

Incorporating Cs and Sr into blast furnace slag inorganic polymers and their effect on matrix properties

Peer-reviewed author version

VANDEVENNE, Niels; Ion Iacobescu, Remus; Pontikes, Yiannis; CARLEER, Robert; THIJSEN, Elsy; GIJBELS, Katrijn; SCHREURS, Sonja & SCHROEYERS, Wouter (2018) Incorporating Cs and Sr into blast furnace slag inorganic polymers and their effect on matrix properties. In: JOURNAL OF NUCLEAR MATERIALS, 503, p. 1-12.

DOI: 10.1016/j.jnucmat.2018.02.023

Handle: <http://hdl.handle.net/1942/25994>

# **Incorporating Cs and Sr into blast furnace slag inorganic polymers and their effect on matrix properties**

Niels Vandevenne <sup>a</sup>, Remus Ion Iacobescu <sup>b</sup>, Yiannis Pontikes <sup>b</sup>, Robert Carleer <sup>c</sup>, Elsy Thijssen <sup>c</sup>, Katrijn Gijbels <sup>a</sup>,  
Sonja Schreurs <sup>a</sup>, Wouter Schroeyers <sup>a,\*</sup>

<sup>a</sup> *Hasselt University, CMK, Nuclear Technological Centre (NuTeC), Faculty of Engineering Technology, Agoralaan,  
Gebouw H, 3590 Diepenbeek, Belgium*

<sup>b</sup> *KU Leuven, Department of Materials Engineering, Kasteelpark Arenberg 44, 3001 Leuven, Belgium*

<sup>c</sup> *Hasselt University, CMK, Research Group of Applied and Analytical Chemistry, Agoralaan, Gebouw D, 3590  
Diepenbeek, Belgium*

\* Corresponding author: Prof. dr. Wouter Schroeyers, e-mail address:

wouter.schroeyers@uhasselt.be

## Abstract

Minimizing harmful effects to the environment in waste-management practices requires continuous innovation. This is especially important in the field of radioactive waste management. Alternatives to the commonly used ordinary Portland cement matrices are being increasingly studied for improved immobilisation purposes. The development of inorganic polymers (IP) from industrial residues has been successfully studied for the immobilisation of caesium ( $\text{Cs}^+$ ) and strontium ( $\text{Sr}^{2+}$ ). However, knowledge of the effect of these introduced elements on the IP-matrix is scarce, especially considering that studied effects are dependent on the IP-precursor characteristics and the form in which the  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  are introduced. In this study, IPs containing varying amounts of  $\text{CsNO}_3$  and  $\text{Sr}(\text{NO}_3)_2$  were developed to study the effect of the introduced elements on the IP-characteristics. IP-samples were developed from ground granulated blast furnace slag (GGBFS) and 6 M NaOH activating solution.  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  were added to account for 0.5, 1 and 2 wt% of the total IP-mass. Throughout the entire study,  $\text{Cs}^+$ -addition showed no significant effects on the studied parameters. Calorimetric results showed that  $\text{Sr}^{2+}$  severely affects reaction kinetics, consuming hydroxide ions necessary for the alkali activation reaction.  $\text{Sr}^{2+}$ -addition also caused a severe decrease in compressive strength, increased calcium leaching, and decreased sodium and hydroxide leaching. Micro-chemical analyses showed that  $\text{Cs}^+$  is almost fully incorporated in the formed IP-matrix, while  $\text{Sr}^{2+}$  mainly precipitates as  $\text{Sr}(\text{OH})_2$  in concentrated regions throughout the IP-structure. The findings presented in this paper give insights on the effect of contaminant elements on the immobilizing matrix.

## Keywords

**Inorganic polymer, waste immobilisation, slag, caesium, strontium, alkali activation**

## 1 Introduction

To address health and environmental risks associated with long-term storage of radioactive waste (RAW), researchers have been looking for better performing alternatives to the ordinary Portland cement (OPC) matrices vastly used by the nuclear industry for RAW-immobilisation; these alternatives include calcium-sulfoaluminate-cement, calcium-aluminate-cement, and geopolymer/inorganic polymer-type matrices (based on metakaolin and sodium silicate) [1]. Immobilising hazardous cations like caesium-137 ( $^{137}\text{Cs}^+$ ,  $T_{1/2} = 30.05$  a) and strontium-90 ( $^{90}\text{Sr}^{2+}$ ,  $T_{1/2} = 28.80$  a) is key in handling RAW, especially concerning nuclear power plants [2,3], since these radionuclides are most often present in cooling water of nuclear reactors [4]. The main solidification mechanism for cationic species in OPC-based binders, which is based on precipitation of the corresponding hydroxides due to the highly alkaline pore solution, is not valid for  $\text{Cs}^+$  causing a low retention and high diffusion towards the biosphere [5]. According to Wieland et al. (2008),  $\text{Sr}^{2+}$ -uptake in OPC occurs mainly as partially hydrated species, binding  $\text{Sr}^{2+}$  to calcium-silicate-hydrate (C-S-H) phases [6]. They concluded that the  $\text{Sr}^{2+}$ -binding is mainly a reversible process, with only a small part of the  $\text{Sr}^{2+}$  being bound in the cement-structure, and that  $\text{Sr}^{2+}$  is bound to surface sites of C-S-H via bridging oxygen atoms through ion exchange interactions with  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  on silanol-groups of the C-S-H-phases (in line with an earlier study of Tits et al. (2006) [7]) [6].

A promising option for a more effective immobilisation matrix is the use of inorganic polymers (IPs). IPs generally demonstrate a higher fire/acid resistance in comparison to OPC and an increasing number of studies is dedicated to the suitability of IPs for RAW-immobilisation, using a variety of industrial wastes as precursors for the IPs [2,4,8–17]. However, introduced species can have a large impact on the properties of the immobilisation matrix, and this effect has been studied to a much lesser extent [18,19]. Also, the conclusions of these studies are not easily generalized due to high variability in precursor composition, and the differences between high-Ca and low-Ca precursors regarding the IP microstructure and strength development. Provis et al. (2008) studied the effect of

caesium and strontium salts (nitrates, sulphates and hydroxides) on metakaolin-based IPs and found that insoluble  $\text{SrCO}_3$  formed in all  $\text{Sr}^{2+}$ -containing samples [18]. They also found that the excess of nitrates precipitates as  $\text{NaNO}_3$  and that addition of  $\text{CsNO}_3$  caused a clear delaying effect on geopolymer binder formation, being significant even at 0.10 or 0.50 wt%  $\text{CsNO}_3$ . In addition, they reported a disruption of the pore structure formation, caused by the presence of ions in the pore solution (particularly the bulky  $\text{NO}_3^-$ ); these anions are repelled by the negatively charged aluminosilicate framework preventing condensation reactions from taking place [18]. This obstruction of gel-hardening was also observed by Komnitsas et al. (2013), who found that the compressive strength of their samples decreased by the presence of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , since these consume part of the alkali activator cations, hindering the geopolymerization reactions [20]. Provis et al. (2008) discussed that  $\text{Sr}^{2+}$  added as a nitrate will probably behave similarly to  $\text{Ca}^{2+}$  during geopolymer formation [18]. They noticed a dramatic decrease in the resistivity of the geopolymer binder and attributed this effect to the presence of the nitrate ion, causing a combination of increased pore size and connectivity, and subsequent mobility of the nitrate ions through the solution-filled pores [18]. They didn't observe this effect as strongly in the  $\text{CsNO}_3$ -containing samples and attributed this to the lower nitrate concentration [18]. According to Kuenzel et al. (2015),  $\text{Sr}^{2+}$  uptake in geopolymer activated by a  $\text{Na}^+$ -activating solution is limited to 0.4 mol  $\text{Sr}^{2+}$  per mol of aluminium, and an excess of  $\text{Sr}^{2+}$  is immobilised by precipitation as hydroxide or carbonate phases [4]. Peng et al. (2016) found that the addition of strontium to metakaolin-zeolite geopolymers caused a hysteresis effect [19]. They attributed the longer setting time to three possible causes: (1) precipitation of  $\text{Sr}^{2+}$  and  $\text{OH}^-$  or  $[\text{SiO}_4]^{4-}$ , passivating the surface of the precursors and slowing down dissolution; (2) reaction of  $\text{Sr}^{2+}$  and  $\text{OH}^-$  or  $[\text{SiO}_4]^{4-}$  resulting in a decrease in the number of hydroxide-ions and silicon-oxygen tetrahedrons; (3) the introduced ions lower the diffusion rate of all ions present in the system as a function of charge attraction and repulsion, and so postponing the geopolymer gel formation [19]. They also reported that  $\text{Sr}^{2+}$  takes part in the polymerization reaction and that the  $\text{Sr}^{2+}$ -ion can replace several  $\text{Na}^+$ -ions for charge balancing purposes [19].

Fewer studies exist on the use of alkali-activated ground granulated blast furnace slag (GGBFS) for immobilising caesium and strontium in comparison with e.g. alkali-activated metakaolin. According to Gong and White (2016), the primary reaction product in GGBFS-based IPs is a C-(N)-A-S-H gel (calcium-sodium-aluminium-silicate-hydrate), resembling a highly disordered C-S-H [21]. The reported use of IPs based on GGBFS for immobilising  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  is scarce [2,9]. Qian et al. (2001) prepared GGBFS IPs containing 0.5 wt%  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  and found them to immobilize  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  better than an OPC matrix [9]. A similar result was reported by Guangren et al. (2002) [2]. Some authors have added GGBFS as an additive in IPs based on different precursors [14,15,22]. However, the effect of caesium- and strontium-addition on the IP-characteristics is not thoroughly investigated. To fill this existing knowledge gap, IPs based solely on GGBFS and a NaOH activating solution are developed for the immobilisation of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$ . This paper discusses the effect of the introduced species on IP reaction kinetics and physical and mechanical properties.

## 2 Materials and methods

Commercially available GGBFS was used as a precursor for the IPs. The slag was first dried at 110 °C to constant weight and then milled for 6 h (Attritor ball mill type 1S, Wiener & Co.). The density of the slag was measured  $2.91 \pm 0.01 \text{ g/cm}^3$  (Quantachrome Multipycnometer MVP-6DC). The fineness of the resulting GGBFS powder was measured according to EN 196-6 [23] and found to be  $5900 \pm 100 \text{ cm}^2/\text{g}$ . The chemical composition of the GGBFS was determined by means of X-ray fluorescence spectroscopy and is shown in **Table 1** (results expressed as oxide, except for Cl).

