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Abel Danezan<sup>1</sup>, Franck Fayon<sup>1</sup>, Cécile Genevois<sup>1</sup>, Emmanuel Veron<sup>1</sup>, Mathieu Allix<sup>1</sup>, Catherine Bessada<sup>1</sup>, Judit Kaknics<sup>2</sup>, Wendy de Seixas<sup>2</sup>, Valérie Montouillout<sup>1</sup>

## **SOLID STATE NMR INVESTIGATION OF TITANIUM'S ROLE ON THE HYDRATION OF INDUSTRIAL SLAGS: A MODEL GLASS STUDY**

*<sup>1</sup>CNRS CEMHTI UPR3079, 1D avenue de la Recherche Scientifique, 45071 Orléans, France*

*<sup>2</sup>ArcelorMittal Global Research and Development (Maizières Process), Voie Romaine, BP 30320 – 57283 Maizières-lès-Metz Cedex, France*

### **Abstract**

Blast furnace slag, by product of pig iron manufacturing, is a glassy material composed mainly of SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub> and MgO, with some minor elements, such as Na, K, P or Ti, present in various quantities depending on the origin of the slag. They have been used for many years as a cement constituent (CEM II, CEM III and CEM V) or as a concrete addition, replacing significant volumes of Portland cement clinker. However GGBS containing cements can display various strength development at early ages depending mainly of their composition. Among minor elements, TiO<sub>2</sub> has been identified to have a negative impact on reactivity, depending on the quantity and the oxidation state.

In this study, we synthesized four model glasses mimicking the chemical composition of an industrial slag with and without titanium, and under oxidizing and reducing atmospheres. The structure of these glasses were characterized using different techniques such as XRD, multi-nuclear high resolution solid state NMR and EPR. The four glasses were then hydrated with a cement pore solution for 2, 7 and 14 days. A combination of XRD and various high resolution solid state NMR experiments was used to monitor specifically the evolution of vitreous network and of the different hydrated phases.

## Introduction

Currently used as cement constituent (CEM II, III or V), granulated blast furnace slag (GGBS) induces various short and long term effects on mechanical strength and durability of the concrete. Many factors could be invoked among which the composition [1] and especially the presence, in addition to the main Si-Ca-Al-Mg elements, of minor elements such as Na, K, P or Ti. Among them, titanium has been identified to have a negative impact on strength development of mortars [2, 3]. However, its role is still unclear on both the reactivity of slags and the kinetic of formation of the hydration products.

From very low contents, titanium significantly affects physical and chemical properties of silicate glasses and melts, including density, viscosity or chemical durability. This strong effect derives mainly from its ability to occupy different coordination environments (four, five or six-folded coordinated) in the structure. Therefore, in glass and liquid phases, titanium may act either as a network modifier, a network former, or both depending on composition, pressure and temperature, explaining the multiplicity and complexity of its interaction with the structure and properties of silicates. The environment of titanium in silicate glasses has been mainly investigated using X-ray absorption spectroscopy in a large range of compositions, from glasses in the  $\text{TiO}_2$ - $\text{SiO}_2$  binary system [4, 5] to Ti-bearing alkali silicate glasses or alkaline-earth silicates glasses [5-12]. All these studies show that titanium atoms are present in the glass with multiple coordination numbers from four to six. The availability of these different environments implies a complex structural role of titanium depending on the overall composition of the glass and the Ti concentration. It is therefore unthinkable to understand the role of this specific component by comparing the reactivity of industrial slags of different origin inducing a wide range of composition.

The aim of this work is to observe selectively the effect of titanium on the reactivity of the vitreous network and the phase development of the hydrates (AFm, C-(A)-S-H). In this context, four model glasses with compositions based on an industrial GBS regarding the main elements (Si, Ca, Al, Mg), were synthesized. The only parameters changing being the presence, or not, of a significant amount of titanium and the oxidizing-reducing conditions of synthesis. The structure of the glasses was fully characterized using EPR, and High Resolution  $^{27}\text{Al}$  and  $^{29}\text{Si}$  solid state Nuclear

Magnetic Resonance. Then, all the glasses were hydrated with a cement pore solution for various delays. A combination of XRD and various high resolution solid state NMR experiments was used to monitor the evolution of vitreous network and the different hydrated phases in our 4 systems. The induced effect of titanium was then highlighted as well as the influence of the nature of atmosphere (oxidizing or reducing) used for the synthesis.

