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| Please fill in your manuscript title.                                       | Designing Wellbore plugging and abandonment materials based on Nature's hydraulic barrier materials: A solution to prevent hydrocarbon leakage over time. |                                                |
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## Abstract

In the oil and gas industry, drilling and completions of wellbores have undergone major technological improvements, that ultimately enabled safer exploration and production of fossil fuels. However, the plugging and abandonment (P&A) of wellbores had not attracted the same level of technological advancements. Wellbore plugging in offshore environments is challenging as the consequence of potential hydrocarbon leakage can cause cumulative damage to the fragile ecosystems for a long time before detection. Gas leakages are especially hard to detect and evaluate for appropriate wellbore intervention and mitigation. Preventing wellbore leakage requires a robust sealing material capable of reducing the permeability through wellbore infrastructure and surrounding formation to zero. One proposed way is to use zeolites as additives. Zeolites could act as scaffoldings for cement hydration reactions to take place and since they have crystal and pore structures similar to Calcium Silicate Hydrate (CSH), they have compatibility. This could act as a bridge between the natural formation and cement. Due to the non-hydraulic nature of zeolites, they could retain some pore water which could be released in an event of fracture providing water for secondary hydration of cement resulting in self-healing properties. Also, zeolites show a very strong skeletal structure despite their large reactive areas and pore sites. Hence, one of the ideas to be explored in this paper is to gain a deep understanding of the zeolite properties before adding it to cement in order to create an ideal hydraulic barrier material. By doing so, ultimately the aim is to achieve a barrier material which could mimic shale which is a natural cap rock and find application in wellbore plugging operation. This paper is focused on evaluation of a natural zeolite ferrierite, primarily microstructural characterization and its chemical stability in contact with fluids that resemble potential subsurface formation fluids. The data suggests that there is no major microstructural change in contact with: low pH aqueous solution, high salinity brine, synthetic oil and water, and some change in contact with high pH Calcium Hydroxide ( $\text{Ca}(\text{OH})_2$ ) solution, after 7days exposure at 95°C.

**Key words: zeolitic structures, wellbore plugging and abandonment, self-healing, hydraulic barrier material.**

## Introduction

Inadequate plugging of the offshore wellbores releases upward migrating hydrocarbons over the course of decades, resulting in cumulative damage to surrounding fragile ecosystems, like the deep-water Ecosystems in the Gulf of Mexico (GoM). The technology developed for the offshore GoM wells can serve as a model for other offshore oil wells. This research seeks to enhance safety by preventing wellbore leakage, protect environment from oil/gas contaminations and catalyze scientific advances benefitting the GoM region in the long run. In the beginning of this work, literature survey was done to understand the drawbacks that are seen in the normal class-H cement like low resistance to chemical attacks, development of microfractures and the like. The literature survey also helped in getting an insight into the various types of supplementary cementitious materials, cement additives that were added to enhance the properties of the cement. Also, the material needs to be compatible with the natural geological formation to ensure a robust plugging.

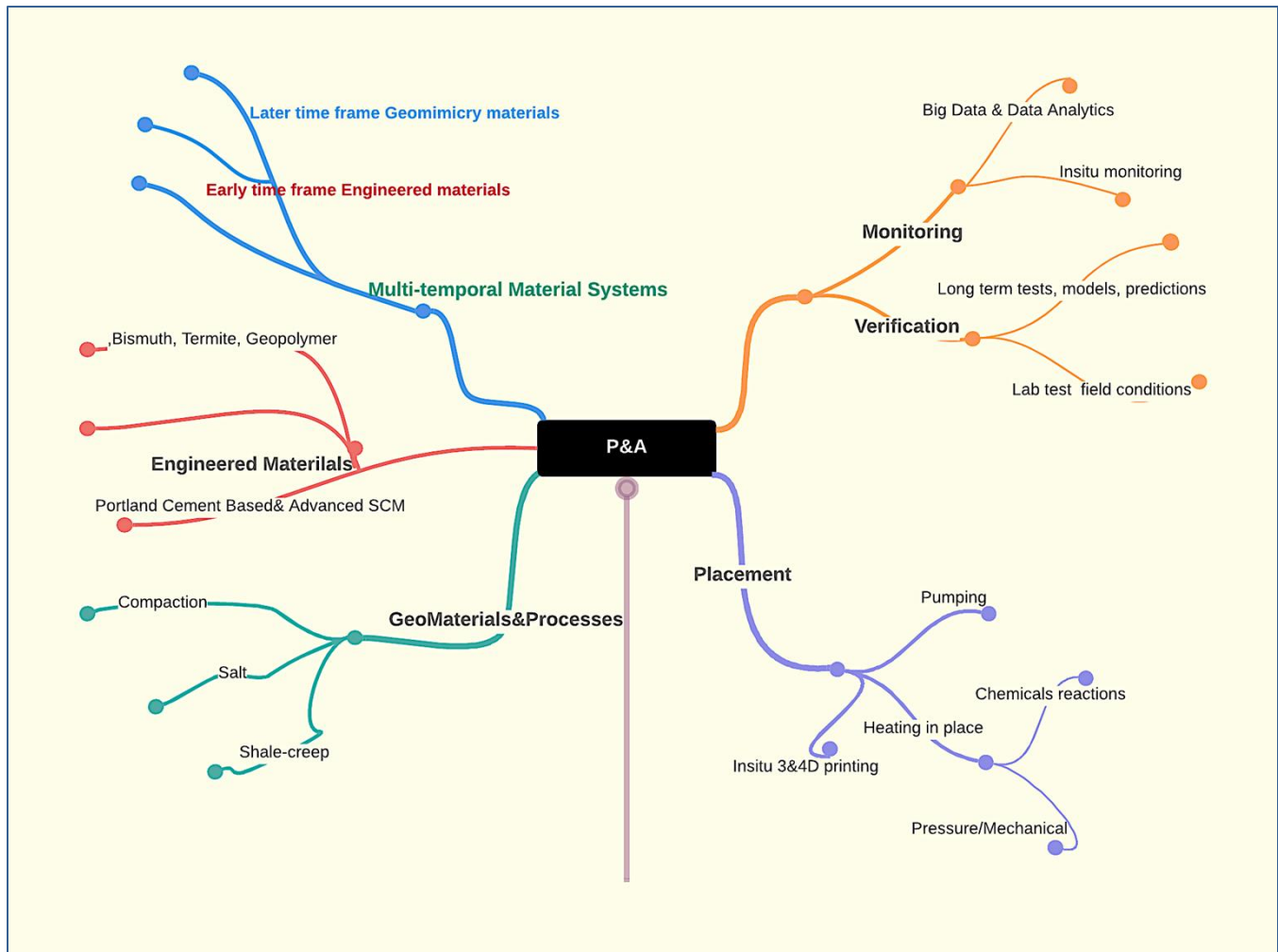


Fig.1: An outlook into designing barrier materials for plugging and abandonment applications.