**Table 1:** GGBFS oxide and chloride composition.

Compound	wt%
CaO	42.4
SiO <sub>2</sub>	33.5
Al <sub>2</sub> O <sub>3</sub>	11.3
MgO	8.5
SO <sub>3</sub>	1.9
TiO <sub>2</sub>	0.7

Na <sub>2</sub> O	0.4
K <sub>2</sub> O	0.4
Fe <sub>2</sub> O <sub>3</sub>	0.4
MnO	0.2
ZrO <sub>2</sub>	0.1
SrO	0.1
Cl	0.1

109

110 IP-pastes were produced by mixing the prepared GGBFS-powder with a 6 mol/L NaOH activating  
 111 solution at a liquid-over-solid ratio (L/S) of 0.37, found to be the optimum in an earlier study [24].  
 112 The activating solution was prepared from NaOH-pellets (Fischer Scientific, 98.44 % pure) and type II  
 113 distilled water. Cs<sup>+</sup> and Sr<sup>2+</sup> were added as nitrates (CsNO<sub>3</sub>, Alfa Aesar 99.8%; Sr(NO<sub>3</sub>)<sub>2</sub>, Emsure  
 114 99.0%) to account for 0, 0.5, 1 and 2 wt% of the final IP-mass (solid precursor + activating solution +  
 115 added nitrates). These amounts were fixed based on literature and earlier experiments (among  
 116 which our earlier study [24]). The mixtures were cast in 20 x 20 x 80 mm<sup>3</sup> moulds and covered with  
 117 plastic foil to prevent dehydration. The hardened samples were demoulded after 1 day, placed in  
 118 plastic containers, and allowed to further cure at 21 ± 2 °C for a total curing time of 28 days. The mix  
 119 designs are given in Table 2.

120

**Table 2:** Inorganic polymer mix design (wt%).

	GGBFS	NaOH (6 M)	Cs <sup>+</sup>	Sr <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>
IP_0	72.96 ± 0.04	27.04 ± 0.04	-	-	-
IP_Cs_0.5	72.45 ± 0.01	26.81 ± 0.01	0.50 ± 0.01	-	0.23 ± 0.01
IP_Cs_1	71.92 ± 0.01	26.61 ± 0.01	1.00 ± 0.01	-	0.47 ± 0.01
IP_Cs_2	70.87 ± 0.02	26.21 ± 0.01	1.99 ± 0.01	-	0.93 ± 0.01
IP_Sr_0.5	72.12 ± 0.01	26.68 ± 0.01	-	0.49 ± 0.01	0.70 ± 0.01

<b>IP_Sr_1</b>	71.24 ± 0.01	26.36 ± 0.01	-	0.99 ± 0.01	1.41 ± 0.01
<b>IP_Sr_2</b>	69.48 ± 0.02	25.71 ± 0.01	-	1.99 ± 0.01	2.82 ± 0.01

121

122

123 All IPs were characterised for heat release and physical and mechanical properties. Additionally,  
124 morphological and micro-chemical analyses were performed at 28 days of curing. Leaching tests took  
125 place at 48 days of curing. To study the effect of Cs<sup>+</sup> and Sr<sup>2+</sup> addition on the heat released during the  
126 alkali activation process, a calorimetric study was performed under isothermal conditions (TAMIII  
127 Thermal Activity Monitor, TA Instruments). A weighed amount of dry precursor was placed in a vial,  
128 while a weighed amount of activating solution was brought into two syringes and placed on top of  
129 the vial. This combination was then inserted into the calorimeter. After a few hours, when the  
130 calorimeter obtained a steady background signal, the activating solution was injected into the vial,  
131 and mixed with the precursor. In this way, the heat release was monitored from the very start of the  
132 reaction.

133 To study morphology and micro-chemistry, a 28-day cured sample of each composition was cut with  
134 a low-speed diamond coated circular saw to 20 x 20 x 5 mm<sup>3</sup>. This sample was then embedded in  
135 resin, polished, and carbon-coated. The micro-chemical analysis was performed with a Jeol  
136 Hyperprobe field emission gun electron probe micro-analyser (EPMA, JEOL JXA-8530F) equipped with  
137 five wavelength dispersive spectrometers (WDS). In addition to a point-based chemical analysis, the  
138 distribution of caesium and strontium was mapped for each of the samples. The EPMA was operated  
139 at 15 kV and a probe current of 15 nA. For quantitative elemental point analysis, the standards  
140 obsidian (for SiO<sub>2</sub>, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>), celestite (for SrO), and apatite (for CaO) were used, except for  
141 caesium, where a factory default standard was used instead, due to the unavailability of a known  
142 standard. Mappings for caesium were collected with a dwell time of 40 ms per pixel in an area of 750



143 x 575 pixels (pixel size 0.4  $\mu\text{m}$ ), and for strontium with a dwell time of 10 ms per pixel in an area of  
144 1300 x 1000 pixels (pixel size 0.8  $\mu\text{m}$ ). The mapped surface area for caesium and strontium was 300 x  
145 230  $\mu\text{m}$  and 1040 x 800  $\mu\text{m}$ , respectively.

146 The flexural ( $f_{cf}$ ) and compressive strength ( $f_c$ ) of the IP-pastes were measured at 1, 8 and 28 days.  
147 Of each composition, and at each time of sampling, three samples were used for the flexural  
148 strength. The sample dimensions were 20 x 20 x 80  $\text{mm}^3$ . For the compressive strength, six  
149 repetitions were performed using cubic samples of 20 x 20 x 20  $\text{mm}^3$ .

150 Determination of water absorption ( $E_v$ ) (vacuum method), apparent porosity ( $P$ ), apparent relative  
151 density ( $T$ ), and bulk density ( $B$ ) were performed following international standard ISO 10545-3 [25].  
152 Results showed that the  $E_v$  and  $P$  were very low ( $< 1\%$ ), and were not influenced by addition of  
153 strontium or caesium.  $T$  and  $B$  were both measured as  $2.1 \pm 0.1 \text{ g/cm}^3$ .

154 The capacity for immobilising  $\text{Cs}^+$  and  $\text{Sr}^{2+}$ , and the release of the structural elements were  
155 determined by means of a dynamic diffusion test based on the standards ASTM C1220-98 [26] and  
156 EN/TS 15863:2015 [27]. IP-subsamples of 20 x 20 x 25  $\text{mm}^3$  were cut from a larger 48-day-cured  
157 sample by means of dry cutting (to avoid premature wash-out). These samples were then cleaned  
158 using a dry brush, measured for dimensions and weight, and submerged in 400 ml of Milli-Q water  
159 while fixed in the centre of the water volume. Both container and sample holder were made of  
160 polypropylene. The containers were tightly closed and placed in an oven at  $90 \pm 2^\circ\text{C}$  for 7 days. At 1  
161 h, 24 h, and 7 d after the start of the leaching experiment, the entire eluate volume was refreshed  
162 and aliquots were taken for further characterization. At each sampling time, 10.0 ml of the eluate  
163 was filtered over a 0.2  $\mu\text{m}$  syringe filter and acidified immediately after sampling to a concentration  
164 of 1 %  $\text{HNO}_3$  (MERCK Suprapur 65 %). The concentration of water-soluble  $\text{Cs}^+$  was measured by ICP-  
165 MS (Perkin Elmer NexION 350S), while the concentrations of  $\text{Sr}^{2+}$ ,  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Na}^+$  were  
166 measured by ICP-OES (Perkin Elmer type Optima 8300). The leaching experiment was performed in  
167 twofold for each of the IP-compositions. The results from the ICP-OES and ICP-MS measurements are

corrected for dilution and sample surface area. One blanc test per repetition was conducted simultaneously, using 400 ml of Milli-Q water in the exact same conditions, excluding the presence of a sample. The experimental results are expressed as the amount of the element released at sampling time ( $t$ ), divided by the surface area of the sample ( $A$ ). The cumulative release of each constituent can be calculated as:

$$R_i = \frac{\sum_0^n [(C_{i,n} - B_{i,n}) \cdot V]}{A} \quad (1)$$

With

$R_i$  = cumulative release of element  $i$  (g/m<sup>2</sup>)

$C_{i,n}$  = concentration of element  $i$  in the filtered aliquot  $n$  (g/ml)

$B_{i,n}$  = concentration of element  $i$  in the filtered blanc aliquot  $n$  (g/ml)

$V$  = initial volume of eluate in bottle containing sample matrix (ml)

$A$  = surface of sample (m<sup>2</sup>)

Each sample was weighed before and after the leaching experiment. The loss of mass is similar for all samples (between 2 % and 6 %) and does not seem to be affected by the addition of caesium or strontium. At each sampling time, a portion of the eluate was used for measuring pH (calibrated electrode HI1043B, Hanna Instruments) and conductivity (Schott Geräte CG 858, calibrated with 0.1 M KCl), while another portion was used for titration purposes, to determine the amount of <sup>-</sup> hydrogen-consuming species released during the leaching process. Titration was performed in threefold using an automated burette (Metrohm Basic Titrino 794) with 0.1 M HCl. The HCl-solution was set with Na<sub>2</sub>CO<sub>3</sub> dried at 110 °C as the primary standard.

### 3 Results and discussion

**Figure 1** shows a visual difference between strontium- and caesium-containing samples. The photographs are taken after 8 days of curing. The white spots observed in the strontium-containing samples are most likely crystals of Sr(OH)<sub>2</sub> (see later section 3.1).



**Figure 1.** Visual difference between samples containing strontium or caesium. Samples from left to right: IP\_0, IP\_Cs\_0.5, IP\_Cs\_1, IP\_Cs\_2, IP\_Sr\_0.5, IP\_Sr\_1, IP\_Sr\_2.

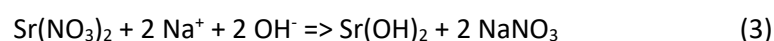
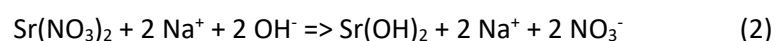
### 3.1 Calorimetry

The isothermal calorimetry results are given in **Figure 2**, showing the evolution of the heat released during the alkali activation process of the GGBFS-precursor, and the effect of caesium and strontium additions. The first stage of the reaction is a very fast and exothermic process, reaching a maximum heat flow of about  $32 \text{ J h}^{-1} \text{ g}^{-1}$  (per gram of solid precursor) for IP\_0. This maximum is reached about 50 min after adding the activating solution. The initial heat release is due to sorption of the activating solution on the precursor surface (weathering) and the dissolution of the solid aluminosilicate. After this, a lower but continuous heat release is measured due to ongoing polymerisation reactions [28].

