic-acid insoluble residue $>45\text{ }\mu\text{m}$, the latter composed of ordinary quartz with minor amounts of glauconite (a complex alkali-calcium-iron-magnesium aluminosilicate). Belite nests are scarce and relatively small; isolated belite is abundant. The clinker is finely crystalline, easily ground, and produces a high strength mortar (typically greater than 49 MPa).

A relatively "hard-to-burn" feed from the western U.S., with a very impure dolomitic limestone, has 6.7% $>125\text{ }\mu\text{m}$ and an acetic-acid insoluble residue of 9.5% $>45\text{ }\mu\text{m}$, the latter comprised of quartz, feldspar, medium to finely crystalline igneous and metamorphic rock fragments, and an abundance of ferro-magnesian minerals (mainly amphiboles and pyroxenes). $Q_{45} = 1.6\%$ and $D_{45} = 4.5\%$. Belite nests (many with tightly packed crystals), solitary belite, and periclase are abundant in this fine- to medium-crystalline clinker. Nevertheless, a high-compressive strength mortar (44.8 to 48.3 MPa) is made, mainly because of the small alite size and the well-scattered solitary belite.

From the southwestern part of Canada, a feed contains coarsely crystalline limestone (actually a marble) and an abundance of siliceous particles such as ordinary

quartz, slag, shale, metaquartzite, finely crystalline feldspathic igneous and metamorphic rocks, chert, metachert, siltstone, mica, plagioclase feldspar, and others; 18.4% of the feed is $>125\text{ }\mu\text{m}$, and the acetic-acid insoluble residue is 8.9% $>45\text{ }\mu\text{m}$. The coarsely crystalline clinker, surprisingly, shows a remarkably uniform distribution of belite and no nests. Mortar strength is high. Belite nests that might have been produced from the coarse silica and siliceous particles were possibly "burned out" by long time at high temperature, as the liquid invaded and facilitated combination.

To illustrate the effects of excessive coarse quartz and other coarse siliceous materials, an extremely nonuniform clinker was made from microcrystalline limestone, a sand containing fragments of quartz and feldspar-rich volcanic rocks, and other rocks and minerals. $IR_{ACE} = 7.6\%$, $Q_{45} = 2.1\%$, and " F_{45} " (feldspar grains) = 2.5%. Belite nests with amber and "muddy" belite are abundant. Predicted mortar strength at 28 days is less than 37.3 MPa. Inability to disperse the siliceous materials uniformly in the feed, the siliceous nature of the coarse fraction, and slow cooling were probably responsible for the low strength.

Variations in predicted 28-day mortar strength among cement producers led Moir (1997) to study the burnabilities of kiln feeds from 15 cement plants in the laboratory, using a horizontal programmable tube furnace. An equation to calculate the temperature required for 1% free lime was given as:

$$\begin{aligned} \text{Temp for 1\% Free Lime} &= 414 + 21(\text{acid insoluble 90-}\mu\text{m kiln feed residue}) \\ &\quad + 10(\text{clinker lime saturation factor}) \\ &\quad + 3(150\text{-}\mu\text{m kiln feed residue}) \\ &\quad + 32(\text{clinker alumina ratio}) \\ &\quad (\text{correlation coefficient} = 0.923) \end{aligned}$$

The single most significant parameter was said to be the percentage of acid insoluble residue, particularly the negative influence of a concentration of silica in the coarse fraction (90- μm acid insoluble residue). An increasing alumina ratio had a greater negative influence on combinability temperature than silica modulus. Among the less quantified variables for the prediction of mortar strength are belite nests and poor assimilation of high-ash coals, both of which generate clinker inhomogeneity, according to Moir, but can be observed microscopically.

These examples, and most of the published literature, suggest the potential hazards in making large-scale generalizations about raw feed burnability, presumably because of the combined effects of variable mineral- and particle-size distributions, the relative proportions of "fluxing" agents, and kiln conditions.

Nevertheless, microscopical analysis of the raw feed, on a *plant-by-plant* or *kiln-by-kiln* basis, helps us understand the combined effects of these variables. The feed can normally be improved, perhaps optimized, with these kinds of data.

Sample Preparation and Method of Counting

The present writer uses particle mounts and thin sections for determination of component percentages in raw feeds. Raw feed examination using powder mounts is described first, followed by analysis with thin sections.

Sample Preparation. Three separate 30-gram portions of the dry raw feed are weighed. While two of the three portions are being digested in 20% acetic acid and 20% hydrochloric acid, respectively, at room temperature, the remaining portion is wet sieved through the 125- μ m screen. The fraction retained on the sieve screen is weighed and the percentage of the original 30-gram portion is calculated.

A representative sample of the coarse wet-sieved fraction ($>125\ \mu\text{m}$) is mounted on a labeled, glass microscope slide with epoxy resin, having an index of refraction (n) of 1.55 to 1.56, or balsam fir resin ($n = 1.537$) as described below, and the limestone particles are counted microscopically to determine their percentage. Counting techniques are given additional discussion later in this chapter.

An epoxy-immersion mount is made by placing a random distribution of particles on the slide. A cover glass is placed over the particles, and, with a dropper or glass rod, a small amount of the resin is placed adjacent to the edge of the cover glass. Capillary forces slowly draw the resin under the cover glass. At this point the grains can be uniformly distributed and many of the bubbles expelled by gently moving the cover glass around with the eraser end of a pencil. The mount is then cured on the slide warmer until the resin hardens, usually approximately one hour at 40°C , depending on the type of epoxy. Prolonged heating or higher temperature causes severe strain birefringence in the epoxy.

The use of balsam fir resin requires heating a drop of resin on a glass slide placed on an electric hotplate at a temperature of approximately 125°C for about three minutes, or until a resin bead is hard and brittle (fracturing with a fingernail). Xylene, commonly used as a diluent, is driven off during the heating step. The particles are sprinkled onto the molten resin, distributed with a needle, and the cover glass is placed edge first in such a way as to avoid entrapment of bubbles. Excess resin can be expelled with the eraser end of a

pencil, and, after removal from the heat and hardening, cut off with a single-edge razor blade.

Insoluble Residues. The second and third 30-gram portions of the raw feed, mentioned above, are used to determine the weights of the $>45\ \mu\text{m}$ insoluble residues IR_{ACE} and IR_{HCl} , using a 20% solution of acetic acid and hydrochloric acid, respectively. Acetic acid is said by Fundal (1980) to concentrate the silicates, dolomite, and other insoluble phases. A digestion period of at least 5 hours for each of the two samples is recommended, but overnight is not unreasonable in the present writer's experience. The insoluble residues are sieved over a 45- μm mesh cloth to establish the $>45\text{-}\mu\text{m}$ IR percentages. Nylon-mesh sieve cloth (Gilson) is particularly helpful because it is not affected by the acids. The residues are then examined microscopically to determine Q_{45} , and, if desired, the dolomite fraction larger than $45\ \mu\text{m}$ (D_{45}). However, one should experiment with the double-acid technique to determine if the dilute HCl removes significant phases other than carbonates.

The dolomite content in these $>45\text{-}\mu\text{m}$ fractions might also be approximated chemically by calculating the percentage difference between the acetic-acid and hydrochloric-acid insoluble residues. Furthermore, one can treat the $>45\text{-}\mu\text{m}$ IR_{ACE} with 20% HCl, the weight loss approximating the $>45\text{-}\mu\text{m}$ dolomite, which can be calculated as a percentage of the original sample weight. Possibly these data, plus the percentage of ferro-magnesian silicates (FM_{45}), could then be used to evaluate the periclase potential.

To approximate chemically the D_{125} factor suggested above, treat two subsamples of the above-mentioned $>125\text{-}\mu\text{m}$ fraction with 20% solutions of acetic and hydrochloric acid, respectively, removing all carbonates in the latter. Consequently, the weight difference of the acid-treated $>125\text{-}\mu\text{m}$ fraction may approximate dolomite content in that size fraction.

One can mount some of the $>125\text{-}\mu\text{m}$ IR_{ACE} in balsam resin or epoxy (or make a thin section) and microscopically determine the D_{125} factor by counting, the result expressed as a percentage of original sample weight just like C_{125} . Dolomite will likely be the dominant (perhaps the only) carbonate mineral in the acetic acid residue. See the discussion below concerning use of Trypan Blue stain to identify dolomite microscopically.

Counting Method. Grain varieties and percentages are microscopically determined by identifying and counting particles in whole-grain mounts, thin sections, or half-sections, the latter two having the advantage of clarifying the mineralogy and microstructure of very finely microcrystalline particles, visible most easily in ultra-thin sections (approximately $15\ \mu\text{m}$ thick).

Determination of percentages commonly entails two steps: (1) identification of the particles with a polarizing-light microscope (the “petrographic” microscope), and (2) counting particle varieties, tallying no less than 200 particles per size fraction. This allows one to calculate the number percentages of quartz, feldspar, metaquartzite, calcite (limestone), dolomite, shale, siliceous polycrystalline rock fragments, opaque particles (mostly from the iron sources), ferromagnesian silicates (mostly amphiboles and pyroxenes), and so on, in the respective sieve fractions, thus leading to the C_{125} , Q_{45} , and A_K values in the F. L. Smidth equation given by Theisen (1992).

Counting is facilitated by manually moving the slide in only one direction with the mechanical X-Y stage, simultaneously identifying and recording *all* the particles that fall under the crosshairs of the eyepiece (or all the grains intersected by one of the eyepiece lines as the mount is moved in a direction perpendicular to the line); this is a very rapid method because it does not rely on a time-consuming, regularly spaced, point-count procedure. Electronic mechanical stages and tallying devices are available and strongly recommended.

Various techniques of making mineral counts and “modal” analysis of particle mounts, thin sections, and polished sections to determine the weight percentages of various phases are summarized in Campbell and Galehouse (1991). These authors discussed methods of quantitative determination of percentages of phases in the raw feed or in clinker, applying both transmitted light in the polarizing microscope and reflected light. For a particle mount, a restricted particle-size range would give reasonably accurate *number* percentages by counting *all* particles intersected along a line of traverse, or all particles within a specified band, or in successive fields of view. A powder mount having a wide range of particle sizes, using the aforementioned methods, cannot produce reliable area (volume) percentages simply because a large number of very small particles recorded normally does not amount to much volumetrically. *Therefore, the less the particle-size range, the more accurate the particle number-to-volume relationship, and, consequently, a better estimate of the weight percentage results.* Additional details of quantitative microscopy, using area counts, ribbon counts, and point counts are presented in some detail by Campbell and Galehouse (1991).

The procedure outlined by Fundal (1979) and Theisen (1992) involves number percentages of particles having a wide size range and without density correction. The number of particles of each rock or mineral type, a restricted size range, multiplied by their respective densities, and recalculating the accumulated weight total, permits precise determination of the *weight* percentages of each particle type which can then be

expressed as percentages of the original amount (weight) retained on the sieve. Fundal’s method, however, may be sufficiently accurate for use as relative comparisons.

Thin-Section and Half-Section Methods for Raw Feeds

Making and using thin sections have been described earlier in this book. Some additional comments, dealing specifically with raw feed thin sections, are made here.

Routine work in evaluating clinker and raw feed in the writer’s laboratory requires an easy, relatively fast method of making thin sections, facilitating the observation and identification of the raw feed particles (petrography and mineralogy). Thin sections or half-sections, especially at thicknesses of approximately 15 to 20 μm , are invaluable in *deciphering the microstructure and mineralogy of finely microcrystalline feed particles* such as shale, and certain other sedimentary, igneous, and metamorphic rock fragments, because the thickness of the section is such that individual crystals can be resolved without the confusing optical effects of crystal stacking. It is mainly for this reason that thin sections are preferred by the writer over powder mounts. If a thin section is not available, then focussing on the thin edges of the finely microcrystalline particles in a powder mount aids in their identification and will, to some extent, replace a thin section. Thin sections, therefore, are optional.

Because the particles of raw feed are small, several fractions of the feed can be separately contained in the same thin section, thereby saving much time and money. The making of thin sections, therefore, begins with a plastic embedding mold or other suitable container divided into two chambers with a properly cut business card. The $>45\text{-}\mu\text{m}$ insoluble residue and $>125\text{-}\mu\text{m}$ sieve fractions of the feed are placed with a few drops of epoxy resin in the chambers of the mold and a partial vacuum is drawn for a few minutes. Then the container is filled with the remaining resin, small labels inserted in each chamber, and the preparation allowed to harden on a slide warmer set at approximately 40° to 50°C.

Alternatively, the writer has found that small portions of plastic fluorescent-light diffuser panels, containing multiple square chambers, can also be used for sample holders. The panel can be cut with a hacksaw into “2-hole,” “3-hole,” or “4-hole” containers, the latter arrangement particularly useful for studying the raw feed — the $>125\text{-}\mu\text{m}$ fraction, the $>45\text{-}\mu\text{m}$ insoluble residue from acetic acid and that from hydrochloric acid, and the feed as received, all in the same thin section. Small fragments of clinkers may also be encap-

sulated similarly. The 4-hole container is placed on a silicone grease-coated glass plate, the bottoms of the chambers are covered with two or three drops of epoxy, and the powders are added to a depth of approximately 2 mm in their respective holes. The container is placed in a vacuum impregnation jar for air removal for approximately 5 minutes, the vacuum is released, the remaining epoxy and small labels are added, and the sample allowed to harden on a slide warmer.

After hardening, a surface on the base of the encapsulation is prepared on the grinding wheels with various diamond or silicon-carbide papers or grinding plates, cleaned, blow-dried, and mounted on a clean glass microscope slide (24 x 46 mm) with epoxy resin and placed on the slide warmer for epoxy curing. After hardening, the encapsulation is cut with a small table-top metallographic saw. The saw-cut surface must be parallel to the surface of the glass slide and the section, therefore, should be of uniform thickness, otherwise a prominent wedge section may produce problems in thinning by hand. One should try to cut a section as thin as possible (<0.5 mm) with the diamond saw to shorten grinding (thinning) time.

Using a machine designed for making thin sections, or detachable metal-bonded diamond discs attached to a rotary grinder/polisher, one can produce a thin section in approximately 5 to 15 minutes, assuming that the encapsulated portion remaining on the glass slide, after cutting off the excess with a small metallographic diamond saw, is no more than 0.5 mm thick. Ahmed (1996) described a method of making thin sections by hand with a grinding procedure utilizing a fine steel mesh and diamond slurries on horizontal rotary wheels. The method appears quite practical, especially for those who do not want to buy a machine specifically designed for thin sections.

