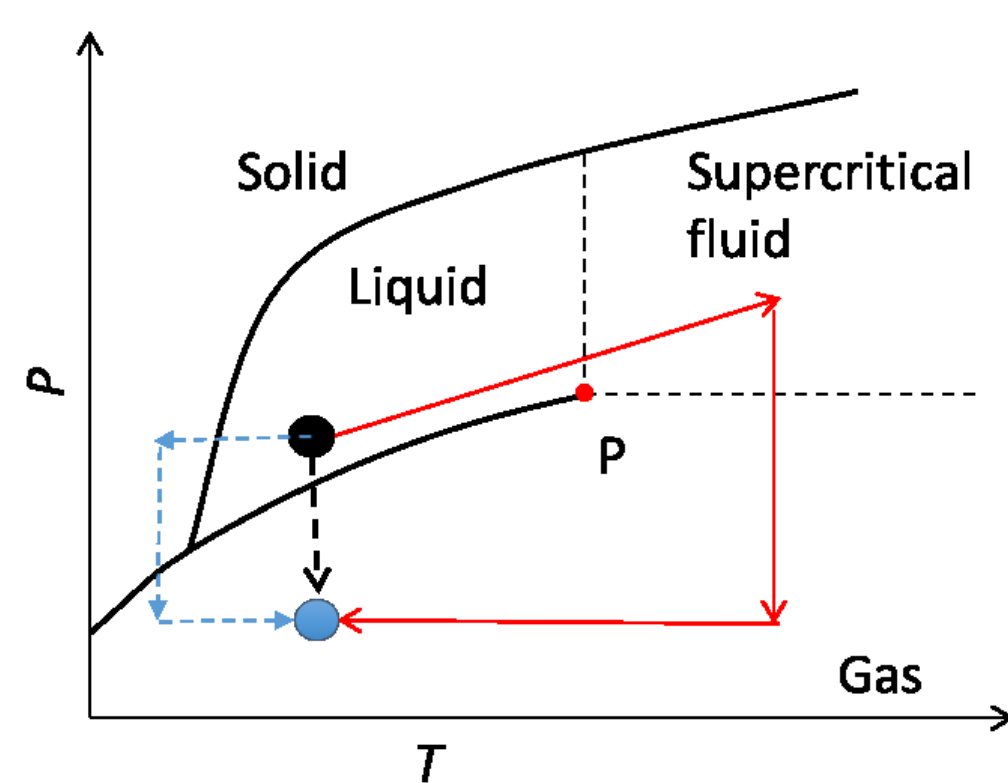


### Introduction

Supercritical drying is a process to remove liquid from the porous media in a precise and controlled way. This drying method is commonly recognized as the best way to preserve microstructure of the porous material during drying. It has been used for decades to prepare aerogels that undergo no shrinkage during drying, even though the gel structure is 99.9% porous. It has been suggested that the initial hydration products in OPC are low-density gels, so supercritical drying is ideally suited for preparation of unaltered samples for microscopic examination.