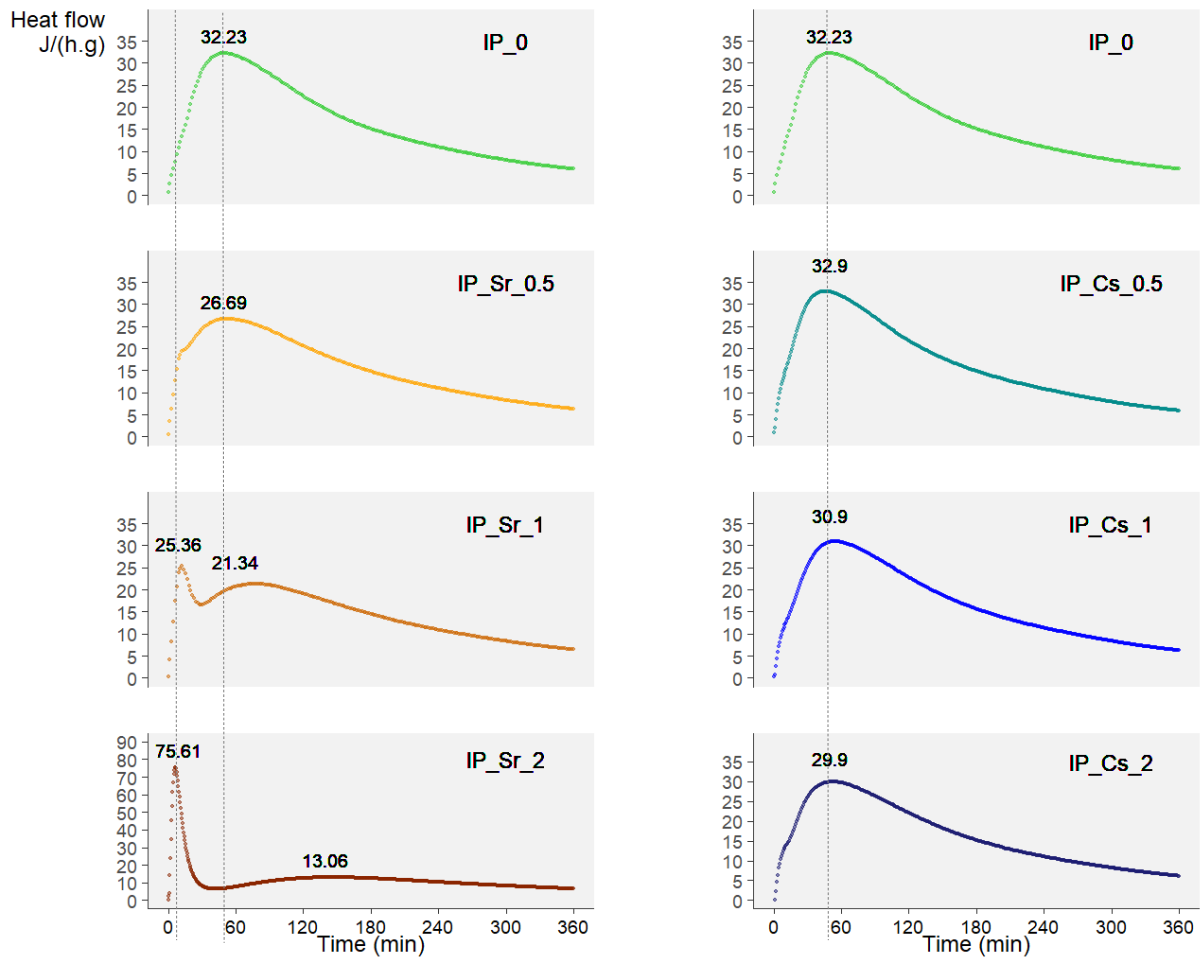
The results from **Figure 2** indicate that addition of  $\text{Cs}^+$  has little to no effect on the heat released during the alkali activation process. Only a small variation in the maximum heat flow can be observed (peak measurement of  $32.2 \text{ J h}^{-1} \text{ g}^{-1}$  for IP\_0 and  $29.9 \text{ J h}^{-1} \text{ g}^{-1}$  for IP\_Cs\_2), while no time delay of the maximum takes place. Addition of  $\text{Sr}^{2+}$ , however, does show a clear effect on the heat flow during the activation process. When increasing the amount of  $\text{Sr}^{2+}$ , an increasingly distinct peak appears before the initial weathering takes place (e.g. the peak of  $25.36 \text{ J h}^{-1} \text{ g}^{-1}$  for IP\_Sr\_1). This initial peak can be attributed to the formation of  $\text{Sr}(\text{OH})_2$  immediately after adding the activating solution to the dry precursor (with  $\text{Sr}(\text{NO}_3)_2$  mixed in). This reaction consumes a portion of the hydroxide ions, preventing them to participate in the alkali activation process. This effect would be manifested in a lower heat flow and a horizontal shift (time delay) of the peak (e.g.  $21.34 \text{ J h}^{-1} \text{ g}^{-1}$  for IP\_Sr\_1) to the right. These slower dissolution kinetics are in line with the observed effect of strontium on the setting time of GGBFS IPs reported in an earlier study [24], where it was found that the setting time of a GGBFS-IP-paste is severely delayed by addition of  $\text{Sr}^{2+}$ . The less profound activation reaction for

IP\_Sr\_1 and IP\_Sr\_2 (measured as lower heat release, **Figure 2**) also leads to a decreased compressive strength (see section 3.3, **Figure 5**). During the mixing and casting procedure of the IP-samples, the addition of strontium also led to a more viscous mixture.

It is assumed that strontium hydroxide is formed immediately when  $\text{Sr}^{2+}$  comes into contact with the activating solution. Equation (2) assumes that the sodium- and nitrate-ions remain dissociated, while equation (3) assumes that the sodium and nitrate will precipitate to form  $\text{NaNO}_3$ . The crystallization of  $\text{NaNO}_3$  from the pore solution has been reported by Provis et al. (2008) [18] and Blackford et al. (2007) [12] (both metakaolin-based IPs) when adding  $\text{Sr}(\text{NO}_3)_2$ , although not immediately during mixing, in contrast to the  $\text{Sr}(\text{OH})_2$  formation.



Since the formation of  $\text{NaNO}_3$  has been reported to take place during a later drying stage [18], it would thus not cause an immediate energy release during initial mixing. In **Figure 2**, however, for sample IP\_Cs\_2 a small “shoulder” in the curve is observed; since the amount of nitrates present in this sample is quite high, this could be due to formation of  $\text{NaNO}_3$  or the prevention of condensation reactions by the  $\text{NO}_3^-$  ions as reported by [18,20]. The consumption of hydroxide ions by the introduced strontium reduces the amount available for the activation reaction, which is also reflected in the decreased  $\text{OH}^-$ -leaching in the strontium-containing samples (later section 3.4.4, **Figure 12**). The white spots observed in the strontium-containing samples (see **Figure 1**) are most likely regions of  $\text{Sr}(\text{OH})_2$ , which precipitate as a fine white crystalline solid.



**Figure 2:** Effect of adding  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  on the heat released per gram of solid precursor ( $\text{J h}^{-1} \text{g}^{-1}$ ) during alkali activation of GGBFS.

### 3.2 Micro-chemical analysis

The results from the WDS micro-chemical analyses on the IP-samples are shown in **Table 3**. It is important to note that the amounts given in **Table 3** are weight-percentages of the IP-matrix formed by the activation process, excluding the undissolved precursor particles (hereafter referred to as *matrix*), and not of the total IP-mass (hereafter referred to as  $IP_m$ ). The fractions of introduced strontium and caesium that are incorporated into the matrix, taking into account the ratio of formed matrix over undissolved precursor, are determined by the following approach: using *Particle (Pores) and Cracks Analysis System (PCAS)* software, a number of images were separately analysed to average the surface ratios of matrix over undissolved precursor, which was found to be about 65/35.

Since this ratio is obtained using different images of randomly cut samples, it can also be assumed valid as a volume over volume ratio. Using this ratio, the density of the matrix phase is found to be 1.7 g/cm<sup>3</sup>, calculated using equation (4). The matrix phase, and the calculated density include possible pores and cracks. But since the open porosity is very low (see section 2), this influence is expected to be limited. The measured amounts of caesium and strontium (**Table 3**) in the matrix are converted to their respective fractions in the total IP-sample using equation (5).

$$\rho_M = \frac{\rho_{IP_m} - 0.35 * \rho_{GGBFS}}{0.65} \quad (4)$$

$$wt\%_{IP_m} = \frac{wt\%_M * 0.65 * \rho_M}{\rho_{IP_m}} \quad (5)$$

With

$\rho_M$  = density of the matrix (g/cm<sup>3</sup>)

$\rho_{IP_m}$  = density of the total inorganic polymer sample (2.1 g/cm<sup>3</sup>, see section 2)

$\rho_{GGBFS}$  = density of the GGBFS precursor (2.91 g/cm<sup>3</sup>, see section 2)

$wt\%_{IP_m}$  = weight-percentage of Cs<sup>+</sup> or Sr<sup>2+</sup> in the total inorganic polymer sample

$wt\%_M$  = weight-percentage of Cs<sup>+</sup> or Sr<sup>2+</sup> in the matrix phase (as tabulated in **Table 3**)

For each measured  $wt\%_M$ , the calculated  $wt\%_{IP_m}$  is given in **Table 4**, together with the fractions of the introduced caesium and strontium that are incorporated in the matrix ( $wt\%_{IP_m}$  divided by 0.5, 1 or 2 wt%, multiplied by 100 %). Because of the uncertainty in the 65/35 ratio, the values in **Table 4** are given as estimates. From these values it can be deduced that for caesium, about all of the introduced Cs<sup>+</sup> is incorporated into the IP-matrix. These findings are in line with the study of Blackford et al. (2007), who reported that Cs<sup>+</sup> is fully incorporated at the nm-scale into the amorphous geopolymers phase [12]. For Sr<sup>2+</sup>, the amounts shown in **Table 4** are corrected for the initial strontium-content measured in IP\_0; the tabulated wt% are thus the amounts of Sr<sup>2+</sup>

incorporated in the IP-matrix in addition to the inherent strontium from the precursor. From these results it can be concluded that in every step of strontium addition (0.5, 1, and 2 wt%), about one sixth is incorporated into the IP-matrix. Results from **Table 3** indicate that addition of strontium or caesium has no effect on the amounts of silicon, aluminium and sodium in the matrix. However, a small effect on the amount of calcium is observed. Adding caesium seems to cause a slight decrease of the  $\text{Ca}^{2+}$ -content, possibly caused by  $\text{Cs}^+$  replacing  $\text{Ca}^{2+}$ , since  $\text{Ca}^{2+}$  can act as a charge balancing ion [29].