Assuming that one is making a thin section by hand with horizontal rotary wheels, the section is held to the No. 200-mesh diamond disc grinding surface with Buehler's slide holder (catalog No. 30-8005). Intermediate grinding with diamond paste (or sprays) on a woven steel-mesh pad (Buehler catalog No. 15-6708) is showing much promise in thickness reduction and production of a relatively flat surface. Final thickness reduction is accomplished on Texmet™ or nylon with 30- to 15-μm diamond paste with oil or propylene glycol. To determine the thickness of the section, observe the concentric multicolored bands in the particle in cross-polarized light. The number of red bands in the particle equals the order of the maximum interference color. When the quartz grains have an interference color no higher than first-order light gray, the section is usable. If preferred, its thickness may be further reduced to a point where the quartz interfer-

ence color is no higher than medium to dark gray. If desired, the thin section can be polished with diamond paste (0.25 μm) on Texmet™ or other suitable polishing cloth. The writer has recently found that food-grade mineral oil or hydraulic oil (Mobil DTE™ FM 32) is an excellent vehicle for grinding and polishing raw feed thin sections. "Baby oil" works quite well, although with all these oils processing time is slightly lengthened.

A cover glass is mounted with epoxy resin (without hardener to facilitate removal later for polishing or staining, the latter technique is described below and is particularly helpful in alkali feldspar and dolomite identification). The epoxy eventually hardens to make a permanent cover-glass binder.

Consequently, the thin sections of sieved raw feed can be used to estimate, or determine by counting, the Q_{45} and C_{125} factors in the burnability equations described above, or used to evaluate the raw feed grinding efficiency, or the size distribution and abundance of "unwanted" constituents, and so on.

As standards for visual comparison, thin sections of >45-μm feed materials, each section with different but known percentages of coarse quartz or other siliceous constituents, as well as >125-μm limestone, can be made. One can also make thin-sections of a relatively narrow particle-size range (for instance, 45 to 75 μm) using that specific size range as a standard for purposes of systematic comparison. Nylon and wire sieve cloths with openings at 5-μm intervals are available. One thin section with half a dozen different laboratory mixes, each containing known variations in phase percentages, is very useful. One could vary the percentages of the siliceous component, for example, or slag, shale, and mill scale. Larger microscope slides, up to 150 x 100 mm, and the equipment necessary for making these giant thin sections, are marketed by Logitech of Westlake, Ohio, and Glasgow, Scotland.*

If the encapsulation contains clinker fragments, a common practice for the writer, the sawcut surface companion to the thin section is ground and polished for use in reflected light in the normal manner for clinker examination. Thus, one can also observe the polished section characteristics of some of the raw feed particles. For example, pyrite (FeS_2), a common constituent in limestones and a major source of sulfur in some plants, is easily detected and identified by its pale yellowish white color in reflected light. Metallic

* Logitech
810 Sharon Drive
Westlake, Ohio, USA 44145
Tel: (800) 321 5834
Fax: (216) 871 8188

Logitech Ltd
Erskine Ferry Road
Old Kilpatrick
Scotland, U.K.
Tel: 44 38 987 5444
Fax: 44 38 987 9042

minerals such as magnetite (Fe_3O_4), which is gray in reflected light, mill scale, and other opaque materials (even coal) can be studied.

Half-Sections. A method has been developed for producing polished surfaces on sections of virtually any type of particulate material embedded in epoxy resin for the purpose of viewing in transmitted plane- or cross-polarized light or reflected light. Data from the scanning electron microscope can be gathered on the same grain, thus strengthening the identification and interpretation of the particle. The procedure is simple and *requires much less time* than making a bona fide thin section because only the upper parts of the epoxy-embedded particles are cross-sectioned.

1. On a cleaned petrographic slide, place a few milligrams of raw feed, clinker, cement, or other particulate materials. Three or more different materials may be placed on the same slide, each separated by match sticks, toothpicks, etc.
2. Add a few drops of epoxy and stir gently with a needle to produce a uniform particle distribution. Place the slide on a level slide warmer set at no higher than 40°C and allow to cure.
3. To reduce the thickness of the particles to approximately 35 to $40\text{ }\mu\text{m}$, use a thin-section grinder or metal-bonded diamond plates ($68\text{-}\mu\text{m}$ diamond) attached to a horizontal rotary wheel, and polishing oil. In other words, grind to a thickness at which the quartz grains, if they are present in the sample, have a maximum interference color of *pale yellow* in transmitted cross-polarized light, checking the interference color occasionally with the petrographic microscope as the sample is thinned. Minerals other than quartz can also be used. A Buehler slide holder (catalog #30-8005) facilitates grinding and polishing by hand. Particle cleavages and fractures that might result from grinding the section are not considered deleterious, but actually helpful in identifying the phase.
4. Using Texmet™ (Buehler) or equivalent cloth, and $15\text{-}\mu\text{m}$ diamond paste or oil slurry, or other suitable grinding pad, and a horizontal rotary grinder/polisher, reduce the section to the final desired thickness (quartz at $25\text{-}\mu\text{m}$ has an interference color no higher than medium first-order gray).
5. Clean the slide with isopropyl alcohol and, using Texmet™ and $6\text{-}\mu\text{m}$ diamond paste or slurry, prepare a rough polish on the section.
6. Wash the section with a sonic cleaner in isopropyl alcohol, rinse with isopropyl alcohol from a spray bottle, and polish with $0.25\text{-}\mu\text{m}$ diamond paste on Texmet™, using the horizontal polish-

ing wheel or the Minimet™, the latter with a thin-section attachment (Buehler catalog #69-1580). Check the surface in reflected light to determine the quality of the polish and possible reactions with polishing media. Be sure the epoxy is not soluble in the acetone which might be used in cleaning.

7. For observation of the particles in ordinary reflected light, no cover glass is required. Oil-immersion, reflected-light techniques, as well as organic and inorganic stains can be applied. For observation of the particles in transmitted light, a cover glass is mounted with epoxy resin (no hardener, for easy removal, if necessary).

Organic and Inorganic Stains for Raw Feed Mineral Identification

Using stains to preferentially color certain minerals in raw feeds greatly facilitates their microscopical and macroscopical observation and identification. The techniques described below were modified from those published by Hutchison (1974) and Carver (1971) to aid in quarry rock and raw feed examination.

Stain Technique No. 1 (Feldspars, Quartz, and Calcite). Chemicals needed in this procedure are concentrated HF (52%), a 5% barium chloride solution in distilled water, a saturated solution of sodium cobaltinitrite, and a solution of amaranth (28 grams of F.D. and C. Red No. 2 pure coal tar dye in 2 liters of water). Amaranth is also called Azorubin S, C. I. 16185, available from Polysciences, Inc., in Warrington, Pennsylvania, and other chemical supply houses. This stain is primarily for silicates, but may include clay minerals when aggregated in shale particles. Testing with the shale, as such, will define the usefulness of the stain in this regard.

1. Sieve the crushed raw materials to produce a 45 - to $125\text{-}\mu\text{m}$ fraction and a fraction greater than $125\text{-}\mu\text{m}$, or other intervals as you wish. Study of the stained $> 45\text{-}\mu\text{m}$ insoluble residue is particularly informative. An alcohol or water wash cleans the sieve fractions by removing the very fine particles held electrostatically.
2. Under a ventilating hood, spread the particles on the flat bottom of a small 100 mL Teflon™ beaker. Place the container on a plastic support within a larger Teflon™ beaker (400 mL), the bottom of which has been covered with HF acid to a depth of approximately 3 to 4 mm . Cover the larger container to trap the HF vapors and leave the sample therein for approximately two (2) minutes. *Because this technique requires the use of HF*

acid, all suitable laboratory precautions should be undertaken. This acid is extremely dangerous. Protective eyewear, an apron, and gloves should be worn.

3. Remove the container with the particles from the acid vapors and, with a small pipette, cover the particles with the sodium cobaltinitrite solution for two (2) minutes.
4. Withdraw the cobaltinitrite solution with a paper towel and wash the particles into a watch glass or suitable beaker with a stream of distilled water from a squeeze bottle, quickly withdrawing the rinse water with a paper towel or decanting. Repeat the rinse procedure and withdraw the water with a towel.
5. Add approximately 10 mL of the barium chloride solution with a small pipette to the particles in the watch glass and, approximately 15 seconds later, withdraw the liquid with a paper towel.
6. Wash the particles twice with distilled water as described in Step 4.
7. Using a small pipette, immerse the particles in the watch glass with the amaranth solution for two (2) minutes. Withdraw the solution with a paper towel.
8. Quickly wash the particles with distilled water as described in Step 4 and dry the sample under a heat lamp or in a low temperature oven (no hotter than approximately 80°C).

The particles may be examined with a stereomicroscope or a "petrographic" microscope. With the latter microscope, in addition to the normal transmitted light, one can use oblique lighting, that is, placing a light source very near and beside the objective; a flexible, fiber optic light works quite well in oblique lighting methods.

Plagioclase feldspar (Na-Ca aluminosilicate), other than albite, stains red; potash feldspar (microcline or orthoclase) stains yellow, and quartz and glassy slag are unstained. Calcite takes on various shades of pink and dolomite may be deep red. The particles are normally examined in immersion mounts, utilizing liquids of known index of refraction and a cover glass.

The technique for staining thin sections is virtually identical, except the section is placed ground surface up in the HF vapor, and dipped in the various liquids, holding the section with forceps. After giving the section the final dip in distilled water, the excess amaranth is swept away with a gentle stream of compressed air, and the section is dried with warm air from a hair dryer. The cover glass can be mounted with epoxy resin (without hardener for possible easy removal later). Be aware that particles exposed on a thin-section surface will have parts below the level of the section and, therefore, will not show the stain.

Stain Technique No. 2 (Evamy Stain for Calcite, Ferroan Dolomite, and Ankerite). Chemicals needed for this method are one (1) gram of alizarin red S mixed with five (5) grams of potassium ferricyanide in distilled water, containing two (2) ml of concentrated HCl. The solution is brought to one (1) liter with distilled water and stored in a dark container. The raw feed can be sieved as described above.

1. Particles representing the selected sieve interval are immersed in a watch glass in a 1% solution of hydrochloric acid for 2 to 3 minutes. For thin sections, a 0.2% solution is used for not more than 30 seconds; however, some experimentation may be necessary.
2. Rinse the particles in the watch glass with distilled water and withdraw the liquid with a paper towel. The thin section can be briefly immersed in distilled water as well.
3. With a micropipette, flood the particles in the watch glass with the Evamy solution and allow it to remain for approximately two (2) minutes.
4. Wash the particles in the watch glass with distilled water and draw off with a paper towel. The thin section may be immersed in distilled water for a few seconds as well.
5. Dry the particles or the thin section under a heat lamp. Be careful not to overheat the thin section with the heat lamp as that may cause delamination. A hair drier works quite well with thin sections, after which a cover glass is mounted with epoxy, without hardener, to make cover glass removal easy if necessary.

The particles or the thin section may be examined under the stereo microscope or, using fiber-optic oblique lighting with the petrographic microscope. Colors obtained are: iron-free calcite, red; iron-poor calcite, mauve; iron-rich calcite, purple; iron-free dolomite, not stained; ferroan dolomite, light blue; ankerite, dark blue.

Stain Technique No. 3 (Dolomite). This stain has been found to be applicable to raw feed particles as well as thin sections.

1. A stain solution is made by dissolving 0.2 gram Trypan Blue in 25 mL methanol. Prepare a 30% solution of caustic soda (30 grams NaOH in 70 mL distilled water) and add it to the stain solution in a dark plastic bottle.
2. Place a few milligrams of the raw feed (a specific sieve fraction if preferred) in a watchglass and flood with 2% hydrochloric acid and allow to react for approximately 3 to 5 minutes. Decant the acid without losing the particles and, using

- a squeeze bottle containing distilled water, gently rinse the particles two or three times.
3. Allow the particles to dry in the watchglass placed over a warm hotplate (no hotter than 80°C).
 4. Add a few milliliters of the Trypan Blue solution to the particles in the watchglass and allow the mixture to gently warm for 3 to 4 minutes.
 5. Decant the solution without losing the particles. Rinse quickly with distilled water from a squeeze bottle and dry the stained residue, still in the watchglass, on the warm hotplate.
 6. Mount the particles on a glass microscope slide with epoxy, refractive index liquids, or, if working with a thin section, put on the cover glass with epoxy resin (without hardener).

The stain may fade with time but can be restored by immersion in a dilute NaOH solution. Methanol lost by evaporation of the stock solution can be replenished. *Trypan Blue is a suspected carcinogen and all suitable precautions should be taken. In the writer's laboratory all paper towels and liquids containing the stain are collected in a pail and incinerated.* It is available from Aldrich Chemicals, 1001 West Saint Paul Ave., Milwaukee, Wisconsin, 53233. Tel: (414) 273-3850, Fax: (414) 273-4979.

The writer has not had extensive experience with the Trypan Blue solution but preliminary tests indicate dolomite is consistently stained blue, and calcite remains colorless. Additional experimentation is necessary, particularly with high-magnesian calcite. Dolomite commonly occurs in limestone and shale; it can be a bedded (layered) quarry deposit or intimately mixed with other minerals in the same feed particle. Dolomite should be an expected constituent.

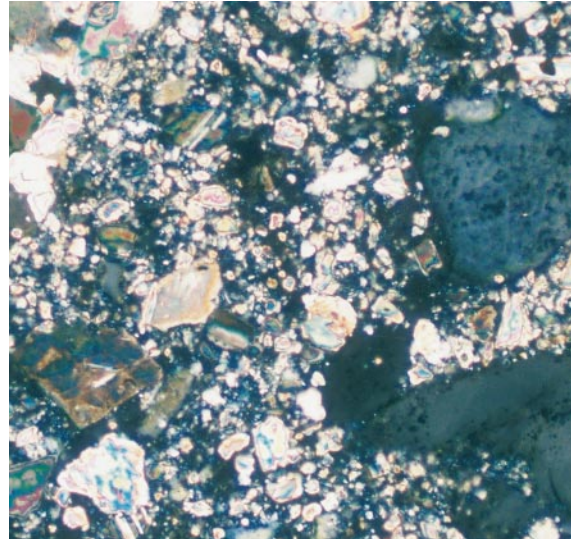
Rhodamine B or methylene blue are organic stains applicable to bentonite, a montmorillonite-rich rock commonly used in drilling muds and for other purposes. A few milligrams of the cement blend, for example, are immersed in the dye solution made by mixing 0.1% dye in ethanol; the solution is allowed to dry around the particles which are then examined microscopically in liquids of known refractive index (Caveny, 1985).