## Materials and methods

All the samples were prepared by ArceloMittal staff using a home-made granulation device. Two powder mixtures based on CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> starting materials were prepared. The composition of the glasses is presented in

*Table 1.* These dry powders were melted at 1600°C for 5 minutes. One batch was made in a Pt crucible under air, corresponding to an oxidizing atmosphere, and the other in a carbon crucible under argon, considered to give reducing conditions. The melts were quenched by spilling them into a water granulation device, under air.

A total of four model glasses were synthesized: two under reducing atmosphere, with and without Ti, denominated G-Ti-R and G-R, and two under oxidizing atmosphere, with and without Ti denominated G-Ti-O and G-O.

	Glass		Glass-Ti	
	mol-%	wt-%	mol-%	wt-%
CaO	44.0	41.8	43.0	40.5
SiO <sub>2</sub>	38.9	39.6	38.0	38.34
Al <sub>2</sub> O <sub>3</sub>	6.7	11.6	6.6	11.28
MgO	10.3	7.0	10.1	6.81
TiO <sub>2</sub>	/	/	2.3	3.10

*Table 1: molar and weight composition of the glasses*

*Figure 1* shows pictures of the different glasses obtained. As can be seen, the titanium bearing model glass synthesized under reducing atmosphere, *Figure 1b* displays a dark purplish colour, while its counterpart without titanium is grey (cf *Figure 1a*). The samples synthesized under oxidizing conditions have the same aspect with and without titanium, both of them displaying a white translucent colour (cf *Figure 1c* and *d*).

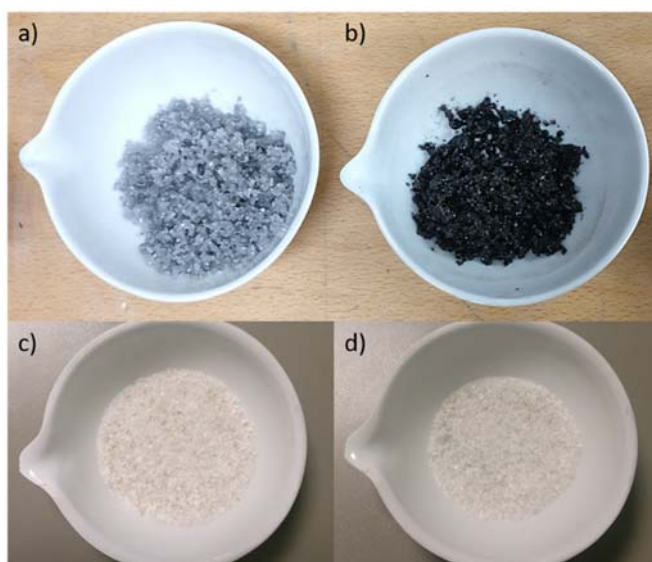


Figure 1 - Synthesized model glasses: a) G-R, b) G-Ti-R, c) G-O and d) G-Ti-O

XRD analyses confirmed the amorphous state of the four samples.  $\text{Ti}^{4+}$  being diamagnetic while  $\text{Ti}^{3+}$  is paramagnetic, EPR investigations were conducted on the Ti-bearing glasses in order to investigate the oxidation state of titanium. These investigations confirmed the presence of titanium as  $\text{Ti}^{4+}$  (no EPR signal) in the G-Ti-O sample and its presence as  $\text{Ti}^{3+}$  in the G-Ti-R samples, confirming the impact of the atmosphere as well as explaining the difference in colour between the oxidized and reduced Ti-bearing samples.

The reactivity of the model glasses was studied using a modified R3 protocol [10, 11]. The samples were mixed with Portlandite with a 1:3 mass ratio. Then, the homogenized powder mix was put in contact with a solution containing  $0.071 \text{ mol.L}^{-1}$  of KOH and  $0.115 \text{ mol.L}^{-1}$  of  $\text{K}_2 \text{SO}_4$  with a liquid to solid ratio of 1. The powder/solution mixes were stirred by hand for 2 minutes in order to obtain a homogeneous paste. The pastes were then left to cure in a room at  $20^\circ\text{C}$  for times ranging from 2 to 14 days. After these periods, the hydration was stopped using a solvent exchange method [12]. The pastes were dipped in acetone for 5 minutes, filtered on a Büchner filter and then dried in a vacuum ( $10^{-3}$  bar) for 15 minutes. The obtain samples were then stored in a glove-box, in order to prevent carbonation, and characterized shortly after.