**Table 3:** Results of micro-chemical analysis using EPMA (calculated from oxides).

Element (wt%)	IP_0	IP_Sr_0.5	IP_Sr_1	IP_Sr_2
$\text{Si}^{4+}$	13 ± 1	13 ± 1	12.6 ± 0.6	13 ± 1
$\text{Al}^{3+}$	5.3 ± 0.3	6 ± 1	5.5 ± 0.3	6.1 ± 0.6
$\text{Ca}^{2+}$	16.2 ± 0.9	17 ± 2	17 ± 1	17 ± 2
$\text{Na}^+$	2.0 ± 0.6	1.9 ± 0.5	2.6 ± 0.7	2.5 ± 0.4
$\text{Sr}^{2+}$	0.20 ± 0.02	0.36 ± 0.01	0.47 ± 0.09	0.9 ± 0.1
$\text{Cs}^+$	-	-	-	-
Element (wt%)		IP_Cs_0.5	IP_Cs_1	IP_Cs_2
$\text{Si}^{4+}$		13 ± 1	13 ± 1	12.5 ± 0.9
$\text{Al}^{3+}$		6.2 ± 0.6	5.8 ± 0.7	5.7 ± 0.8
$\text{Ca}^{2+}$		12 ± 2	13 ± 1	12.8 ± 0.7
$\text{Na}^+$		3.6 ± 0.4	2.5 ± 0.8	2.9 ± 0.4
$\text{Sr}^{2+}$		0.19 ± 0.02	0.19 ± 0.03	0.19 ± 0.02
$\text{Cs}^+$		1.32 ± 0.09	1.8 ± 0.4	3.6 ± 0.4

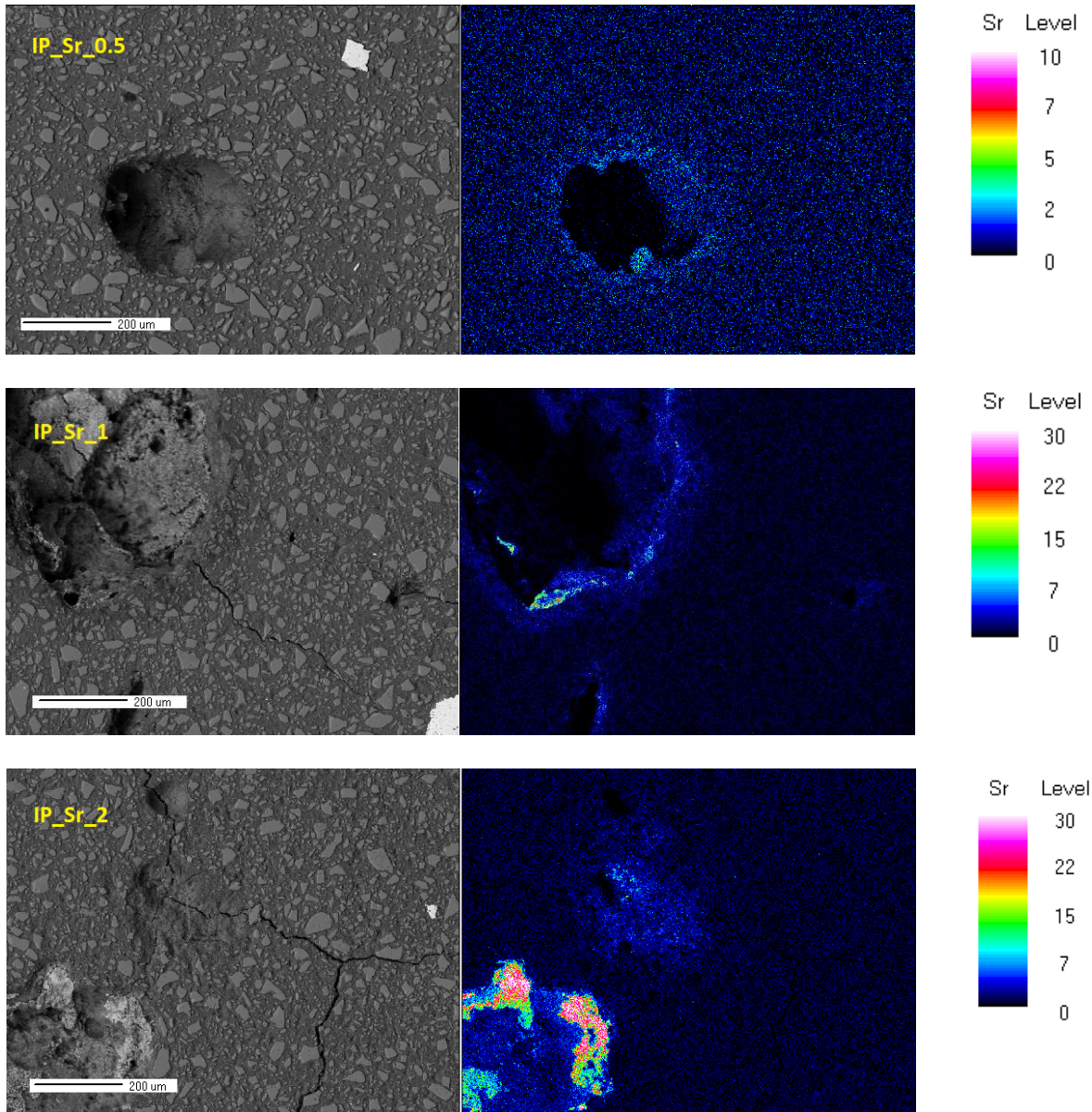
**Table 4.** (a) Weight-percentages of caesium and strontium incorporated in the matrix phase, recalculated for the entire IP-mass, and corrected for initial strontium content. (b) Percentages of introduced caesium and strontium that are incorporated into the matrix.

(a) wt% <sub>IP<sub>M,cor</sub></sub>	IP_Sr_0.5	IP_Sr_1	IP_Sr_2	IP_Cs_0.5	IP_Cs_1	IP_Cs_2
<b>Sr<sup>2+</sup></b>	0.08	0.14	0.36	-	-	-
<b>Cs<sup>+</sup></b>	-	-	-	0.68	0.93	1.86
(b) Fraction incorporated into matrix (%)						
<b>Sr<sup>2+</sup></b>	17	14	18	-	-	-
<b>Cs<sup>+</sup></b>	-	-	-	100*	93	93

\* This value is rounded down since the calculated value is 137 % (probably due to statistical variation in the concentrations at the measurement points)

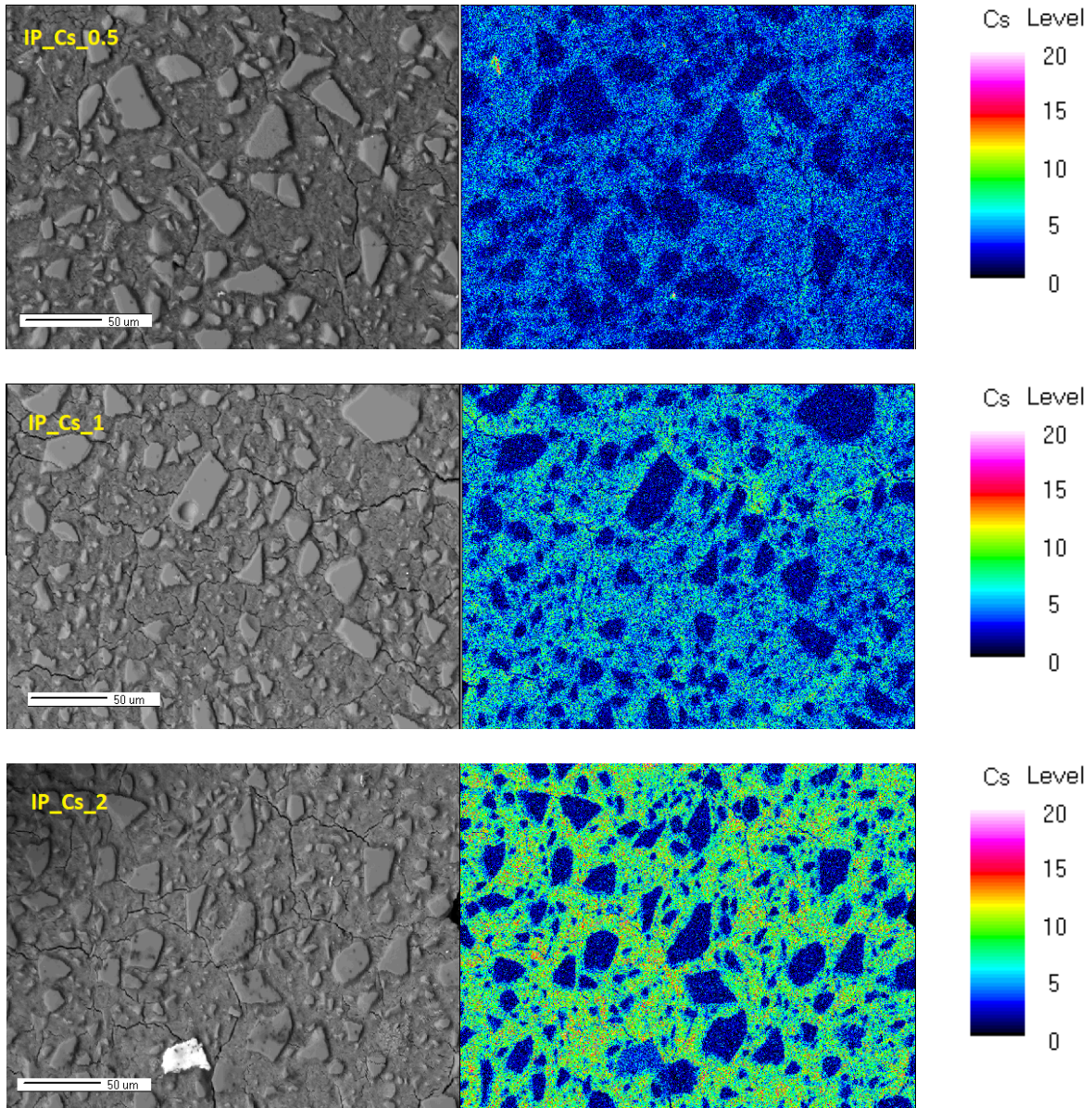
**Figure 3** and **Figure 4** show mappings of these same samples to study the distribution of caesium and strontium throughout the microstructure. Mapping of the Sr<sup>2+</sup>-containing samples is done at a larger scale than for the Cs<sup>+</sup>-samples because this allows a clear view of precipitation sites for Sr(OH)<sub>2</sub>, while the smaller scale for the Cs-samples allows a clearer view of the incorporation of Cs<sup>+</sup> in the binder. For the samples containing added strontium, precipitation sites are clearly visible where large amounts of strontium are concentrated. From **Figure 3**, sample IP\_Sr\_0.5, it can be observed that a small amount of strontium is distributed evenly throughout the microstructure. **Figure 3** also shows large pores where the Sr<sup>2+</sup> seems to be concentrated. **Figure 4** shows that Cs<sup>+</sup> is incorporated homogeneously throughout the binder-phase. This difference in incorporation is also reflected in the leaching results (see further, section 3.4), where Cs<sup>+</sup> leaches out more easily since it is distributed evenly throughout the structure (and thus being more available at the sample surface), while Sr<sup>2+</sup> is more physically encapsulated (and thus less available at the sample surface).





