Mineralogical and microtextural characterization of eco-friendly concrete for marine infrastructures: Methodologies for the MARINEFF Project

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1. Project MARINEFF

- **Enhance and protect** costal and transitional **water ecosystems** in the cross-border **Channel regions**.
- The main innovation aspects are the **integration of habitats directly into the marine infrastructures** and the inclusion of **recycled shellfish waste** into the concrete.
- Funded by the European Union through the **Interreg VA (France-England) programme**.
- **9 partner institutions** across France and England:

  France: ESITC Caen (coordinator), Muséum National d'Histoire Naturelle, Ports de Normandie, TPC, Vinci Construction, Université Caen Normandie;

  United Kingdom: University of Southampton, Bournemouth University, University of Exeter.

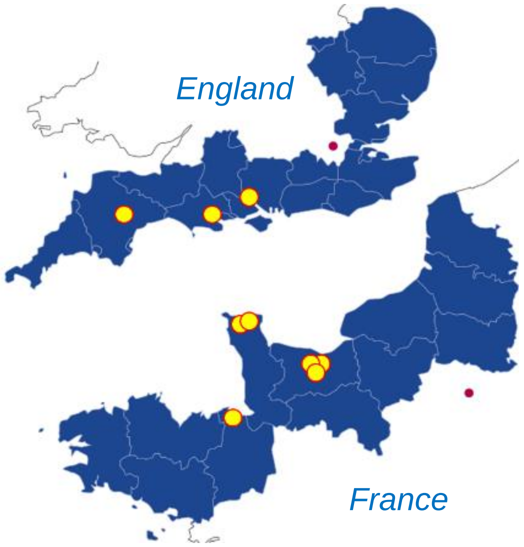
1. Project MARINEFF

- Marine structures - **oyster prism modules**, **dykes**, **boat moorings** and **rockpools**.

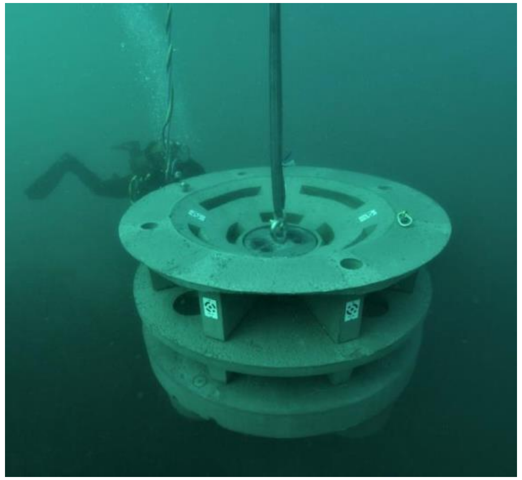
Oyster prism modules

Waterbreak blocks

Rockpools



Map of the eco-engineering deployment sites in FR and UK.



Underwater boat moorings

2. The University of Exeter team

Jens Andersen

John Coggan

Kate Littler

Rich Crane

Gavyn Rollinson

- Investigate the **mineralogy and microtexture of the raw materials**, namely of aggregates, seashells and cements, in order to contribute to the **design of the most adequate concrete mix**.

- Monitor how the **materials perform** technically as well as with respect to **bio-colonisation and bio-diversity upon immersion in the sea**.