### Theory

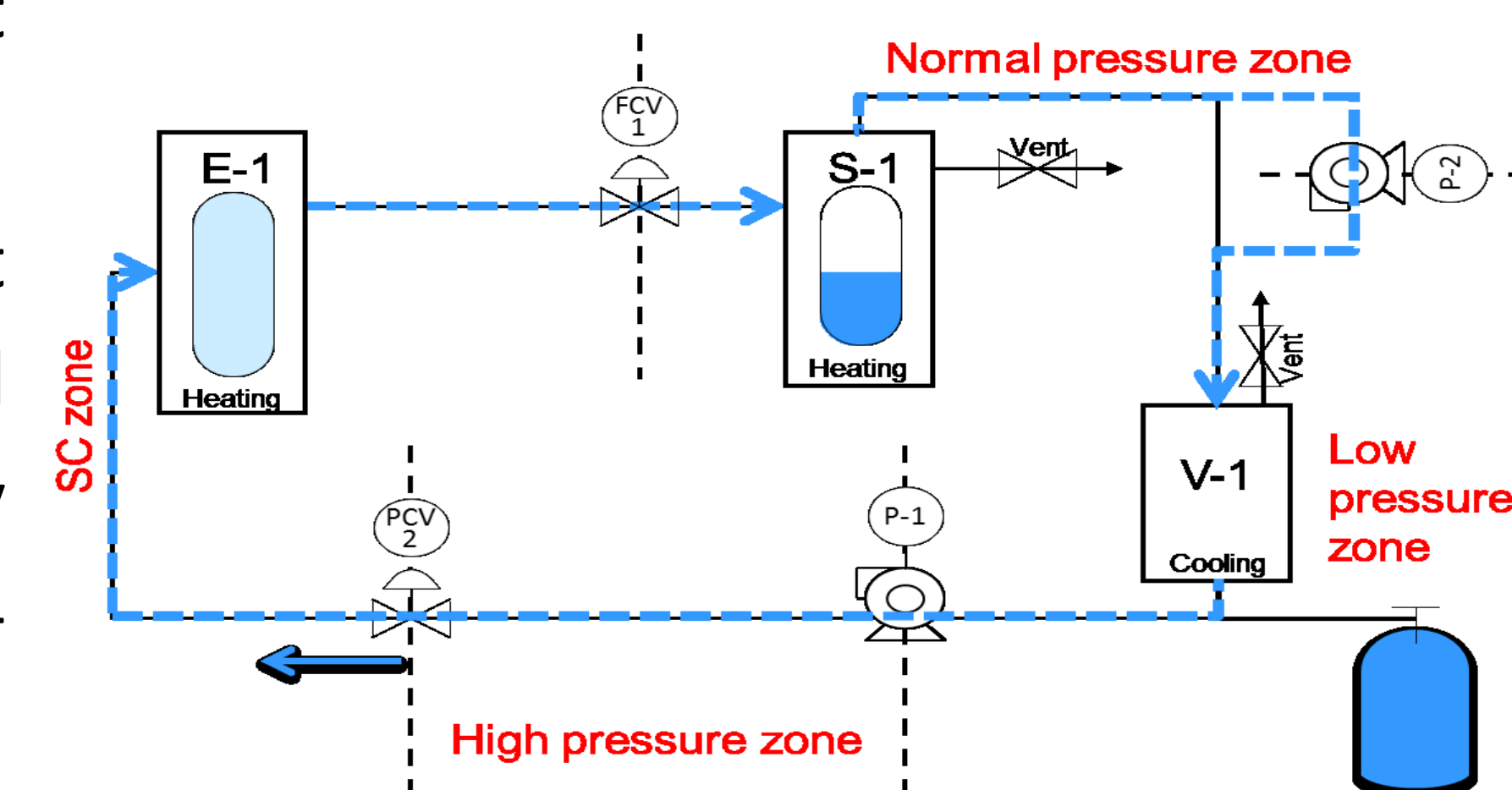
When temperature and pressure both increase to a certain point, a liquid body will become the supercritical fluid, in which no liquid-gas boundary exists. Traditional drying methods either let the liquid to cross the liquid-gas boundary or freeze the liquid to solid and then cross the solid-gas boundary. The former method creates capillary pressure due to surface tension. For most porous media, this pressure is strong enough to destroy the pore structures. It is commonly known as drying shrinkage. Freeze drying can cause damage to the solid during freezing the liquid, because of the expansion of total fluid volume. The alternative way is to let the liquid become a supercritical fluid and then vent it without crossing liquid-gas/solid-gas boundary.



### Experiment setup

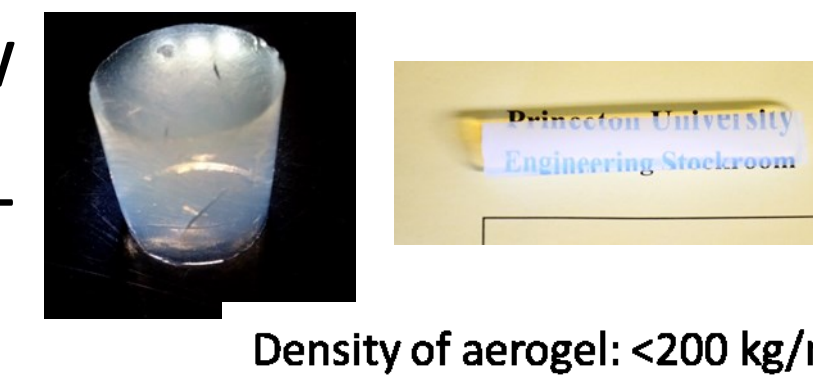
Most liquids in porous media are not suitable for supercritical drying due to very high temperature and pressure needed. Generally, the liquid needs to be exchanged with liquid CO<sub>2</sub> which has a low critical point (7.38 MPa at 31.1 °C).

