

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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Mileva Radonjic, Sai Vamsi Krishna Vissa
Oklahoma State University



Introduction

- **Abstract Summary:**

- Efficient plugging and abandonment (P&A) – an age old problem
- Need to develop better barrier materials – enhancement of cement properties
- Zeolites – potential way forward – Zeolite of interest - **Ferrierite**
- Exploring the suitability as additive, chemical and morphological properties of zeolite

Problems faced in P&A

- Off shore oil wells – Growing in number.
- Challenging sub surface conditions / offshore P&A:

Reservoir Condition	Geocompatibility Effect
High temperatures and pressures	Drying, shrinkage, development of microfractures
Salinity, pH anomalies	Carbonate leaching and loss of phases
Chemical attacks	Loss of strength, erosion, formation of micro annuli

Table 1: Different sub surface conditions and their effects on cement

Objectives

- To develop Engineered barrier materials for P&A in Gulf of Mexico
- Ultimate goal - developing a robust material for offshore P&A applications
- Achieve geocompatibility of engineered barrier materials
- Overcome drawbacks of Class-H cement

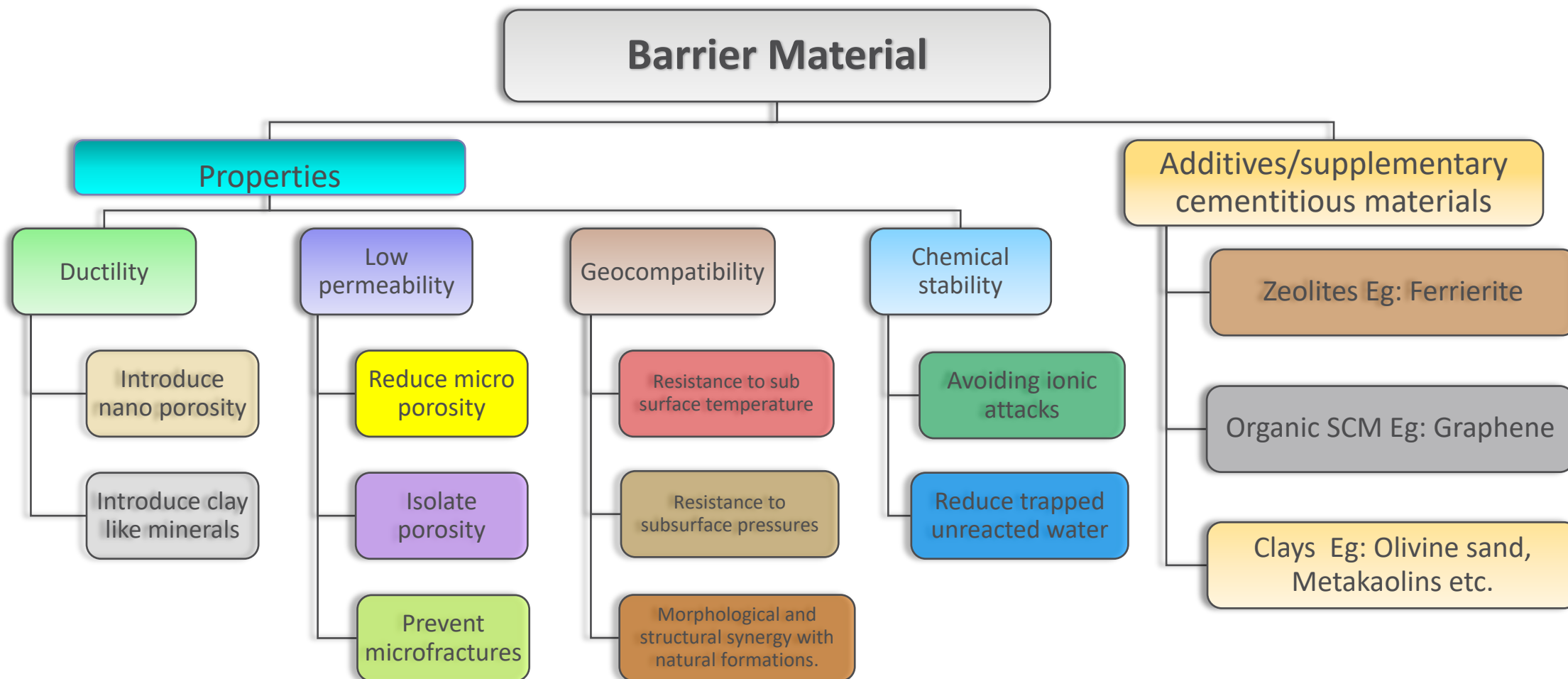
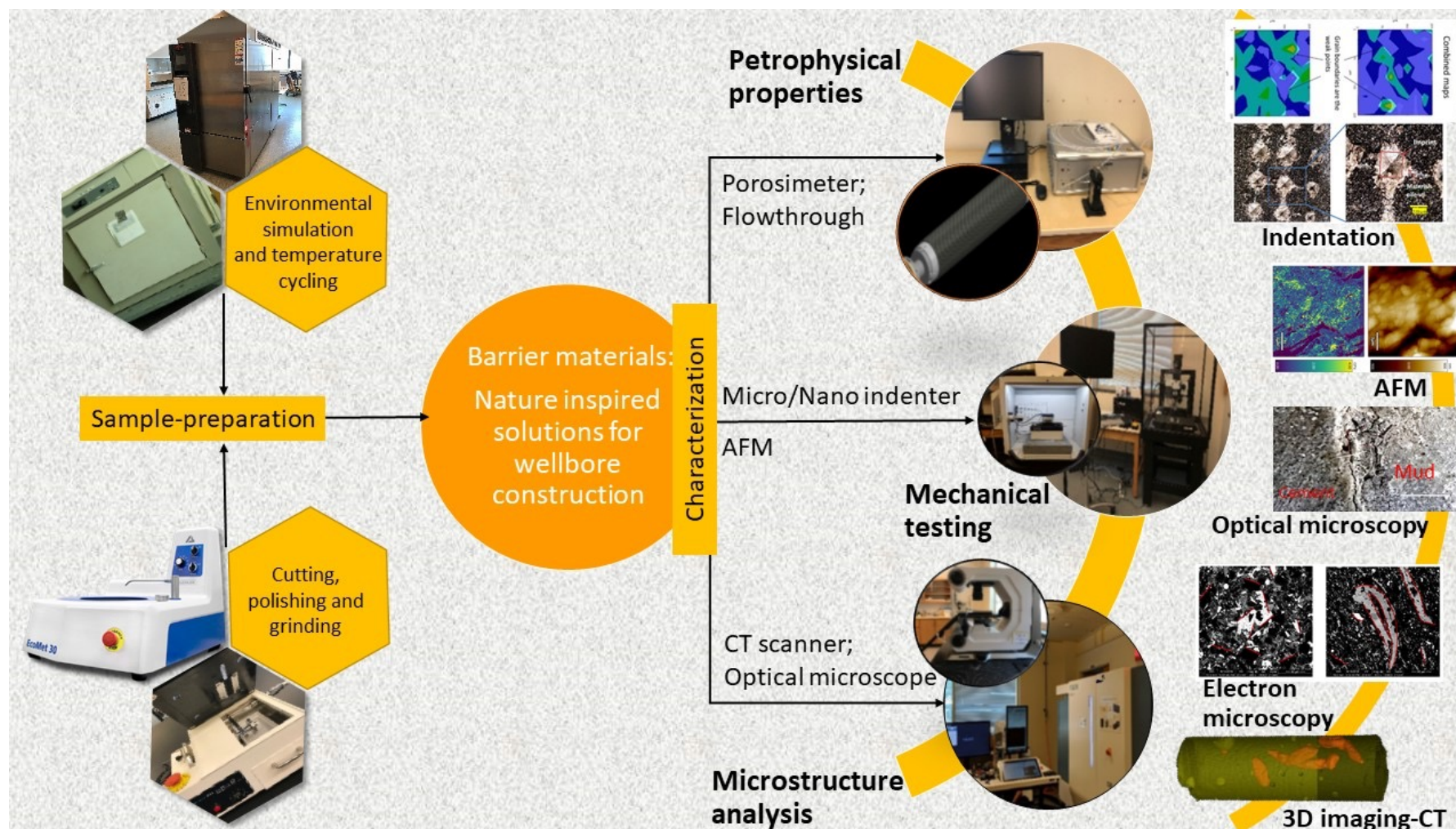
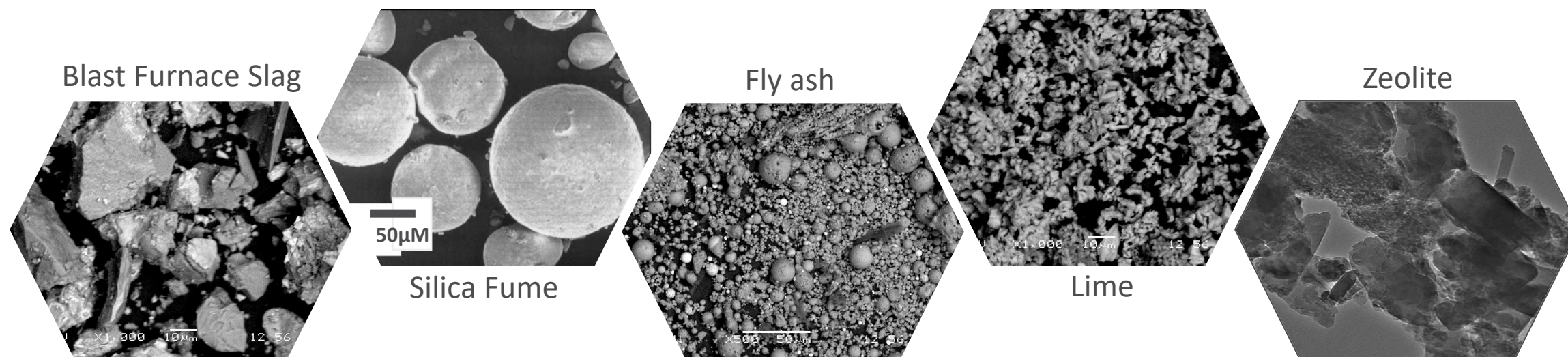


