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## Designing model system for low-pH cement carbonation

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### Introduction

Low-alkalinity (a.k.a. Low-pH) cementitious materials are likely to be used in the framework of the French geological disposal facility for intermediate level and long lived wastes (Cigeo project). The use of low-pH materials is justified by the will to limit the impact of the alkaline plume on clayey rock and to decrease the temperature during the concrete hardening. Those cementitious materials are obtained by incorporation of large amount of siliceous bearing supplementary cementing materials such as fly ash, slag, and silica fume. Low-pH cementitious materials have been studied for several years but some information pertaining to durability remain to be acquired. Especially those materials' evolution upon carbonation. <sup>1</sup>Auroy *et al.* brought to light a substantial increase of cracking coupled to an increase of transport properties in low-pH cement upon atmospheric carbonation compare to OPC. <sup>2</sup>Serdar *et al.* showed that the rate of carbonation-induced corrosion of steel was increased.

Within the framework of waste management research and development, several studies' approach involve the design of representative model systems in order to gain a better understanding of complex phenomena. We formulated model cementitious materials of controlled mineralogy and increasing chemical composition complexity. Those model materials are hardened cement pastes with Ca/Si ratio between 0.80 and 3.0 with a microstructure generated by their hydration. They are part of a study focusing on atmospheric carbonation and its consequences (modifications in mineralogy and microstructure) but this aspect will not be discussed here. We will focus instead on the hardened cement pastes properties such as mineralogical assemblage, chemistry and microstructure.

### Materials

Hardened cement paste based on C<sub>3</sub>S and colloidal silica mixed in stoichiometric ratio were fabricated with targeted molar C/S ratio of 0.80, 0.87, 0.95; 3.00. The paste workability was adjusted using a commercial polycarboxylate superplasticizer. The water/cement ratio (in mass), of these pastes ranged between 0.5 for C/S: 3.00 to 0.7 for C/S: 0.80. A volume of 1.40 L of each paste was fabricated using a planetary mixer. The pastes were kept into PTFE cylindrical mold (Ø30 mm x H110 mm) during one month then kept in curing water during at least 2 months.

### Results and discussion

After the curing period, the model pastes were characterized using several complementary methods including, Thermogravimetric Analysis (TGA), X-ray Computed Tomography (X-ray CT) and Dynamic Vapor Sorption (DVS). The corresponding results will be addressed during the conference. Figure 1 shows the XRD patterns of the model pastes (mixtures of C<sub>3</sub>S and nanosilica). The presence of C-S-H mains peaks is plain to see for the pastes. Traces of anhydrous C<sub>3</sub>S (noted as *an* on XRD pattern) are detected within the pastes of higher C/S ratio (1.40 and 3.00). Portlandite is present in the sample of the higher C/S ratio (3.00), contrarily, residual amount of portlandite is found in the sample of C/S 1.40.

Samples of lower C/S (<1.40) show no content on portlandite.

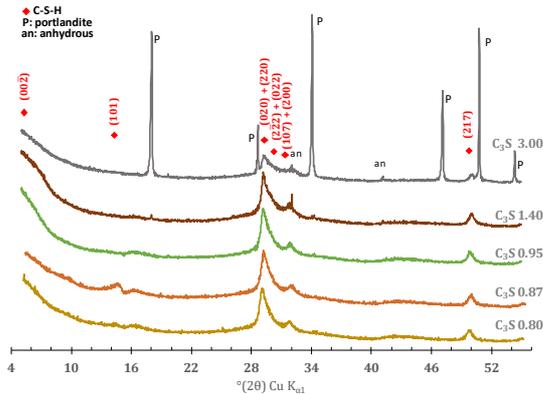


Figure 1: XRD  $C_3S$  pastes

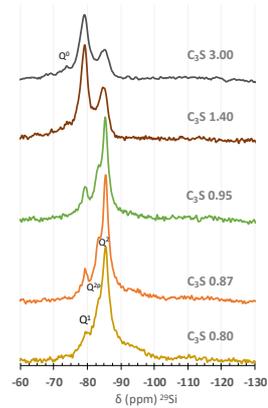


Figure 2:  $^{29}Si$  NMR  $C_3S$  pastes

The pastes show broadened and asymmetric C-S-H peaks induced by nanocrystallinity and disorder. This property could probably be induced by the strain within the paste during the hydration. Figure 2 shows  $^{29}Si$  NMR spectra of the model pastes, expected environment are found for each pastes, *i.e.* decreasing silicate polymerization (from  $Q^2$  to  $Q^1$ ) when increasing C/S values. The pastes show expected characteristics both on their XRD patterns and  $^{29}Si$  NMR spectra, bringing thus to light the tunable mineralogical properties of these model pastes.