**Figure 3:** EPMA mappings of IP\_Sr\_0.5, IP\_Sr\_1 and IP\_Sr\_2. The level-scale of IP\_Sr\_0.5 is smaller for improved visibility of the distribution of strontium throughout the matrix. The chemical composition of the samples is given in **Table 3**.



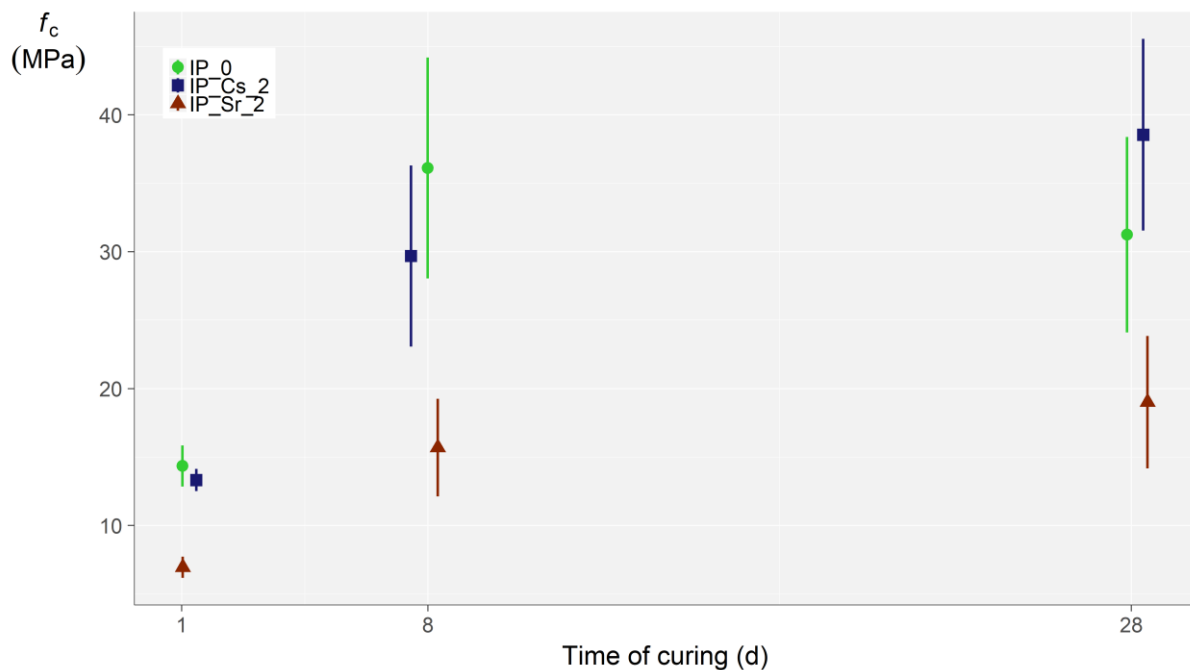


**Figure 4:** EPMA mappings of IP\_Cs\_0.5, IP\_Cs\_1 and IP\_Cs\_2. The chemical composition of the samples is given in **Table 3**.

### 3.3 Compressive and flexural strength

The compressive strength data shown in **Figure 5** indicate that addition of  $\text{CsNO}_3$  does not significantly affect the strength development. Addition of  $\text{Sr}(\text{NO}_3)_2$ , however, does show a deleterious effect on the compressive strength. After 1 day and 8 days of curing, the compressive strength of IP\_Sr\_2 is only about 45 % of the values for IP\_0. This difference is reduced with increased curing time. At 28 days of curing, IP\_Sr\_2 ( $19 \pm 5$  MPa) reaches about 60 % of the

compressive strength of IP\_0 ( $31 \pm 7$  MPa). This negative effect on the compressive strength is probably caused by the less profound alkali activation reaction due to the formation of  $\text{Sr}(\text{OH})_2$  and  $\text{NaNO}_3$ , causing a less concentrated activating solution and resulting in slower dissolution kinetics (as discussed in section 3.1, and observed in an earlier study [24] as a longer setting time). The occurrence of  $\text{Sr}(\text{OH})_2$  precipitation spots and accompanying pores (see **Figure 1** and **Figure 3**) can also cause weak spots in the IP-structure. Provis et al. (2008) found that, in a metakaolin-based system, the addition of  $\text{CsNO}_3$  caused a clear delaying effect on geopolymer gel formation, being significant even at 0.10 or 0.50 wt%  $\text{CsNO}_3$ , and attributed this to the presence of  $\text{NO}_3^-$  [18]. Since no negative effect is observed in the caesium-containing samples in this study, the decrease in compressive strength for the strontium-containing samples cannot be attributed to the presence of nitrates, but rather the presence of  $\text{Sr}^{2+}$ . A similar conclusion can also be drawn from an earlier study [24] where it was found that adding up to 2 wt%  $\text{Cs}^+$  (in the form of nitrates) only showed a small effect on the final setting time (delay of up to 40 %), while strontium-addition retarded final setting severely (delay of 140 % at 0.5 wt%  $\text{Sr}^{2+}$ ). For the flexural strength of the samples, the standard deviations are much too high to distinguish clearly between the results. Only at 1 day and 8 days of curing, there is a small discernible difference between IP\_0 (1d:  $9 \pm 1$  MPa; 8d:  $12 \pm 1$ ) and IP\_Sr\_2 (1d:  $7 \pm 1$  MPa; 8d:  $9 \pm 2$  MPa). At 28 days of curing, no significant difference was observed.



**Figure 5:** Compressive strength of IP\_0, IP\_Sr\_2 and IP\_Cs\_2. Measurement points have been randomly offset from the times of curing (1 d, 8 d, and 28 d) for increased discernibility.

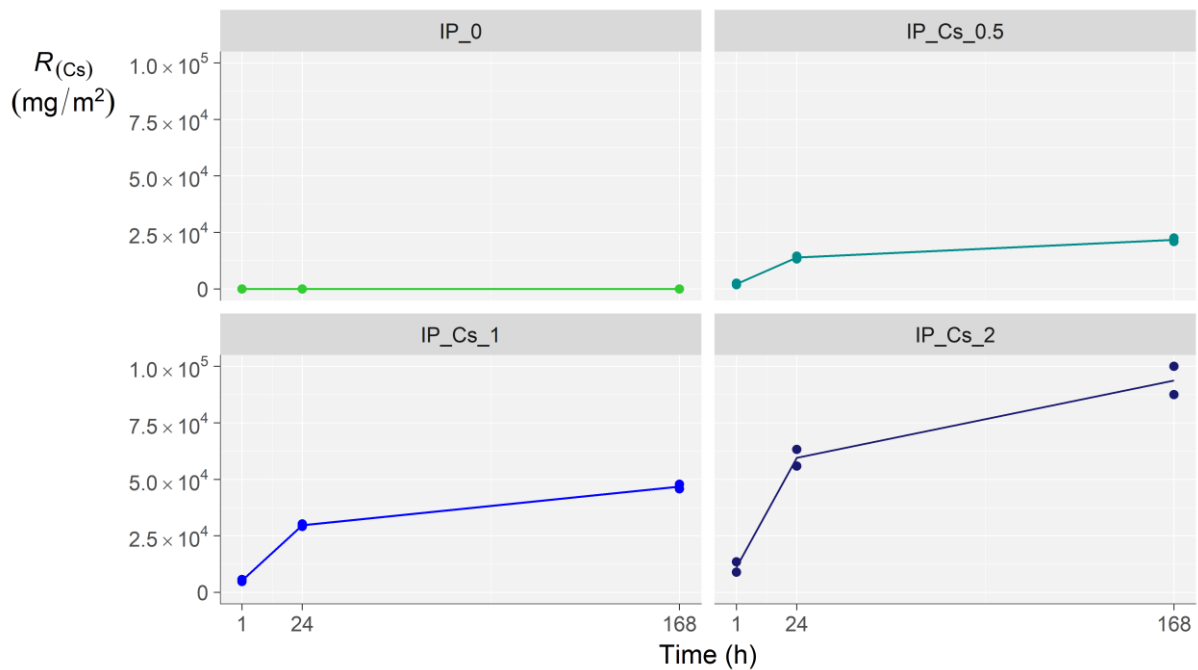
### 3.4 Leaching of structural and added elements

By use of a dynamic accelerated leaching test, the amount of  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ , and structural elements released has been studied. For the release of caesium and strontium, only results are shown from the samples where the respective elements were added, together with IP\_0. Overall, the measurement points lie very close together.

#### 3.4.1 Release of $\text{Cs}^+$

The results of IP\_Cs\_0.5, IP\_Cs\_1 and IP\_Cs\_2 (**Figure 6**) show that the amount of  $\text{Cs}^+$  released increases proportionally with the amount of  $\text{Cs}^+$  introduced in the IP-matrix. There is no obvious change in leaching behaviour when adding more  $\text{Cs}^+$ , only an increase in the total amount released. When taking into account the amount of  $\text{Cs}^+$  introduced into each sample, the mass of the sample, and the total amount of  $\text{Cs}^+$  leached out, the percentage of introduced  $\text{Cs}^+$  that was released can be determined. For IP\_Cs\_0.5, IP\_Cs\_1, and IP\_Cs\_2 this is respectively 63 %, 66 %, and 62 %. This