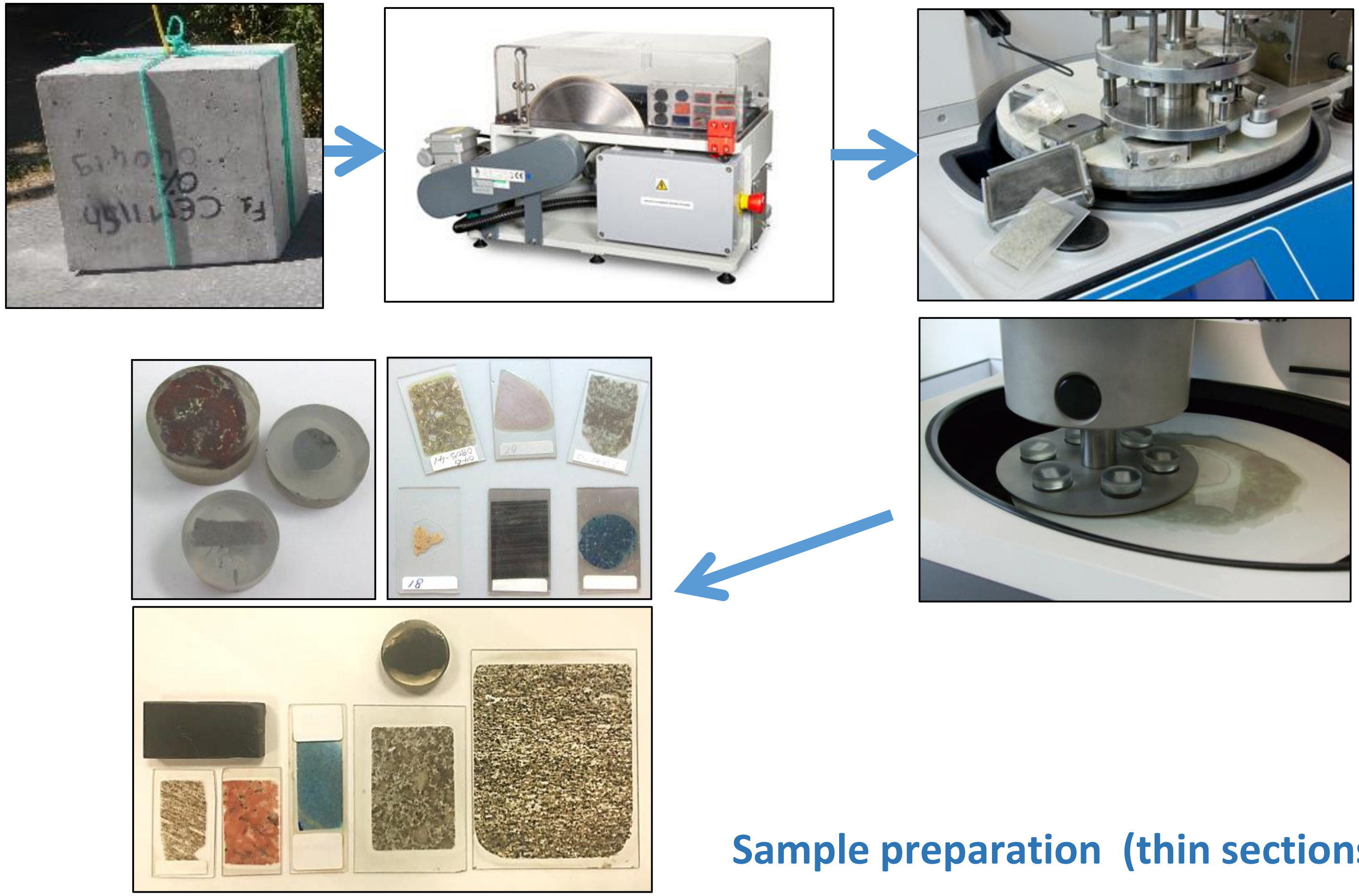
Concrete block immersed for 6 months.

Bio-colonisation present on concrete blocks. (Photo: Jenny Mallinson)

3. Methodologies

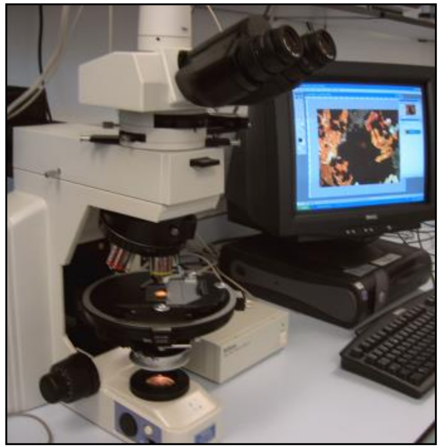
- Optical petrography;
- Scanning electron microscopy analysis;
- Electron probe micro-analysis;
- Automated scanning electron microscopy analysis (QEMSCAN®);
- X-ray diffraction analysis.