Aim of this research is to design a better barrier material. The key points to be considered for a good barrier material are:

- 1) Reduction of porosity and permeability;
- 2) Increasing the strength and resilience;
- 3) Compatibility with the geological formations;
- 4) Resistance to chemical attacks;
- 5) Durability in high temperature and pressure conditions.

In order to achieve these properties, it is a matter of utmost importance to choose the right material. Class-H cement is by far the most reliable base hydraulic barrier material which had been used for wellbore construction and plugging applications. In this research, the aim is to decide a right additive that can be added to Class-H cements. Various materials like pozzolans, Blast furnace slag, Silica fume and fly ash had been studied and are being commonly used with cement for various applications. Among all of them, zeolites had piqued our interest as they provide a means for engineerable properties. In addition, the fibrous and porous morphology of the zeolites act like a substrate for the crystal growth of cement during hydration and had shown an increase in the strength and chemical stability of the cement.

Poon C.S. et al [1], Chen J.J. et al [2] Ahmadi B et al [3], and Feng N.Q et al [4], had shown an increase in the strength of the cement composition on addition of zeolites. V. Lilkov et al [5], had done an extensive study on how addition of various zeolites effects the hydration of cement by studying the hydration products of cement. Poon C.S. et al had also shown that the porosity of cement samples was affected by the addition of zeolites. Th. Perraki et al [6] had studied the early hydration characteristics of cement on addition of zeolites. The effect of zeolite addition had also been compared with silica fume and metakaolin additions by Valipour M. et al [7]. Markiv T. et al [8] had tested the freeze thaw resistance, as well as the drying shrinkage properties of zeolite added cement. Pyatina T et al., [9] had shown that a special zeolite composition could show self-healing properties. Rice S.B. et al [10] had done an extensive morphological study to understand the natural zeolite formation. Pacewska et al [11] had studied the effect of waste zeolites from Fluidized Bed Catalytic cracking on hydration properties of cement. Najimi M. et al [12] had studied the effect of adding zeolites on resistance towards sulfate attack, workability as well as freeze thaw resistance. Nagrockiene, D. et al [13] had shown the effect of zeolite additions on strength, freeze thaw resistance and lowered water absorption.

With the available information from literature, we chose zeolites as our materials of choice. The first step is to study the properties of these zeolites to have an idea of how they would react with cement under sub surface conditions. In most of the literature studied, the morphological characters of various types of plain zeolites like clinoptilolite were studied and it was noted that they had close resemblance to the CSH particles which are observed in cement hydration. This similarity results in a synergistic effect since zeolite gets homogeneously distributed in cement without separating out as different phases which could add to the overall strength of the cement. Once the zeolites are studied to get an idea of chemical, physical and morphological properties, they could be used to be added to cement in various compositions to check the physical, petrophysical and morphological properties of cement.

## Methods and materials

In this study, the chemical properties of a zeolite of interest Ferrierite was studied. In the first part, the plain zeolite rock was carefully cut into small pieces with at least two parallel faces and then polished to a uniformity of up to 3 $\mu$ m by using high precision polishing. These polished samples were dried, and carbon coated to be observed under the scanning electron microscope. Ferrierite was then powdered and passed through a 425 $\mu$ m sieve to achieve a uniform size distribution with particles no larger than 425 $\mu$ m. Some plain ferrierite powder was studied under the SEM to get an idea of the basic elemental composition and morphological features.

This powdered form of ferrierite was then exposed to different chemical conditions like those observed at the sub-surface. The focus of this research is to check whether the ferrierite retains its zeolitic morphology of aluminosilicate networks after exposure to these harsh conditions. It is required that the zeolite maintains the chemical and elemental composition without showing any signs of phase change or hydraulic activity in order to be considered as a good supplementary cementitious material. The following

solutions had been prepared to simulate sub-surface chemical conditions. Also, Oil was added to see if there would be any change on interaction with organic material like organic based drilling fluids.

| Condition       | solution              | Quantity                  |
|-----------------|-----------------------|---------------------------|
| High pH         | CaOH solution (pH 13) | Until pH reaches 13       |
| Acidic (Low pH) | HCl solution (1N)     | 500mL                     |
| Brine           | NaCl Solution (35ppt) | 17.5gms in 500mL DI water |
| Water           | DI water              | 500mL                     |
| Oil             | Mineral oil           | 50mL                      |

Table 1: Compositions of different solutions to simulate sub-surface conditions

2.5 grams of Ferrierite was immersed in 250 mL of pH 13 CaOH (Calcium Hydroxide) solution, 1N HCl (Hydrochloric acid) solution, 35ppt NaCl (Sodium Chloride) solution, de-ionized water and 25mL of mineral oil. CaOH, HCl and NaCl were acquired from fisher scientific. The Change of atomic percent of the various elements in Ferrierite were studied after keeping them in the above solutions for a week at 95°C. The samples were regularly checked, and the solution level was maintained all through out. After one week, the powders were washed, clean repeatedly with DI water to remove excess of the chemicals and collected on Millipore paper. The sample which was suspended in oil was washed repeatedly with isopropyl alcohol to remove the oil from the sample and collected in Millipore paper similar to the other samples. They are then slowly transferred off to petri dishes, labelled and left for drying. Once the samples were dried thoroughly, they were taken on to carbon taped microscopy holders and carbon coated before performing electron microscopy.