In summary, evaluating a raw feed on the basis of the petrography of the several size fractions and their insoluble residues, with grain mounts or thin sections, stained or otherwise, is an immediately rewarding method of quality control. Petrographic "standard" slides are highly recommended. If clinker particles are added to the thin section or powder, then the cause of numerous belite nests in the clinker might be seen in the same microscope slide. Feed microscopy, in many cases, allows one to state precisely where manufacturing changes should be made to meet the competitive challenge. Even if one does not want to calculate the potential free lime at 1400°C, the F.L. Smidth formula (Theisen, 1992) for burnability can be used, modified or not, as a routine raw feed quality control tool to measure the feasibility of combination. Perhaps the burnability equation(s) should include thermal energy units, heating rate, particle-size distribution (PSD), and other mineralogical factors. Certain PSD factors (percentile parameters) combined with microscopical data are probably far better than our current method of using one or two sieve residues.

PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS

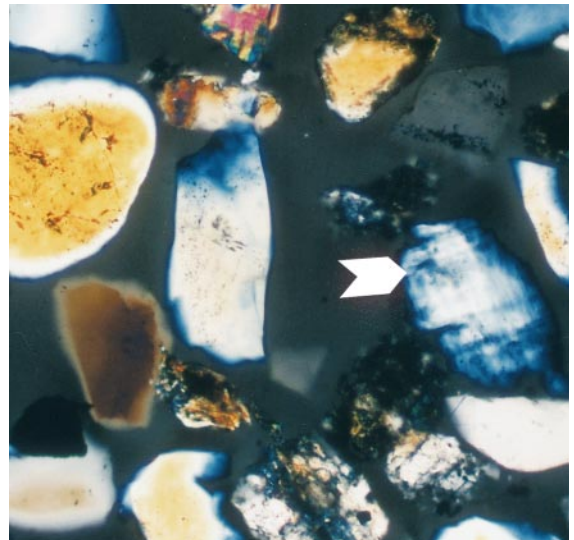
Photograph 10-1 Kiln feed in thin section. Multicolored particles are grains of dolomitic limestone (calcite). Gray quartz at lower right, feldspar at upper right. Clinker produced contains an abundance of belite nests and periclase. (S#A6869)

Crossed polars
Field dimensions = 0.3 mm x 0.3 mm



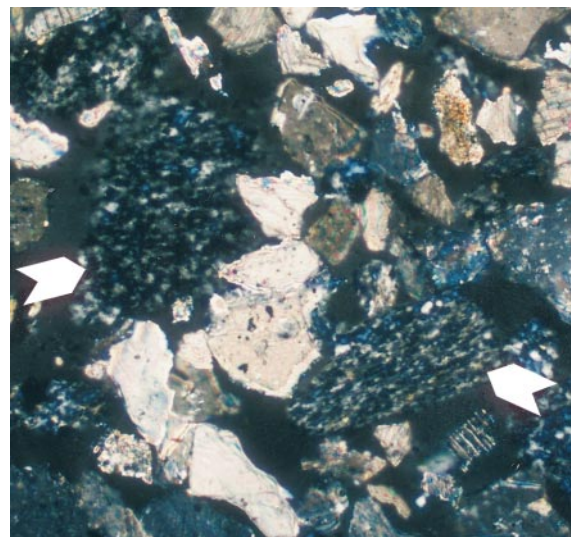
Photograph 10-2 Feed particles representing the insoluble residue from acetic acid in a thin section which is slightly thicker than normal. Gray and yellow quartz, microcline feldspar (arrow), and other silicates. $Q_{45} = 2.05\%$, $A_K = 5.1\%$, the latter comprised largely of finely microcrystalline volcanic rock fragments. Silicate distribution in the clinker is exceedingly nonuniform, belites are yellow and amber, and strengths are low. (S#A6870)

Partially crossed polars
Field dimensions = 0.3 mm x 0.3 mm



Photograph 10-3 Thin section of kiln feed containing an abundance of coarse micaceous siltstone (arrows), providing the silica for the clinker and producing a uniform distribution of clinker silicates, suggesting the ease with which combination can occur with fine-grained, polycrystalline, impure, siliceous raw materials. (S#A6871)

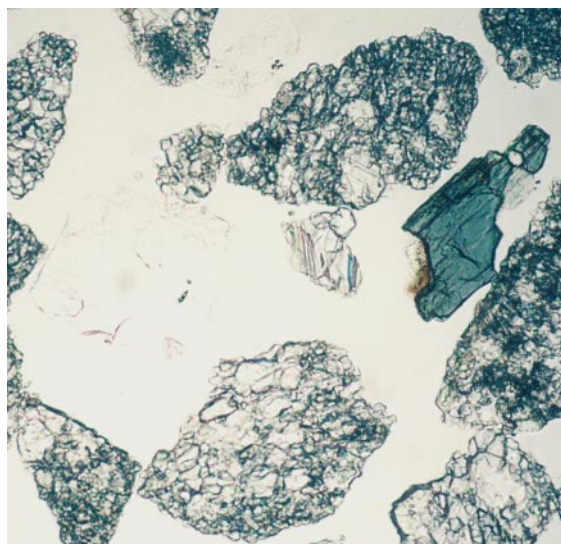
Crossed polars
Field dimensions = 0.6 mm x 0.6 mm



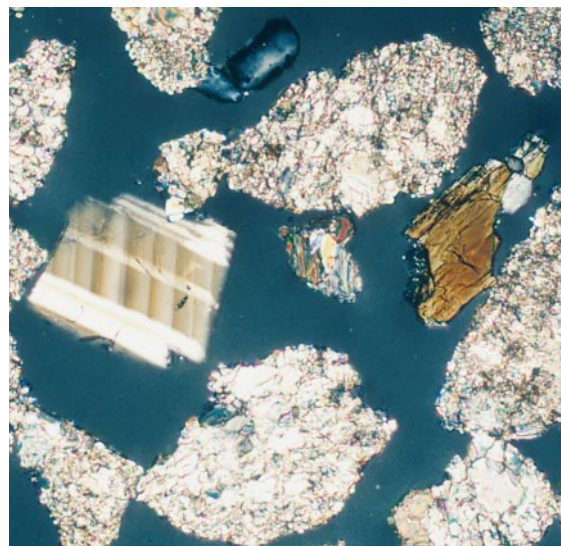
PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

Photograph 10-4 Thin section of $>125\text{-}\mu\text{m}$ fraction of raw feed showing twinned feldspar (left) surrounded by fine- to medium-crystalline limestone, with ferro-magnesian silicate (hornblende) on right. (S#A6872)

Transmitted, plane-polarized light
Field dimensions = $0.6\text{ mm} \times 0.6\text{ mm}$

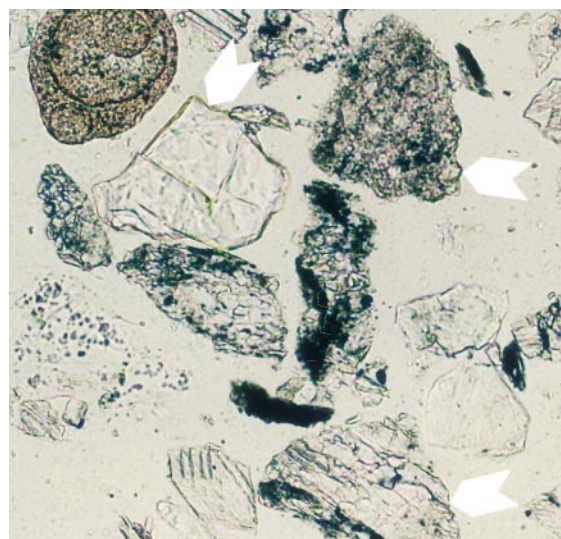


Photograph 10-5 Same as 10-4 but with crossed polars. (S#A6873)



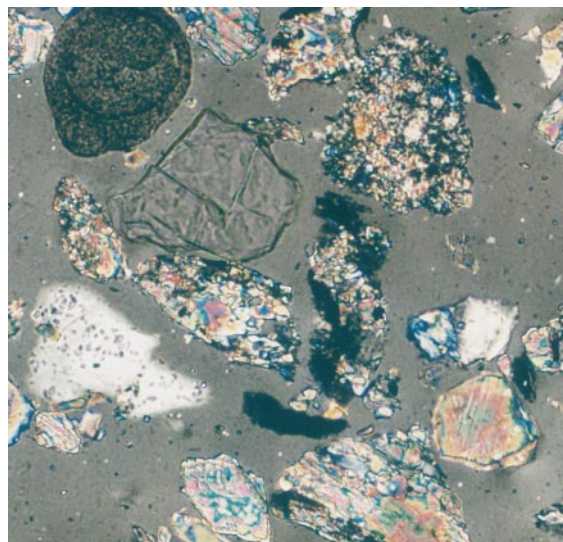
Photograph 10-6 Thin section of easily burned raw feed ($>45\text{-}\mu\text{m}$ fraction) showing round polycrystalline petroleum catalyst (upper left), glassy ceramic waste (magenta arrow), quartzite (green arrow), and iron-bearing limestone (yellow arrow). (S#A6874)

Transmitted, plane-polarized light
Field dimensions = $0.3\text{ mm} \times 0.3\text{ mm}$



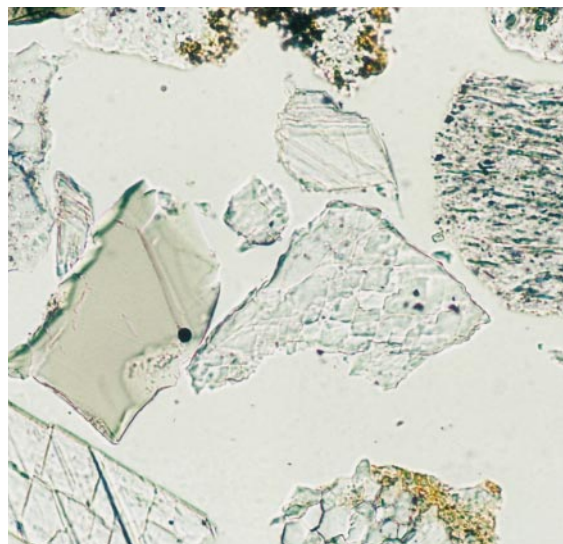
PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

Photograph 10-7 Same field of view as 10-6 but with crossed polars. (S#A6875)

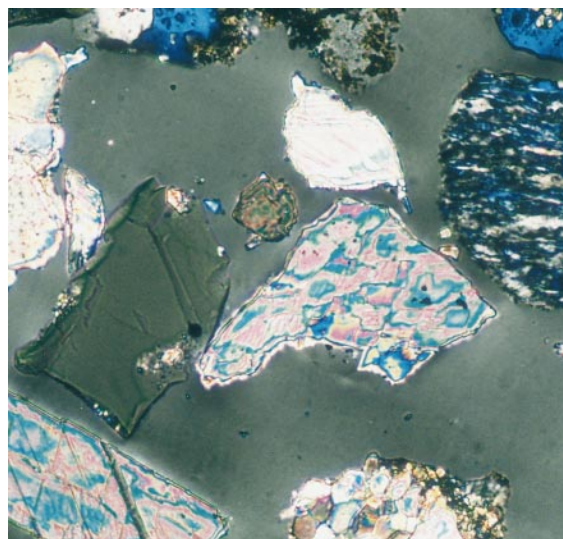


Photograph 10-8 Thin section of raw feed, 45- to 125- μ m fraction, showing pale green glassy slag (left), shale (right), and calcite marble (center). (S#A6876)

Transmitted, plane-polarized light.
Field dimensions = 0.3 mm x 0.3 mm



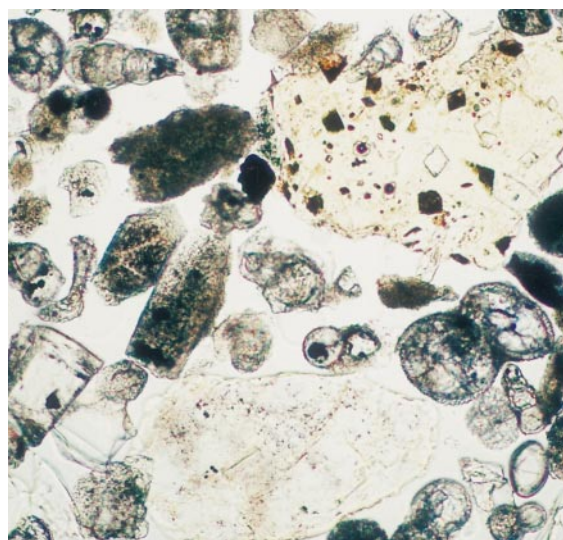
Photograph 10-9 Same field of view as 10-8 but with partially crossed polars. (S#A6877)



PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

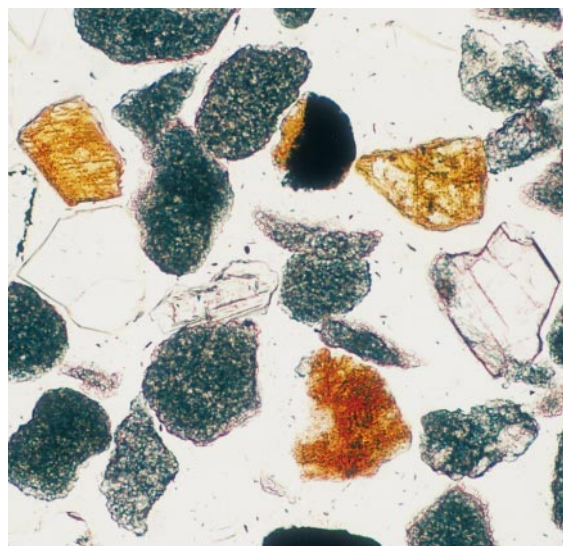
Photograph 10-10 Thin section of easily burned raw feed (45- μm fraction) composed largely of calcite fossil shells (foraminifera), many of which contain opaque crystals of pyrite (FeS_2). Chert (microcrystalline quartz) with iron stain and dolomite at upper right, and large quartz at bottom. (S#A6878)

Transmitted, plane-polarized light
Field dimensions = 0.6 mm x 0.6 mm

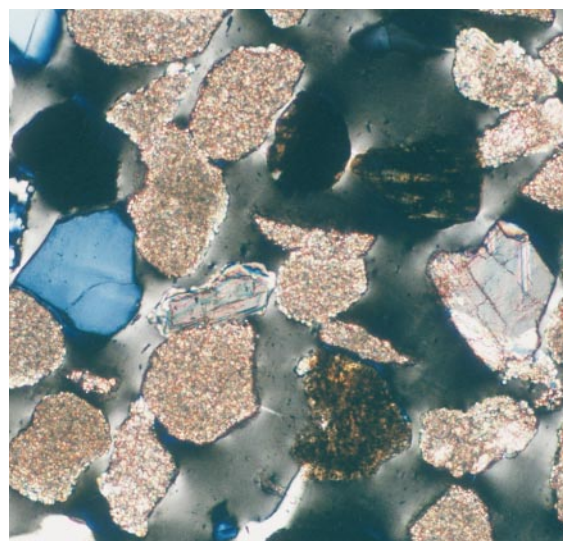


Photograph 10-11 Raw feed thin section of 45- to 75- μm material stained with a sodium cobaltinitrite-barium chloride-amaranth solution, revealing potash feldspars (yellow) and calcite (pink to red). (S#A6879)