3.1 Optical petrography



Sample preparation (thin sections & mounts)

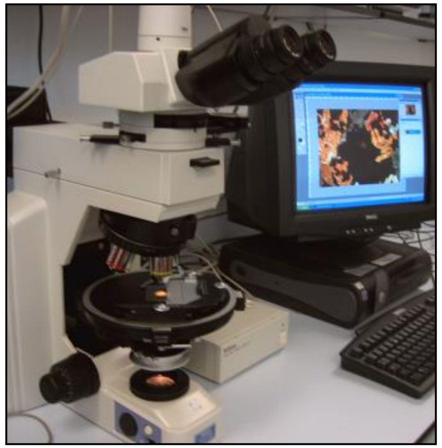
3.1 Optical petrography



Nikon Eclipse E600 Pol microscope, reflected and transmitted light modes with a 5MP digital camera.

- Image magnifications up to 50x;
- Mineralogy, compositional features, quality, workmanship and conformity with standards and specifications (e.g. ASTM C856/C856M, 2020);
- Size, distribution and types of aggregate and their mineral abundances;
- Size, distribution and abundances of phases in the binder;
- Voids, micro-fracturing and other structural defects;
- Presence of supplementary cementitious materials (e.g. blast furnace slag, fly ash, silica fume);

3.1 Optical petrography



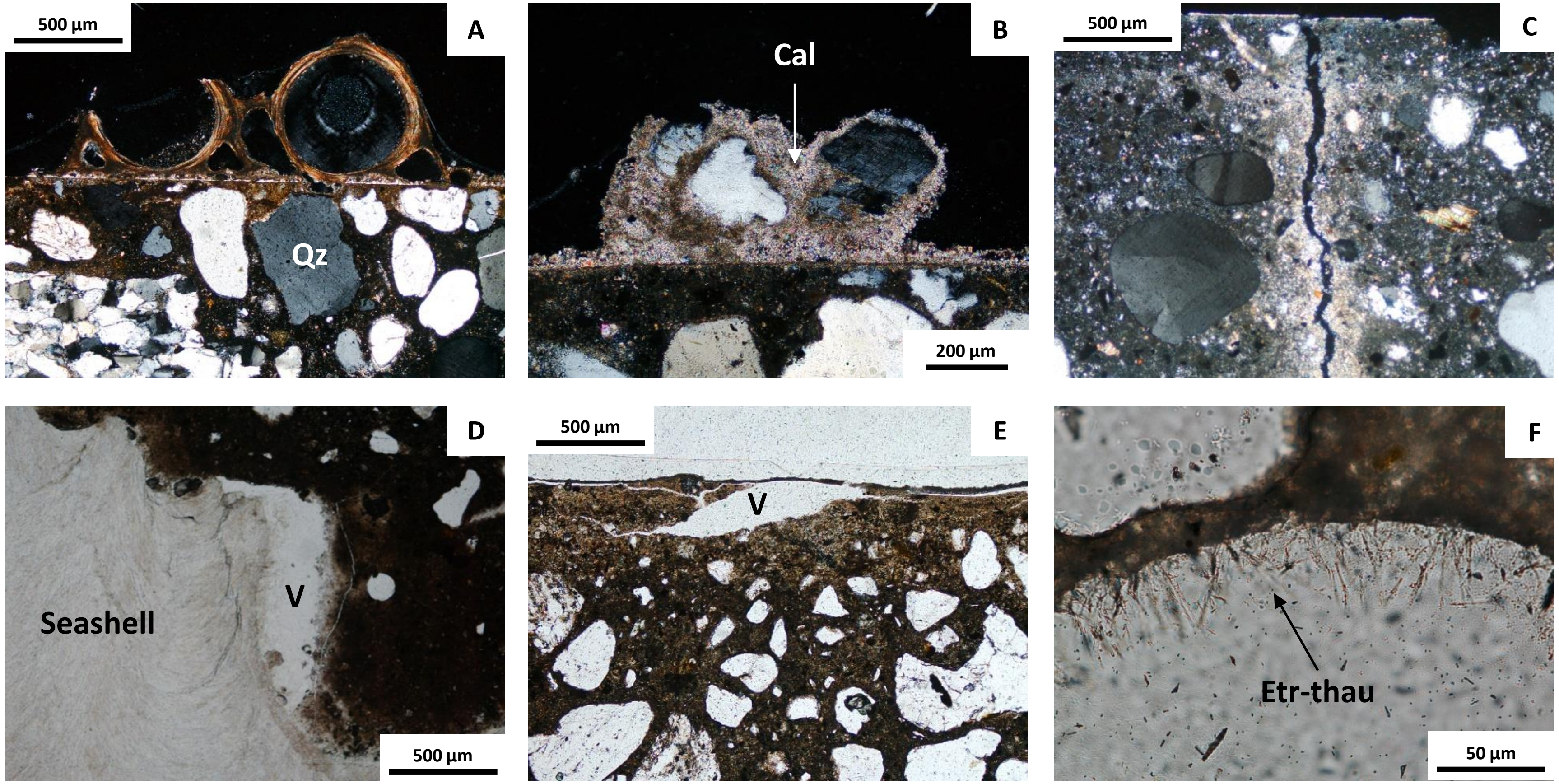
Nikon Eclipse E600 Pol microscope, reflected and transmitted light modes with a 5MP digital camera.