Fig 1. Properties to be achieved in order to obtain a robust hydraulic barrier material and additives to be added



Literature review summary

- Additives - enhance cement properties;
- supplementary cementitious materials – Examples: Blast Furnace Slag, Silica Fume, Fly ash, pozzolanic materials, zeolites.



Adapted from Murmu et al., (2009); J. Yajun, J.H. Cahyadi, (2003).

Zeolites

- SCM (Supplementary Cementitious material) of choice
- Ferrierite – zeolite shown to self heal fractures [1]
- Morphology similar to CSH crystals $\Rightarrow$ Structural synergy
- Chemical stability $\Rightarrow$ ability to act as scaffolding/substrate for hydration

Ferrierite

- Orthorhombic zeolite mineral with high variation in cation distribution.
- Radiating spherical aggregates with thin needle like translucent crystals.
- Three different Types in Ferrierite group:

Ferrierite-Mg $[\text{Mg}_{0.5}\text{K, Na, Ca}_{0.5}]_6(\text{H}_2\text{O})_{20} [\text{Al}_6\text{Si}_{30}\text{O}_{72}]$

Ferrierite-K $[\text{K, Na, Mg}_{0.5, \text{Ca}_{0.5}}]_6(\text{H}_2\text{O})_{20} [\text{Al}_6\text{Si}_{30}\text{O}_{72}]$

Ferrierite-Na $[\text{Na, K, Mg}_{0.5, \text{Ca}_{0.5}}]_6(\text{H}_2\text{O})_{20} [\text{Al}_6\text{Si}_{30}\text{O}_{72}]$



Fig 3: Clusters of ferrierite-Mg blades from the type locality at Kamloops Lake, British Columbia, Canada. Width of view 10 mm. (3)