The data was obtained by performing EDS and SEM analysis of the samples. EDS would give us an understanding of the elemental composition of the ferrierite. The reason for this kind of an analysis is to observe if there is any change in the elemental composition after interaction with the sub-surface chemical conditions. SEM is used to take high magnification images of the ferrierite in order to observe the morphological properties and if there is any change after interaction with the sub-surface chemical conditions. This was done using FEI Quanta 600 Scanning electron microscope equipped with a Bruker EDS system. XRD was done using Bruker D8 advance X-ray diffractometer to confirm the phase present in our material and compare it with the standard ferrierite XRD data from the International Centre for Diffraction Data.

In order to get an understanding of how this cement composition is going to work, we use an existing zeolite cement formulation in which ferrierite is interground with cement clinker, which had been used for geothermal applications called Flexcem®. Intergrinding produces a bimodal particle size distribution between the harder clinker and the softer zeolite resulting in increased strength properties. This cement is claimed to be showing self-healing properties[9] in geothermal wells. One of the purposes of this research is to see similar characteristics when added to Class-H cement which is currently in use for wellbore plugging applications. The study would include getting an understanding of how the zeolite would interact at different sub surface chemical conditions and with impurities observed in drilling and completions.

Once the properties of this zeolite (ferrierite) are thoroughly studied, it would be mixed with Class-H cement in varying proportions and tested for physical and petrophysical properties. The goal as mentioned earlier is to optimize this cement design for wellbore plugging application.

## Results and discussion

The EDS results obtained for the chemically treated ferrierite had shown a variation in the atomic percentages of the various elements present in it. These variations could be related to the interactions of ferrierite with these chemical solutions. Further, we would like to investigate the interactions of this material with cement and relate the changes in the elemental compositions to the amount of zeolite that is added to the cement hydration. Cement samples would be prepared after adding ferrierite and the physical and petrophysical properties of the material would be tested.

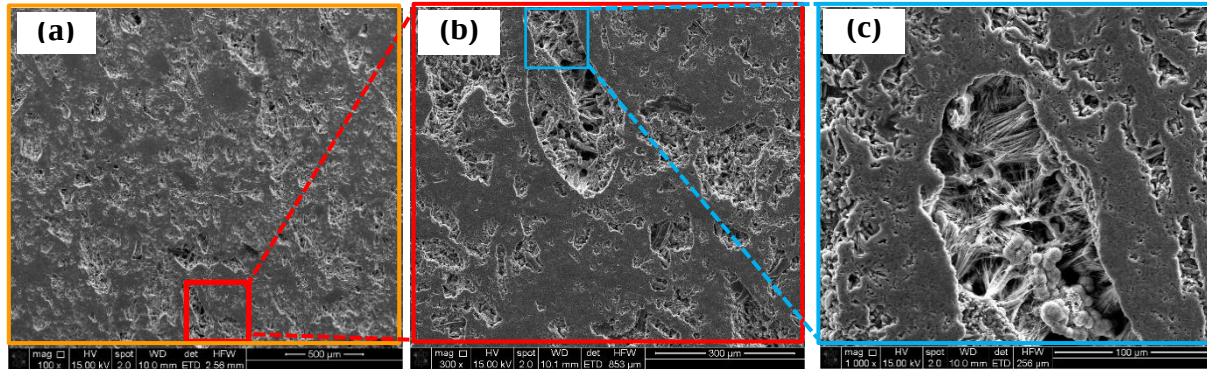


Figure 2: SEM images of Ferrierite samples polished and carbon coated: **(a)** Low magnification image of Ferrierite at 100x; **(b)** Higher magnification at 300x; **(c)** High magnification image at 1000x showing the ferrierite crystal networks.