- Type of cement clinker;
- Presence of high alumina cement;
- Original total water to cement ratio;
- Identification of products, causes and progression of cement paste deterioration (e.g. alkali-aggregate reaction, sulphate attack, seawater attack, etc.).

- Does not give direct information on the chemical composition of concrete;
- Not adequate for the investigation of chloride ingress or the presence of plasticisers;
- Optical observation is invariably subjective and dependent on the skills of the observer.

3.1 Optical petrography

- Main mineral phases with special emphasis on minerals formed during seawater attack;
- Carbonated cement paste;
- Effectiveness of the aggregate/seashell-cement paste bonding;
- Cracking, shape and distribution of voids and presence of infillings.



Photos A to C in cross-polarized light. Photos D to F in plane polarized light. Qz – quartz; Cal – calcite; V – void; Etr-thau – ettringite-thaumasite.

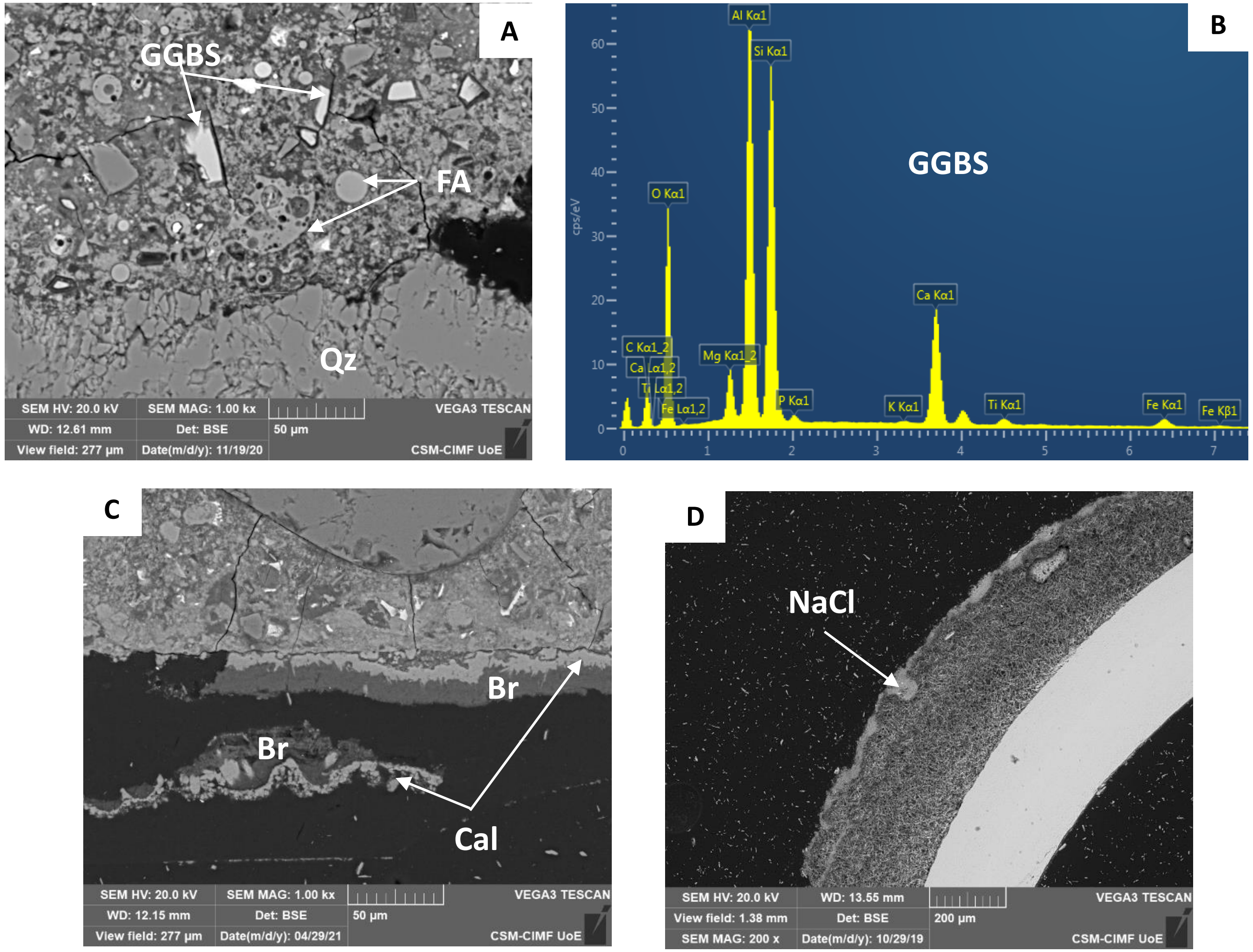
3.2 Scanning electron microscopy analysis