Transmitted, plane-polarized light
Field dimensions = 0.6 mm x 0.6 mm



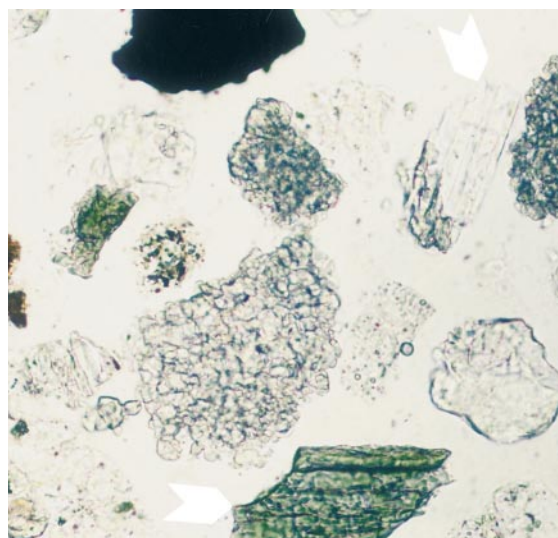
Photograph 10-12 Same field of view as 10-11 but with partially crossed polars. Note quartz and quartzite on left. (S#A6880)



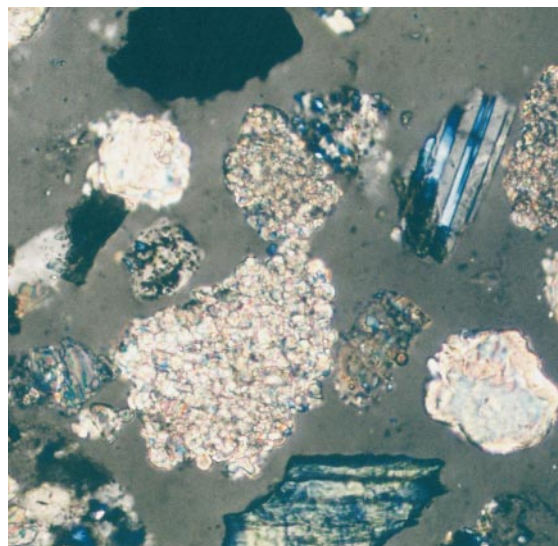
PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

Photograph 10-13 Hard-to-burn silica-rich raw feed in thin section, acetic-acid insoluble residue ($>45\text{ }\mu\text{m}$), showing cleavage on plagioclase feldspar (sodium aluminosilicate, green arrow), and hornblende (a ferromagnesian silicate, magenta arrow). Iron-rich particles are dark brown and opaque. (S#A6881)

Transmitted, plane-polarized light
Field dimensions = $0.3\text{ mm} \times 0.3\text{ mm}$

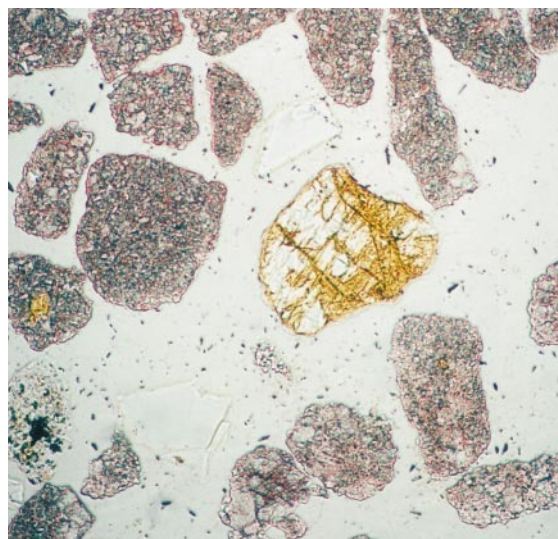


Photograph 10-14 Same field of view as 10-13 but with partially crossed polars. (S#A6882)



Photograph 10-15 Thin section of 45- to $75\text{-}\mu\text{m}$ fraction of raw feed stained with a sodium cobaltinitrite-barium chloride-amaranth solution, showing yellow potash feldspar and pink calcite. (S#A6883)

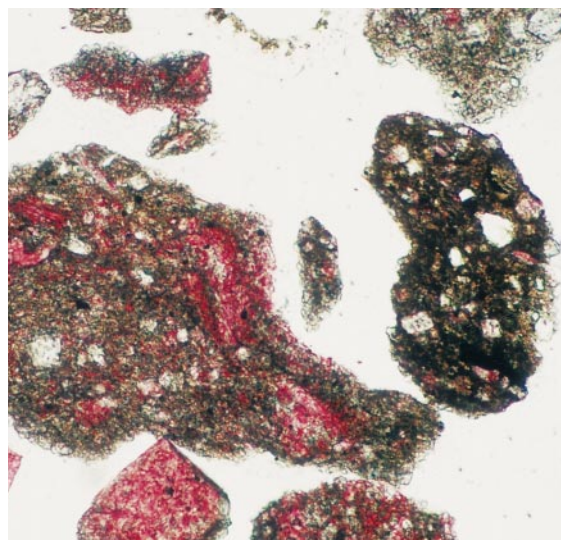
Transmitted plane-polarized light
Field dimensions = $0.3\text{ mm} \times 0.3\text{ mm}$



PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

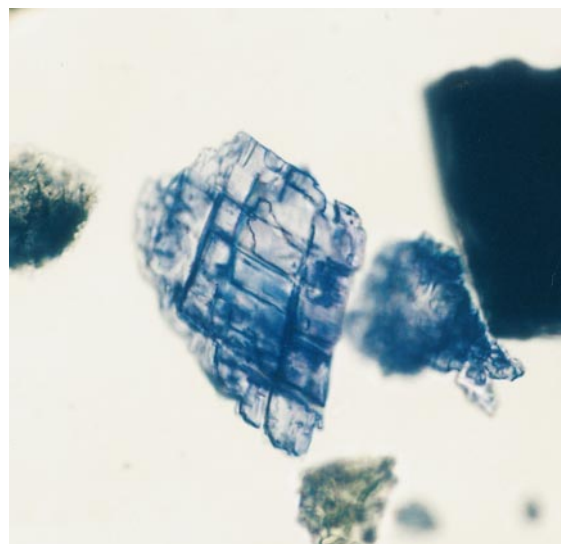
Photograph 10-16 Easily burned raw feed in a thin section stained with the Evamy solution. Calcite is red, rhombic crystals of dolomite are clear (unstained) in brown shale (right). (S#A6884)

Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm



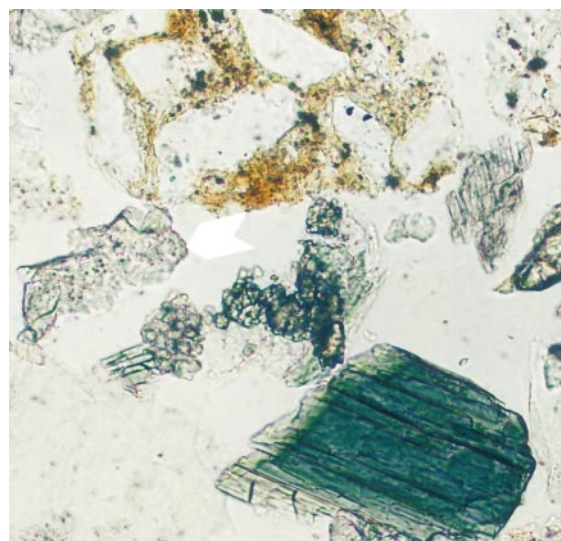
Photograph 10-17 Powder mount of acetic-acid insoluble residue ($>45\text{ }\mu\text{m}$) stained with Trypan Blue. Dolomite cleavage fragment exhibits typical stain coloration and rhombohedral cleavage. (S#A6885)

Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm



Photograph 10-18 Thin-section view of feed containing iron-bearing clayey brown sandstone (upper center) in acetic-acid insoluble residue ($>45\text{ }\mu\text{m}$). Green hornblende shows typical cleavage. Dolomite (arrow) exhibits cleavage and prominent optical relief. (S#A6886)

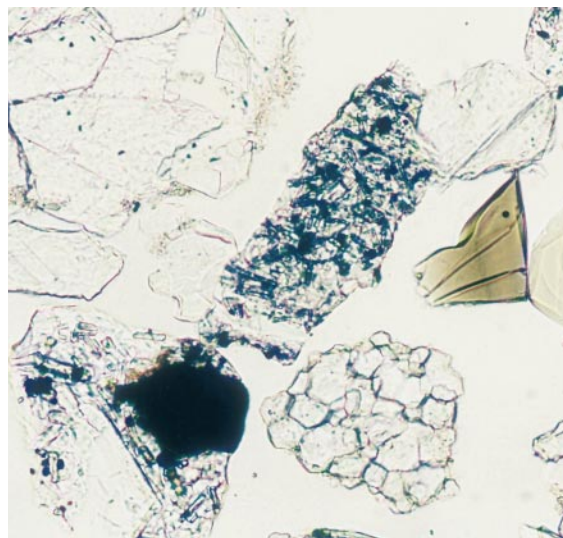
Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm



PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

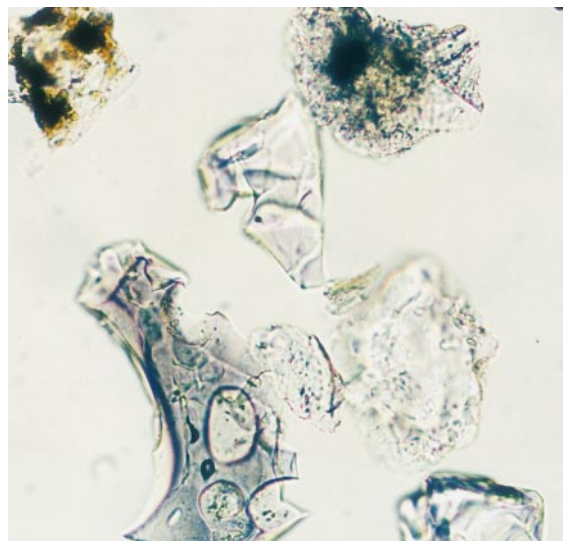
Photograph 10-19 Thin section of 45- to 125- μm feed showing brown and pale yellow glassy slag, and microcrystalline basalt fragments containing dark iron-oxide minerals (magnetite) and feldspar. Calcite marble particle below slag and at upper left. (S#A6887)

Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm



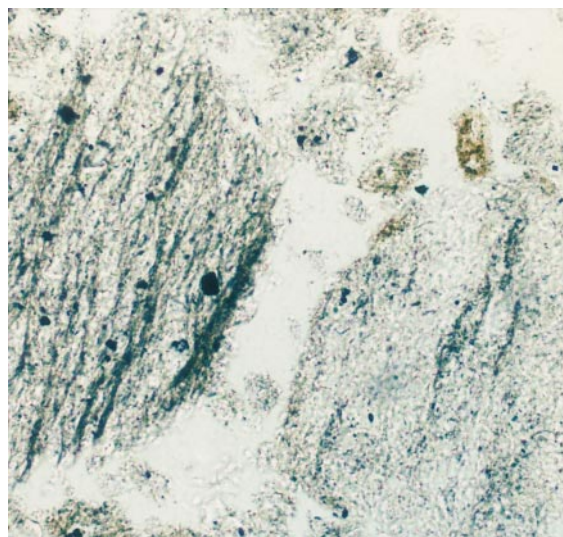
Photograph 10-20 Acetic-acid insoluble residue in powder mount of $>45\ \mu\text{m}$ fraction in epoxy resin, showing glassy slag particles (lower left) and iron-bearing basalt (top). (S#A6888)

Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm



Photograph 10-21 Thin section of high-silica shale particles in white-cement raw feed. Grain at left has well-oriented sericite mica flakes; grain on right shows very finely microcrystalline assemblage of quartz, clay, and mica. (S#A6889)

Transmitted, plane-polarized light
Field dimensions = 0.6 mm x 0.6 mm



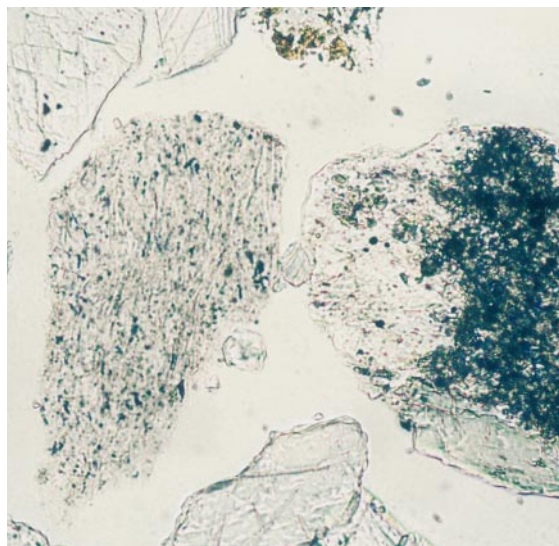
PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

Photograph 10-22 Same field of view as 10-21 but in cross-polarized light. (S#A6890)



Photograph 10-23 Thin section of the feed coarse fraction, showing a shale particle (left), with an igneous rock fragment (right) containing quartz, feldspar, and ferro-magnesian silicates. Calcite marble fragments. (S#A6891)

Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm



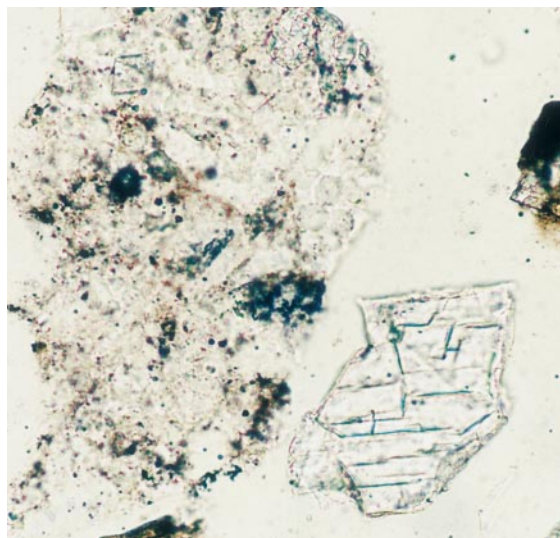
Photograph 10-24 Same field of view as above, but with slightly uncrossed polars. (S#A6892)