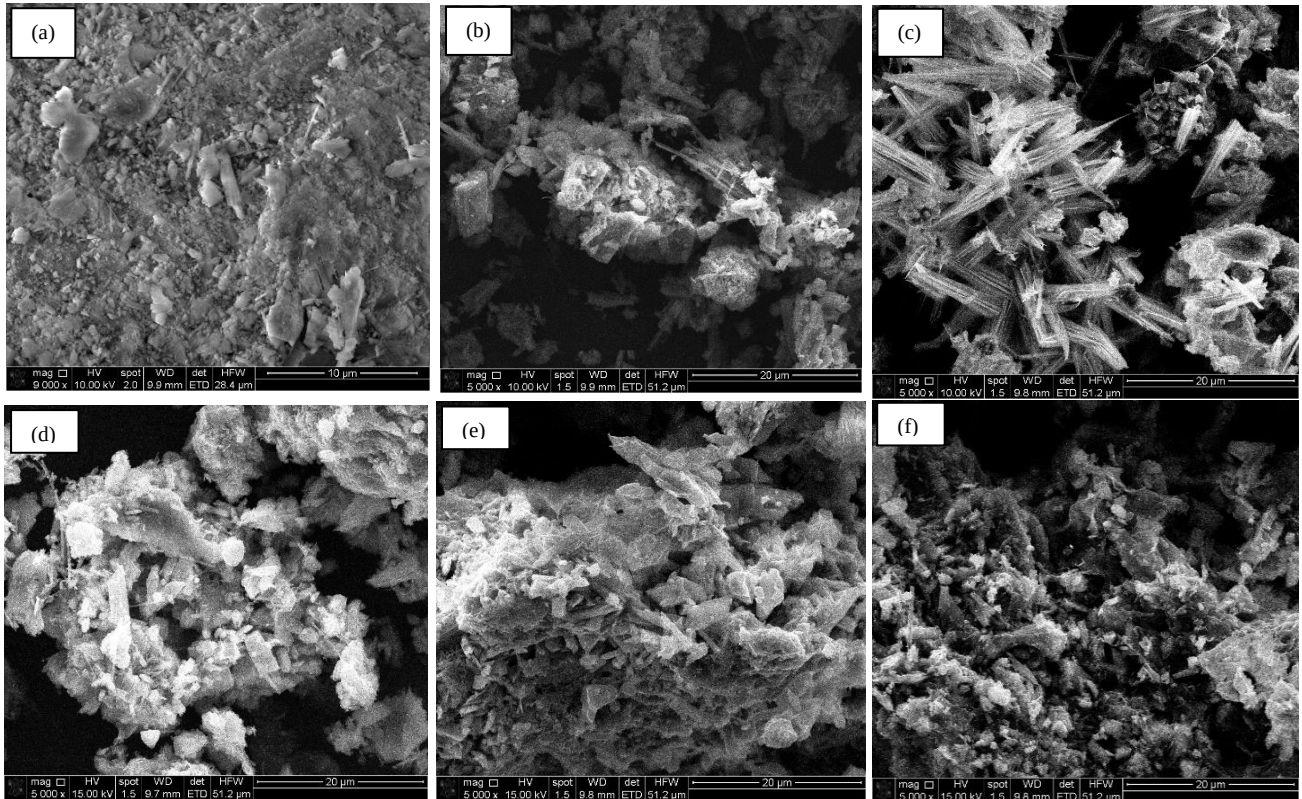


Fig.3: (a) Plain ferrierite (Control); (b) ferrierite in HCl; (c) ferrierite in CaOH; (d) ferrierite in NaCl; (e) ferrierite in DI Water, (f) ferrierite in oil.

|           |               | Fer.<br>Control | Fer.CaOH | Fer.HCl | Fer.NaCl | Fer. Oil | Fer.<br>Water |
|-----------|---------------|-----------------|----------|---------|----------|----------|---------------|
| Element   | At.<br>Number | Atom%           | Atom%    | Atom%   | Atom%    | Atom%    | Atom%         |
| Oxygen    | 8             | 65.69           | 41.57    | 63.32   | 58.72    | 64.03    | 60.30         |
| Sodium    | 11            | 1.1             | 0.10     | 0.01    | 2.46     | 1.13     | 1.06          |
| Magnesium | 12            | 0.72            | 0.36     | 0.28    | 0.49     | 0.56     | 0.46          |
| Aluminum  | 13            | 5.37            | 2.20     | 2.70    | 4.68     | 4.34     | 4.71          |
| Silicon   | 14            | 24.43           | 19.54    | 33.36   | 30.95    | 26.60    | 30.08         |
| Potassium | 19            | 2.04            | 0.06     | 0.31    | 1.86     | 2.19     | 2.57          |
| Calcium   | 20            | 0.45            | 35.72    | 0.00    | 0.00     | 0.23     | 0.17          |
| Iron      | 26            | 0.21            | 0.45     | 0.01    | 0.83     | 0.93     | 0.64          |

Table 2: atomic percentages of various elements in ferrierite after treating them in aforementioned chemical conditions.

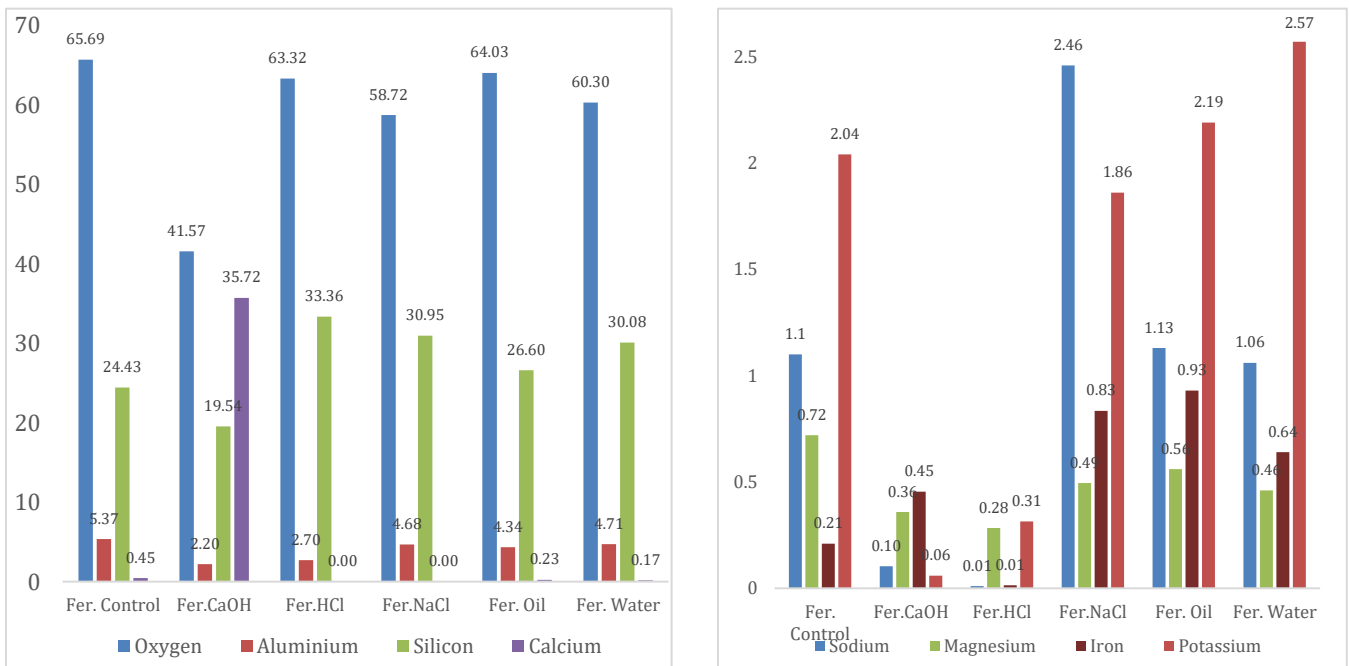


Fig.4: The atomic percentage variation of various elements in the zeolite on exposure to sub-surface chemical conditions.