TESCAN Vega

- Image magnifications up to more than 50.000x and resolutions down to 1 nm;
- Observations of very small structures and fine materials (e.g. concrete binder);
- Equipped with energy dispersive detector (EDS) which allows *in situ* chemical analysis and **identification of minerals or phases**;
- Electron imaging involves the collection of: **secondary electrons** (SE) and **backscattered electrons** (BSE).
- **SE imaging** – most reliable for the study of the topography of the sample;
- **BSE imaging** – show contrast due to variations in the chemical composition of a specimen.

3.2 Scanning electron microscopy analysis

- Concrete phases;
- Seawater chemical attack reaction phases (e.g. ettringite, thaumasite and brucite);
- Microtextures and fractures at the nanometre scale.



GGBS – ground-granulated blast furnace slag; FA – fly ash; Qz – quartz; Br – brucite; Cal – calcite.

3.3 Electron probe micro-analysis

JEOL JXA-8200 Superprobe

- Optimised for **quantitative chemical analysis**;
- Fitted with wavelength dispersive spectrometers (WDS) that have **higher sensitivity and better spectral resolution** than the SEM-EDS;
- The signals are calibrated against **standard reference materials** for quantitative analysis;
- The analysis allows for detailed **determination of mineral compositions and formulae**.

Lower spatial resolution in comparison to the SEM-EDS.

