

1 Effect of gypsum content on CSAB cement-based immobilization of Se and
2 SO₄ from industrial filter sludge and sodium-selenium salts

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19 Abstract

20 Release of different heavy metals from various industries is a significant environmental hazard worldwide.
21 In order to reduce the threat from these chemicals, different treatment methods are needed to make them
22 harmless. This study approaches the problem by examining the effect of gypsum content for immobilization
23 of selenium oxyanions selenite and selenate, and sulphate, with calcium sulphotoaluminate belite (CSAB)
24 cement based ettringite binder systems. The study has two experimental sections. In the first section, an
25 industrial filter sludge with high concentrations of selenium and sulphate is immobilized with CSAB and
26 varying amounts of gypsum. The immobilization is efficient and reducing gypsum amount in the hydrating
27 mixture enhances the incorporation of both selenium and sulphate. The binding occurs through
28 encapsulation and incorporation into ettringite and other hydrated phases. In the second section, two
29 reagent grade sodium-selenium salts, sodium selenite and sodium selenate, are mixed with CSAB and
30 varying amounts of gypsum. The immobilization is not effective and ettringite is not formed in large
31 quantities, most likely due to high sodium content in the reacting system.

32

33 Introduction

34 Heavy metals are a common and harmful contaminate in industrial waste, and different kinds of treatments
35 are used to prevent the heavy metals from spreading into the environment (Fu and Wang 2011; Guo et al.
36 2017a). Unlike harmful compounds, heavy metals cannot be decomposed, as the element is harmful as
37 itself, and therefore commonly the most practical solution is immobilization of the hazardous elements.
38 The methods for heavy metal immobilization include for instance stabilization/solidification, encapsulation,
39 chemical incorporation, ion exchange and adsorption (Ji and Pei 2019; Vu and Gowripalan 2018). In this
40 study stabilization/solidification is applied for the immobilization of industrial waste rich in anionic
41 selenium (Se) and sulphate (SO₄). The presence of sulphate is important to consider, since it has a negative
42 effect on the immobilization of selenium.

43 Stabilization/solidification methods target in binding the heavy metals into a solid binder matrix such as
44 Ordinary Portland cement (OPC) (Guo et al. 2017a). In stabilization, the hazardous component is bound
45 chemically to the solid matrix, while solidification refers to incorporating the heavy metals into a solid with
46 low permeability and physically prevent them from escaping (Wang et al. 2012). Stabilization/solidification
47 is a very common method for treatment of hazardous waste due to being simple, low cost, good
48 compatibility with a wide range of different kinds of wastes and contaminants, and being available both in
49 situ and ex situ (Derakhshan Nejad et al. 2018). Furthermore, stabilization/solidification may allow
50 utilization of the immobilized material (Badur and Chaudhary 2008). On the downside, the stability of the
51 immobilizing solid over time can be a matter of concern (Derakhshan Nejad et al. 2018).

52 One of the most studied mineral phases for stabilization/solidification applications is ettringite
53 (Ca₆Al₂(SO₄)₃(OH)₁₂*26H₂O). It is an effective ion exchanger that can bind a large variation of both cations
54 and anions into its structure (Chen et al. 2009). There are two main methods for incorporating heavy
55 metals into ettringite structure: stabilization/solidification for solid waste materials and precipitation for
56 contaminated water solutions (Chrysochoou and Dermatas 2006). Stabilization/solidification contains
57 different mechanisms of immobilization, such as encapsulation and chemical incorporation, and due to the

58 chemically complex nature of the system, the heavy metals are typically immobilized into the binder matrix
59 with several different methods simultaneously (Chen et al. 2009; Guo et al. 2017b; Ji and Pei 2019).

60 Ettringite forming binder materials include various cement replacers, for example CSAB cement and various
61 industrial side streams, such as ladle slag (Chen and Juenger 2011; Nguyen et al. 2019).