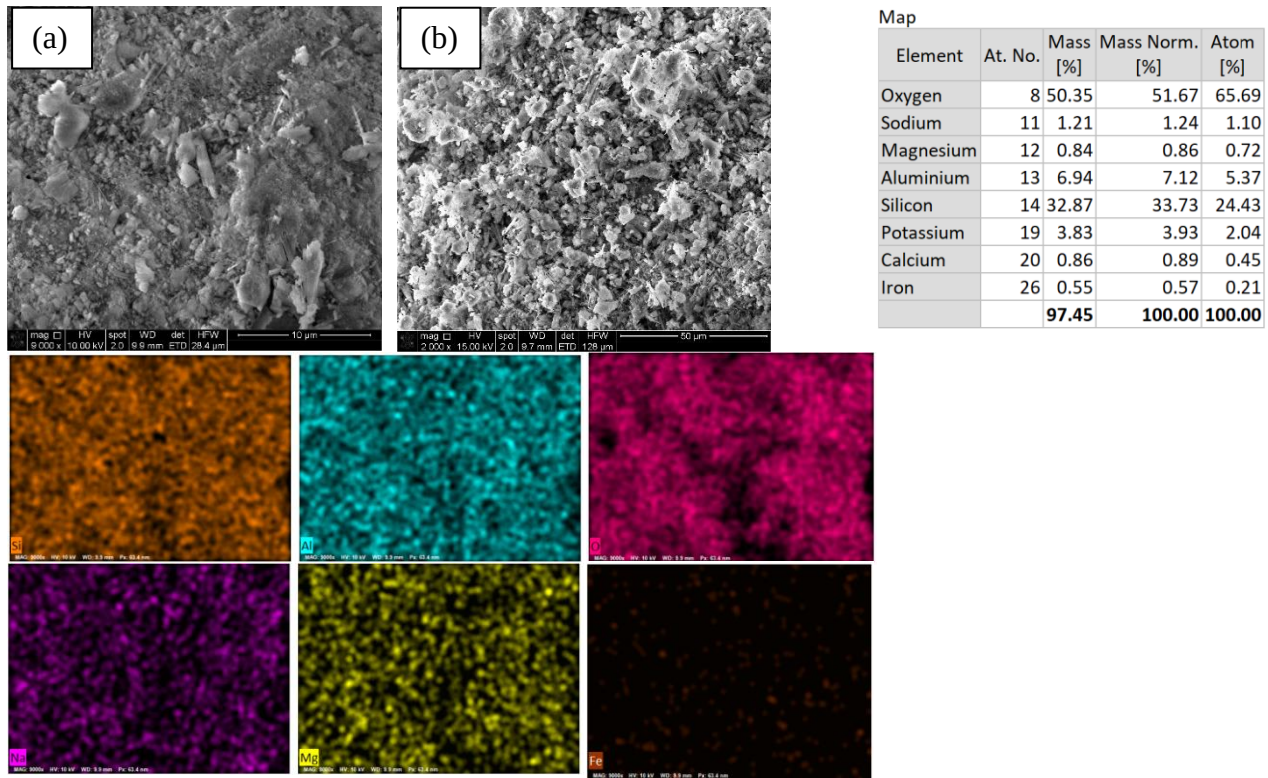


Fig.5: Plain ferrierite (Control); elemental maps.(a) Low mag 100x; (b)High mag 5000x

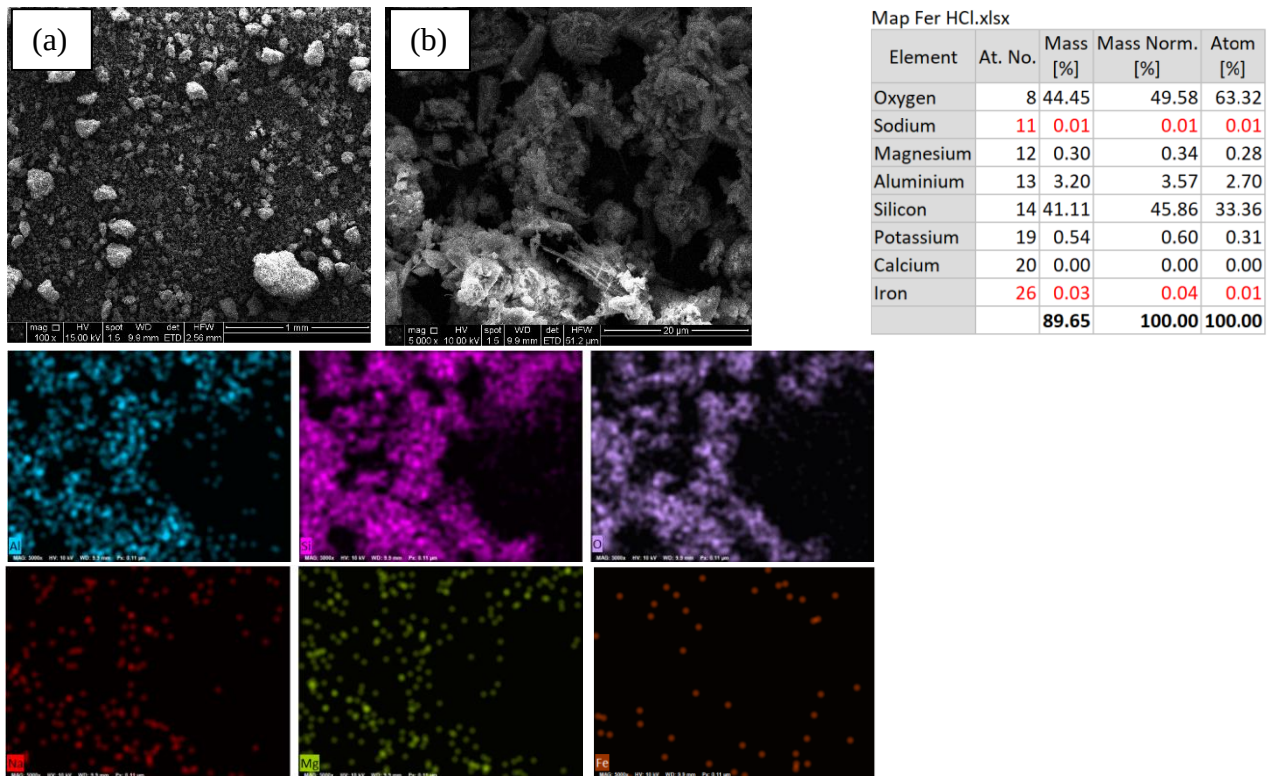
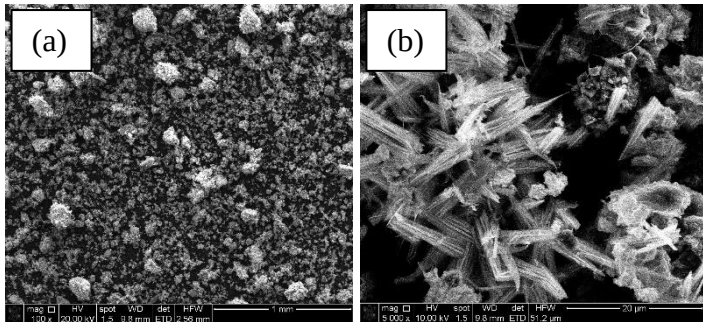


