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About The Effect Of Portland Cement Activation On Supersulfated Cements Properties

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ABSTRACT

Supersulfated cements (SSC) were first discovered more than hundred years ago, but were abandoned after the 70's. Nowadays, this technology is experiencing a new boom, due to its durability towards sulfate attacks and to its ultra-low carbon footprint. These cements are composed of ground granulated blast-furnace slag (GGBS), calcium sulfate, and less than 5% Portland clinker (PC) according to the European standard. However, despite numerous studies on this subject, the role of PC content on the hydration of SSCs is still not well controlled and understood. As PC content increases, nonlinear and sometimes pessimum effects are observed for strength development in the short- and long-terms.

In this study, the effect of PC content variation is assessed with GGBS from various origins. It is shown that the optimized PC content for strength development is dependent on GGBS chemistry. Slight variations of PC content can lead to either optimum or pessimum of activation. With some GGBS sources, a 0.5% wt. increase of PC could lead to a 50% diminution of compressive strength of SSC at 28 days. Variations of mechanical strength cannot be correlated to hydration heat alone. Water accessible porosity and hydrates formation are also assessed to try to understand these phenomena.

KEYWORDS: *Supersulfated cement, activation, hydration, isothermal calorimetry, porosity*

1. Introduction

Supersulfated cement (SSC) technology is described in the European standard EN 15743-1+A1 (AFNOR (2015)), where it must contain at least 75% wt. of ground granulated blast-furnace slag (GGBS), between 5 and 20% wt. of calcium sulfate, and less than 5% wt of Portland clinker. Despite this normative definition, the formulation principles detailed in the literature are often empirical and the effect of each component is sometimes unclear. While the calcium sulfate content as well as the GGBS nature have been more carefully evaluated (e.g. Gruskovnjak et al (2008), Angulski da Luz and Hooton (2019)), the impact of the Portland cement activator is still under debate. The nature and content of activators have been studied by several authors, with sometimes contradictory observations. Bijen and Niel (1981) found that increasing clinker content from 2 to 5% wt. led to loss of strength while Baux et al (2014), showed the opposite. Angulski da Luz and Hooton (2019) found out that, with one GGBS source, increasing the activator content (KOH) led to better results, but it was the opposite with a second source. Kondo et al (1980) and Rubert et al (2018) also showed the high sensitivity of SSC to non-Portland activator content (Ca(OH)₂ and KOH respectively).

Unfortunately, all these authors often performed only few activator content variations, on few different GGBS sources. Thus, it remains difficult to analyse the role of activator and how SSC should be formulated to optimize its strength development.

This study aims to show the sensitivity of SSC to OPC dosage, with 8 different clinker contents and 3 GGBS of different origins. A methodology is proposed, by comparing compressive strength, isothermal calorimetry, hydrates formation and water accessible porosity.

2. Materials & Methods

Table 1 presents main characteristics of the materials used in this study. Three granulated slag sources were used. Source A was milled in two different ways: industrially with a vertical mill and in laboratory with a ball mill to have the comparison with other sources. The activation of SSC was realized with an ordinary Portland cement (OPC), and natural anhydrite served as a calcium sulfate source (Cs). All SSC were formulated by keeping a constant GGBS/Cs ratio equals to 7.33.

Table 1: Materials properties

	physical properties		Chemical composition (% wt)									
	grinding	d50 (μm)	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	Na ₂ O	K ₂ O	SO ₃	LoI
GGBS - A1	Vertical Mill	10.1	43.1	37.5	10.0	0.4	6.6	0.6	0.2	0.4	0.9	-
GGBS - A2	Ball Mill	5.5	42.9	36.9	10.6	0.4	6.8	0.6	0.3	0.4	1.0	-
GGBS - B	Ball Mill	4.7	42.2	33.9	14.6	0.9	6.0	0.5	0.2	0.3	1.1	-
GGBS - C	Ball Mill	5.4	35.7	36.4	18.1	1.0	6.1	0.6	0.3	0.4	0.9	-
OPC	-	10.4	63.4	20.4	3.8	3.0	1.5	0.2	0.2	0.9	3.2	1.2
Anhydrite	-	7.9	37.9	4.3	0.0	0.4	2.1	0.0	0.2	0.4	40.8	0.6

Compressive strength of SSC was either realized on mortars, (cured at 20°C, under water after 24h according to EN 196-1 standard), or on cement pastes (with 6 cubes of dimensions 2cm x 2cm x 2cm, per age of test). All pastes were casted with a water-to-binder ratio of 0.40 and cured at 20°C in autogenous conditions until tested. Hydration heat was followed by isothermal calorimetry. X-Ray diffraction (XRD) was performed at 28 days after hydration was stopped by solvent exchange. SSC dry powder was mixed with ~5%wt. of fluorite as internal calibration standard for Rietveld refinement. Water accessible porosity was estimated on paste, using a protocol consisting in drying at 50°C, after imbibition under vacuum.