62 The ettringite crystal has a needle-like shape, and it consists of columns of Ca and Al oxides, with sulphate
63 ions and water molecules between them (Guo et al. 2017b). The ions Ca^{2+} , Al^{3+} and SO_4^{2-} can be replaced by
64 ions of similar atomic size and ionic charge (Chen et al. 2009). In practice, a variation of ions can substitute
65 them, and previous studies include testing the immobilization of Cr^{3+} , Pb^{2+} , Cu^{2+} , and Zn^{2+} (Niu et al. 2018,
66 2019; Wu et al. 2012) into the columns, and SeO_4^{2-} , CrO_4^{2-} , AsO_4^{3-} , and MoO_4^{2-} replacing SO_4^{2-} and water
67 (Guo et al. 2017b; Kiventerä et al. 2019; Zhang and Reardon 2003). The results are promising, showing that
68 with the right methods ettringite can be used for binding heavy metals form a variety of harmful and
69 hazardous wastes.

70 The requirements for the similarity are not very strict for SO_4^{2-} , for which sustaining total ionic charge
71 seems to be more crucial than sustaining stoichiometry (Gougar et al. 1996). The anionic compounds are
72 holding the positively charged columns together with electrostatic forces. The structure allows the anions
73 to be re-substituted by sulphate, which can cause them to leach out in sulphate rich conditions (Guo et al.
74 2017a). Selenite is observed to have stronger incorporation to the structure than selenate, since it can bind
75 to the surface of the columns with hydroxide bonds replacing OH^- and H_2O groups (Guo et al. 2017b).

76 In this study, the immobilization of sulphate (SO_4^{2-}) and two selenium oxyanions, selenite (SeO_3^{2-}) and
77 selenate (SeO_4^{2-}) are studied. Ettringite and monosulphate are generally recognized as phases that are
78 especially suited for binding oxyanions, since they form and are stable in highly basic conditions, where the
79 oxyanions are at their most leachable (Chrysochoou and Dermatas 2006). The immobilization of oxyanions
80 is affected by the fact that sulphate is always the first anion to incorporate into ettringite structure (Guo et
81 al. 2017c; a). On the other hand, the presence of sulphate is needed for a fast precipitation of selenate
82 ettringite (Guo et al. 2017c).

83 In this study calcium sulfoaluminate-belite (CSAB) cement is used as the ettringite forming binder. The main
84 phases of CSAB are typically ye'elimite ($\text{Ca}_4\text{Al}_6(\text{SO}_4)\text{O}_{12}$), belite ($\text{Ca}_2(\text{SiO}_4)$) and some ferrite ($\text{Ca}_2(\text{Al,Fe})\text{O}_5$),
85 and calcium sulphate is added before hydration (Glasser and Zhang 2001). CSAB is widely acknowledged as
86 a promising alternative to OPC mostly due to its lower carbon footprint (Hanein et al. 2018; Scrivener et al.
87 2018). Ettringite is the main hydration product of CSAB, and the final amount of ettringite in the hydrated
88 product depends on the amount of ye'elimite in the clinker (Juenger et al. 2011).

89 Previous studies have proven CSAB to be a promising medium for heavy metal and sulphate immobilization
90 (Kiventerä et al. 2019). In our previous research, highly hazardous filter sludge was stabilized by CSAB
91 cement (Piekkari et al. 2020). An effective immobilization was achieved for several cationic heavy metals.
92 However, the Se and SO_4 did not stabilize effectively probably due to excessive gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)
93 content in the system. In this research, CSAB is used for immobilizing the same filter sludge with a
94 decreasing gypsum content in order to observe the effect of a declining sulphate content on the efficiency
95 of the oxyanion immobilization. Another target is to study closer the differences in behavior of selenite and
96 selenate components in a CSAB hydration system, which has not been studied in past articles. For this study
97 the ye'elimite content of the used CSAB clinker was increased from 36.5% that was used in (Piekkari et al.
98 2020) to 56.5 % in order to encourage ettringite formation.

99 This study consists of two separate experimental sections researching the immobilization of selenium and
100 sulphate in a CSAB matrix. In the first section, the filter sludge that was also studied in the earlier article, is
101 immobilized with CSAB and gypsum. The filter sludge originates from the sulfuric acid plant of a nickel and
102 copper smelter. In the second section, pure selenium salts sodium selenite (Na_2SeO_3) and sodium selenate
103 (Na_2SeO_4) were immobilized with the same binder mixture in order to get a better understanding of the
104 incorporation of Se and SO_4 in a more simple experimental setting.