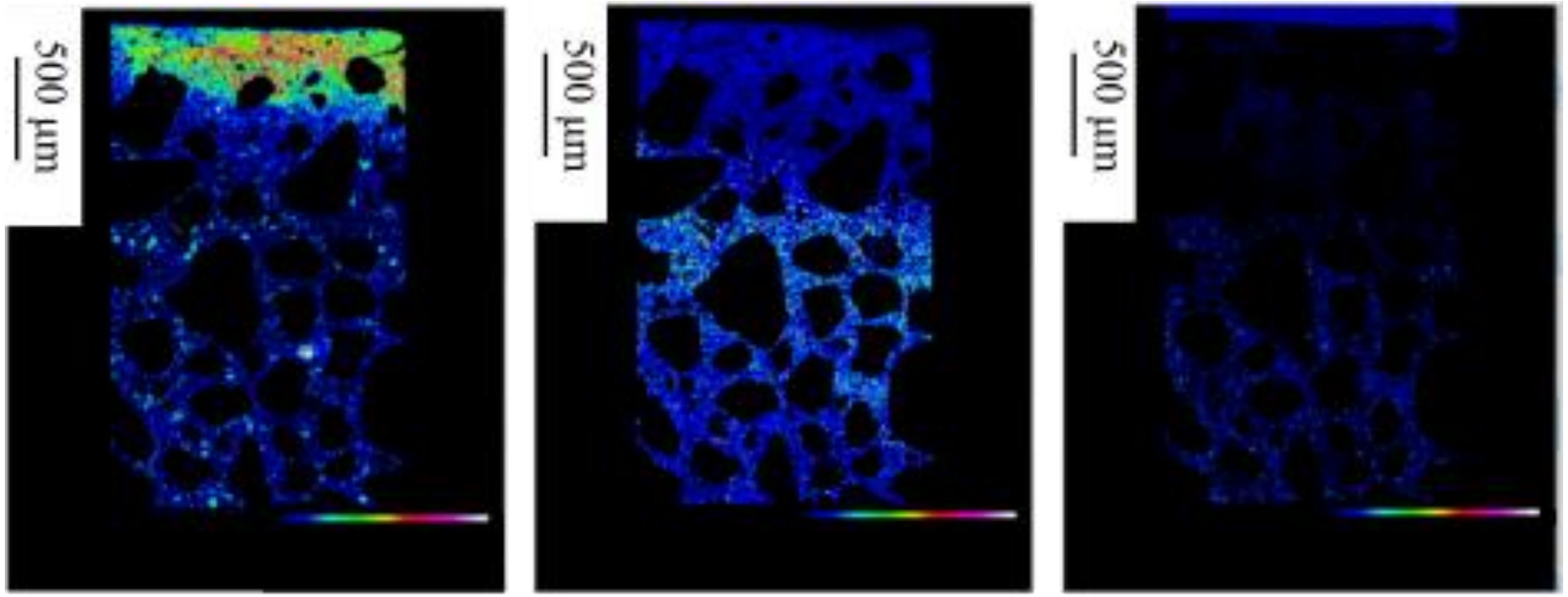
3.3 Electron probe micro-analysis

Chemical zonation due to seawater attack.

- Chemical substitution in minerals;

- X-ray elemental mapping at micron-scale

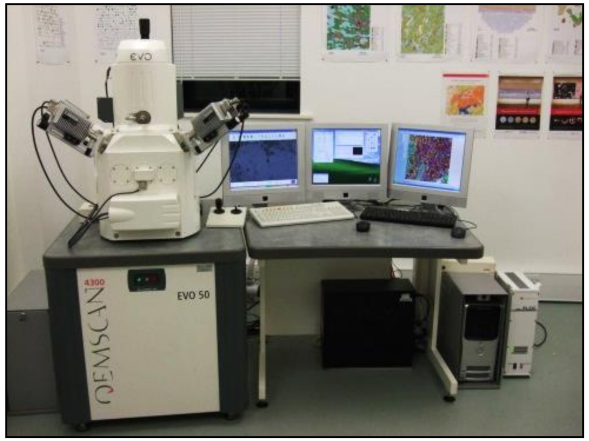
(e.g. determination of the penetration depths for chloride, magnesium and sulphate ions).



Mg S Cl

Elemental maps from a concrete block immersed for 3 months using CEM V.