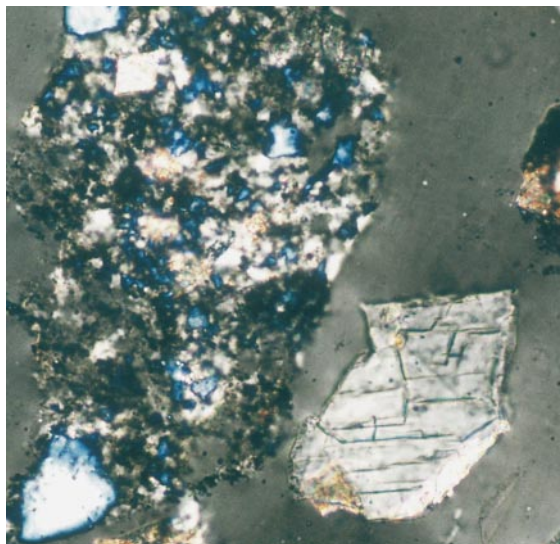
PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

Photograph 10-25 Thin section insoluble residue from acetic-acid treatment of feed, showing large grain of chert and smaller particle of feldspar, the latter exhibiting a pale pink color and well-developed cleavage. (S#A6893)

Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm

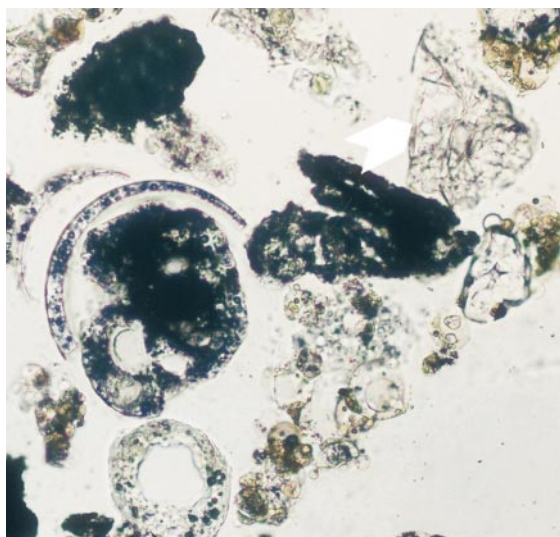


Photograph 10-26 Same field of view as 10-25 but in partially crossed polars. (S#A6894)



Photograph 10-27 Polished thin section of fly ash, >75 μm , showing black opaque carbon particles, glassy particles (some with a variety of included phases and colors), and quartz (arrow). (S#A6895)

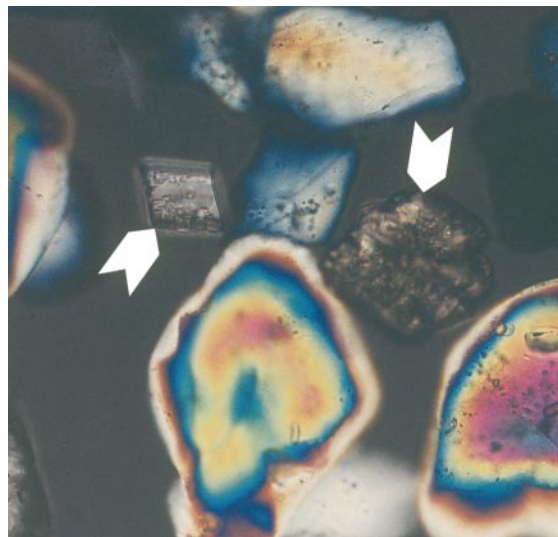
Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm



PHOTOMICROGRAPHS OF PORTLAND CEMENT RAW MATERIALS (CONTINUED)

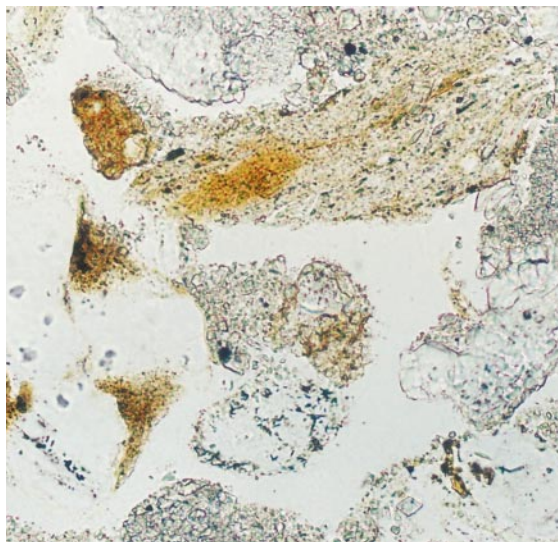
Photograph 10-28 Powder mount of acetic-acid insoluble residue, $>45\mu\text{m}$, showing abundant large quartz grains (multicolored) and rhombohedral dolomite crystals (arrows). Raw feed for white portland cement. (S#A6896)

Transmitted light, partially crossed polars
Field dimensions = 0.3 mm x 0.3 mm



Photograph 10-29 Thin section of raw feed, centrifuged in epoxy (Campbell, 1986), showing the coarse fraction at the base of the test tube. Large shale particle (upper center), sandstone and limestone, left and right, respectively. (S#A6897)

Transmitted, plane-polarized light
Field dimensions = 0.3 mm x 0.3 mm



Photograph 10-30 Same field of view as 10-29 but with crossed polars. (S#A6898)



CHAPTER 11

Recommended Formats and Materials

The suggested format for detailed clinker examination given in this chapter requires more observation than a “routine” analysis would necessitate. However, answers to many of the questions posed in the suggested format have not been published, and, therefore, the outline may point to some needed research that may have very practical consequences. For example, little is known about belite inclusions in alite (their size, abundance, and composition) in relationship to burning conditions and raw feed characteristics. Crystal size distributions of most of the matrix phases in relation to burning conditions are also poorly known. In short, detailed quantitative studies of phase varieties are needed, not only as subjects of scientific inquiry but also for the purpose of improving the quality and extending the usefulness of portland cement. *The format is designed to elucidate the variation within and among clinker nodules or fragments.*

SUGGESTED FORMAT FOR DETAILED CLINKER EXAMINATION*

- A. **Production date and time**
- B. **Examination date**
- C. **Megascopic properties**—hardness, color, porosity, shape; note variations in these properties within and between clinkers and establish predominant characteristics; agglomerated or single nodules.

Size variation—if sieving is impractical, estimate the following, in metric terms, from a random sample:

modal clinker size—the most frequently occurring diameter

16th and 84th percentiles—determine which clinker diameter has 1/6 of the clinker diameters larger than itself . . . this is the 84th percentile diameter on a cumulative percent-

age curve. Next, determine which clinker diameter has 1/6 of the clinker diameters smaller than itself . . . this is the 16th percentile diameter. The difference between these percentiles includes approximately $\pm$ one standard deviation(s) from the median clinker size, i.e., $(84\text{th} - 16\text{th}) \div 2 = \pm s$, assuming a population with a normal size distribution.

- D. **Microscopical description** (powder mount, polished section, polished thin section). Each clinker phase is described in this recommended order:

1. Percentage (state method, such as point count, line count, etc., if other than estimation with comparison charts).
2. Occurrence and distribution pattern—uniformly, randomly, or patchily distributed; occurrence near or in pores, near certain other phases, clinker core, shell, sharply bounded groups (nests) of crystals, diffuse boundaries, and so on.
3. Orientation of crystals—random or preferred, local or general.
4. Crystal size—mode, extreme range, and gradation (estimation of s as described above); unimodal or bimodal; comparison within and among clinkers. In order to establish a classification and nomenclature for clinker texture (that is, crystal size), the following scheme is proposed, based on the most commonly occurring alite crystal length:

* Modified after Folk, R.L., *Petrology of Sedimentary Rocks*, Hemphill Publishing Co., Austin, Texas, 1980, 184 pp.

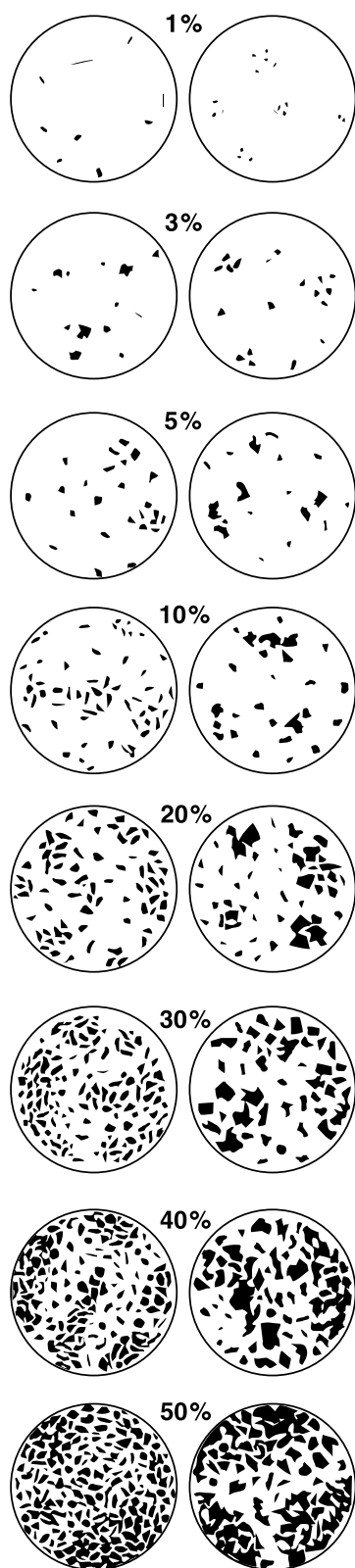


Figure 11-1. Comparison chart for visual percentage estimation (after Terry and Chilingar, 1955).

Alite crystal length (in micrometers)	Descriptive term
< 10	Extremely finely crystalline
10 to 20	Very finely crystalline
20 to 30	Finely crystalline
30 to 40	Medium crystalline
40 to 50	Coarsely crystalline
50 to 60	Very coarsely crystalline
> 60	Extremely coarsely crystalline

5. Facial development on crystals—euhedral, subhedral, anhedral; areas of preferential development in a single clinker.
6. Contact features—is phase indented by others, or does it indent its neighbors?
7. Cleavage, fracture, or parting—how many cleavage directions, intersecting at what angles and parallel to which crystal faces? Are microcracks preferentially oriented in the clinker? Do they exhibit phase-specific patterns?
8. Zoning and internal structure—note differences in zonal birefringence and refractive index (on broken crystals); twinning or crystal intergrowths; number of sets of lamellae; lamellar width variations.
9. Refractive index, color, and pleochroism in transmitted light; luster and color in reflected light (without etch); characteristics in reflected light (oil immersion); note variations within species.
10. Interference color, birefringence; straight or wavy extinction; biaxial or uniaxial; negative or positive $2V$; dispersion in transmitted light.
11. Etch or stain effects—consistent or variable within individual crystals? Within clinkers? Within species?
12. Inclusions—identify and describe each type with above outline as completely as necessary; note size, distribution among and within host crystals, and abundance of each.
13. Freshness, alteration products, homogeneity of decomposition or alteration within same species.
14. Definition of species varieties and description—for example, raggedy, round, vs. dendritic varieties of belite or euhedral, large periclase vs. anhedral, or dendritic periclase; state relative abundance and preferred locations of each.
15. Affinities and antipathies of occurrence—for example, does alkali aluminate selectively occur in more porous zones or is free lime preferentially associated with periclase?

16. Age relations—is one phase being replaced or attacked by others; is it euhedral against others; formed earlier or later?

The extensive list of observations given above requires far more time than a normal investigation would allow. For practical reasons, the following format is used by the writer.

CLINKER and RAW FEED MICROSCOPY

Project No.:

Company:

Date:

Sample No.:

Number of Nodules Examined:

Crushed or whole.

Nodule granulometry:

Mode* =

s = $(84\text{th}-16\text{th}) \div 2 =$

Ave. =

Porosity: Low, moderate, high. Porosity distribution (variation) within and between nodules.

Alkali Sulfate:** Percentage; location; association; average size. Size and abundance variations in and among clinkers; varieties and individual abundances, if possible. Determine varieties and percentages with XRD.

Periclase: Percentage; crystal morphology; average crystal size; percentage larger than 15 microns; association. Size and abundance distribution in and among clinkers.

Free Lime: Percentage; crystal morphology; average crystal size; packing; association. Size and abundance distribution in clinkers. Note amount of epeizite in KOH-sugar solution residue.

Aluminates: Percentage; varieties and crystal morphologies; association; average crystal size. Size variations in and among clinkers. Matrix percentage and distribution; aluminate/ferrite ratio, ratio variations within and among clinkers. General texture of the matrix (finely crystalline = less than 2.0, medium crystalline = 2 to 4, and coarsely crystalline = greater than 4 microns), and textural variation within and between nodules. Note and describe occurrences of aluminates other than C_3A or $(\text{N},\text{K})\text{C}_8\text{A}_3$. Salicylic acid residue can be used to concentrate matrix phases facilitating refractive index determination.

Ferrite: Percentage; crystal morphology; association; average crystal size; color, size. Abundance variations within and among clinkers.

Alite: Percentage

Mode =

s = $(84\text{th}-16\text{th}) \div 2 =$

Ave. =

Apparent birefringence =

Etch reactivity variations (specify etch and length of time). Crystal morphology; crystal surface characteristics (depth of alteration); internal structure; tendency for coarse cannibalism (masses greater than 5 times the average alite crystal size); inclusions. Size and abundance variations within and between clinkers.

Belite: Percentage

Mode =

s = $(84\text{th}-16\text{th}) \div 2 =$

Ave. =

Crystal colors*** in percentages are _____.

Etch reactivity variations; crystal morphologies; internal structure varieties (Types "A," "B," or "C"); inclusions; percentages of nests and types of crystal packing and their percentages; nest boundaries; if nest crystals are different from others, *describe separately*. Crystal size, morphology, and abundance variations within and among clinkers.

Raw Feed: Determine the weight percentages in the >125-micron and 45- to 125-micron fraction by wet sieving and list particle varieties in order of decreasing volume percentages in each by counting at least 200 grains. Determine weight percentages of insoluble residues 20% acetic acid and 20% HCl treatment, calculate difference, and study the >45-micron insoluble residues, listing volume percentages of each particle type or counting same to determine C_{125} , Q_{45} , A_K , etc. *Describe differences within each fraction*. Use stains and refractive index liquids where practical.

* Crystal size measurements in microns, nodule size in millimeters. "Mode" is most frequently occurring size; 16th and 84th percentiles refer to estimated points on an imaginary crystal- or particle-size curve, the difference divided by two is an estimate of one standard deviation (s) on each side of the median. "Ave." = $(\text{"mode"} + 84\text{th} + 16\text{th percentiles}) \div 3$. KOH-sugar extraction facilitates determination of alite birefringence and belite color.