The autoclave was built to carry out supercritical drying. It can precisely control pressure and temperature cycles.



### Supercritical drying of silica gels

The preliminary experiment was drying of silica gel to make aerogels. Measured temperature and pressure closely follow the recipe. Transparent and uncracked aerogels indicate that the autoclave works well.



### Applied to cementitious materials

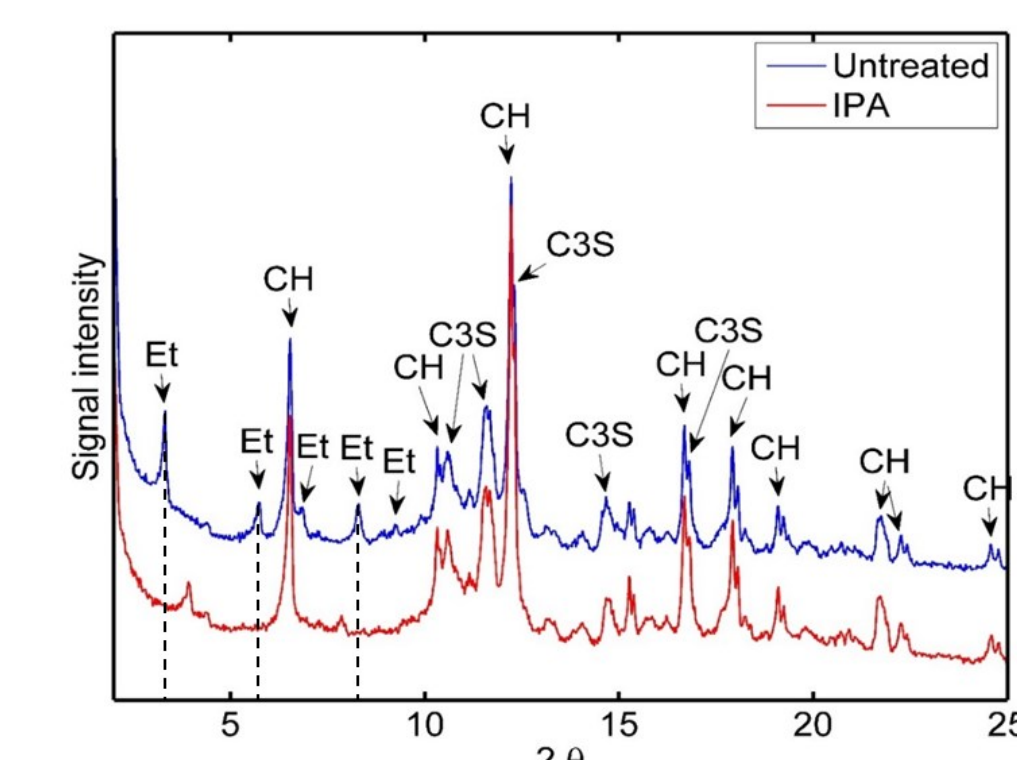
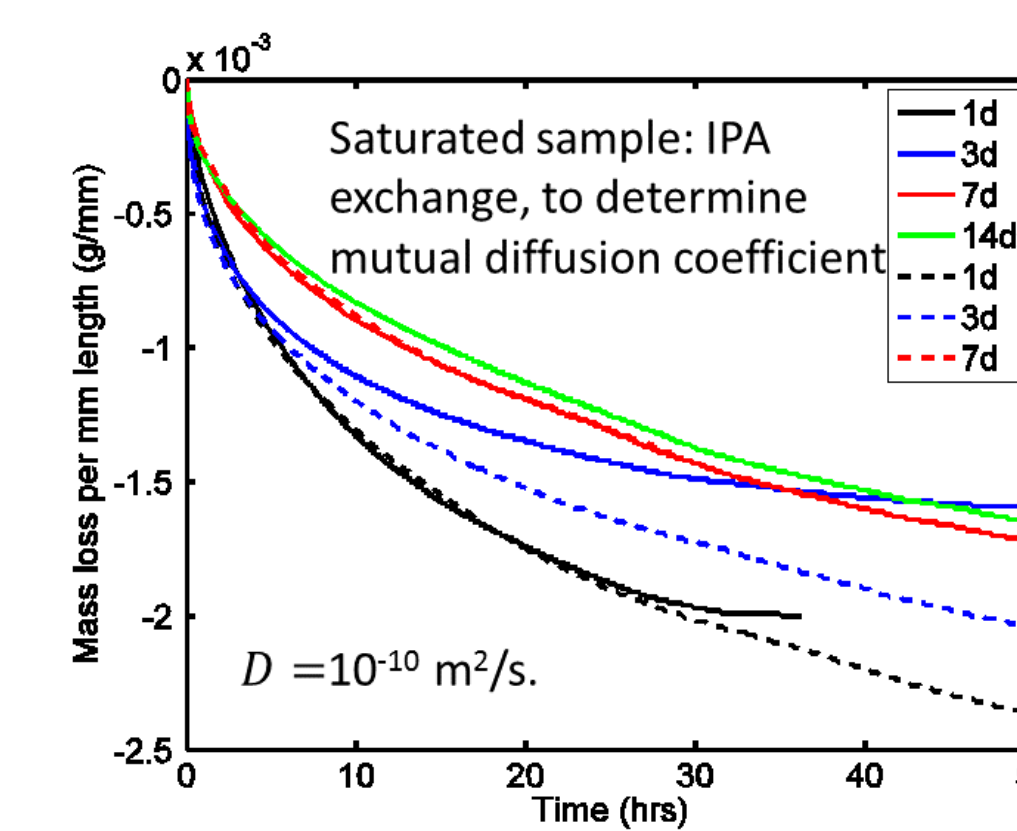
#### Questions to be answered?