Ferrierite SEM

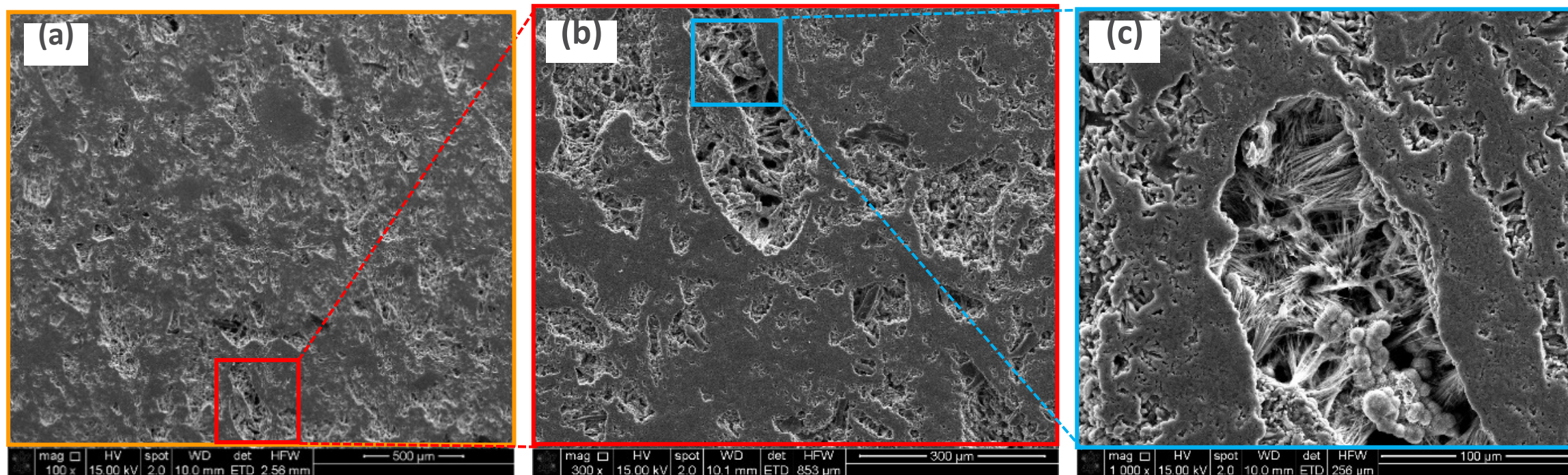


Fig 4. SEM images of Ferrierite samples polished and carbon coated: (a) Low magnification image of Ferrierite at 100x; (b) Higher magnification at 300x; (c) High magnification image at 1000x showing the ferrierite crystal networks