Fig.6: ferrierite in HCl; elemental maps. (a) Low mag 100x; (b)High mag 5000x



Ferrierite CaOH.xlsx

| Element   | At. No. | Mass [%] | Mass Norm. [%] | Atom [%] |
|-----------|---------|----------|----------------|----------|
| Oxygen    | 8       | 32.53    | 24.24          | 41.57    |
| Sodium    | 11      | 0.12     | 0.09           | 0.10     |
| Magnesium | 12      | 0.43     | 0.32           | 0.36     |
| Aluminium | 13      | 2.91     | 2.17           | 2.20     |
| Silicon   | 14      | 26.84    | 20.00          | 19.54    |
| Potassium | 19      | 0.11     | 0.08           | 0.06     |
| Calcium   | 20      | 70.02    | 52.18          | 35.72    |
| Iron      | 26      | 1.24     | 0.92           | 0.45     |
|           |         | 134.20   | 100.00         | 100.00   |

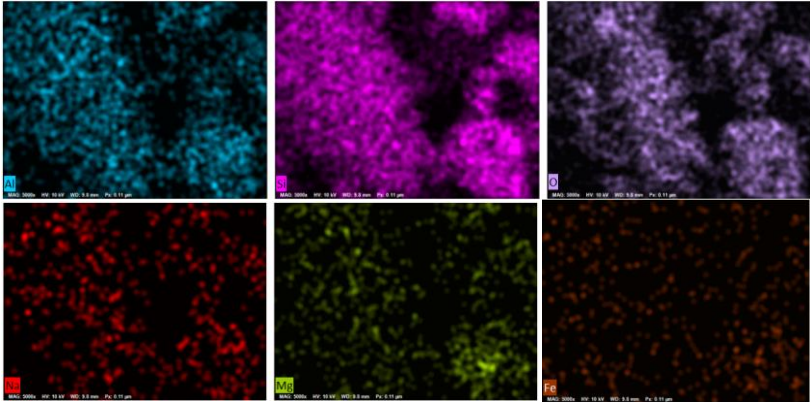
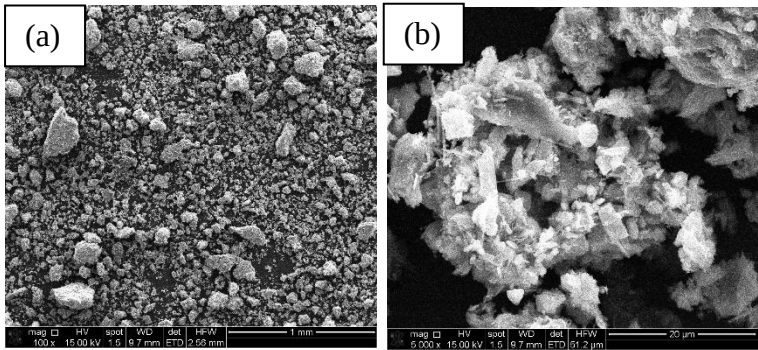


Fig.7: ferrierite in CaOH; elemental maps. (a) Low mag 100x; (b)High mag 5000x



Map Ferrierite NaCl.xlsx

| Element   | At. No. | Mass [%] | Mass Norm. [%] | Atom [%] |
|-----------|---------|----------|----------------|----------|
| Oxygen    | 8       | 36.69    | 44.26          | 58.72    |
| Sodium    | 11      | 2.21     | 2.66           | 2.46     |
| Magnesium | 12      | 0.47     | 0.57           | 0.49     |
| Aluminium | 13      | 4.93     | 5.95           | 4.68     |
| Silicon   | 14      | 33.95    | 40.95          | 30.95    |
| Potassium | 19      | 2.84     | 3.43           | 1.86     |
| Calcium   | 20      | 0.00     | 0.00           | 0.00     |
| Iron      | 26      | 1.82     | 2.19           | 0.83     |
|           |         | 82.91    | 100.00         | 100.00   |