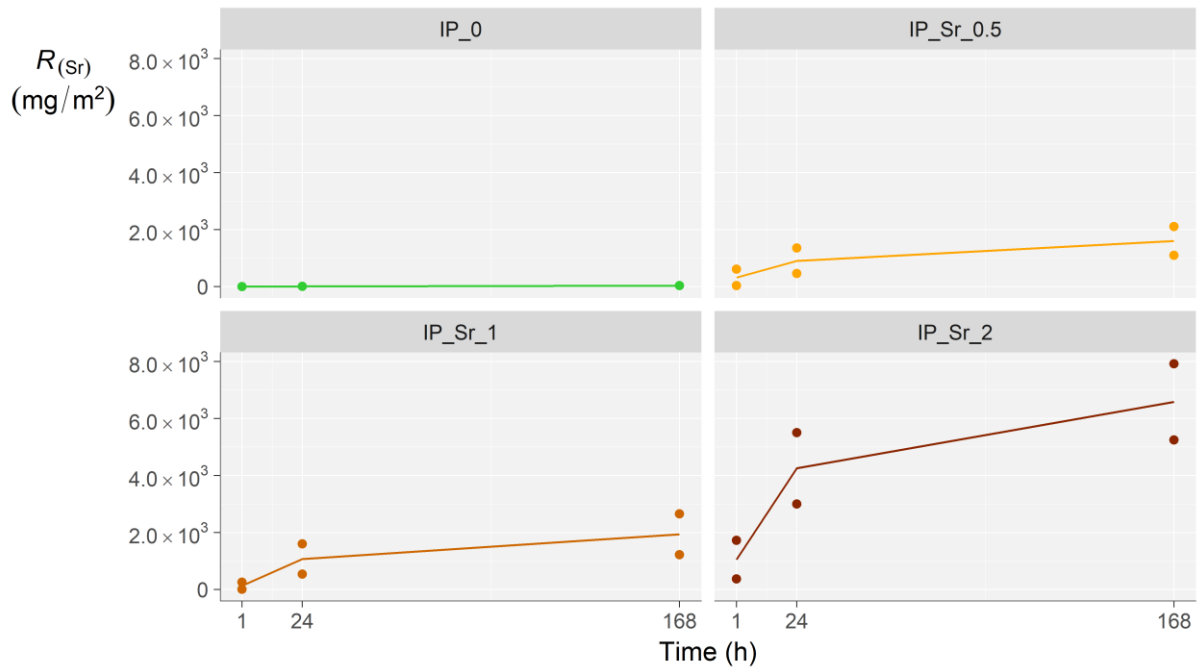
finding is in line with the proportional caesium-incorporation in the IP-binder, discussed in paragraph 3.2.



**Figure 6:** Cumulative release of  $Cs^+$  during a 7-day dynamic leaching test.

#### 3.4.2 Release of $Sr^{2+}$

A small amount of  $Sr^{2+}$ , present in the GGBFS, leaches out from the base sample IP\_0 (about 35 mg/m² after 7 days). When adding increasing amounts of  $Sr^{2+}$ , a proportional increase in  $Sr^{2+}$ -release is not immediately observed (see **Figure 7**). The measurement results are also less precise than the results for the other elements. This is most likely due to the fact that a large part of the  $Sr^{2+}$  is precipitated in the IP-structure as  $Sr(OH)_2$  (as discussed in sections 3.1 and 3.2). This causes a distribution of precipitation sites (see **Figure 1**). Due to the casting process and cutting of the samples into smaller subsamples, a variation occurs in the amount of precipitated  $Sr(OH)_2$  spots on or near the surface of the samples. This causes a variation in the amount of  $Sr(OH)_2$  available for immediate dissolution from these precipitation spots. The amounts of introduced  $Sr^{2+}$  that were released, are 3 %, 2 %, and 4 % for IP\_Sr\_0.5, IP\_Sr\_1, and IP\_Sr\_2 respectively.

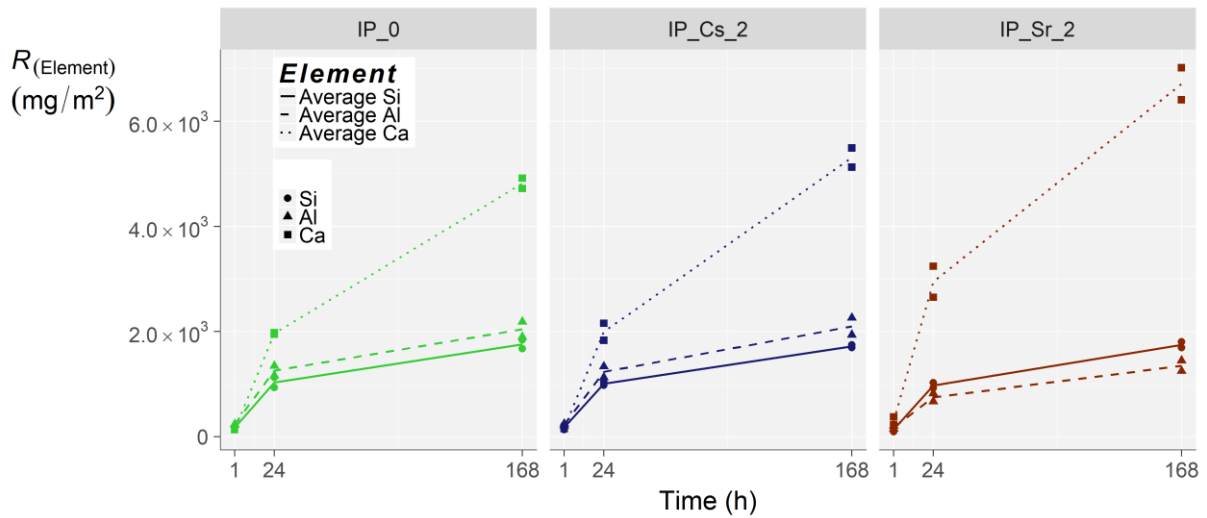


**Figure 7:** Cumulative release of  $\text{Sr}^{2+}$  during a 7-day dynamic leaching test.

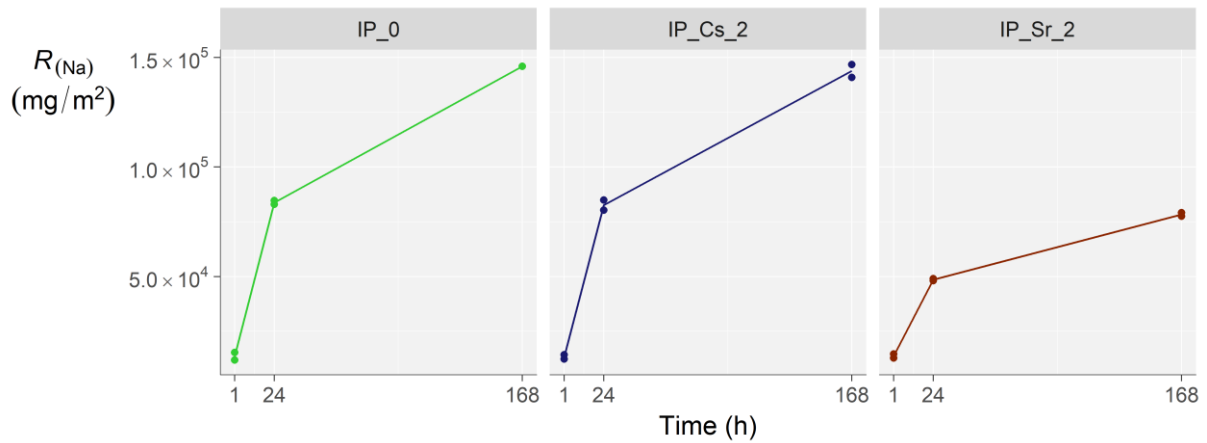
### 3.4.3 Release of structural elements

**Figure 8** and **Figure 9** show the cumulative release of  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  respectively.  $\text{Al}^{3+}$ -release of about 2000  $\text{mg/m}^2$  for IP\_0, IP\_Cs\_0.5, IP\_Cs\_1 and IP\_Cs\_2 is observed. Addition of  $\text{Cs}^{+}$  to the base IP does not seem to affect the leaching of  $\text{Al}^{3+}$  from the IP-matrix. Addition of  $\text{Sr}^{2+}$ , however, does show a decrease in the amount of  $\text{Al}^{3+}$  released during leaching, dropping to a value of about 1400  $\text{mg/m}^2$  for IP\_Sr\_2. The reason for this is unclear. **Figure 8** shows cumulative  $\text{Si}^{4+}$ -release of about 1750  $\text{mg/m}^2$  for all samples. Addition of  $\text{Cs}^{+}$  or  $\text{Sr}^{2+}$  does not seem to have any effect on the amount of  $\text{Si}^{4+}$  released. Cumulative  $\text{Ca}^{2+}$ -release of about 5000  $\text{mg/m}^2$  is reached for IP\_0, IP\_Cs\_0.5, IP\_Cs\_1 and IP\_Cs\_2. Addition of  $\text{Cs}^{+}$  to the base IP does not seem to affect the leaching of  $\text{Ca}^{2+}$  from the IP-matrix. Addition of  $\text{Sr}^{2+}$ , however, does show a slight increase in the amount of  $\text{Ca}^{2+}$  released during leaching, rising to a value of about 6500  $\text{mg/m}^2$ . A possible explanation for this is that the added  $\text{Sr}^{2+}$  can replace  $\text{Ca}^{2+}$  as a charge-balancing ion, since  $\text{Sr}^{2+}$  can behave similarly to  $\text{Ca}^{2+}$  during IP formation [18]. Also, since high-calcium GGBFS precursors give rise to calcium-(aluminium)-silicate-hydrate (C-(A)-S-H) formation [21], it could be that  $\text{Sr}^{2+}$  replaces  $\text{Ca}^{2+}$  in the C-S-H, giving rise to a C-(Sr)-A-S-H phase. This is in line with the findings of Wieland et al. (2008) and Tits et al. (2006), where

strontium-uptake in cementitious materials occurred through ion exchange with  $\text{Ca}^{2+}$  on silanol-groups of the C-S-H-phases [6,7]. Both options would result in a structure where  $\text{Ca}^{2+}$  is less strongly bound in the microstructure. This can also be seen in section 3.2, **Table 3** where the amount of  $\text{Ca}^{2+}$  measured in the IP-matrix decreases slightly when adding more  $\text{Sr}^{2+}$ . **Figure 9** shows cumulative  $\text{Na}^{+}$ -release of about  $1.5 \times 10^5 \text{ mg/m}^2$  for IP\_0 and IP\_Cs\_2. Addition of  $\text{Sr}^{2+}$  seems to cause a significant decrease in the amount of  $\text{Na}^{+}$  released during leaching, dropping to a value of about  $7.5 \times 10^4 \text{ mg/m}^2$  for IP\_Sr\_2, which is half of the  $\text{Na}^{+}$ -release from IP\_0. This could be caused by the formation of  $\text{NaNO}_3$  as discussed in section 3.1, and further elaborated in the next section (3.4.4). The formation of  $\text{NaNO}_3$  seems to be a plausible cause, since Kuenzel et al. (2015) observed an increase in  $\text{Na}^{+}$ -leaching when adding strontium in the form of  $\text{Sr}(\text{OH})_2$  to their IP-mixture (and thus having no nitrates in their samples) [4]. Since the EPMA measurements (see section 3.2, **Table 3**) do not indicate a difference in  $\text{Na}^{+}$  content in the IP-matrix, it can be deduced that the formation of  $\text{NaNO}_3$  occurs after 28 days (EPMA was performed on 28-day-cured samples, while leaching was performed on 48-day-cured samples). Since the samples for the leaching test were cut and transported in ambient conditions, it is also likely that some drying occurred, increasing the formation of  $\text{NaNO}_3$  (as mentioned by Provis et al. (2008) that  $\text{NaNO}_3$  crystallization from the pore solution could occur during drying of the sample [18]). Addition of  $\text{Cs}^{+}$  to the base IP does not seem to affect the leaching of  $\text{Na}^{+}$  from the IP-matrix. This indicates that adding  $\text{CsNO}_3$  does not cause the formation of  $\text{NaNO}_3$ . The latter was also reported by Blackford et al. (2007), who observed no formation of  $\text{NaNO}_3$  when adding  $\text{CsNO}_3$ , while  $\text{Sr}(\text{NO}_3)_2$  addition did cause  $\text{NaNO}_3$  crystallization [12].