3.4 Automated scanning electron microscopy analysis (QEMSCAN®)



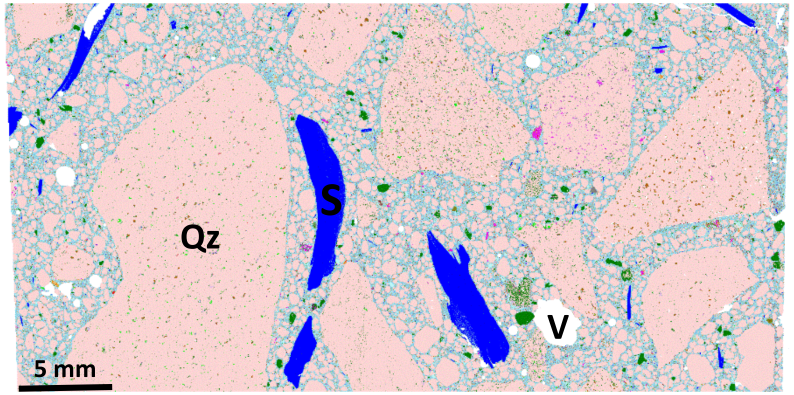
QEMSCAN® 4300

- Full **identification and quantification of the minerals** present on a sample as well as of particle size distributions and systematic relationships between the different mineral phases;
- Creation of **false colour image or map** at a micron-scale corresponding to a chemical image of the mineralogy.

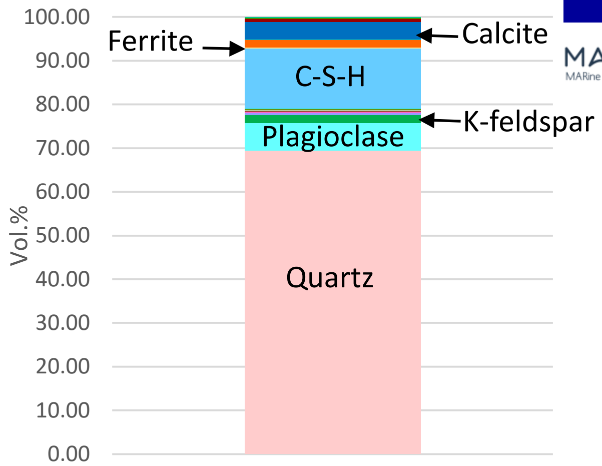
- Particle size data suffer from the problem of stereology (2D particle data representing a 3D particle) underestimating true sizes;
- Touching particles of the same mineral are not distinguishable (e.g. quartz touching quartz gives a single grain);
- Cannot distinguish polymorphs (e.g. calcite/aragonite/vaterite).

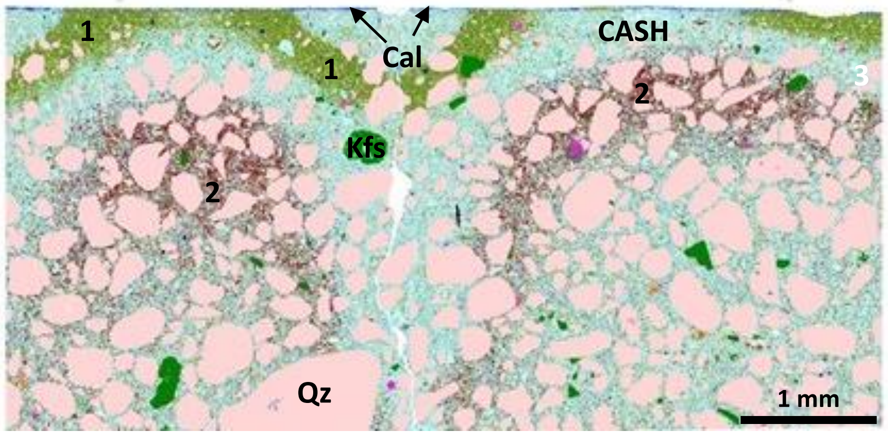
3.4 Automated scanning electron microscopy analysis

- Full and intuitive identification of the concrete mineralogy and its relations;
- Shape, size and distribution of aggregates/seashells, voids and porosity;
- Effectiveness of aggregate/seashell bonding with the binder;
- Presence, extension and width of cracks and the potential existence of infillings;
- Extent of carbonation;
- Secondary products resultant from seawater attack.



False colour mineral map of a non-immersed concrete block using CEM II. Qz – quartz; S – seashell; V – void.





False colour mineral map of a concrete block immersed for 3 months using CEM V.
Qz – quartz; Cal – calcite; Kfs – K-feldspar; CASH – calcium aluminium silicate hydrate; V – void;
1 – Mg-rich zone, 2 – S-rich zone.