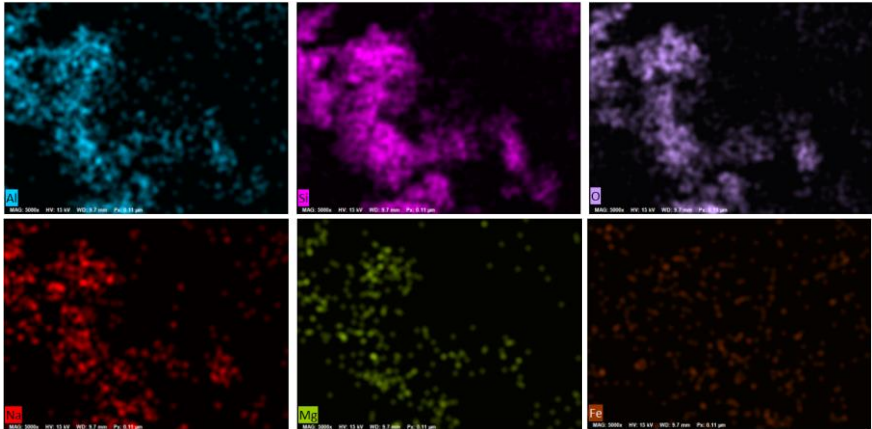
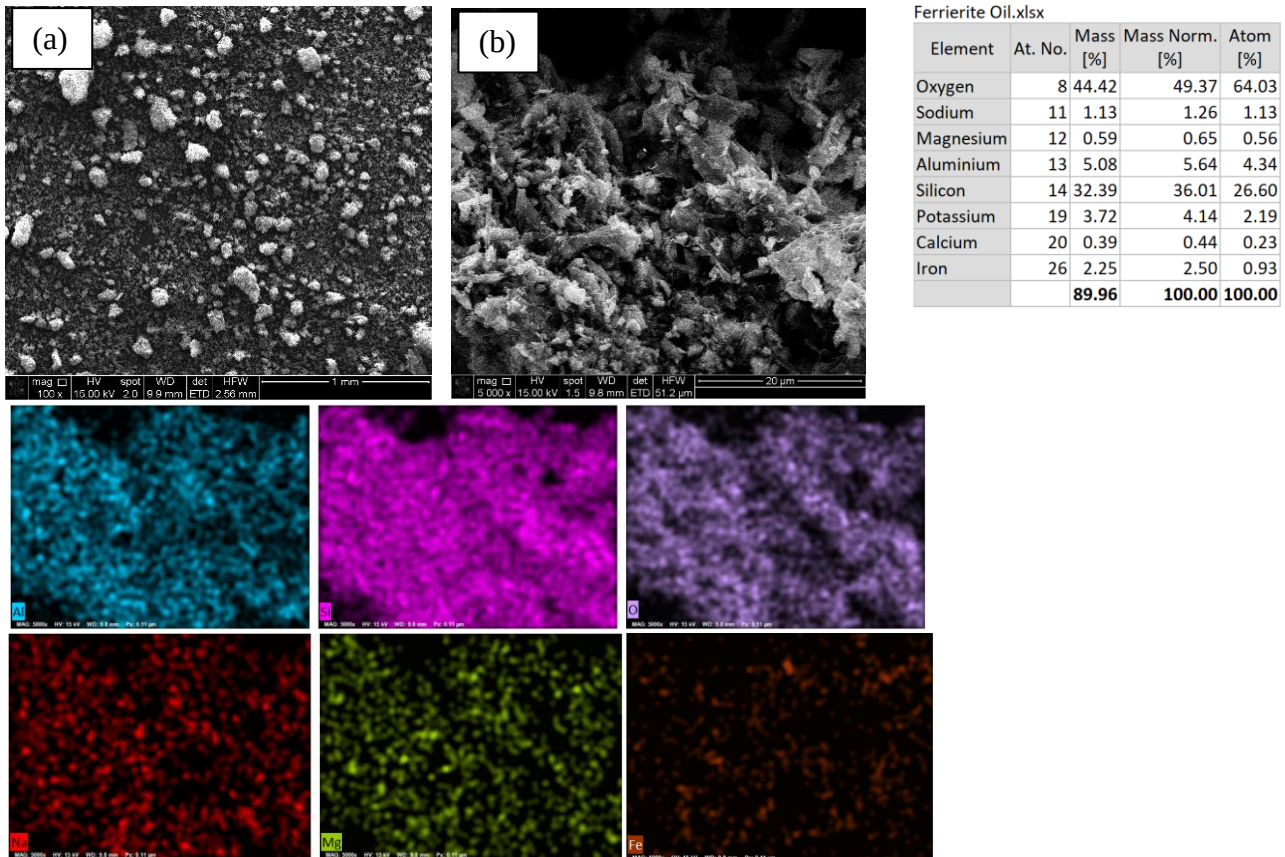
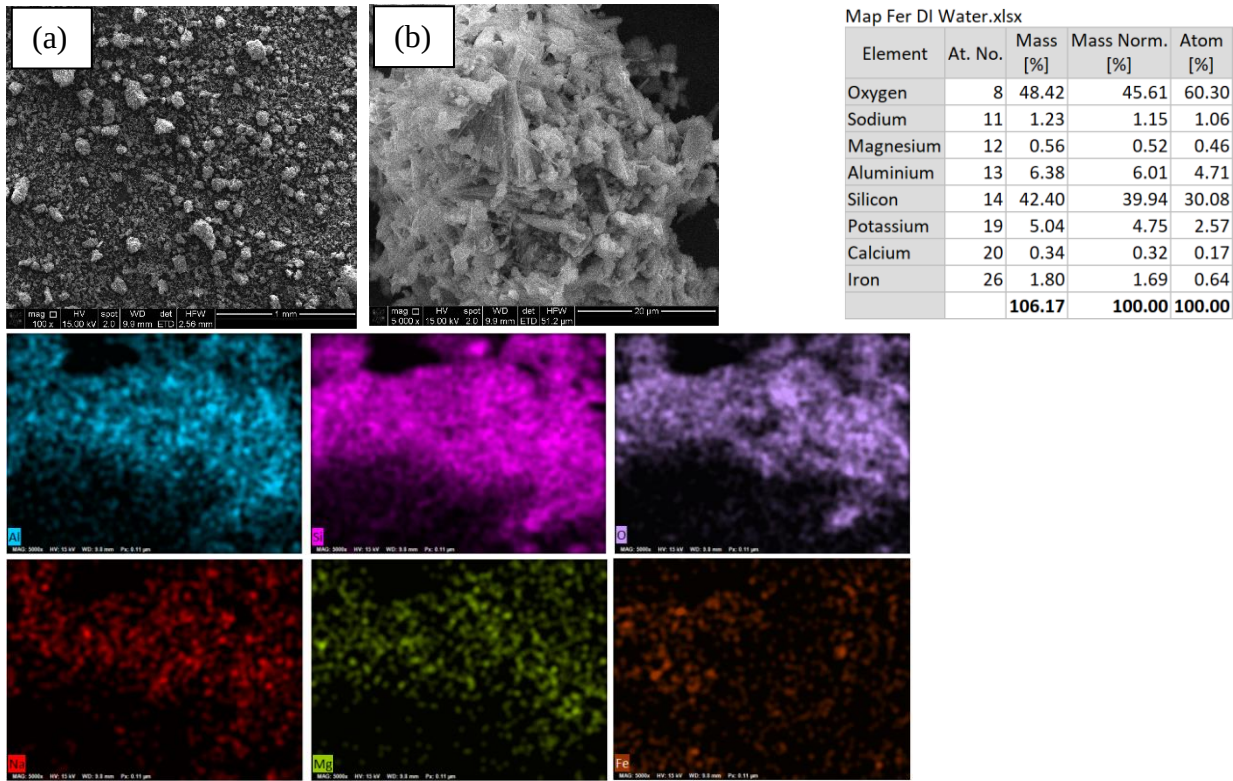