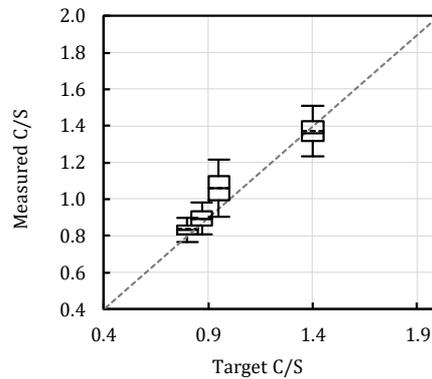


Figure 3: EDS analyses of  $C_3S$  based pastes

Figure 3 shows the quantitative chemical analyses obtained by dispersive X-ray spectroscopy in back-scattered electron mode for the  $C_3S$  based pastes. The C/S values obtained between the first and the third quartile and the C/S values between the first and the ninth decile of each sample are represented by the box height and the whiskers, respectively. The median and the mean C/S ratio are represented by line and dot line within the box. The targeted C/S values for the pastes are obtained, only the paste with C/S ratio of 0.95 shows a slight discard to the target C/S.

Table 1: Pastes' macroscopic properties

Target C/S	Samples				
	3.00	1.40	0.95	0.87	0.80
Porosity (80°C)	38%	52%	≈ 56% (*)	≈ 52% (*)	na
Saturated density	1.89	1.76	1.68	1.67	na
Water/binder (wt%)	0.50	0.60	0.65	0.65	0.70
SiO <sub>2</sub> content (wt%)	0.26	0.43	0.53	0.55	0.57
#NA: not available (*) complete drying not achieved yet					

Some properties related to the microstructure are given in the Table 1. When the C/S ratio is decreased both the water/ binder ratio and the silica content are increased, the two latter affect highly the porosity.

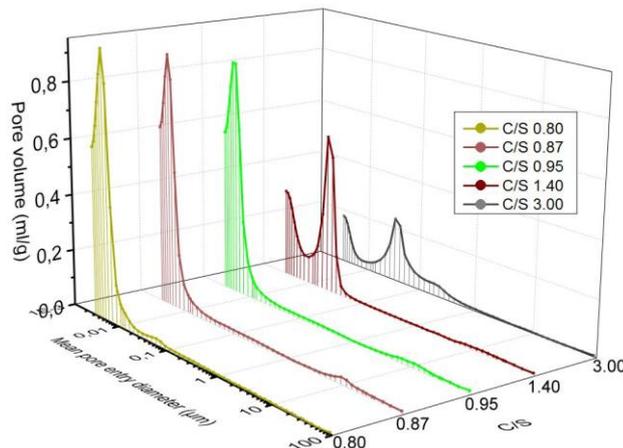


Figure 4: Distribution of the mean pore entry diameter for the pastes (Mercury intrusion porosimetry)

Mercury intrusion porosimetry data for the pastes are presented in Figure 4. C/S ratio impacts the porosity distribution. C/S 3.00 paste shows similar porosity as usual cement (OPC). The pastes of high C/S ratio (3.00 and 1.40) show two types of porosity. The smaller mean pore entry diameter (<10 nm) are associated with the intrinsic porosity of the C-S-H, the second type of porosity, the capillary porosity (< 1 μm) is mainly associated with void between hydrates. Pastes of smaller C/S ratio show different porosity distribution. The main porosity related to those materials are associated with C-S-H, one can see the increase of this type of porosity from pastes with high C/S ratio to pastes of lower C/S ratio. This indicates higher C-S-H content for paste with lower C/S ratio. We could explain the absence of capillary porosity by the high content on silica, generating thus more C-S-H, filling therefore the capillary void. Addition of reactive silica leads to an increase of pozzolanic reaction, C-S-H engendered by the latter lead to refined pore structure. This is supported by the higher pore volume observed when the C/S ratio is lowered. The porosity distribution shown by smaller C/S ratio is similar to those demonstrated by Low-pH.

## Conclusion

In this study, we designed cementitious materials of controlled mineralogy intended to be used as model low-pH materials for durability studies. Using C<sub>3</sub>S and nanosilica in stoichiometric amounts made it possible to obtain pastes of controlled C/S ratio only composed of C-S-H. The microstructure of lower C/S

model paste reveals their close similarity to low-pH materials in terms of type of porosity and porosity distribution<sup>1</sup>.

The pastes' main properties (mineralogy, chemical composition and microstructure) were investigated. The results obtained support the relevancy of our methodology to fabricate model cementitious materials with controlled chemistry, and mineralogy.

### **Acknowledgment**

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### **References**

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- 2) Serdar *et al.* "Carbonation of low-alkalinity mortars: influence on corrosion of steel and on mortar micro-structure", *Cement and Concrete Research* 101, 33-45 (2017)