

# THE EFFECT OF Cs AND Sr ON THE MECHANICAL PROPERTIES OF BLAST FURNACE SLAG INORGANIC POLYMER FOR RADIOACTIVE WASTE IMMOBILISATION

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## Introduction

In pursuit of a sustainable society, researchers and industries have been increasingly studying the conversion of industrial residues into valuable construction materials such as inorganic polymers (IPs). These IPs can often be developed from both a single residue stream (*e.g.* metallurgical residue) or a combination of residue streams (typically amorphous/non-crystalline), mixed with an activating solution (*e.g.* Na-, K-hydroxides and silicates). The superior properties of IPs over OPC-based structures (fire resistance, chemical resistance, *etc.*) have led to different studies for their application as an immobilisation matrix for hazardous and radioactive substances<sup>1-4</sup>. The effectiveness in immobilising elements such as cesium (Cs) and strontium (Sr) has been proven in several studies<sup>1-3</sup>. However, the effect of the introduced elements on the properties of the IP-matrix has been studied to a much lesser extent<sup>5,6</sup>. Also, due to high variability in precursor compositions and the differences between high-Ca and low-Ca IP strength development, the conclusions of these studies cannot easily be generalised. This study focusses on the effect of Cs<sup>+</sup> and Sr<sup>2+</sup> on the setting time, strength development, and microstructure of IPs developed from ground granulated blast-furnace slag (GGBFS).

## Materials and Methods

The chemical composition of the GGBFS was analysed by X-ray fluorescence spectroscopy (Philips PW 2400). For producing IPs, GGBFS was used as precursor and NaOH as activating solution. GGBFS was milled to a Blaine-value of  $5430 \pm 40 \text{ cm}^2/\text{g}$  (EN 196-6) and the concentration of the solution used was 6 mole NaOH/L. IP-pastes were produced by mixing GGBFS with the activating solution at a liquid-over-solid ratio (L/S) of 0.37. This was chosen based on preliminary tests and allowed to attain pastes fluid enough for casting. Cs<sup>+</sup> and Sr<sup>2+</sup> were added (in the form of CsNO<sub>3</sub> and Sr(NO<sub>3</sub>)<sub>2</sub>) to account for 0, 0.5, 1 and 2 wt% of the final IP-mass (Table 1). The pastes with Sr(NO<sub>3</sub>)<sub>2</sub> were less fluid, thus a slight increase in the L/S ratio (Table 1) deemed necessary. The resulting pastes were cast in 20 x 20 x 80 mm<sup>3</sup> moulds and covered

with plastic foil to prevent evaporation of water. The samples were demoulded after 1 day and placed in plastic containers to further cure at  $21 \pm 2^\circ\text{C}$  for 28 days. The setting time of the different pastes was determined by EN 196-3. The flexural ( $f_{cf}$ ) and compressive strength ( $f_c$ ) of the obtained samples were determined at 1, 8 and 28 days according to EN 196-1. After 28 days, a spare sample of each formulation was cut with a low-speed diamond coated circular saw, embedded in resin, polished, and carbon-coated for WDS micro-chemical analysis using an electron probe micro-analyser (EPMA, JEOL JXA-8530F). The results expressed herein are the average of 3 to 6 measurement points, collected in the hardened IP-binder, for each formulation studied.