105 The target of this article is to throw more light on the earlier erratic behavior of Se and SO_4 and bring
106 insight to the effect of gypsum and SO_4 content on the hydration of the waste/contaminant-binder mixture.
107 The hydrated samples were exposed to leaching tests, X-ray powder diffraction (XRD), thermogravimetric

108 analysis (TGA) and field emission scanning electron microscopy with energy dispersive spectroscopy
109 (FESEM-EDS) in order to observe the efficiency and mechanisms of oxyanion immobilization.

110 Materials

111 This article covers two different stages of experiments, where selenium and sulphate were incorporated
112 into the crystalline structure of ettringite. The first series was prepared with an industrial filter sludge with
113 high contents of heavy metals, including selenium and sulphate, while the other one focused on samples
114 made with pure selenium salts. In both series of samples, the same CSAB clinker and reactants were used
115 to create an ettringite rich binder material. The samples with filter sludge is later referred to as series FS,
116 and the samples with the selenium salts is referred as series SS.

117 CSAB clinker

118 The CSAB clinker that was used to form the immobilizing solid binder was prepared from pure reagent
119 grade chemicals (RGC) from Alfa Aesar (ThermoFisher (Kandel) GmbH, Germany): calcium oxide, reagent
120 grade powder (CaO), calcium sulphate, anhydrous powder (CaSO₄), metal basis aluminum oxide, fine
121 powder (Al₂O₃), metal basis silicon(IV)oxide, mesh fused amorphous powder (SiO₂), and metal basis iron(III)
122 oxide (Fe₂O₃). The relative amounts of RGC corresponded with the chemical composition of the clinker
123 (Table 1), and they were calculated based on the target phase composition of the prepared clinker (Table
124 2). Before weighting the RGC, CaO was fired at 800°C for 12h in a Nabertherm GmbH muffle furnace
125 (Lilienthal, Germany) to remove possible traces of CaCO₃ and Ca(OH)₂. Similarly, CaSO₄, Al₂O₃, SiO₂ and
126 Fe₂O₃ were fired at 500°C in order to ensure that they would not contain any moisture during weighting.

127 To achieve homogenous mixture, the raw materials were milled for total 25 min with a tumbling ball mill
128 (Germantec TPR-D; Germantec, Ransbach-Baumbach, Germany), using a 10 L stainless steel jar (d=250 mm)
129 and 80 stainless steel balls (d=30 mm) as grinding media with 84 rpm speed. The milled raw material mix
130 was compressed into cylinder shaped corundum crucibles (d = 100 mm and h = 100 mm). The crucibles
131 were fired in the muffle furnace by the following method; The crucibles were placed into the furnace at the

132 temperature of 800°C held for 30 min and then heated up to 1300°C at a rate of 10°C/min. The crucibles
133 were held in 1300°C for 1h 30 min and then cooled down to room temperature.

134 The fired clinker was crushed with a jaw crusher and ground with the tumbling ball mill for 90 min with
135 grinding speed of 69 rpm. The clinker was sieved through a 63 µm sieve, and the section left on the sieve
136 was ground again until it passed the sieve. The particle size distribution was measured with a Beckman
137 Coulter LS 13320 particle size analyzer (Beckman Coulter, Brea, CA, USA) and 2-isopropanol as medium. The
138 actual phase composition of the prepared clinker (Fig. 1, Table 2) was analyzed via XRD. For hydration
139 gypsum was added to the clinker in a clinker-gypsum ratio of 7:3.

140 Composition of series FS samples

141 The industrial filter sludge (FS) originated from a sulfuric acid production plant attached to a fume gas
142 washing process on a nickel and copper smelter, and therefore it contained very high ratios of several
143 heavy metals (Table 3). The chemical components and their abundancies were determined with XRF for
144 pressed pellets (Omnian Panalytical AXIOS, Malvern Panalytical, Malvern, UK). The median particle size d_{50}
145 of the material was 1.17 µm with 99.6 % of the particles falling under 20 µm. The most abundant crystalline
146 phases were analyzed with XRD and they were identified as anglesite (PbSO_4), mercury selenide bromide
147 ($\text{Hg}_3\text{Se}_2\text{Br}_2$), and nickel iron oxide ($\text{Fe}_{1.85}\text{Ni}_{1.25}\text{O}_4$).