Supercritical drying is needed for study of cementitious materials to answer these questions:

- ◆ How do hydration products grow? Needle growth? Two stages growth (low and high density products)? [1]
- ◆ High resolution TEM/SEM images are needed for hydration products, but do the common drying methods alter them?
- ◆ Does rapid drying preserve structures better than slow drying [2]?

#### Main issues?

- Water in cementitious materials cannot be directly supercritically dried. A solvent exchange with isopropanol is needed. IPA preserves solid structure better than other solvents [3]. However, different diffusion rates of water and isopropanol cause contraction of sample.
- Supercritical CO<sub>2</sub> cannot be used to dry cement due to carbonation. Trifluoromethane (critical point 26°C and 4.8 MPa) seems the ideal gas for this purpose. But trifluoromethane can damage the ozone sphere and is expensive so it cannot be vented like CO<sub>2</sub>.
- Depressurization can damage the structure of porous materials [4]. For cementitious materials no such study has been done yet.

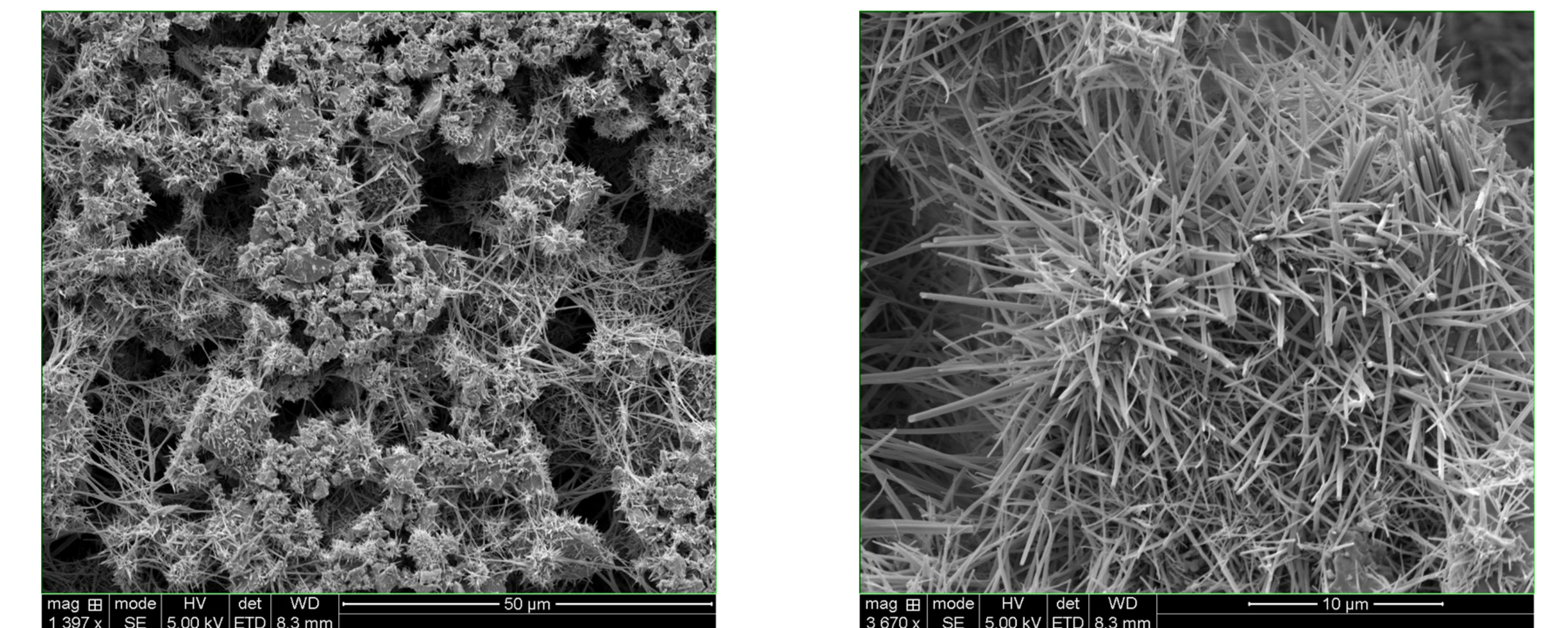


### Results

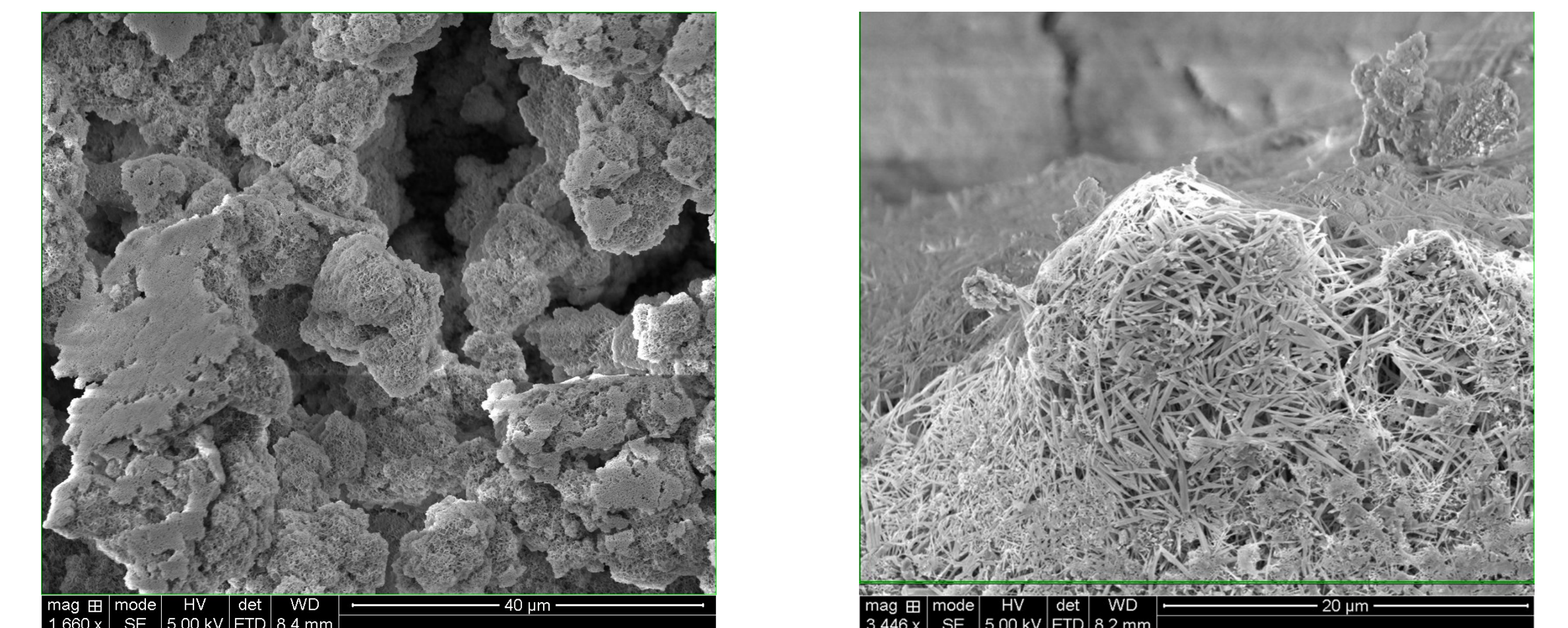
Cement paste is less permeable than silica gel, so a very small amount of paste was dropped on SEM stub to create a thin layer. A sample holder was fabricated to stabilize the SEM stubs. After drying, the sample holder was capped to avoid carbonation.