**Figure 8:** Cumulative release of Si<sup>4+</sup>, Al<sup>3+</sup>, and Ca<sup>2+</sup> during a 7-day dynamic leaching test.



**Figure 9:** Cumulative release of Na<sup>+</sup> during a 7-day dynamic leaching test.

#### 3.4.4 Characterizing eluate

**Figure 10** shows the measured pH-values of the eluate at different sampling times (1 h, 24 h, and 168 h after start leaching). These results show that the addition of caesium to the base IP-mixture does not have a significant effect on the pH of the eluate. Adding strontium, however, does show an influence on the pH of the eluate, decreasing gradually with increasing amounts of strontium (from pH 11.9 for IP\_0 to pH 11.6 for IP\_Sr\_2). This decrease in pH is to be expected when Sr(OH)<sub>2</sub> is formed, trapping part of the introduced hydroxides in the IP-structure, and thus preventing them from leaching out. Regarding the conductivity of the eluate (**Figure 11**), the addition of caesium to

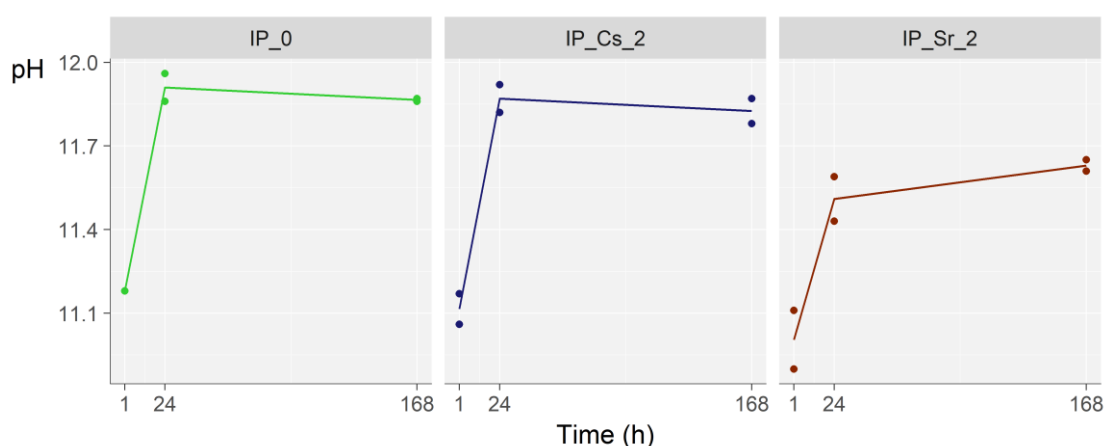


the base IP-mixture again doesn't show any significant change, while a clear change is observed when adding strontium. When adding 2 wt% of strontium to the base IP-mixture, a drop to about half is observed in the conductivity of the eluate (at 24 h and 168 h after the start of the leaching test). Taking into account the measured ions in the eluate (section 3.4), this change in conductivity seems most likely to be the cause of the lower  $\text{Na}^+$ -leaching in the strontium-containing samples. However, since the conductivity is also influenced by other charged species, the amount of hydrogen-consuming ions released in the eluate is also determined by use of automatic titration.

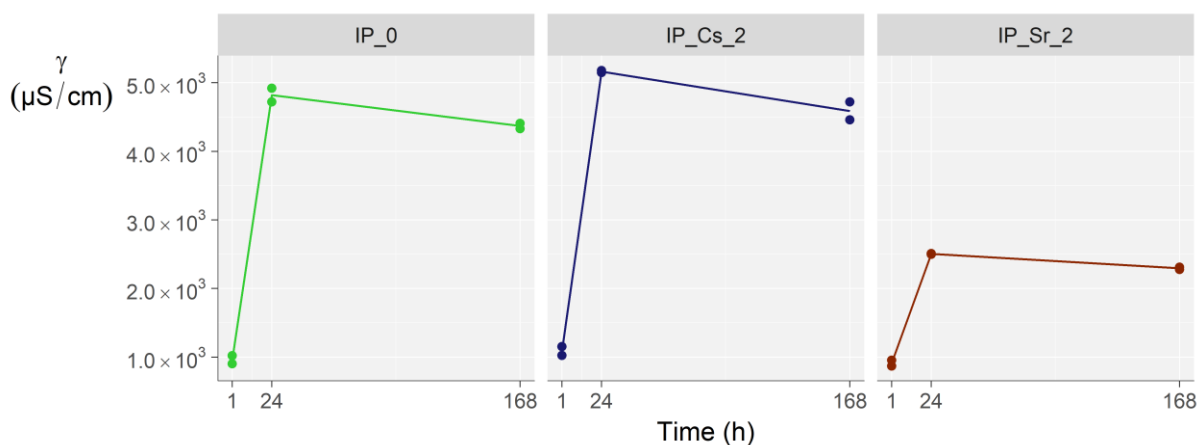
**Figure 12** shows the results of the titration tests. During titration, 3 equivalence points were measured (around pH 10, pH 8.5, and pH 5). The positions of these equivalence points did not depend on the sampling time of the leaching test (1 h, 24 h, 168 h). The presence of these three equivalence points indicates that other hydrogen-consuming species (besides hydroxides) are present in the eluate. When comparing the results in **Figure 12** from the base IP-mixture (IP\_0) and the caesium containing samples (IP\_Cs\_0.5, IP\_Cs\_1, and IP\_Cs\_2), no clear difference is observed in the amount of  $\text{H}^+$ -ions necessary to reach equivalence, and thus in the release of hydrogen-consuming species during leaching. The results from the strontium-containing samples (IP\_Sr\_0.5, IP\_Sr\_1, and IP\_Sr\_2), however, do show an effect on the amount of  $\text{H}^+$ -ions necessary for equivalence. After 1 h of leaching a small difference is already visible for IP\_Sr\_1 and IP\_Sr\_2. At the 24 h and 168 h sampling times, this difference has increased, indicating that the eluate from e.g. IP\_Sr\_2 contains about half the amount of hydrogen-consuming species compared to the eluate of IP\_0. The number of hydroxide-ions released, calculated from the measured pH-values, is  $37 \pm 2$  % of the amount of total hydrogen-consuming species (see **Figure 12**) for all samples over the total leaching period, leaving about 60 % for other unidentified hydrogen-consuming species.

Calculated from the measured pH-values, the eluates of IP\_Sr\_0.5, IP\_Sr\_1 and IP\_Sr\_2 contain respectively about 17 %, 40 % and 50 % less hydroxide-ions than the eluate of IP\_0. The trend observed when adding increasing amounts of strontium to the base mixture is similar for the

measured  $\text{Na}^+$ -concentration, conductivity, and  $\text{OH}^-$ -concentration. Results for all three parameters seem to drop slightly when adding 0.5 wt% strontium, while dropping by about 35-40 % and 50 % when adding 1 and 2 wt% respectively. From this, it can be concluded that the amounts of  $\text{OH}^-$  and  $\text{Na}^+$  released during leaching are closely linked, and affected similarly when adding strontium. A first possible explanation for the lower release of both  $\text{OH}^-$  and  $\text{Na}^+$  when adding increasing amounts of strontium can be that strontium hydroxide is formed immediately when  $\text{Sr}^{2+}$  comes into contact with the activating solution (see section 3.1). Since the positive  $\text{Sr}^{2+}$ -ions are consumed by the hydroxide-ions, the remaining  $\text{NO}_3^-$ -anions could cause the  $\text{Na}^+$ -cations to be more strongly retained due to ionic interaction or  $\text{NaNO}_3$  precipitation. The possible interactions between strontium, sodium and hydroxide are shown as equations (2) and (3).

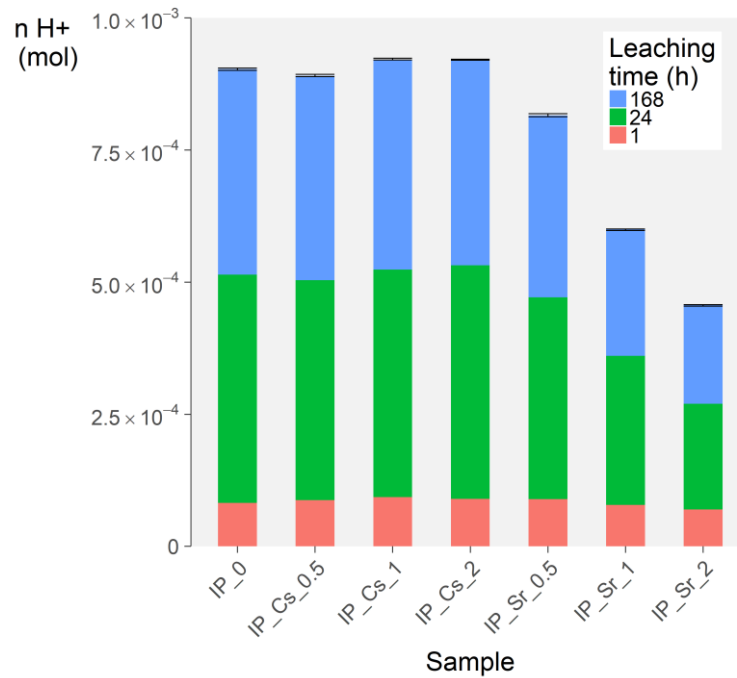


**Figure 10:** pH-values of eluates at different sampling times.



442

**Figure 11:** Conductivity  $\gamma$  ( $\mu\text{S}/\text{cm}$ ) of eluates at different sampling times.



443

**Figure 12:** Cumulative amounts of  $\text{H}^+$ -ions added to neutralize the eluate (covering three equivalence points of  $\text{pH} \approx 10$ ,  $\text{pH} \approx 8.5$ , and  $\text{pH} \approx 5$ ).