3.5 X-ray diffraction analysis

Siemens D5000

- Requires the **powdering of the sample material** (<50 µm) in order to achieve a homogeneous sample and an average random orientation of crystallites;
- X-ray diffraction **patterns are unique for each crystalline mineral** and are used for direct identification usually by automated comparison with an electronic library of known and indexed patterns;
- Identification of **mineral polymorphs**;
- Can be used for the **quantification of minerals**.

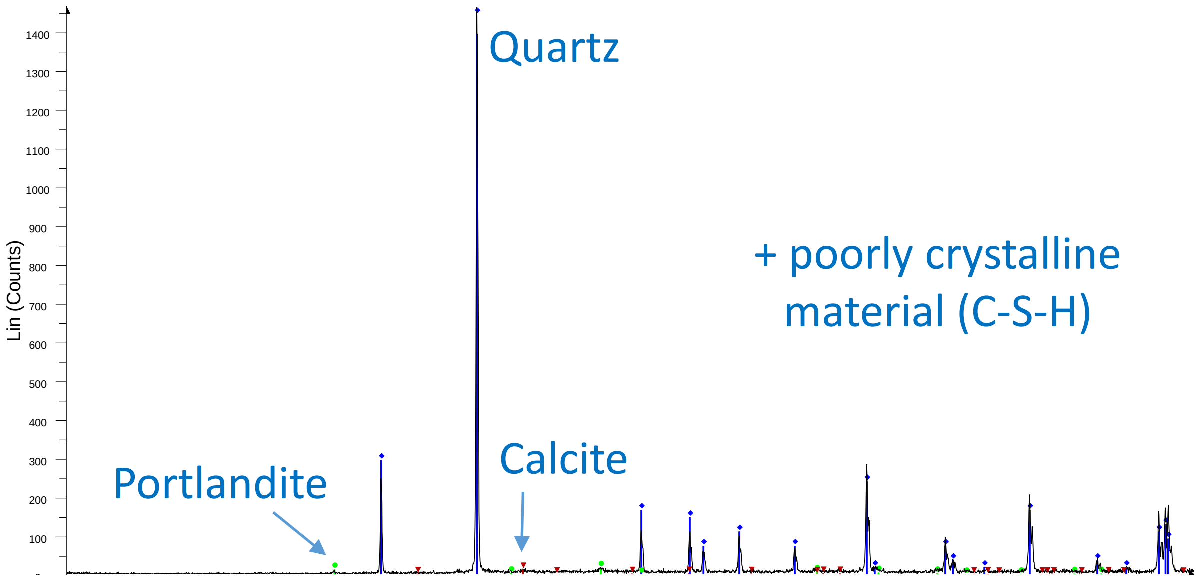
- Detection limit of 5%;
- Poorly-crystalline and amorphous phases (e.g. C-S-H) give weak broad diffraction peaks and do not generate unique diffraction patterns, respectively.

3.5 X-ray diffraction analysis

- Identification of abundant mineral phases present in concrete samples;

- Discrimination of minerals that are chemically similar or polymorphs
(e.g., calcite/aragonite/vaterite);

- Identification of some forms of concrete deterioration
(e.g. surface deposits and crack infillings that formed, for example, in response to sulphate attack).



Diffractogram of a concrete block immersed for 3 months using CEM II.
T – top section; M – middle section; B – bottom section.

Conclusions

- The integrated results from optical microscopy, SEM-EDS, EPMA, QEMSCAN® analysis and XRD give **unparalleled insight** into the variable and complex mineralogy and microtextures of concrete;

- The information range from the **quantification of the bulk mineralogy, identification of secondary mineral phases in the cement paste resulting from seawater attack, morphology and distribution of aggregates, seashells and porosity to the presence of cracks and their infilling products**, among others;

- The mineralogical analysis should be **integrated with data provided through engineering investigations**, such as compression strength, porosity, chloride ion ingress tests, and also **bio-colonization studies**;

- A wider appreciation of these tools can **advance the knowledge of concrete degradation**.

Acknowledgements

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QEMSCAN® is a registered trademark of FEI Corporation (now part of ThermoFisher Scientific).

Merci beaucoup de votre attention!