**Table 1:** Inorganic polymer mix design (wt%)

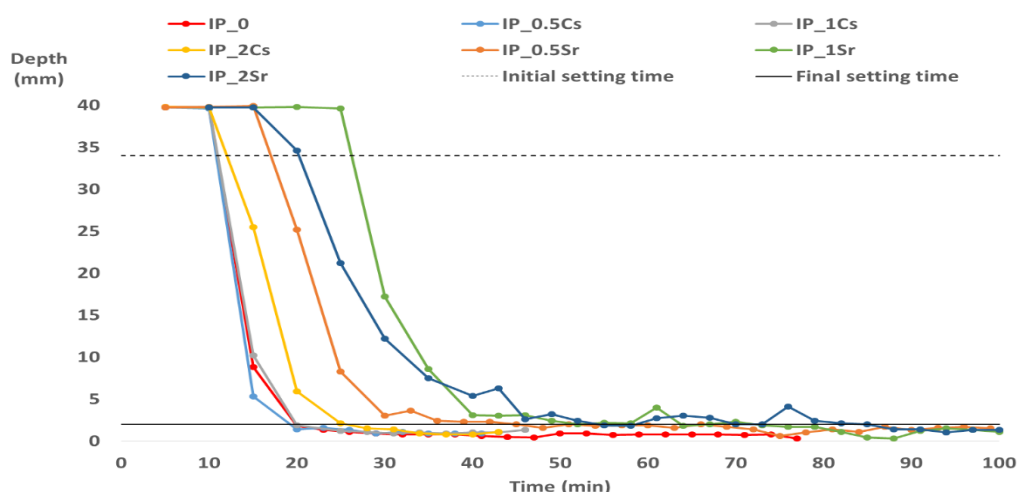
	GGBFS	NaOH (6M)	Cs <sup>+</sup>	Sr <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	L/S
IP_0	72.93	27.07	-	-	-	0.37
IP_0.5Cs	72.35	26.92	0.50	-	0.23	0.37
IP_1Cs	71.82	26.72	1.00	-	0.46	0.37
IP_2Cs	70.75	26.32	2.00	-	0.93	0.37
IP_0.5Sr	71.59	27.22	-	0.49	0.70	0.38
IP_1Sr	70.73	26.91	-	0.98	1.38	0.38
IP_2Sr	69.13	26.27	-	1.90	2.70	0.38

## Results and Discussion

In this paragraph the effect of Cs<sup>+</sup> and Sr<sup>2+</sup> on the setting time, mechanical properties, and WDS micro-chemical analysis of the developed IPs will be discussed. XRF analysis of the GGBFS showed as main constituents (wt%):  $40.3 \pm 0.5$  CaO,  $36.2 \pm 0.2$  SiO<sub>2</sub>,  $11.4 \pm 0.2$  Al<sub>2</sub>O<sub>3</sub> and  $8.2 \pm 0.1$  MgO.

### Setting time

Figure 1 shows the results for the setting time of the IPs doped with Cs<sup>+</sup> and Sr<sup>2+</sup>. The results show that setting time is only marginally affected when Cs<sup>+</sup>-addition does not exceed 1 wt%. A final setting time of about 20 min is obtained for IP\_0, IP\_0.5Cs and IP\_1Cs. Addition of 2 wt% Cs<sup>+</sup>, however, does show a retarding effect on the setting time of the IP-paste, resulting in a final setting time of about 28 min. Addition of Sr<sup>2+</sup> retards the setting time of the IP paste to a larger extent. The final setting time was approximately 48 min for IP\_0.5Sr, 64 min for IP\_1Sr and 88 min for IP\_2Sr, accounting for an increase of about 140%, 220% and 340% compared to IP\_0.



**Figure 1:** Initial and final setting time of IP-pastes with different wt% of Cs<sup>+</sup> and Sr<sup>2+</sup>

### Mechanical properties

The flexural ( $f_{cf}$ ) and compressive strength ( $f_c$ ) test results are shown in Table 2. Because of the low sample count, these results are indicative. At 28 days, IP\_0 shows a final  $f_c$  of  $64 \pm 3$  MPa and a  $f_{cf}$  of 11 MPa. Addition of 0.5 wt% Sr<sup>2+</sup> results in a decrease in  $f_c$  of about 30% at the same age; however, the decrease is larger with the increase in Sr<sup>2+</sup> to 2 wt%. In contrast, the addition of 0.5 wt% Cs<sup>+</sup> seems to enhance the  $f_c$  by about 15% at 28 days of curing compared with IP\_0. Doping with 1 and 2 wt% Cs<sup>+</sup> causes an increase in the  $f_c$  at 1 and 8 days of curing.