The environment of silicon and aluminum were studied by quantitative High Resolution Solid State  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR.  $^1\text{H}$ - $^{29}\text{Si}$  and  $^1\text{H}$ - $^{27}\text{Al}$  Cross Polarization Magic Angle

Spinning (CP-MAS) experiments were performed to edit specifically the signals consistent with Al and Si in close proximity to  $^1\text{H}$  atoms, allowing for the observation of the signals coming only from hydrated phases. The  $^{29}\text{Si}$  and  $^1\text{H}$ - $^{29}\text{Si}$  CP-MAS experiments were acquired on a Bruker AVANCE 400MHz spectrometer ( $B_0=9.4\text{T}$ ,  $\nu_{\text{RF}}(^1\text{H})=400\text{MHz}$ ,  $\nu_{\text{RF}}(^{29}\text{Si})=79.4\text{MHz}$ ,  $\nu_{\text{rot}}=10\text{kHz}$ ) and the  $^{27}\text{Al}$  and  $^1\text{H}$ - $^{27}\text{Al}$  CP-MAS experiments were acquired on a Bruker AVANCE 750MHz spectrometer ( $B_0=17.6\text{T}$ ,  $\nu_{\text{RF}}(^1\text{H})=750\text{MHz}$ ,  $\nu_{\text{RF}}(^{27}\text{Al})=195.4\text{MHz}$ ,  $\nu_{\text{rot}}=23\text{kHz}$ ). All the spectra were simulated using the DMFit software [13]. The CP-MAS experiments' simulation allowed for the determination of the parameters of the signals consistent with the hydrated phases, which were then used to fit the quantitative MAS experiments. The relative quantities of Si and Al species were estimated from the deconvolution of the quantitative MAS spectra.

## Results and discussion

### Unaltered glasses

Figure 2(a) shows the  $^{29}\text{Si}$  MAS NMR spectra obtained for the unaltered model glasses. The spectra appear very similar, composed of a single broad signal centered at around -75 ppm and spreading out from -65 ppm to -90 ppm (FWHM of about 11.5ppm). This lineshape results from the overlapping of numerous contributions corresponding to the different silicon environments making impossible an unambiguous deconvolution. The position and width of the lines are consistent with depolymerized silicate networks mainly composed of  $\text{Q}^1_{(0\text{Al})}$ ,  $\text{Q}^2_{(1\text{Al})}$  and  $\text{Q}^2_{(0\text{Al})}$  units. This observation is consistent with theoretical number of non-bridging oxygen (NBO) per Si tetrahedron value calculated by

$$\frac{\text{NBO}}{T_{\text{Si}}} = \frac{2(\text{CaO} + \text{MgO} - \text{Al}_2\text{O}_3)}{\text{SiO}_2}$$

The value obtained is the same for both composition (with and without Ti) and is 2.45 NBO per tetrahedron

No differences are observed according to the presence or not of titanium and its degree of oxidation