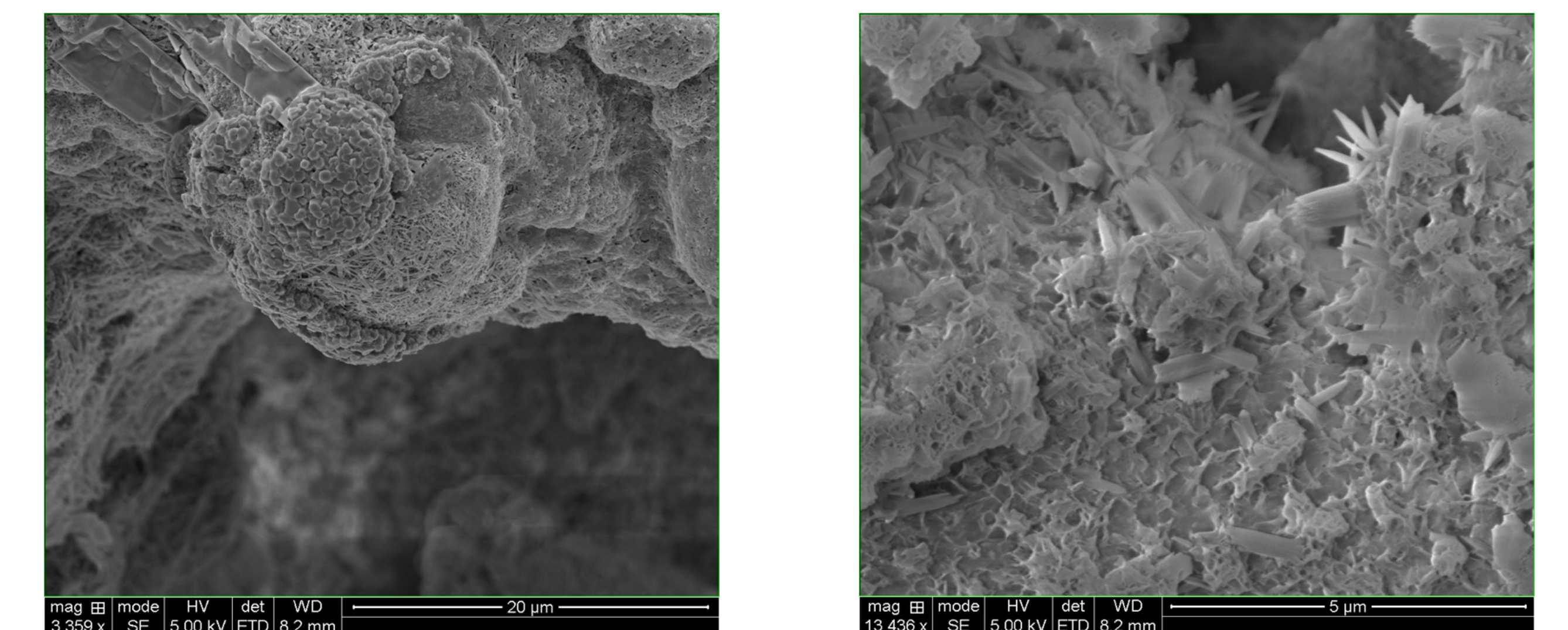
Supercritically dried specimens (w/c=1) were observed by high magnification SEM along with specimens dried by other methods.



Supercritically dried specimens (15h curing)



Directly dried by N<sub>2</sub> gas (Left: 1h; Right: 15h)



Submerged in IPA, and then dried by N<sub>2</sub> gas (15h curing)

### Conclusion and future work

Preliminary results show supercritical drying can well preserve the needle-structure hydrated products, while this structure collapses for traditional methods. More tests are needed to confirm this conclusion.

**References:** [1]. S. Bishnoi & K.L. Scrivener, CCR 39 (2009) 849–860. [2]. P.C. Fonseca & H.M. Jennings, CCR 40 (2010) 1673–1680. [3]. J. Zhang & G. W. Scherer, CCR 41 (2011) 1024–1036. [4]. G. W. Scherer, J. Non-Crys. Solids 145 (1992) 33-40.