** Phase abundances are estimated volume percentages unless otherwise noted.

*** Crystal color scale: 4=clear, 3=pale yellow, 2=yellow, 1=amber; crystals with abundant dotlike products of exsolution are ranked as 1; estimate the percentages, or determine by counting at least 200 crystals.

Note: Record observations of nodule color variations, and other unusual occurrences such as refractory fragments, weathered clinkers, and clinker nodule disintegration.

EXTRACTION TECHNIQUES FOR CONCENTRATION OF CLINKER SILICATES AND MATRIX

Removal of the matrix phases (aluminates and ferrite) and concentration of the silicates in the residue using a warm potassium hydroxide-sugar solution greatly facilitates the observation of belite color and determination of apparent birefringence of alite. The procedure given below is a modification of that presented by Guttridge (1979) of the Cement and Concrete Association in the United Kingdom. Routine use of the KOH-sugar extraction technique is highly recommended. Saini and Guilani (1995) emphasize the KOH-sugar extraction method for XRD analysis and microscopy of clinker, illustrating the close similarity of the data. Indeed, the present writer always combines polished section examination in reflected light with powder studies in transmitted light.

1. If a clinker sample is to be subjected to the extraction, a random sample of 1- to 2-mm crushed clinker particles, taken from the same fraction as previously prepared for polished section examination, is further crushed in a mortar and pestle until all the subsample passes a 75- μ m screen (No. 200 mesh). If a cement is to be treated, a random sample of approximately 10 grams is sieved to produce the 45- to 75- μ m fraction (325 to 200 mesh); particles left on the 75- μ m screen could be further crushed to pass the screen or, perhaps, studied microscopically to determine belite nest percentage. Sieving, however, is an optional step; the main benefit is that it provides a uniformly sized powder promoting a relatively uniform level of focus by removing "boulders" that may interfere with examination and particle manipulation. If sieve contamination is a likely problem, one can use disposable nylon with the proper mesh opening.

Wet sieving with isopropyl alcohol produces a dust-free powder and dries quickly. Some workers prefer to treat the sample without sieving or washing, thus wet sieving is also considered optional.

2. Place the dried powder in a small labeled vial or other suitable storage container.
3. On a 125-mm diameter, heavy duty watch glass or small beaker (200 mL) placed on a ceramic triangle on a hot plate, add approximately 10 mL of the

KOH-sugar solution (10 grams of KOH + 5 grams of sugar + 20 mL deionized water). The liquid temperature for digestion should be approximately 80°C. *This solution is extremely caustic and proper laboratory safety precautions such as eye protection, apron, and rubber gloves are recommended.*

4. Add a few milligrams of the clinker or cement to the warm liquid and stir with a glass rod occasionally or use a swirling motion to distribute the particles.
5. After warming for approximately 15 to 20 minutes, remove the beaker from the hot plate, add a few milliliters of distilled water to reduce viscosity, and decant the liquid. Withdraw the remaining liquid with the edge of a paper towel.
6. Rinse the wet residue with a stream of deionized water from a squeeze bottle, decanting the liquid. Do this three times within a 3-minute interval. Do not be concerned with traces of a precipitate that may form or tiny crystals that may grow on the silicate particles. Withdraw the remaining liquid with the edge of a paper towel.
7. Flood the residue with acetone or isopropyl alcohol and decant the liquid. Do this three times within a 3-minute interval.
8. Allow the residue to dry on a hotplate and transfer to a labeled vial for storage. An artist's paintbrush and slick paper (old photographic paper) facilitates this transfer.
9. Prepare a powder mount, using a liquid with a refractive index of approximately 1.715, for examination in transmitted polarized light at 400X. The microscope should be equipped with a day-light blue filter over the light source. Light intensity settings and the substage aperture diaphragm should be constant from sample to sample.

Belite crystals (nested or single) and whole alite crystals are amazingly easy to find and observe with this technique. One is able to count the number of belite nest fragments in the powder mount, possibly relating these data to coarse quartz percentages in the raw feed. At liquid boiling temperatures, however, most of the belite nests commonly lose their integrity and are dissolved into single crystals. Thus the proposed procedure is not designed to destroy the belite nests and, therefore, one can easily see the preferential colors that nested belite commonly exhibits compared to solitary belite.

For details of crystal counting to determine belite color percentages and a discussion of some of the problems involving color observations, see Campbell (1994) and parts of Chapter 6. Alkali sulfate, epeizite, periclase, some free lime, and other phases are present in the residue.

For removal of the silicates and concentration of the matrix phases, a solution of 30 grams salicylic acid, added to 250 mL methanol, is made, and a few milliliters of the liquid are placed in a beaker or watch glass. The clinker or cement particles (sieved or otherwise) are added to the container and the mixture placed on a warm hotplate (80°C) for approximately 30 minutes. The methanol lost by evaporation can be replenished periodically. Decant and withdraw the remaining liquid with paper towels and rinse the residue with methanol or acetone three times over a 3-minute interval and allow the preparation to dry on the hotplate. Gather and store the particles as described above, and study with a polarizing-light microscope, keeping in mind that the powder mount may also contain phases in addition to aluminates and ferrite. Fragments of tightly packed belite nests may remain but can perhaps be removed by boiling in the methanol-salicylic acid solution instead of merely warming.

QUANTITATIVE MICROSCOPY

Determination of the percentages of clinker phases can be accomplished by (a) visual comparison with known (measured) clinker standards (Long, 1982a), (b) visual comparison with percentage diagrams (Figure 11-1), (c) point counts, or (d) linear traverse. Point counts entail the identification and recording of the phase under cross-hair intersections or dots in an eyepiece reticle.

Hofmänner (1973) has clearly discussed the problem of accurate determination of phase abundance and recommends a point count of at least 4000 points on a polished section of epoxy-encapsulated, crushed clinkers, using a 25-point grid reticle placed in the microscope eyepiece. According to Hofmänner, a competent microscopist can count approximately 1000 points per hour with a distance between points approximately equal to the average diameter of the crystals. The following equation was given by Hofmänner (1973) to estimate the measuring error, Δ , in point counting:

$$\Delta = 2.0235 \sqrt{\frac{P(100 - P)}{n}} \quad (\text{Eq. 14})$$

where P = percent of points representing a given phase, and

n = total number of points

This equation indicates that the measuring error changes only slightly after 4000 points have been tallied.

Semiautomatic tallying devices (multiple channel counters) and automatic mechanical microscope stages are available to streamline the counting and make it less time-consuming. Voice-activated data recorders with simple statistical calculations should, theoretically, make quantitative microscopy much easier by

permitting an almost continuous eye-to-eyepiece relationship for the observer. Software for geologic point-count data manipulation are presently on the market and could, perhaps, be modified for clinker (or raw feed) use. A second person to keep a tally sheet is very helpful.

Confidence in using percentage diagrams for abundance estimates could be strengthened by combining point counts on the same clinkers until the microscopist feels that his or her visual estimates are sufficiently accurate, that is, within a tolerable range of error. For normal clinker investigations, however, a simple estimate, either based on comparison with point-counted standards or percentage diagrams, will often suffice. Corroboration by XRD analysis can be quite rewarding, especially with computer-integrated systems.

Midgley and Dharmadhikari (1964) described methods of point counting polished sections of clinkers, using an HF vapor etch and 1000 to 2000 points. These authors stated that the standard deviation of the alite and belite weight percentages were estimated at 1.0 and 1.5, respectively, and that the microscopical method is as accurate as that obtained from Bogue calculations and better than that from X-ray diffraction.

Comparisons of statistical analyses of phase percentages determined microscopically by various workers, laboratories, and techniques have been presented by the Chemical Commission of the Technical Studies Committee of the Cement Industry (1978), a French organization. The methods and principal conclusions from their analyses are:

1. The sample is made from 5 kg of clinker, crushed in a jaw crusher with a gap of 2 mm and screened on a 150- μ m sieve. The fraction larger than 150 μ m is used.
2. A polished section is etched with an ammonium nitrate solution in a mixture of water and alcohol to reveal the silicates, followed by a nital etch, which in turn is followed by a sodium hydroxide solution etch to reveal the interstitial phases.
3. Magnification is adapted to the dimensions to be measured, with 4000 points tallied. Chemical dissolution of clinkers with salicylic acid to selectively remove silicates and free lime, followed by removal of C_3A by sugar-water, results in a fairly good microscopic correspondence with the silicates but poor correlations with aluminates and ferrite.
4. Alite and belite percentages determined by microscopy are generally higher and lower, respectively, than the values calculated by the Bogue equations. Major errors in microscopical percentages of matrix phases are mainly due to small crystal sizes.

Ono (1995) presented a series of correction factors in the calculation of phase percentages by the Bogue equations. The factors involve: minor components, solid solution of C_3S and C_2S , solid solution of $C_6A_2F-C_4AF$, and glass. Taylor (1990) also provided formulas for correcting the Bogue calculations.

Chromy (1983), utilizing a 2000-point count on 22-mm diameter polished sections of a sieved crushed clinker sample, demonstrated the usefulness of the microscope in determining the mineralogical composition of clinker, the data from which were related mathematically to clinker and raw mix composition, and cement strength. He concluded, "If conversion constants linking the equilibrium clinker composition and strength are determined, it is not necessary to carry out the quantitative phase analyses of the clinker produced. Monitoring the free lime content will suffice."

Chromy (1992) described his quantitative microscopical method of clinker quality control in Czechoslovakia, using both powder mounts (Ono's technique) and polished sections, the latter made and analyzed in what appears to be less than 30 minutes. Chromy's procedure is: (1) The encapsulation mold, with its floor just covered with 0.5- to 1.0-mm size particles of crushed clinker is heated to approximately 110°C and the epoxy introduced in drop fashion. The initial epoxy quickly hardens in a few minutes, after which the remaining epoxy is added, producing a frothy mass which also hardens and completes the encapsulation. After grinding and polishing the bottom of the encapsulation, the areas of alite, belite, and matrix are estimated at 100X, followed by estimation of the matrix phase percentages at 400X. The microscopist, in regularly scheduled intervals, checks mainly for deviations from optimum target compositions, indicating changes in the production process. Free-lime percentage is given major emphasis in quality control and for this parameter free-lime "aggregates" are counted microscopically in 11 fields of view, each field having a diameter of 2.2 mm. The free lime in weight percent of the clinker is then calculated by dividing the number of aggregates by the number of fields, providing a determination said to be as good as that by chemistry. Chromy stated that any increase in the level of free lime may be due to underburning, high lime saturation factor, high silica modulus (deficient liquid phase), feed fineness too low, or insufficient homogenization of the raw mix (which can be recognized by an uneven distribution of the alite and belite). "Operational microscopy," as Chromy calls it, can replace the traditional method of determining liter weight and free lime.

Linear traverse methods, which record crystal chord lengths and calculate volume and weight percentages as well as specific surfaces of alite and belite, have recently been used to study clinker thermal history and

grindability (Scheubel, 1983). Quantitative microscopy, like that in the previously mentioned paper, is greatly needed in clinker analysis.

Hicks and Dorn (1982) have shown the practicality of using a computer to calculate correlation coefficients from Ono test data, stating, "The computer remains a powerful tool for drawing correlations from masses of data and discovering new paths of usefulness as the program matures."

Statistical methods were used by O'Kelly and Fortune (1983) to relate microscopically determined silicate percentages and clustering tendencies to grindability.

Marciano, Zampiere, and Centurione (1987) gave emphasis to quantitative (statistically designed) clinker microscopy, using an eyepiece micrometer scale for phase abundance determination. These authors summarized the microscopical differences between a well-granulated clinker and one with an excess of fines, the latter said to be due to poor raw material grinding and blending, and use of coarsely ground high-ash (35%) coal.

Hargave and others (1983) quantitatively related (a) phase assemblage (weight ratios), (b) stabilization of phase modifications, (c) silicate crystal size, (d) silicate crystal morphology, and (e) clustering of phases to type of burning process (wet, semidry, and dry). Least square linear regression techniques established some general trends in relation to compressive strength and showed the negative effect of phase clustering (Hargave and others, 1985 and 1988).

The procedure of microscopically superimposing a grid of lines or curves on a microscopical field of view and counting the number of points, averaging for a selected number of fields, has been standardized by ASTM Subcommittee Task Group C1.23.02 for use in point counting of portland cement clinker polished sections, the present author writing the original draft of the procedure for the Task Group. The ASTM designation is C 1356-M, titled *Standard Test Method for the Quantitative Determination of Phases in Portland Cement Clinker by Microscopical Point-Count Procedure*.

Weigand (1994) reported the point-count results of the ASTM microscopy task group on one of the Standard Reference Clinkers supplied by the National Institute of Standards and Technology (Gaithersburg, Maryland). Compared to the Bogue calculations, the microscopical data are roughly 5% higher for alite, 5% lower for belite, 4% lower for C_3A , and 0.5% lower for ferrite. It was further shown that 3000 points per sample would provide sufficient data for statistical acceptance of portland cement clinker polished sections.

The National Institute of Standards and Technology (NIST) offers a set of Standard Reference Clinkers for phase abundance. Analysis of these clinkers by SEM, light microscopy, and QXRD is found in Stutzman

and others (1989). Purchase and study of these Standard Reference Materials is strongly recommended.

MICROSCOPICAL EQUIPMENT, SUPPLIES, AND THIN SECTION SERVICES

Equipment needed for microscopy in a cement plant may range from only a polarized-light microscope required for powder mount analysis to sawing, grinding, and polishing equipment necessary for thin-section and polished-section study. Two somewhat idealized lists of equipment are given in Table 11-1. The "Economy" column in the table contains only the minimum equipment for powder-mount study and polished-section examination. The other column also contains items for preparation of thin sections.

Refractive-index liquids are normally used in transmitted light. However, some liquids when continuous between the polished section and the oil-immersion objective lens, utilizing reflected light, reveal an amazing detail, especially in the clinker matrix. Cedarwood oil ($n = 1.51$) and a 100X specially designed objective are recommended for oil-immersion reflected-light studies. For use in transmitted light, a set of refractive-index liquids, ranging from $n = 1.40$ to 2.00 , will suffice for most examinations. Many of these liquids are toxic and adequate ventilation is required.

A list of common permanent mounting media is given in Table 11-2, followed by names and addresses of some of the companies specializing in commercial thin-section preparation (Table 11-3).