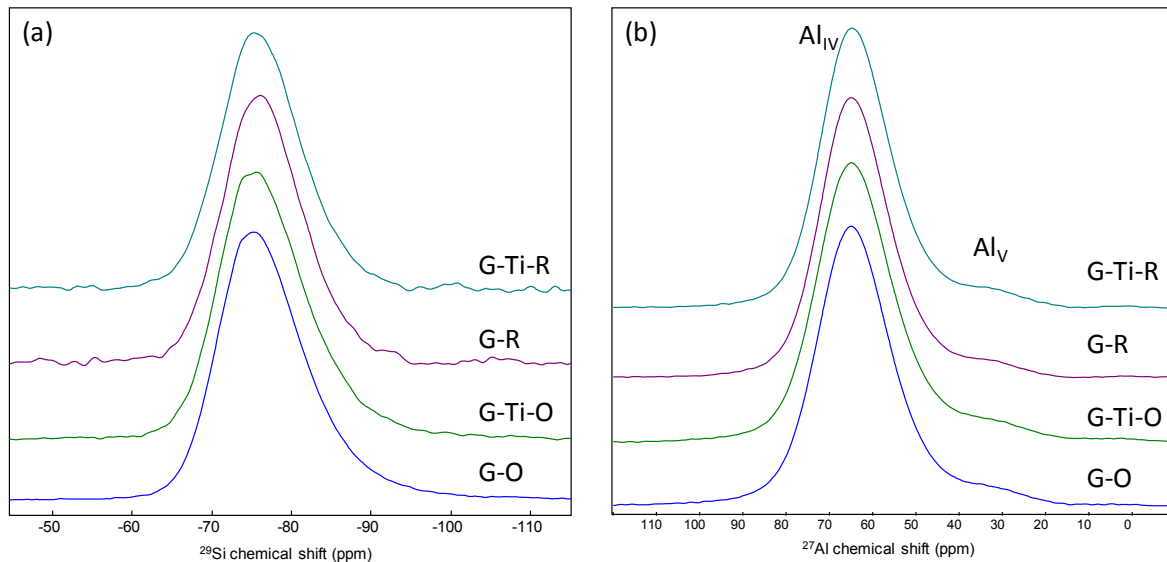


Figure 2 –  $^{29}\text{Si}$  (a) and  $^{27}\text{Al}$  (b) MAS NMR spectra of the four glasses

The  $^{27}\text{Al}$  MAS NMR spectra of the four glasses are presented on *Figure 2(b)*. Again they appear very similar, with a main signal centered at about 65 ppm and a smaller shoulder around 35 ppm assigned respectively to aluminum in four-fold and five-fold coordination. The lineshapes are characteristic of Al in disordered materials and result from local environment distribution. The spectra were simulated using the DMFit software [11]. The extracted parameters and relative  $\text{Al}_{\text{IV}}$  and  $\text{Al}_{\text{V}}$  quantities are grouped in Table 2.

	$\text{Al}_{\text{IV}}$			$\text{Al}_{\text{V}}$		
	$\delta_{\text{iso}}$ (ppm)	$C_{\text{Q}}$ (MHz)	%	$\delta_{\text{iso}}$ (ppm)	$C_{\text{Q}}$ (MHz)	%
G-Ti-R	69.8	6.1	95	37.2	4.3	5
G-R	69.8	6.1	96	37.2	4.3	4
G-Ti-O	70.2	6.1	94	37.2	4.3	6
G-O	70.4	6.0	94	37.2	4.3	5

Table 2:  $^{27}\text{Al}$  NMR parameters and proportion of aluminum species extracted from simulation of MAS spectra

As for the silicon environment, it seems that the presence of titanium and the atmosphere under which the samples are synthesized have no significant impact on the aluminum environment.

### Hydrated samples

The reactivity of the samples were followed by NMR characterization of hydrated and quenched glasses after 2, 7 and 14 days of curing.

Figure 3 shows the experimental and simulated  $^{29}\text{Si}$  (a) and  $^{27}\text{Al}$  (b) spectra of the G-R 2 days hydrated sample. The  $^{29}\text{Si}$  MAS NMR spectrum displays a main broad signal consistent with the residue of unaltered slag as well as two distinguished thin signals assigned to  $Q_1$  and  $Q_2$  silicon species (i.e. four-fold connected silicon with 1 and 2 bonding oxygen respectively). These species compose the  $\text{SiO}_4$  tetrahedra chains of the C-(A)-S-H phase and their assignment was confirmed by  $\{^1\text{H}\}$ - $^{29}\text{Si}$  CP-MAS experiments. In the same way, the  $^{27}\text{Al}$  NMR spectrum exhibits a broad signal consistent with the residue of unaltered slag as well as thinner signals attributed to hydrated aluminate products (confirmed by  $\{^1\text{H}\}$ - $^{27}\text{Al}$  CP-MAS NMR experiments). The chemical shift associated to these thin signals are consistent with the four-fold coordinated aluminum present in the C-(A)-S-H phases (74 ppm) [14], the aluminum of Ettringite (13ppm) [14], the aluminum in AFm phases (10ppm) [14] (i.e. monosulfate, monocarbonate, hemicarbonate...) and the aluminum of Third Aluminum Hydrate (~6ppm) [15].