Ferrierite TEM

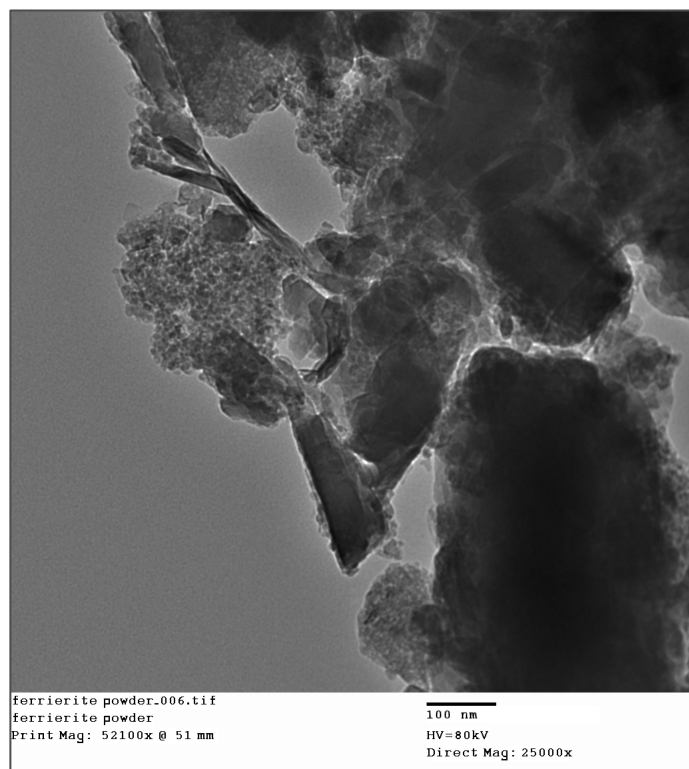


Fig 5. Complex morphology of finely ground Ferrierite at 25000x under TEM

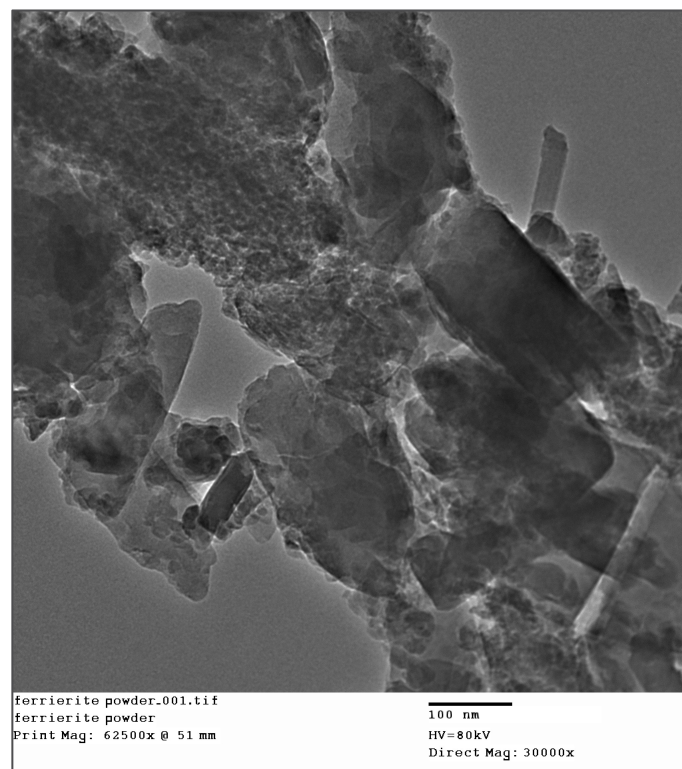


Fig 6. Different crystal phases observed in finely ground Ferrierite at 30000x under TEM

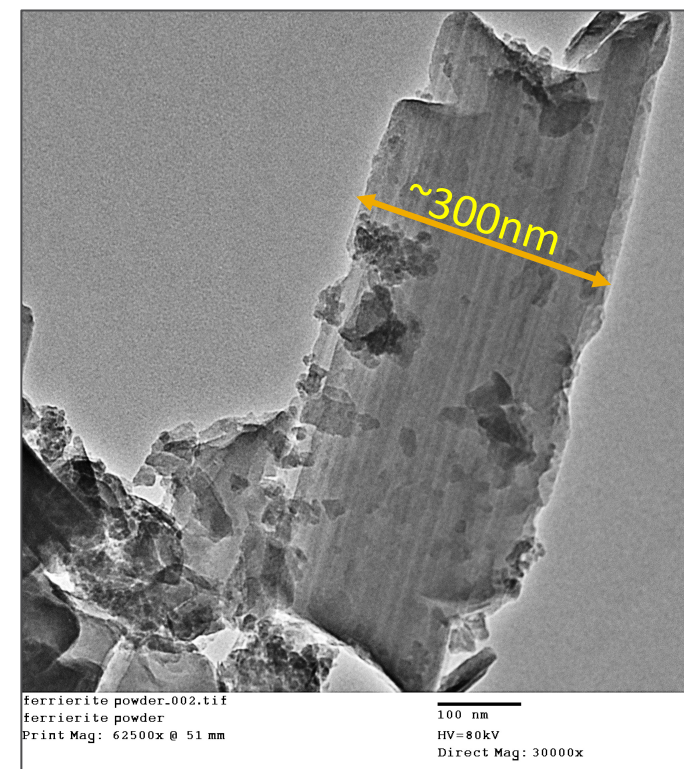


Fig 7. Orthorhombic crystals observed in finely ground Ferrierite at 30000x under TEM

Ferrierite

Study of chemical stability:

- Chemical stability of as received raw zeolite rock was tested.
- Dissolved powdered Ferrierite in following solutions:

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 2: Different chemical solutions to which ferrierite was exposed to at 95°C for one week.