**Table 2:** Flexural ( $f_{cf}$ , 1 sample) and compressive ( $f_c$ , 2 samples) strength

	1 day		8 days		28 days	
Sample	$f_c$ (MPa)	$f_{cf}$ (MPa)	$f_c$ (MPa)	$f_{cf}$ (MPa)	$f_c$ (MPa)	$f_{cf}$ (MPa)
IP_0	$23 \pm 5$	9	$43 \pm 2$	13	$64 \pm 3$	11
IP_0.5Cs	$28.5 \pm 0.1$	13	$46 \pm 5$	14	$74 \pm 1$	8
IP_1Cs	$31 \pm 1$	11	$64 \pm 10$	14	$68 \pm 5$	8
IP_2Cs	$32 \pm 2$	11	$52 \pm 7$	15	$65 \pm 7$	10
IP_0.5Sr	$13 \pm 2$	9	$32.5 \pm 0.9$	9	$45 \pm 6$	12
IP_1Sr	$15.8 \pm 0.1$	8	$26 \pm 9$	7	$32 \pm 2$	10
IP_2Sr	$11.8 \pm 0.4$	7	$23 \pm 5$	7	$30 \pm 2$	11

### Micro-chemical analysis

The results from the WDS micro-chemical analyses on the IP-pastes doped with Cs<sup>+</sup> and Sr<sup>2+</sup> are shown in Table 3. The addition of 0.5, 1 and 2 wt% Cs<sup>+</sup> caused a gradual increase in the amount of Cs<sup>+</sup> in the IP-binder up to  $3.6 \pm 0.4$  wt%. This indicates that Cs<sup>+</sup> is incorporated very well in the IP-binder. Note that the results in Table 3 are wt% of the binder mass, and not of the total IP mass. Future experiments will be performed to study how much of the GGBFS-precursor is consumed to form the IP-structure. The amount of Sr<sup>2+</sup> incorporated is about 4 times less than Cs<sup>+</sup>. A possible saturation is also visible, since the fraction of Sr<sup>2+</sup> incorporated seems to decrease with increasing Sr<sup>2+</sup>

addition. The remaining  $\text{Sr}^{2+}$  will probably tend to be physically encapsulated as a precipitate (e.g.  $\text{Sr}(\text{OH})_2$  or  $\text{SrCO}_3$  <sup>3</sup>). It is also possible that, when mixing the ingredients, not all of the  $\text{Sr}(\text{NO}_3)_2$  dissolved, preventing the  $\text{Sr}^{2+}$  from being incorporated in the IP-matrix. Different mixing procedures (e.g. high shear mixing) will be tested in the future to see if more of the  $\text{Sr}(\text{NO}_3)_2$  can dissolve.

**Table 3:** Results of microstructural analysis using EPMA

Constituent (wt%)	IP_0.5Cs	IP_1Cs	IP_2Cs
Cs <sub>2</sub> O	1.4 ± 0.1	1.9 ± 0.4	3.8 ± 0.4
Cs <sup>+</sup>	1.3 ± 0.1	1.8 ± 0.4	3.6 ± 0.4
	IP_0.5Sr	IP_1Sr	IP_2Sr
SrO	0.43 ± 0.01	0.6 ± 0.1	1.0 ± 0.2
Sr <sup>2+</sup>	0.36 ± 0.01	0.47 ± 0.09	0.9 ± 0.1

## Conclusions

In this work, the effect of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  on the setting time, mechanical properties, and micro-chemistry of IPs developed from GGBFS was studied. For more than 0.5 wt%  $\text{Sr}^{2+}$  addition, there was a noticeable delay in the setting time, whereas for  $\text{Cs}^+$  the delay only occurred with 2 wt% addition. Compressive strength of the IPs decreased significantly by adding  $\text{Sr}^{2+}$ . Adding  $\text{Cs}^+$ , however, caused an increase of up to 15% in compressive strength at 28 days of curing, compared to IP\_0. Micro-chemical analysis showed that  $\text{Cs}^+$  is incorporated very well in the IP-binder, while  $\text{Sr}^{2+}$  is incorporated about 4 times less. To evaluate the effectiveness of GGBFS-based IPs for immobilising radionuclides, future leaching studies will be performed.

## References

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