Fig.8: ferrierite in NaCl; Elemental maps. (a) Low mag 100x; (b)High mag 5000x



The above figures (Fig.5 -Fig.10) are the low and high magnification images of the various ferrierite samples after exposure to chemical conditions synonymous to sub-surface. Also, the elemental compositions were given in terms of atomic percentage of each element. The elemental maps of the main components of the zeolite namely Aluminum, Silicon, Oxygen, Sodium, Magnesium and traces of Iron are shown below the electron micrographs.

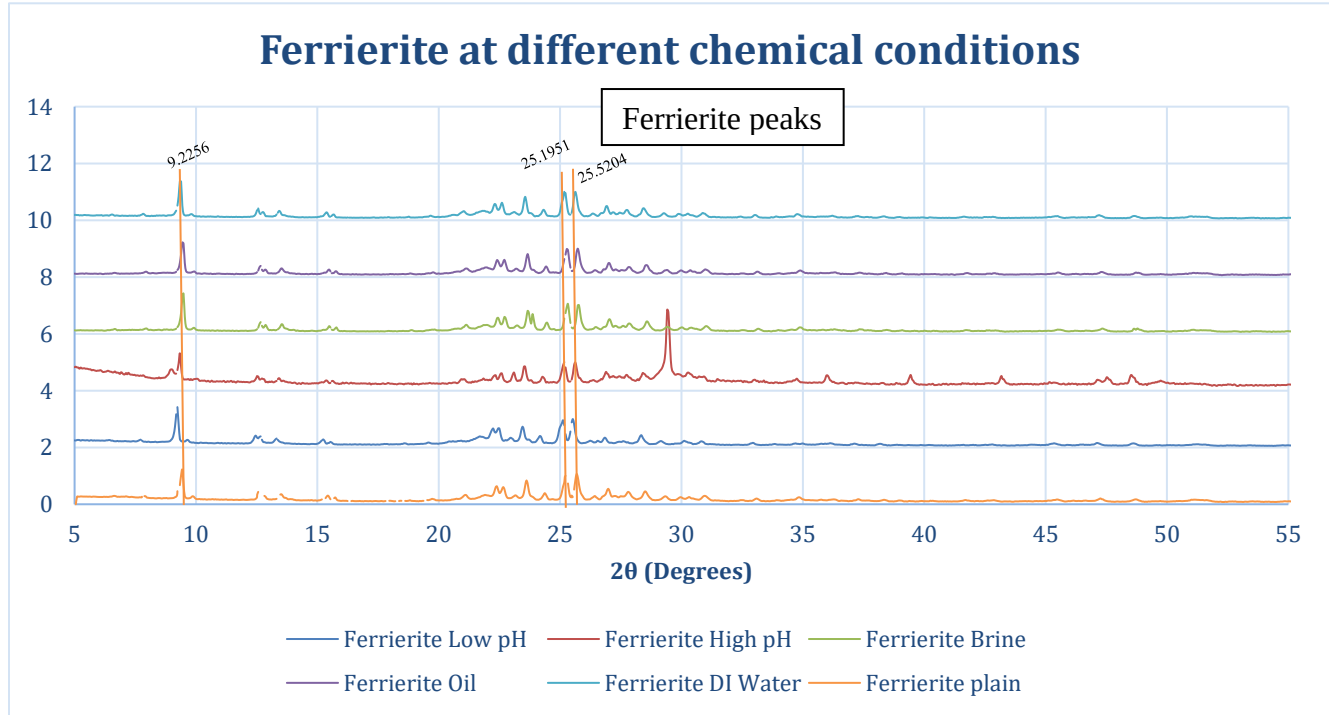


Fig.11: XRD data of ferrierite powder after exposure to various chemical conditions compared with the control sample. Standard ferrierite peaks are highlighted

#### Discussion:

The elemental and morphological analysis shows that these zeolites are slightly affected by these tests in terms of the surface elemental composition but retained the aluminosilicate networks. The addition of CaOH had shown formation of CH crystals in the electron micrographs. Though the EDS results show a change in the composition, the XRD results remain the same showing peaks prominently corresponding to ferrierite. This shows that there is no phase change observed that reinforces the fact that ferrierite is not hydraulic in nature and the retention of phases would be favorable for cement during hydration. It can still act as a scaffolding structure providing a substrate for the hydration to take place. This synergistic nature of zeolite could be the strongest reason for considering ferrierite as an ideal supplementary cementitious material. Also, the possibility of self-healing capabilities makes it an interesting candidate to be studied as an addition to cement.

## Conclusions

Based on the observations, it is a safe choice to use ferrierite as a supplementary cementitious material. Like all other zeolites observed in the literature, ferrierite showed morphological characteristics similar to cement phases which would act as a scaffolding structure or substrate for the cement hydration to take place. This would add to the hydration of cement by homogeneously being a part of the cement phases. Zeolite showed slight changes in the surface elemental compositions on exposure to CaOH and HCl. CH crystals had been observed in the samples exposed to CaOH. The iron content was found to be

the lowest in samples exposed to HCl. Despite these changes in elemental compositions, the XRD results indicate that there are no changes in the phases which reinforces the non-hydraulic nature of ferrierite and its stability when exposed to sub-surface chemical conditions. With these considerations, ferrierite can be chosen as a supplementary cementitious material. Future work is planned to study the effect of the addition of this zeolite to Class-H cement in various compositions and studying their properties.

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