The use of X-ray diffraction (XRD) data can clearly be supportive to microscopy in almost all materials investigations. One obvious advantage of XRD analysis is that it is a reliable mode of identification and quantification for almost all of the major phases commonly seen in raw feed, clinker, and cement. However, XRD analysis suffers one major disadvantage: it cannot tell you where, in the examined mass of clinker, the belite is located or how the belite is related to alite. XRD analysis can indicate the presence of belite and, with some calibrated standards, the amounts of belite polymorphs, but only the microscope can tell you that the belite occurs mostly as decomposition of alite crystals or that the belite occurs only as inclusions in alite. XRD analysis may indicate the presence and quantity of more than

trace amounts of free lime, but only microscopy will tell you that the free lime occurs within alite or that the free lime is associated with periclase. The human eye can microscopically detect phases that, because of their small percentage or amorphous character, are not detected by XRD. XRD analysis, therefore, should be used in a corroborative manner with microscopy.

Photography* is virtually essential in providing pictorial evidence for the interpretations drawn from microscopical examination. A Polaroid-type** camera (large format) is most convenient, producing photomicrographs quickly and easily for reports. For projection screen presentation, a 35-mm color slide is, thus far, unexcelled. Films such as Kodak Kodacolor II (VR-100), Ektachrome 64, 64T, and VT1000, AGFA-RSX 100, and AGFA 100 have been used satisfactorily by the writer for color photographs. Tungsten 160 film is recommended by Dorn (personal communication, 1985); this slide film requires no filters. Ilford Pan F film, in the author's opinion, is excellent for black and white photographs.

One of the most effective means of quickly conveying microscopical information is through the use of a video camera and monitor with which one can show a wide range of clinker features while the audience, in a sense, participates in observation and analysis. As a teaching tool, the video system is unsurpassed. The video camera and monitor, combined with videotape and videoprint attachments, provides a permanent visual data base for clinker comparisons. And lastly, the computer, having already been proven adept at data analysis, may find routine application in image and phase analysis, storing the visual data acquired during an automatic linear traverse of a polished and suitably etched section on CD-ROM or other storage devices. Such information can be transmitted in "real time" via the Internet to waiting computers in, for example, a cement-plant laboratory.

Image analysis and description of its methodological problems, discussed in papers by Mårten, Strunge, and Knöfel (1994), Theisen (1997), and Anwender (1998), are quite instructive. These authors recommend the use of HF vapor as an etchant and real color processing to determine phase percentages (alite, belite, and matrix). Research by the present writer suggests the feasibility of the technique.

* Most of the photomicrographs in this publication were custom printed by Doug Goddard, Gamma Inc., Chicago, Illinois.

** Manufacturers and products are listed for reference or to assist in locating various products; this does not imply Portland Cement Association endorsement or approval.

Table 11-1. Microscopical Equipment and Suppliers*

Equipment		Microscopical Equipment Suppliers	
Complete Lab	Economy Lab		
Trim saw (150-mm diam., oil coolant) ¹		Buehler Ltd. 41 Waukegan Road Lake Bluff, IL 60044 Tel: 847-295-6500 Fax: 847-295-7979	McCrone Accessories & Components 850 Pasquinelli Drive Westmont, IL 60559-5531 Tel: 800-622-8122 Fax: 630-887-7764
Table-top saw with small flanges and appropriate chucks	Table-top saw		
3 Grinder-Polishers with extra wheels and Minimet™ (Buehler), the latter with slide holder for thin sections	1 Grinder-Polisher with 2 extra wheels or Minimet™	Fryer Company Inc. 11177 East Main Street Huntley, IL 60142-7147 Tel: 847-669-2000 Fax: 847-669-2056	Microtec Engineering Lab P.O. Box 636 Clifton, CO 81520 Tel: 970-434-8883 Fax: 970-434-4747
2 Glass plates (300x300 mm)	2 Glass plates (300x300 mm)		
Vacuum impregnator		Hacker Instruments, Inc. P.O. Box 657 Fairfield, NJ 07006 Tel: 973-226-8450 Fax: 973-808-8281	Wards Natural Science Establishment, Inc. P.O. Box 1712 Rochester, NY 14603 Tel: 800-962-2660 Fax: 800-635-8439
Epoxy and hardener and polyethylene cups (several varieties of each)	Epoxy and hardener and polyethylene cups		
Cyanoacrylate adhesive (Super Glue™)	Cyanoacrylate adhesive (Super Glue™)		
Slide warmer		South Bay Technology, Inc. 1120 Via Callejon San Clemente, CA 92673 Tel: 800-SBT-2233 Fax: 714-492-1499	Gilson Company, Inc. P.O. Box 200 Lewis Center, OH 43035 Tel: 800-444-1508 Fax: 800-255-5314
Polaroid™ and 35-mm cameras, video recorder, monitor, video printer	Polaroid™ camera		
Hot plate		Struers, Inc. 810 Sharon Drive Westlake, OH 44145	
Thin-section grinder ²			
Thin-section cut-off saw ²			
Oil coolant (lapping oil) ^{1,2}			
Stereomicroscope			
Polarized-light microscope	Polarized-light microscope		
Sénarmont compensator	Sénarmont compensator		
Reflected-light (metallo-graphic) microscope	Reflected-light (metallo-graphic) microscope		
Petrographic slides (46x24 mm)	Petrographic slides (46x24 mm)		
Diamond pencil or electric engraver	Diamond pencil or electric engraver		
Cover glasses	Cover glasses (several sizes)		
Refractive-index liquids	Refractive-index liquids		
Mortar and pestle	Mortar and pestle		
Alcohol (isopropyl) and spray bottles	Alcohol (isopropyl) and spray bottles		
Propylene glycol	Propylene glycol		
Acetone			
Stage micrometer	Stage micrometer		
Polishing cloths and powders	Polishing cloths and powders		
Adhesive-backed grinding papers	Adhesive-backed grinding papers		
Sieves, 76-mm diam.	Sieves, 76-mm diam.		
Hot air blower	Hot air blower		
Calculator	Calculator		
Vials and caps (15 mL) for powders or plastic bags	Vials and caps (15 mL) for powders or plastic bags		
Sample jars and caps	Sample jars and caps		
Steel file (fine)	Steel file (fine)		

* Manufacturers and products are listed for reference or to assist in locating various products; this does not imply Portland Cement Association endorsement or approval.

¹ Propylene glycol or mineral oil may be substituted for lapping oil. Mobil DTE™ FM 32 is available from:
Mobil Oil Corp.
Products and Technology Dept.
3225 Gallows Rd.
Fairfax, Virginia, USA 22037
MSDS Fax: 800-662-4524, Tel: 703-849-3265

² For thin-section preparation

Table 11-2. Permanent Mounting Media

Canada Balsam Resin, index of refraction $n = 1.537$, and **Lakeside 70** (a synthetic resin, $n = 1.54$) available from most chemical and petrographic supply houses.

Meltmount, $n = 1.539, 1.582, 1.662, 1.704$ for grain mounts:
 Cargille Laboratories, Inc.
 Cedar Grove, NJ 07009
 Tel: 973-239-6633
 Fax: 973-239-6096
 McCrone Accessories & Components
 850 Pasquelli Drive
 Westmont, IL 60559-5531
 Tel: 800-622-8122
 Fax: 630-887-7764

Quickmount, a medium-viscosity resin mixed at 2 parts powder to 1 part liquid, by volume, for grain mounts and clinker encapsulations:

Fulton Metallurgical Products Corp.
 P.O. Box 118A, Saxonburg Blvd.
 Saxonburg, PA 16056
 Tel: 724-265-1575
 Fax: 724-898-3192

Epoxy Resins*

Araldite 506 Resin with **Hardener HY-2964**, low-viscosity, mixed at 2 parts resin to 1 part curing agent for $n = 1.56$:

Ciba-Giegy Corp.
 Mktg. Resins Division
 Brewster, NY 10509
 Tel: 800-222-1906
 Fax: 914-785-3477

Epoxide Resin with **Hardener** and **Epo-Kwick**: mixed at 5 parts resin to 1 part hardener, by weight, for $n = 1.565$; or **Epo-Thin**, a low viscosity resin mixed at 10 parts resin to 3.6 parts hardener:

Buehler Ltd.
 41 Waukegan Road
 Lake Bluff, IL 60044
 Tel: 847-295-6500
 Fax: 847-295-7979

Struers Epofix and **Hardener**, a low-viscosity medium mixed at 9 parts resin to 1 part hardener by weight (8:1 by volume), for $n = 1.57$:

Struers Inc.
 810 Sharon Drive
 Westlake, OH 44145
 Tel: 800-321-5834
 Fax: 440-871-8188

Spurr Resin (soluble in xylene) with four-part kit:

Ladd Research Industries Inc.
 P.O. Box 901
 Burlington, VT 05401
 Tel: 503-253-2843

Epo-Tek 301, low-viscosity, mixed at 4 parts resin to 1 part hardener for $n = 1.56$:

Epoxy Technology Inc.
 14 Fortune Drive
 Billerica, MA 01821
 Tel: 978-667-3805
 Fax: 978-663-9782

Bubble pack (Epo-Tek 301):

APS, Inc.
 P.O. Box 31
 103 Foster St.
 Peabody, MA 01960
 Tel: 800-222-1117
 Fax: 978-532-8901

Regular Setting Epoxy (Black Label, 45 min., in small bubble packages for mounting specimens on glass slides for thin sectioning, $n = 1.56$):

Hardman, Inc.
 Belleville, NJ 07109
 Tel: 973-751-3000
 Fax: 973-751-8407

Table 11-3. Commercial Thin-Section Makers

American Petrographics, Inc. 40 Appletree Lane Roslyn Heights, NY 11577 Tel: 516-625-9162 Fax: 516-625-5804	National Petrographic Service, Inc. 5933 Bellaire Blvd., Suite 108 Houston, TX 77081 Tel: 713-661-1884 Fax: 713-661-0625
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Balsam Petrographics 7611 South Springbook Dr. West Jordan, UT 84084 Tel: 801-562-2570	San Diego Petrographics 27118 North Broadway P.O. Box 3615 Escondido, CA 92026 Tel: 760-749-9272 Fax: 760-751-1772
Burnham Petrographics 846-1 South Myrtle Ave. Monrovia, CA 91016 Tel: 800-772-3975 Fax: 626-359-1811	Spectrum Petrographics, Inc. 499 Dillard Gardens Rd. Suite 2 Winston, OR 97496 Tel: 800-625-2476 Fax: 541-679-5173

D.M. Organist Petrographic Lab P.O. Box 176 Newark, DE 19711 Tel: 302-368-5361 Fax: 302-453-1988	Struers Inc. 810 Sharon Drive Westlake, OH 44145 Tel: 800-321-5834 Fax: 440-871-8188
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Marathon Oil Co. 7400 South Broadway Littleton, CO 80122 Tel: 303-794-2601 Fax: 303-794-1720	Texas Petrographic Service, Inc. 15608 South Brentwood, Suite D Channelview, TX 77530 Tel: 281-862-0666 Fax: 281-862-0777
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Mineral Optics Lab P.O. Box 828 Wilder, VT 05088 Tel: 802-295-9373 Fax: 802-295-7540	
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* For thin sections, whole grain mounts, clinker impregnations, and encapsulations.

CHAPTER 12

Conclusions

The industrial application of the microscopical study of portland cement and clinker is comprised of several fundamental and interrelated parts: (a) data-gathering, consisting of phase identification, description of the phases and their mutual arrangements, measurement of crystal sizes, and estimation of phase abundances; (b) analysis, encompassing the correlation of microscopical data with raw-feed characteristics, burning conditions, and cement performance with and without admixtures; and (c) prediction of clinker grindability, cement performance, and, perhaps most importantly, the formulation of microscopical criteria for maintaining optimum kiln conditions.

As an economical and rapid method to control the quality of portland cement, the value of routine clinker microscopy should be an inescapable conclusion from the numerous observations and interpretations given on previous pages. Quality control of clinker without microscopy of raw feed, in the writer's opinion, is less than adequate. Profound cause-effect relationships exist between the raw feed/particle size distribution, energy required for grinding and burning, clinker quality, and cement performance. Visually appreciating the characteristics of raw feed via microscopical examination gives additional comprehension to quality control.

"Standard" samples of clinker, cement, and raw materials, studied microscopically, with the results of chemical analysis and x-ray diffraction, form the data base for subsequent comparisons. Study of acetic-acid residues is strongly recommended. "Half-sections" can replace thin sections, thus saving much time.

A choice between reflected-light or transmitted-light techniques for plant use may, of necessity, be made on the basis of personal ease of application, tradition, equipment availability, or other reasons. In the writer's opinion, a combination of the two modes of analysis is best. Reflected-light observations of polished sections of whole or crushed clinkers from the

modal size class is recommended for silicate crystal morphology, size, and internal structure and for matrix and void phase descriptions. Transmitted-light observation of powder mounts, half sections, or thin sections is best for belite colors and apparent birefringence of alite. The potassium hydroxide-sugar solution for extraction of the matrix and concentration of the silicates makes transmitted-light microscopy easy for clinker and cement.

With quickly setting epoxy resins or similar materials, such as cyanoacrylate ester (Super Glue™), and modern semiautomatic grinding and polishing equipment, polished sections can be made within a few minutes, while an alcohol-washed, sieved clinker powder, mounted in refractive-index oil, is studied.

Ono's theory, on which the "Ono Method" is based, succinctly set forth in 1981 by Ono (pp. 200-204) and restated in 1995, appears to have a wide and growing acceptance, judging by the numerous research reports by Asian and South American microscopists and the increasing use of the method in North America. Whether called the "Ono Method" or not, the principal variables in clinker quality control are maximum temperature, time at high temperature, rates of heating and cooling, and the nature of the raw feed.

The Ono method, however, is not the only technique of kiln control through microscopy, nor is it a complete analysis. The results of transmitted-light microscopy using the Ono method are almost always fortified by reflected-light observations of polished sections. One must be proficient, therefore, in powder-mount and reflected-light microscopy to gain maximum benefit with Ono's Method. Proficiency is developed only by diligent practice ("eye-training"), adhering to the methodological habits of patience and perseverance.

Above all, when examining anything microscopically, avoid giving undue importance to rare occur-

rences. Always pause when about to make an interpretation and ask "Is this observation characteristic (typical, common) for most of the sample? Does the observation represent a significant, but minor, portion of the sample, or merely a rare occurrence?" It has been said that one can find "almost anything" in clinker. Therefore, be constantly aware of a normal tendency to exaggerate the minutiae.

Now that phase analyses with electron microscopy are available, one might foresee a routine, somewhat automated microscopical basis for quality control. Computer programs and equipment for automating simultaneous microscopical and chemical analyses of polished sections do not appear to be beyond our reach and may, indeed, already be employed on a day-to-day basis in some plants. Application of the computerized scanning electron microscope and chemical analysis via energy dispersive x-ray was demonstrated by Diamond and Olek (1990) for a cement. The techniques were suggested to be applicable to supplementary cementitious materials, blended cements, and fly ash. However, the utility of computer-generated data, like all data, is only as good as the quality of the interpretations. Consequently, the microscopist should continue to serve in a role of objective verification, using the finely honed techniques of observation and inference to relate cause and effect. The value of x-ray diffraction can hardly be understated. XRD and microscopy combined are like two sides of the same coin.