Ferrierite SEM

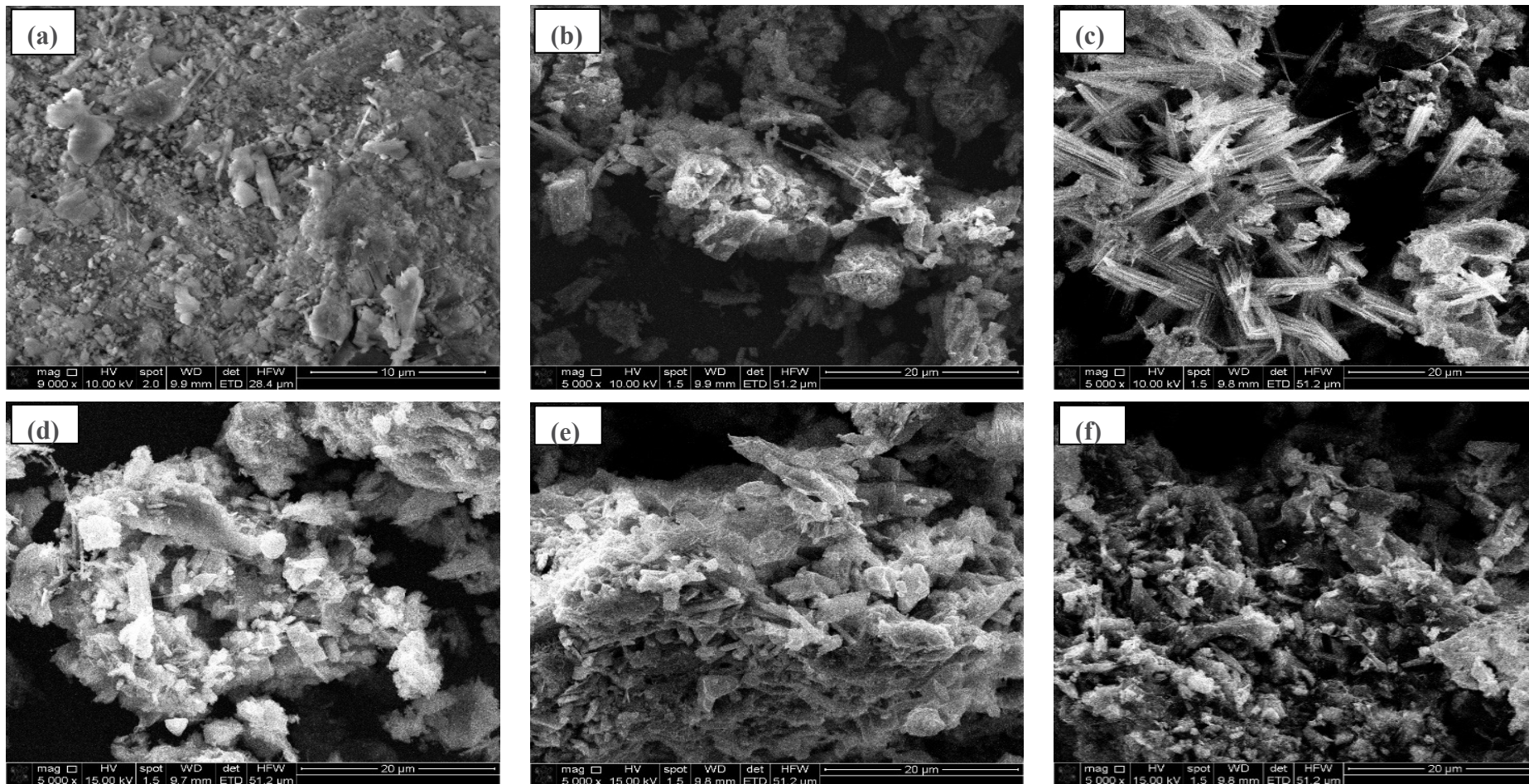


Fig 8. (a) Plain ferrierite (Control); (b) ferrierite in HCl; (c) ferrierite in CaOH; (d) ferrierite in NaCl; (e) ferrierite in DI Water, (f) ferrierite in oil.