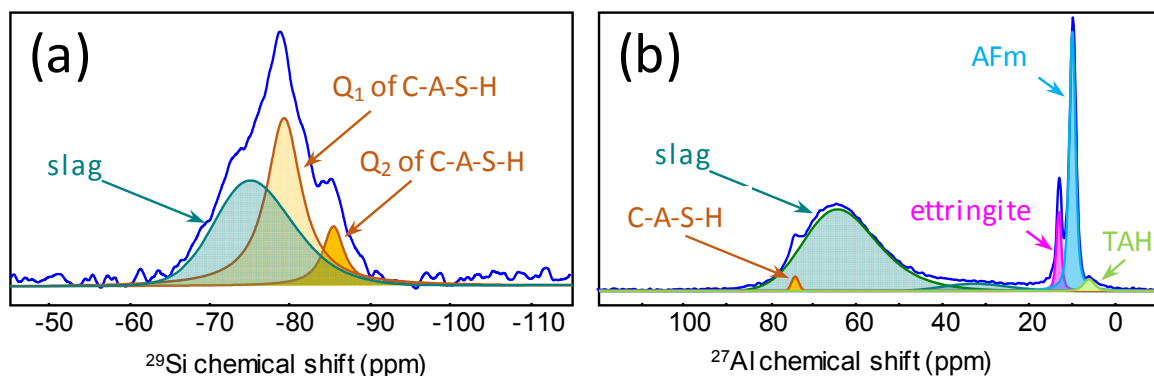


Figure 3:  $^{29}\text{Si}$  (a) and  $^{27}\text{Al}$  (b) NMR spectra with their deconvolution of G-R sample hydrated during 48h

All the quantitative MAS spectra obtained for hydrated G-R, G-Ti-R, G-O, and G-Ti-O were simulated based on the previous deconvolutions, allowing for the determination of the proportion of silicon and aluminum in the residual glass and in the hydrated phases. It is then possible to estimate the molar % of each phases, assuming that C-A-S-H is defined by  $\text{Ca}/\text{Si}=1$  and  $\text{Al}/\text{Si}=0.1$ . Figure 4 shows the evolution of these proportions as a function of curing time.