148 The sludge was immobilized with a mixture of the CSAB clinker and gypsum so that gypsum was replaced
149 with FS and calcium hydroxide ($\text{Ca}(\text{OH})_2$) (Table 4). The aim was to replace the SO_4 of the gypsum by
150 sulphate and selenium originating from the FS. At first, the total content of sulphate and selenium in FS was
151 defined based on the XRF.

152 Since the reactivity of selenium and sulphate in FS was not known, some percentage ratios were assumed
153 for the total fractions participating in the hydration reaction. The binder composition was planned with the
154 initial clinker-gypsum-rate of 7:3. A constant amount of FS was added to the binder, and based on the
155 different assumed reactive ratios of FS, gypsum was removed from the mixtures. The amount of added

156 calcium hydroxide in each mix was equal to the molar amount of replaced gypsum. The FS/binder ratio was
157 held constant by adding extra clinker. The liquid/solids (L/S)-ratio of the mixtures was 0.6.

158 Composition of series SS samples

159 In addition to the clinker, the materials used in sample making included reagent grade gypsum
160 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (VWR International, Leuven, Belgium), calcium hydroxide ($\text{Ca}(\text{OH})_2$), (Merck KGaA, Darmstad,
161 Germany), sodium selenite (Na_2SeO_3) (Sigma-Aldrich, St. Louis, MO, USA) and sodium selenate (Na_2SeO_4)
162 (Sigma-Aldrich, Tokyo, Japan). The sodium-selenium salts were mixed with the clinker and gypsum as solid
163 powders. Water was added with a LS-ratio of 0.55. The clinker and gypsum formed the original binder, and
164 a reference sample was prepared without selenium in order to observe the properties of the pure binder.

165 In order to substitute sulphates from gypsum with selenium oxyanions, gypsum was gradually replaced
166 with the selenium compounds by matching the molar amount of the selenium compound with the amount
167 of the replaced gypsum (Table 5). Sodium selenite and sodium selenate were used in sample series SS3 and
168 SS4 respectively. Only one selenium compound was used at a time to observe differences between the
169 different oxyanions. Calcium hydroxide was then added according to the molar amount of reduced gypsum
170 in order to ensure availability of calcium in the reacting paste.

171 The L/S-ratio of the mixtures was set to constant 0.55, but samples SS3-50, SS3-75 and SS3-100 required
172 extra water to be added in order to ensure proper mixing of the components. It was decided to prioritize
173 sufficient mixing instead of maintaining the L/S-ratio, because the homogeneity and proper reaction rate of
174 the mixture were more elemental to this study than the physical properties of the hardened samples.

175 Methods

176 The samples were prepared so that first the dry ingredients were mixed thoroughly by hand, and then
177 water was added. The paste was mixed carefully by hand, ensuring that no heterogeneity remained. The
178 paste was then molded and set to harden in airtight plastic containers in room temperature. After

179 unmolding the samples were stored inside airtight plastic bags in order to avoid carbonation reaction with
180 air on the sample surface.

181 The leaching of selenium and sulphate from FS was defined by a one stage leaching test following the
182 Finnish Standard Association's European Standard SFS-EN 12457-2. For the immobilized samples (both
183 series FS and S) the standard method was modified by reducing its volume. For the test, the hardened
184 samples were crushed until they went through a 2 mm sieve. The sample was then leached in water with a
185 L/S-ratio of 10 for 24 hours with constant shaking. The test was performed to the immobilized samples
186 after 28 days of curing. The samples were mixed during the leaching by placing the containers in an end-
187 over-end tumbler (Retsch, Haan, Germany) with 10 rpm rotation speed.

188 In order to observe and identify the phase composition of the samples, XRD analysis was executed for all
189 samples in the age of 28 days with a SmartLab analyzer (Rigaku, Tokyo, Japan) with Co K α X-ray source with
190 voltage 40 kW and current 135 mA. The following scan parameters were used: scan speed of 4°/min, step
191 width of 0.02°, and scan range of 5-130°. The ratios of the detected phases were calculated by using
192 Rietveld refinement. In order to include the amorphous section in the results, internal standard with 20
193 wt% added rutile was used (TiO₂). Rigaku PDXL 2 software was used for identifying the crystalline phases
194 from the XRD-patterns with ICDD database/ PDF-4+ 2020 RDB database.