Ferrierite EDS

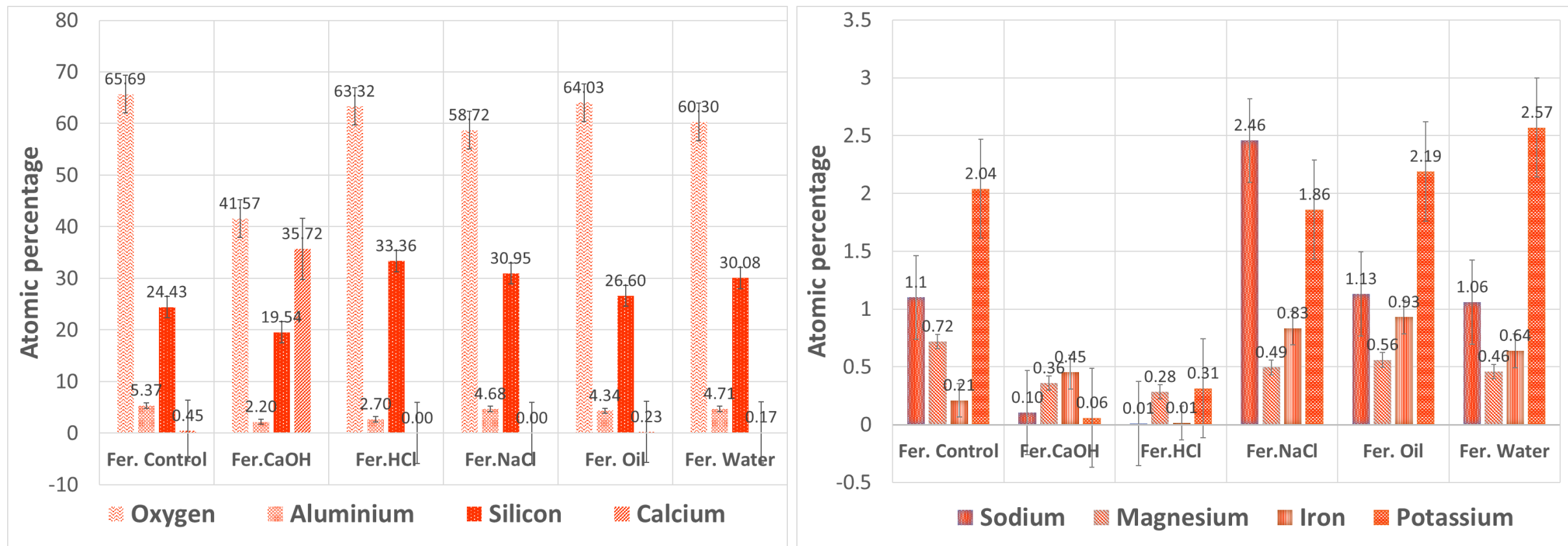
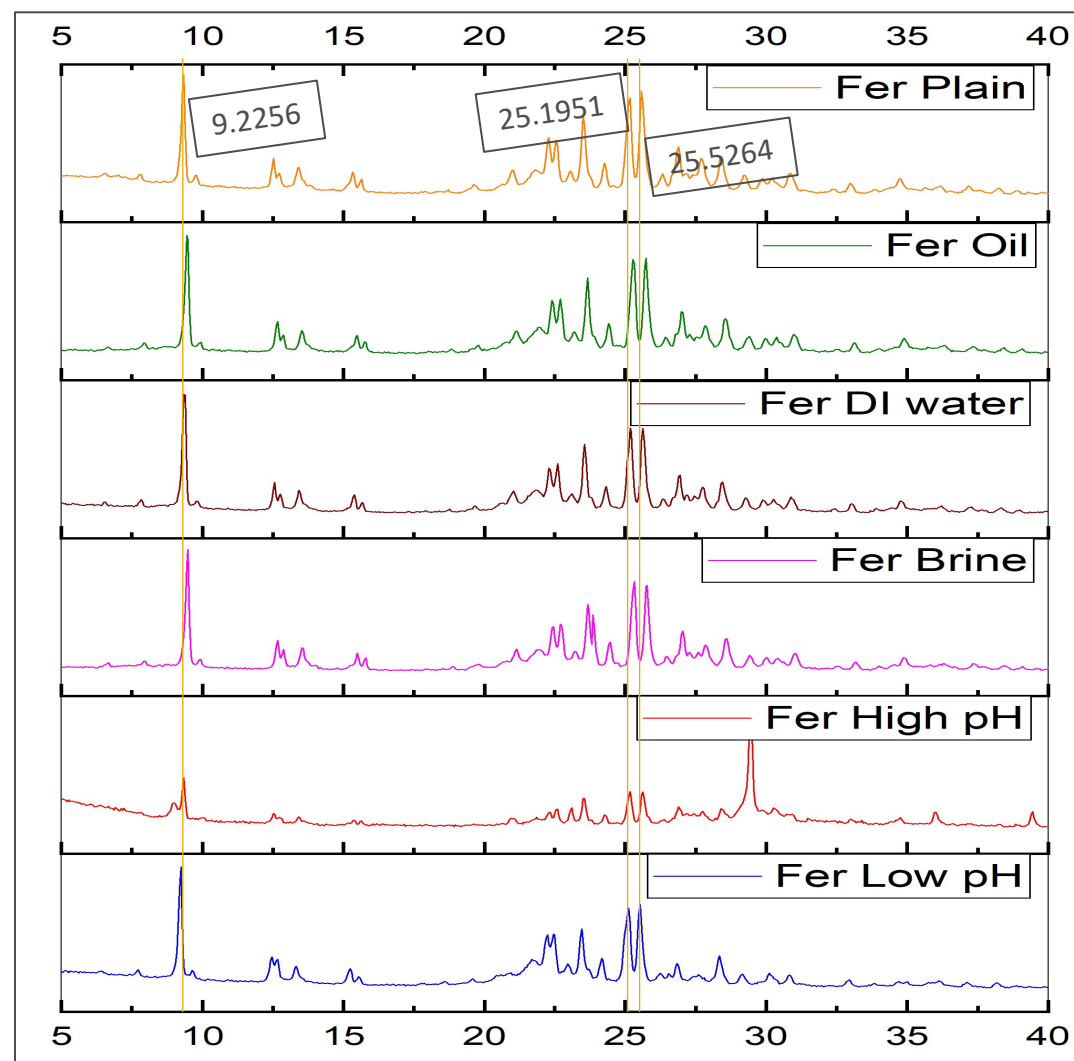