#### 446 4 Conclusion

447 In this paper, the effect of adding  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  to a GGBFS-based IP was discussed.  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  were  
 448 added, as nitrates, to a base IP-mixture to account for 0.5, 1, and 2 wt% of the final IP-mass.  
 449 Calorimetric results indicate that  $\text{Cs}^+$  did not show any significant effect on the early reaction kinetics.  
 450  $\text{Sr}^{2+}$ , however, severely affected the reaction kinetics by forming  $\text{Sr}(\text{OH})_2$  immediately after  
 451 introducing the activating solution to the dry precursor. This consumed part of the available  
 452 hydroxides resulting in a reduced dissolution of the precursor and thus a reduced polymerization  
 453 reaction. This is also visible in the lower compressive and flexural strength. The micro-chemical  
 454 analysis shows that almost all of the introduced  $\text{Cs}^+$  is incorporated in the IP-matrix, while only about  
 455 one-sixth of the introduced  $\text{Sr}^{2+}$  is incorporated into the matrix phase. It was also observed that  
 456 adding caesium caused a decrease in the  $\text{Ca}^{2+}$ -content in the IP-matrix. Water absorption

experiments show that water absorption and apparent porosity of the samples is very low, and not significantly affected by the addition of caesium or strontium. From the leaching experiments, results show that  $\text{Cs}^+$ -leaching is proportional to the amount of  $\text{Cs}^+$  added. For all caesium-containing samples, the final amount of  $\text{Cs}^+$  released were all around 65 % of the introduced amount. The total  $\text{Sr}^{2+}$ -release was around 3 % of the introduced amount for each strontium-containing sample. Strontium-addition resulted in an increased  $\text{Ca}^{2+}$ -leaching while causing a significant decrease in the amount of  $\text{Na}^+$  and  $\text{OH}^-$  leached. In general, the addition of  $\text{Cs}^+$  did not show any significant effect on the studied parameters. Adding  $\text{Sr}^{2+}$ , however, caused an important decrease in the number of hydroxides available for the dissolution of the precursor resulting in a lower overall strength. For IP\_Sr\_0.5, the 1-day and 28-day compressive strength show no significant decrease compared to IP\_0. Since the addition of 0.5 wt%  $\text{Sr}^{2+}$  results in a delayed setting time of 140 % in addition to the base sample[24][24][24][24], the application of strontium as a retarder in inorganic polymer development seems very promising. In future work, optimisation of the IP-composition for improved  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  immobilisation will be studied.

## Acknowledgements

The authors would like to thank the research group of Applied and Analytical Chemistry (TANC) of Hasselt University for the ICP-OES and ICP-MS measurements. The authors would also like to thank the research group of Physical Chemistry and Polymer Science of the Vrije Universiteit Brussel (VUB), and in particular Prof. dr. ir. Hubert Rahier and ir. Antigoni Katsiki, for the calorimetric measurements.

## References

- [1] International Atomic Energy Agency, The behaviours of cementitious materials in long term storage and disposal of radioactive waste : results of a coordinated research project, Vienna, 2013.
- [2] Q. Guangren, L. Yuxiang, Y. Facheng, S. Rongming, Improvement of metakaolin on radioactive

- 482 Sr and Cs immobilization of alkali-activated slag matrix, *J. Hazard. Mater.* 92 (2002) 289–300.  
483 doi:10.1016/S0304-3894(02)00022-5.
- 484 [3] M. Ochs, D. Mallants, L. Wang, *Radionuclide and Metal Sorption on Cement and Concrete*,  
485 Springer International Publishing, 2016. doi:10.1007/978-3-319-23651-3.
- 486 [4] C. Kuenzel, J.F. Cisneros, T.P. Neville, L. Vandeperre, S.J.R. Simons, J. Bensted, C.R.  
487 Cheeseman, Encapsulation of Cs/Sr contaminated clinoptilolite geopolymers produced from  
488 metakaolin, *J. Nucl. Mater.* 466 (2015) 94–99.
- 489 [5] S. Goni, A. Guerrero, M.P. Lorenzo, Efficiency of fly ash belite cement and zeolite matrices for  
490 immobilizing cesium, *J. Hazard. Mater.* 137 (2006) 1608–1617.  
491 doi:10.1016/j.jhazmat.2006.04.059.
- 492 [6] E. Wieland, J. Tits, D. Kunz, R. Dähn, Strontium Uptake By Cementitious Materials, *Environ. Sci.*  
493 *Technol.* 42 (2008) 403–409.
- 494 [7] J. Tits, E. Wieland, C.J. Müller, C. Landesman, M.H. Bradbury, Strontium binding by calcium  
495 silicate hydrates, *J. Colloid Interface Sci.* 300 (2006) 78–87. doi:10.1016/j.jcis.2006.03.043.
- 496 [8] M.Y. Khalil, E. Merz, Immobilization of intermediate-level wastes in geopolymers, *J. Nucl.*  
497 *Mater.* 211 (1994) 141–148. doi:10.1016/0022-3115(94)90364-6.
- 498 [9] G. Qian, D.D. Sun, J.H. Tay, New aluminium-rich alkali slag matrix with clay minerals for  
499 immobilizing simulated radioactive Sr and Cs waste, *J. Nucl. Mater.* 299 (2001) 199–204.  
500 doi:10.1016/S0022-3115(01)00700-0.
- 501 [10] A. Fernandez-Jimenez, D.E. MacPhee, E.E. Lachowski, A. Palomo, Immobilization of cesium in  
502 alkaline activated fly ash matrix, *J. Nucl. Mater.* 346 (2005) 185–193.  
503 doi:10.1016/j.jnucmat.2005.06.006.
- 504 [11] C. Shi, a. Fernández-Jiménez, Stabilization/solidification of hazardous and radioactive wastes  
505 with alkali-activated cements, *J. Hazard. Mater.* 137 (2006) 1656–1663.  
506 doi:10.1016/j.jhazmat.2006.05.008.
- 507 [12] M.G. Blackford, J. V. Hanna, K.J. Pike, E.R. Vance, D.S. Perera, Transmission electron  
508 microscopy and nuclear magnetic resonance studies of geopolymers for radioactive waste  
509 immobilization, *J. Am. Ceram. Soc.* 90 (2007) 1193–1199. doi:10.1111/j.1551-  
510 2916.2007.01532.x.
- 511 [13] Q. Li, Z. Sun, D. Tao, Y. Xu, P. Li, H. Cui, J. Zhai, Immobilization of simulated radionuclide  
512  $^{133}\text{Cs}^+$  by fly ash-based geopolymer, *J. Hazard. Mater.* 262 (2013) 325–331.  
513 doi:10.1016/j.jhazmat.2013.08.049.
- 514 [14] J.G. Jang, S.M. Park, H.K. Lee, Physical barrier effect of geopolymeric waste form on diffusivity  
515 of cesium and strontium, *J. Hazard. Mater.* 318 (2016) 339–346.  
516 doi:10.1016/j.jhazmat.2016.07.003.
- 517 [15] J. Wang, J.X. Wang, Q. Zhang, Y.X. Li, Immobilization of simulated low and intermediate level  
518 waste in alkali-activated slag-fly ash-metakaolin hydroceramics, *Nucl. Eng. Des.* 300 (2016)  
519 67–73. doi:10.1016/j.nucengdes.2016.01.011.
- 520 [16] Z. Li, T. Ohnuki, K. Ikeda, Development of Paper Sludge Ash-Based Geopolymer and  
521 Application to Treatment of Hazardous Water Contaminated with Radioisotopes, *Materials*  
522 (Basel). 9 (2016) 633. doi:10.3390/ma9080633.
- 523 [17] Z. Xu, Z. Jiang, D. Wu, X. Peng, Y. Xu, N. Li, Y. Qi, P. Li, Immobilization of strontium-loaded  
524 zeolite A by metakaolin based-geopolymer, *Ceram. Int.* 43 (2017) 4434–4439.

- doi:10.1016/j.ceramint.2016.12.092.
- [18] J.L. Provis, P.A. Walls, J.S.J. van Deventer, Geopolymerisation kinetics. 3. Effects of Cs and Sr salts, *Chem. Eng. Sci.* 63 (2008) 4480–4489. doi:10.1016/j.ces.2008.06.008.
- [19] X. Peng, Y. Xu, Z. Xu, D. Wu, D. Li, Effect of Simulated Radionuclide Strontium on Geopolymerization Process, *Procedia Environ. Sci.* 31 (2016) 325–329. doi:10.1016/j.proenv.2016.02.043.
- [20] K. Komnitsas, D. Zaharaki, G. Bartzas, Effect of sulphate and nitrate anions on heavy metal immobilisation in ferronickel slag geopolymers, *Appl. Clay Sci.* 73 (2013) 103–109. doi:10.1016/j.clay.2012.09.018.
- [21] K. Gong, C.E. White, Impact of chemical variability of ground granulated blast-furnace slag on the phase formation in alkali-activated slag pastes, *Cem. Concr. Res.* 89 (2016) 310–319. doi:10.1016/j.cemconres.2016.09.003.
- [22] J. Jang, S. Park, H. Lee, Cesium and Strontium Retentions Governed by Aluminosilicate Gel in Alkali-Activated Cements, *Materials (Basel)*. 10 (2017). doi:10.3390/ma10040447.
- [23] European Committee for Standardization, EN 196-6:2010 - Methods of testing cement - Part 6: Determination of fineness, 2010.
- [24] N. Vandevenne, R.I. Iacobescu, Y. Pontikes, K. Gijbels, S. Schreurs, W. Schroevers, THE EFFECT OF Cs AND Sr ON THE MECHANICAL PROPERTIES OF BLAST FURNACE SLAG INORGANIC POLYMER FOR RADIOACTIVE WASTE IMMOBILISATION, in: 5th Int. Slag Valoriz. Symp., 2017: pp. 401–404.
- [25] ISO, International Standard ISO 10545-3:1995 - Determination of water absorption, apparent porosity, apparent relative density and bulk density, 1997.
- [26] ASTM, C 1220 - 98 Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste, (1998).
- [27] European Committee for Standardization, CEN/TS 15863:2015: Characterisation of waste - Leaching behaviour test for basic characterisation - Dynamic monolithic leaching test with periodic leachant renewal, under fixed test conditions, 2015.
- [28] E. Najafi Kani, A. Allahverdi, J.L. Provis, Calorimetric study of geopolymer binders based on natural pozzolan, *J. Therm. Anal. Calorim.* (2016) 1–10. doi:10.1007/s10973-016-5850-7.
- [29] J.G.S. van Jaarsveld, J.S.J. van Deventer, L. Lorenzen, Potential use of geopolymeric materials to immobilize toxic metals: Part I. Theory and applications, *Miner. Eng.* 10 (1997) 659–669. [http://dx.doi.org/10.1016/S0892-6875\(97\)00046-0](http://dx.doi.org/10.1016/S0892-6875(97)00046-0).