3. Results

Figure 1 presents the influence of OPC content on SSC mortars' compressive strength at 1, 7 and 28 days, depending on GGBS source. For GGBS A, it appeared that the best OPC content to optimize both 1- and 28-days strength was around 0.25 to 0.5% wt. A pessimum phenomenon emerged for an OPC content of

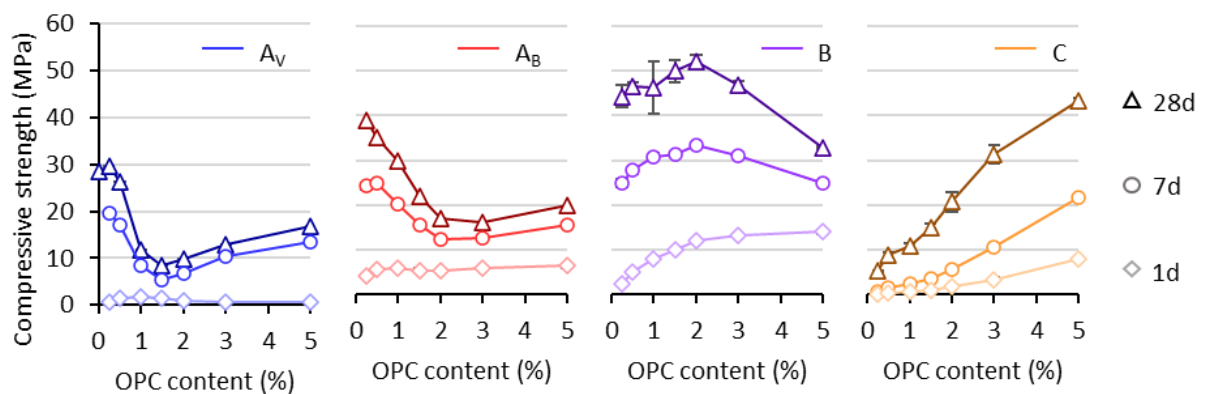


Figure 1: Compressive strength on standardized mortars of SSC at 1, 7 and 28d, depending on the GGBS source and OPC content in their formulation

1.5 to 2% wt. While grinding method had an impact on absolute strength development ($A_B > A_V$) at all curing ages, it had little to no consequence on OPC optimal content. GGBS B led to high strength due to its high Al_2O_3 and CaO content and presented an optimum effect for 2% wt. OPC. With GGBS C, considering the limits of formulation set by the standard, 5% wt. of OPC led to the best results. For the three GGBS tested, a linear correlation appeared between the optimal OPC content that would maximize long term strength and the Al_2O_3/CaO ratio of the GGBS.

Complementary analyses to understand the role of OPC on SSC hydration were only realized on GGBS A_V for the moment.

Figure 2a shows the normalized heat flow of SSC pastes made with GGBS A_V and variable OPC content. OPC content influenced the duration of induction period, the evolution of the hydration heat flow, and the time of appearance and value of maximum heat release. Increasing the OPC from 0.5 to 2% wt. extended the induction period, leading to a delayed maximum, single, heat flow peak. However, with 5% wt. OPC, at least 2 main peaks of hydration were visible. Without any OPC, SSC hydration started after 96h or later in some repetition trials.

Figure 2b presents the corresponding 7-day compressive strength plotted in function of the heat of hydration. Represented linear trend line do not consider the point without OPC as confidence interval on heat of hydration was too important. As revealed by the low R^2 value, despite a general tendency linking strength with hydration heat, it did not explain the zone where a small change of OPC content led to the largest loss in strength development (from 0.25 to 1.5% wt).

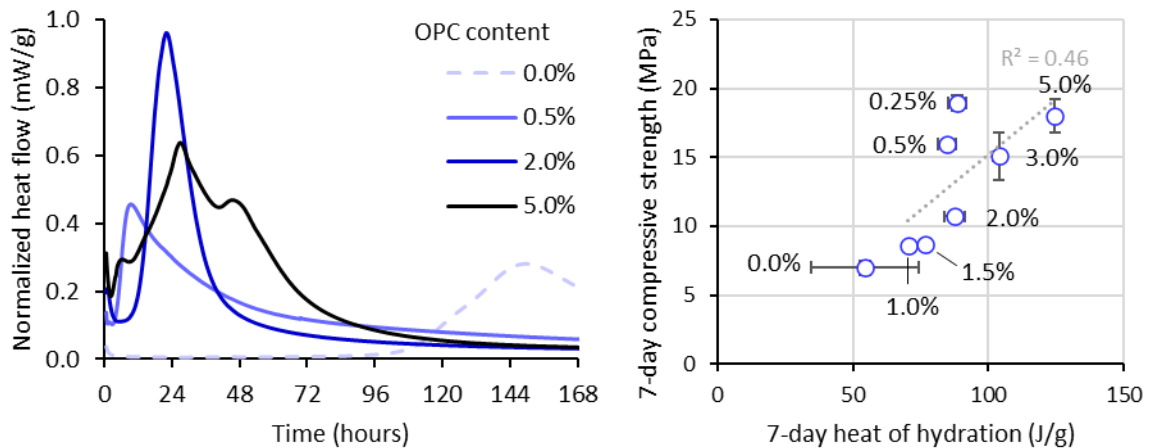


Figure 2: a) Normalized heat flow of SSC pastes made with GGBS A_V and variable OPC content and b) corresponding 7-day compressive strength plotted in function of the heat of hydration – indexed numbers corresponds to the OPC content