Fig 9. The atomic percentage variation of various elements in the zeolite on exposure to sub-surface chemical conditions.

Ferrierite XRD

- XRD data of ferrierite powder after exposure to various chemical conditions compared with the control sample.
- Standard ferrierite peaks are highlighted.
- Observed no change in the phases after exposure for one week at 95°C.

Fig 10. XRD data of ferrierite powder after exposure to various Chemical conditions- Low pH, High pH, Brine, water, oil and plain ferrierite for reference.



Flexcem®

- Ferrierite based Cement – Developed for Geothermal wells.
- Self healing observed [1].
- 16 PPG formulations based on Class-H slurry designs – showed micro fractures.
- New 16PPG slurry design developed by industry experts – To be tested



Fig 11. Trial Flexcem cement cores Ready for testing

Flexcem®

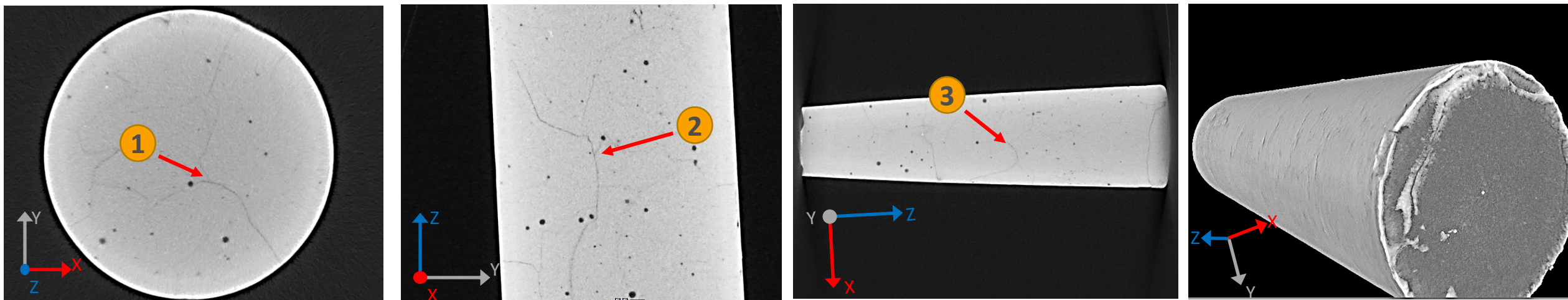


Fig 12. Flexcem® CT images of Class-H based 16PPG slurries; 1,2,3-micro fractures.

Discussion

- The elemental and morphological analysis – chemical stability
- The addition of $\text{Ca}(\text{OH})_2$ – CH crystal formation – affinity to cement phases.
- EDS – Elemental changes
- XRD – Peaks predominantly corresponding to Ferrierite data.
- synergistic nature of zeolite – Scaffolding – expected geocompatibility
- Possibility of self-healing capabilities – Expected to hold pore water

Conclusions

- EDS – Elemental composition suggests chemical stability.
- XRD – Phase stability.
- Ferrierite – Potential seed crystals for hydration.
- Possible holding of pore water – release in event of fracture.

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Image sources

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Thank you

Questions??