Unfortunately, some of the observations and interpretations presented in Chapter 7 ("Microscopical Interpretation of Clinkers") do not appear to be founded in systematic experimental design or statistical analysis. Statistical measures to determine the degrees of correlation and association of the observations, and their relationship to the various physical and chemical causal factors of the production process, are essential and urgently needed for several very important reasons:

1. To quantify microscopical data in order to remove as much subjectivity as possible;
2. To strengthen the science of clinker and cement microscopy in general, that is, to fortify the foundation with statistical rigor; and
3. To enable the microscopist to communicate precisely with others who are interested in quality control at the cement plant.

Little has been said in the present publication regarding these specific operational modifications because of the wide variety in types of kilns, and the large number of possible equipment changes that may be necessary to modify burning conditions. However, a few examples can be cited:

Of major importance in future work is the quantification and statistical treatment of microscopical data from systematic investigations. Results of an extensive statistical study involving 754 clinker samples over a period of approximately two years to develop a database were described by McKenzie (1991). Specific changes in the microscopy were related to equipment variations, failures, and other process fluctuations. For example, a drop in alite birefringence was related to inefficient coal mill grinding, resulting in a reduction of flame temperature. A partial blockage in a primary air duct, due to a snowman in the firing hood and cooler throat, led to an oxygen deficiency, reducing conditions, and a decrease in the burning zone temperature, indicated by lower birefringence of alite and high ash values. Cariou, Ranc, and Sorrentino (1988) utilized a statistical computer program to analyze the microscopical and chemical data from more than 60 clinker samples representing many methods of pyroprocessing. As a result, after determination of the chemical composition of the raw material and definition of some of the burning-condition parameters, a clinker mineralogy could be predicted and subsequently checked in actual production.

As a result of data from powder-mount study and polished-section examination, Prout (1985) recommended the following production process changes: location of burner pipe, feed rate, primary air, and the intergrinding of gypsum with kiln feed so as to produce a molecular sulfur to alkali ratio of not less than 0.8. Cement quality greatly improved after the proposed changes were made, providing a clear-cut illustration of the successful application of the microscope to cement quality problems and, no less importantly, establishing support from operational personnel. For details concerning microscopical effects of changing burner pipe positions, the reader is referred to a paper by McKenzie (1989a).

Other recommended equipment changes related to the improvement of clinker quality can be found in papers by Hansen (1983) and Miller (1978). Jany and Love (1993) presented microscopical data corresponding to specific changes in flame profile, initial cooling, cooler bed depth, and I.D. fan, in a 158.6-meter, dry-process kiln.

Quality control of cement using microscopy finds daily use in Venezuela (Arbelaez, 1988) where statistical analysis of microscopical data from transmitted and reflected light, and other production variables, provides baseline parameters for problem solving and product improvement. Arbelaez described the following process changes: (1) use of the correct amount of compressed air in feed homogenization in the slurry tank to eliminate belite nests, (2) by modifying the

flame and position of the burner pipe, a shorter burning zone and faster cooling rate resulted in smaller alite and better belite form, (3) maintenance of a uniformly high heating value of the gas, combined with higher flow of primary air, to eliminate overburning but retain the high birefringence of the alite, (4) increase in bed depth in the grate cooler, increasing the secondary air temperature and the flame intensity, (5) a decrease in the lime saturation factor resulted in smaller alite and a minimum percentage of free lime, and (6) the feed retained on the 75- μm screen (No. 200-mesh) was corrected to 12%-14% for the wet plant and 20%-22% for the dry process.

The microscopical effects of improved clinker coolers, a new, innovative coal mill system, and control of kiln feed blending and composition were described by Miller and Venable (1988). Changes in these items resulted in significant increases in 7- to 28-day concrete strengths. Specific details of equipment modifications were described along with the microscopical effects, illustrating several practical techniques to produce a clinker with relatively small alite, large belite, and a fine-grained matrix. Improvement of clinker appearance by cooler modification is described by Jany and Warmkessel (1987).

Recent work by Hamilton and Hamilton (1997) suggests that increasing kiln rotational speed (specific feed rate held constant) results in the following benefits: (a) shortening of the burning zone by 50%, (b) lower exit gas NO_x , (c) decrease in alite size, (d)

increase in quantity and quality of primary belite, (e) permits a quick quench of the clinker, reducing dust, (f) improves vaporization of alkali, (g) increases grinding rates by 15%, (h) increases kiln productivity, and (i) 90% to 100% return of kiln dust by insufflation.

Effects of common minor and trace elements derived from recycling waste materials in fuels and as raw materials for clinker production, as well as cement hydration, are summarized by Uchikawa and Hanehara (1997). Crystal size and optical property variations in clinker phases (alite, belite, aluminates, and ferrite), and their hydraulic reactivities, are shown to be related to concentrations of sulphur, magnesium, phosphorous, fluorine, chlorine, chromium, manganese, zinc, and many other elements. The cement industry is based in crystal chemistry.

Finally, microscopical examination alone may not provide sufficient answers to the questions of clinker microstructure or a cement's inferior performance. Cement particle size distribution, variations in crystal chemistry, mineral and chemical admixtures, as well as the effectiveness of the set-controlling material (normally gypsum or similar minerals), may have stronger effects on cement hydration than the clinker production problems inferred by routine microscopy. Some clinker and cement problems, however, are simple and easily solved; others require the analysis of a tangled set of multiple causes and effects. Microscopy should be one of the first steps in that analysis.

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GLOSSARY

amorphous. Said of a substance having no detectable regular atomic structure or crystal lattice, disordered in all directions, typical of glasses, liquids, gases.

anhedral. A crystal showing no crystal faces; syn. xenomorphic.

anisotropic. Material whose physical properties vary in different directions; in optical terms, the property of dividing light into two rays with differing velocity and direction (double refraction); all crystals, except those of the isometric system, are anisotropic. Alite and belite are examples.

basal pinacoid. A pinacoid of two parallel faces that intersect only the "c" crystallographic axis.

Becke line. A band of relatively high-intensity light, visible around or in nonopaque particles observed under the microscope; apparent movement of the band during focus adjustment relates to differences in indices of refraction between the particle and adjacent liquid or solid medium.

biaxial. A crystal having two optic axes and three principal indices of refraction; for example, a monoclinic, orthorhombic, or triclinic crystal.

birefringence. The difference between the greatest and least indices of refraction of an anisotropic crystal.

cleavage. A preferred direction of breakage in crystalline materials, forming planar stepped or flat surfaces. Described in terms of number of directions or relation to crystallographic forms.

crystalline. Said of a substance in which crystallographic structure (lattice) is evident, and normally evidenced by x-ray diffraction patterns and response to plane-polarized light. Also used to describe the sizes of crystals making up a polycrystalline solid, such as marble, granite, or portland cement clinker.

dendritic. A branching pattern of crystallization; may resemble a tree.

euohedral. A crystal on which the faces are well developed; syn. idiomorphic.

extinction. In crystal optics, darkening an anisotropic crystal four times during a 360° rotation in cross-polarized light; darkening occurs when light vibration directions of the crystal are parallel to those of the microscope polars. A shadowy, non-uniform extinction, called "undulatory," is common in alite, quartz, and feldspar.

feldspar. A group of rock forming minerals, the most abundant in the earth's crust, ranging in composition from a potassium alumino silicate (microcline and orthoclase) to a sodium-calcium solid solution series of alumino silicates (plagioclase).

feldspathic. A rock containing feldspar as a principal ingredient, such as granite and arkose.

form. A crystallographic body having all faces occupying a similarly related position with respect to the planes or axes of symmetry. Forms are said to be open (for example, a prism) if they do not enclose space, or closed (for example, a cube) if they do enclose space. Various closed forms include octahedron, tetrahedron, dodecahedron, and others; open forms include pinacoids, prisms, pyramids, and others.

fracture. A pattern of breakage, other than cleavage, described as conchoidal, splintery, rough, fibrous, hackly, uneven, smooth, etc.

glass. A solid material in which no discernable crystallographic order (crystal lattice) is detectable.

hexagonal system. A crystal system characterized by one unique axis of threefold or sixfold symmetry that is perpendicular and unequal to three lateral and equal axes, the latter mutually intersecting at an angle of 120°; that group of crystals showing the threefold symmetry are, in some classifications, separated to form the trigonal system. Axes are labeled a_1 , a_2 , a_3 , and c .

idiomorphous. Describes a crystal completely bounded by crystal faces. Alite is typically idiomorphous. Obsolescent synonym for euohedral.

index of refraction, n . A constant number equal to sine of the angle of incidence (i) divided by the sine of the angle of refraction (r): $n = \sin i / \sin r$, a relationship also known as Snell's Law. The index of refraction is, in common usage, the inverse of the velocity of light within the studied material. Subscripts such as e , o , E , O , X , Y , and Z , etc., indicate certain light vibration directions in the crystal. Refractive index (RI) is synonymous with n .

isometric system. A crystal system in which the symmetry is characterized by four threefold axes as body diagonals in the cubic unit cell of the lattice; synonymous with cubic system. Crystal axes (a_1 , a_2 , a_3) are of equal length and mutually perpendicular.

isotropic. A material in which physical properties do not vary with direction; in optical terms, light rays pass through a substance at the same velocity without dividing (that is, without double refraction); isometric crystals and amorphous substances are isotropic. Free lime is isotropic.

lamella. A thin plate, lamina, or layer; one of the units in a polysynthetically twinned mineral (such as plagioclase feldspar); or a unit within a set of lamellae in belite.

lath. A crystal habit in which the crystal is long and thin and of moderate to narrow width; cross sections of platy or tabular crystals are lathlike.

length slow. Certain anisotropic crystals in which the slow vibration direction of light is parallel to the length of the crystal; determined by use of accessory plates and observation of interference colors.

monoclinic system. Crystal system characterized by a single, twofold axis of symmetry; a single plane of symmetry; or a combination of the two: three unequal axes (a , b , c), two of which are perpendicular and form a plane at an angle (β) to the third axis.

nest. A concentration of several crystals within a small area; crystals may be tightly packed or loosely packed, the latter nest exhibiting a relatively large amount of matrix between belite crystals, for example. "Cluster" can be used synonymously.

optic axis. A direction in a crystal along which both refracted light rays travel at the same velocity.

orthorhombic system. A crystal system characterized by three unequal, mutually perpendicular axes (a , b , c).

pinacoid. An open crystal form consisting of two parallel faces.

plane-polarized light. An electromagnetic wave in which the electric vector and the magnetic vector reach simultaneous maximum and minimum intensities and vibrate in mutually perpendicular planes.

pleochroism. The ability or property of an anisotropic crystal to absorb various wavelengths of transmitted light differentially in certain crystallographic directions, thereby showing different colors as the crystal is rotated. Ferrite is pleochroic.

polycrystalline. Said of a solid material in which crystals are assembled as a mosaic. Limestone and granite are examples.

polymorphism. The characteristic of a substance to crystallize in more than one form, such as α and β quartz or α , α' , β , and γ belite.

prism. A crystal form having three, four, six, eight, or twelve faces, with parallel intersection edges, and which is open only at the two ends of the axis parallel to the face intersection edges; prisms are closed by other forms.

pseudomorph. A mineral sample with the external form of one mineral and the internal chemistry of another.

pyramid. An open crystal form consisting of three, four, six, eight, or twelve nonparallel faces that meet at a point. An alite crystal is said to be construction of pyramids (Maki, Haba, and Takahashi, 1983).

retardation. The path difference between two light waves, referring to the fact that one wave has fallen behind or advanced ahead of the other wave by a certain number of whole or fractional wavelengths. Path difference is measured between similar points on each wave and has a dimension of length (normally nanometers).

rhombohedron. A trigonal crystal form comprised of a parallelepiped whose six identical faces are rhombs. According to Ono, Kawamura, and Soda (1968), alite is comprised of two rhombohedra.

scaleno-hedron. A twelve-faced crystallographic form in the rhombohedral class of the hexagonal system. Each face is a scalene triangle. Calcite commonly crystallizes in this form.

subhedral. A crystal on which faces are incompletely or only partly developed; syn. hypidiomorphic.

tetragonal system. A crystal system characterized by a fourfold rotation or rotary inversion axis of symmetry. Three crystallographic axes ($a_1 = a_2$, c) are mutually perpendicular.

triclinic system. A crystal system characterized by three axes (a , b , c) intersecting at angles of α , β , and γ , none of which are 90° ; crystals in this system have a onefold axis of symmetry.

trigonal system. See hexagonal system.

twin. The intergrowth of two or more single crystals of the same mineral, described in terms of crystallographic symmetry (rotation axis, reflective plane, center). Twinning is the development of a twin crystal by growth, transformation (as from higher to lower symmetry), or gliding (slip along a crystal plane).

uniaxial. A crystal having one optic axis and two principal indices of refraction; for example, a tetragonal or hexagonal crystal.

vitreous. A type of material luster resembling that of broken glass or china.

xenomorphous. A crystal showing no outward crystal form (crystal faces); an anhedral crystal.

zoning. Variation in the composition of a crystal from core to margin; may result from crystallographic or chemical changes.

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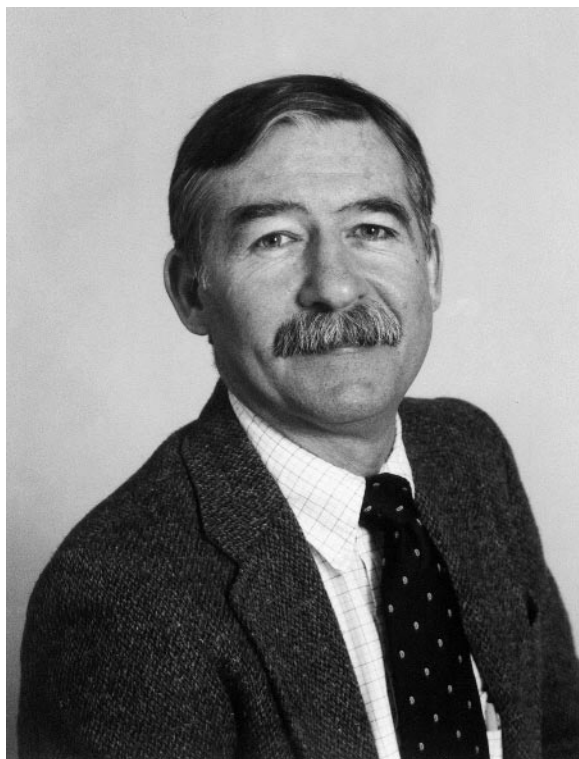
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