Figure 3 presents the XRD patterns obtained after 28 days of hydration of SSC paste made with GGBS A_V and various OPC contents. Diagrams were truncated in intensity so that all the hydrates are visible without being overwhelmed by the larger anhydrite and fluorite (used as reference) peaks. It was observed that these SSCs still contained unreacted anhydrite, and small gypsum content (coming from anhydrite surface hydration). Unsurprisingly, main crystallized hydrate was ettringite, but a poorly crystallized tobermorite like C-(A)-S-H phase could also be identified around 29° (Grangeon et al. (2016)). No modification in hydrates nature was identified for different OPC contents. However, ettringite production appeared to be positively correlated with the OPC dosage in SSC. After a Rietveld refinement, ettringite content was found to be around 5% wt. in all mixes with an OPC content below 1%, and 9% wt. for the SSC paste made with 5% wt. OPC (also correlated with a diminution of anhydrite).

Figure 4 shows the 28 days compressive strength of SSC pastes made with GGBS A_V , versus estimated water accessible porosity. This porosity was calculated after drying the samples at $50^\circ C$ until mass stabilization, instead of $105^\circ C$ as usually recommended (to avoid ettringite deterioration). Obviously, this method tends to reduce the calculated porosity since part of the smallest pores are not emptied at such a

low temperature. If the 5% wt. of OPC point is set aside, it was observed that compressive strength was well correlated with SSC porosity at 28 days.

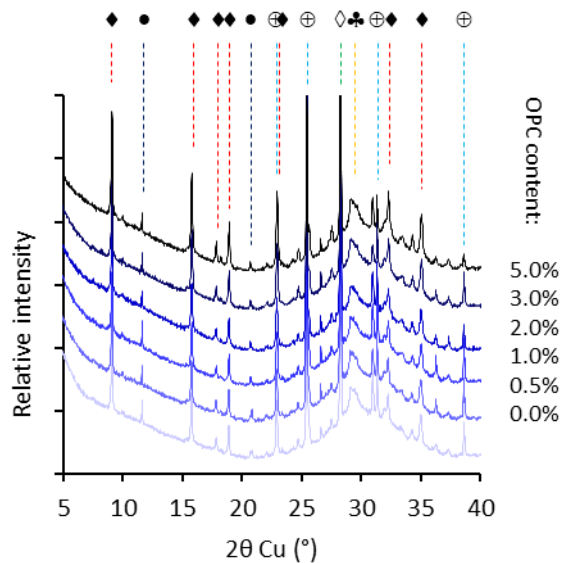


Figure 3: XRD of hydrated SSC pastes made with GGBS A_v and variable OPC content after 28 days – mineral phases are illustrated as follows: ⊕ Anhydrite ◆ Ettringite ◇ Fluorite ● Gypsum ♣ Tobermorite

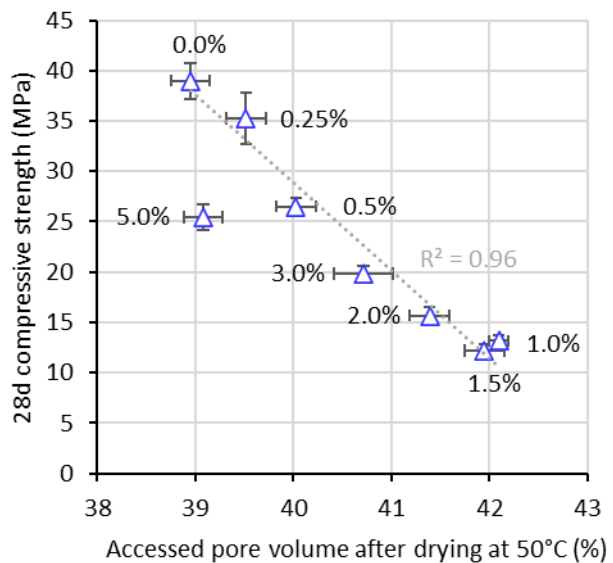


Figure 4: 28-day compressive strength of SSC pastes made with GGBS A_v and variable OPC content plotted in function of the water accessible porosity estimated after drying the samples at 50°C

4. Conclusions

Several conclusions were drawn from this study:

- The optimal OPC content to maximize SSC compressive strength was highly dependent on GGBS source. The chemical composition could have a preponderant influence.
- For a given GGBS, increasing OPC above 1% led to more ettringite formation. However, cumulative heat (associated to hydration rate) was not well correlated to compressive strength development. Thus, it would seem the degree of hydration alone could not explain why a major loss of strength can appear for a slight OPC variation.
- Strength was mostly driven by porosity development. It would suggest that along hydration of GGBS, formation of ettringite in the paste structure could be the main factor influencing its porosity. More in-depth analyses, realized on several GGBS sources, would be required to precise this phenomenon.

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