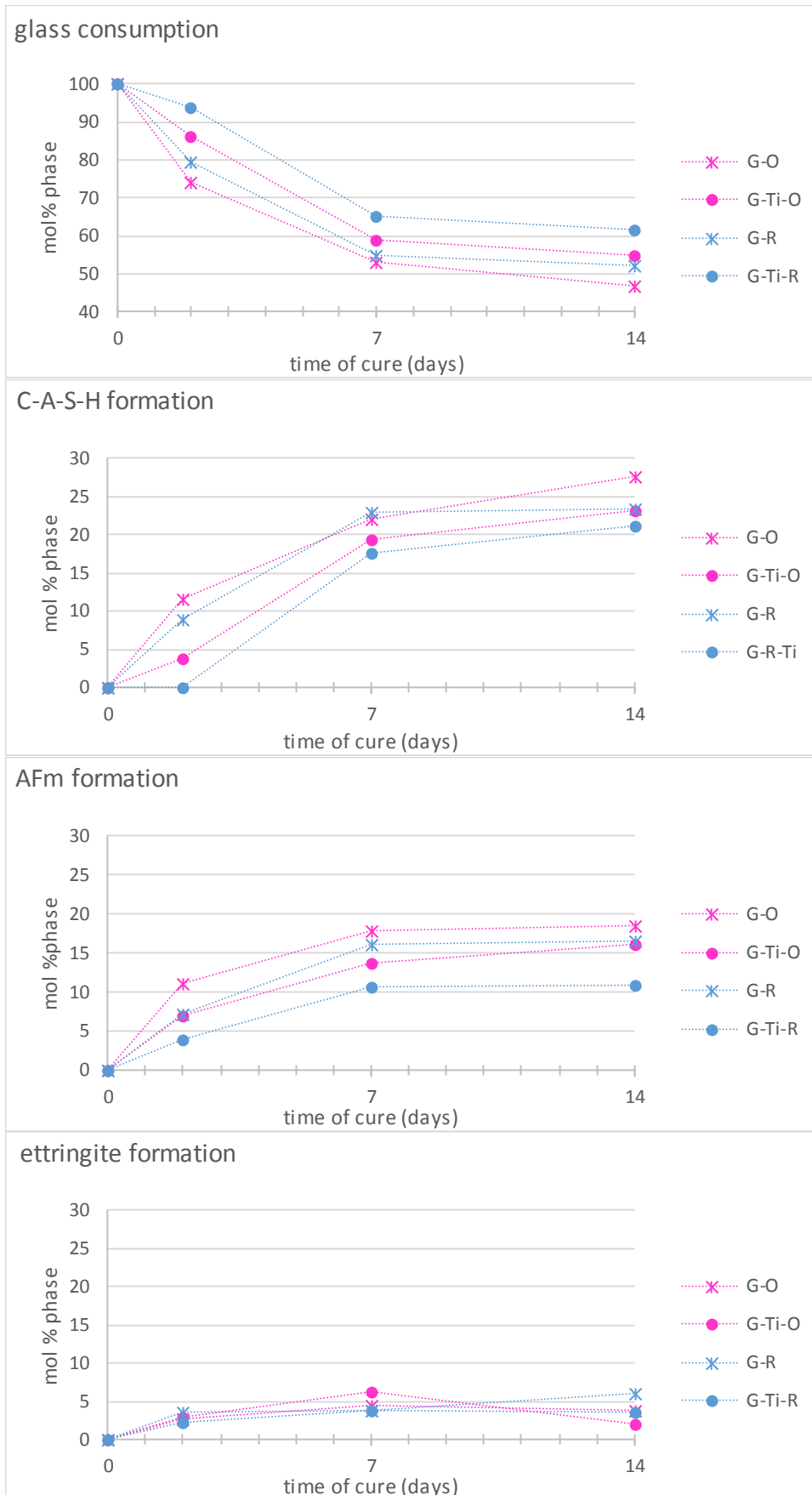


Figure 4: Kinetics of glass dissolution and hydrated phases formation for the 4 systems

We observe clear differences between the 4 systems as well for the glass dissolution than AFm and C-A-S-H precipitation. The dissolution rate of glasses are ordered as follow  $G\text{-Ti-R} < G\text{-Ti-O} < G\text{-R} \leq G\text{-O}$ . As expected, the presence of titanium slows down the vitreous network dissolution, but surprisingly we evidence also an influence of the nature of atmosphere (oxidizing or reducing). It seems that  $\text{Ti}^{3+}$  is more detrimental than  $\text{Ti}^{4+}$ . In the case of no Ti-bearing sample, the consumption of the glass is also faster in G-R than in G-O, to a lesser extent.

In parallel, in exception of ettringite, the precipitation of hydrated phases is minimized by the presence of titanium in the initial glass. After a 2 days curing, it created half less AFm in G-Ti-R than in G-R glass and no C-A-S-H are distinguishable in G-Ti-R while around 10% are present in G-R. The same limiting effect of titanium is also observed in G-O and G-Ti-O glasses, but the amount of the two phases is more important due to the best dissolution of the initial glasses, and then the largest amount of ions in solution. Then, the effect of titanium seems to be equivalent on the precipitation of hydrated phases. This is coherent with the fact that during its passage in solution, the  $\text{Ti}^{3+}$  ion is reduced in  $\text{Ti}^{4+}$ .

## **Conclusion**

In this work the induced effect of the presence titanium on Si-Al-Ca-Mg vitreous network has been investigated. Four GBS model glasses, with and without titanium were granulated under oxidizing and reducing atmosphere. While no difference can be detected in the structure of the initial glasses, the impact of titanium is particularly noticeable on the glass reactivity when mixed with a cement pore solution. The presence of titanium slows down the vitreous network dissolution and more remarkably  $\text{Ti}^{3+}$  seems to be more detrimental than  $\text{Ti}^{4+}$ . The effect is also determinant on AFm and C-(A)-S-H precipitation which are strongly minimized in presence of titanium whatever the atmosphere of synthesis. These observation can explain the low strength development of Ti-bearing GGBS.

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