195 The visual imaging of the material matrix and chemical composition of the different phases were analyzed
196 with a ZEISS Ultra Plus (Oberkochen, Germany) FESEM-EDS setup. The analysis was executed for crushed
197 samples that were cast in epoxy resin under vacuum and polished. TGA in nitrogen gas (N₂) with STD 650
198 simultaneous thermal analyzer (TA Instruments, New Castle, DE, USA) was used to further observe the
199 phase composition of the samples. The used TGA sequence contained equilibrating in 50.00 °C followed by
200 a ramp of 5.00 °C/min to 1005.00 °C.

201 Results

202 Reference sample

203 The phase composition of the reference sample after 28 days of hydration was determined through XRD
204 analysis to be 44 % ettringite, 12 % belite, 6 % gypsum and 1 % ye'elite (Fig. 2). The unknown fraction
205 was 37 %, which represents the amorphous components present. FESEM imaging revealed a highly
206 heterogenous binder matrix suggesting that ettringite and monosulphate dominated the matrix in volume
207 as large structures (Fig. 3).

208 Series FS

209 Leaching

210 The leaching rates are expressed as immobilization efficiency, where the section of the component that
211 immobilized has been divided with the total amount of the component in the solid sample. Both selenium
212 and sulphate immobilization improved as gypsum was substituted with calcium hydroxide (Fig. 4). This was
213 the desired outcome of the experiment, since it implies the sulphate and selenium from FS incorporating
214 into the binder in the absence of sulphate. From the shape of the trends across the samples it can be
215 deduced that sulphate from FS began incorporating into the matrix as soon as the gypsum amount started
216 to decrease, while the selenium only started incorporating in sample FS3.

217 This observation is in line with sulphate being prioritized over selenium in ettringite formation (Guo et al.
218 2017c; a). Based on the result it can be stated that the Se and SO_4 in the FS samples were effectively
219 immobilized by the gypsum reduction. This strongly implies that the problems concerning the two
220 components in the previous study were indeed caused by an excessive gypsum content in the samples.

221 Binder structure

222 The samples mainly compose of agglomerated clusters of the filter sludge inside a highly heterogenic
223 binder matrix (Fig. 5). The ettringite content declined as the amount of FS in the sample was increased (Fig.
224 6). Despite the decline, ettringite remained as the most abundant crystalline phase in all the samples.

225 In addition to ettringite, monosulphate resembling structures were found in the binder matrix. The binder
226 structure implies that the filter sludge is most likely encapsulated inside the binder matrix, just as in the
227 earlier experiments (Piekkari et al. 2020). In addition, EDS analysis also found selenium spread out into the
228 binder matrix. Remnants of unreacted clinker phases were commonly detected with XRD and EDS. Iron-
229 nickel oxide was observed as a separate phase among the sludge.

230 It seems that such as in the earlier study, encapsulation was the major immobilization mechanism, but also
231 incorporation into the binder was observed. However, since the ettringite formation declined rapidly as
232 gypsum amount depleted, there is a reason to believe that Se and SO_4 incorporated into another,
233 undefined binder phase, such as monosulphate that is known to incorporate ions into its structure in a
234 similar manner as ettringite (Guo et al. 2017a; Saikia et al. 2006).

235 Series SS

236 Observations from sample preparation

237 The LS ratio of 0.55 was suitable for the SS4-series, but for SS3-samples the water amount was inadequate.
238 Therefore, extra water was added to enable a proper mixing (Table 5). As a result, the SS3-samples had
239 highly different molding properties compared to the SS4-series. SS3 samples also hardened significantly
240 slower and remained moist and soft for several weeks after molding.

241 The larger water demand of the SS3-samples was most likely a consequence of difference in the particle
242 sizes of the selenium salts. The used sodium selenite was obtained as a fine powder, while the sodium
243 selenate appeared as cubic crystals. The smaller particle size of the sodium selenite corresponds with a
244 significantly larger surface area, which in turn results in a larger water demand during the mixing.

245 Leaching

246 Unlike for FS samples, the immobilization of Se and SO_4 did not increase as more gypsum was substituted
247 (Fig. 7). Se immobilization was inefficient compared to FS experiments and showed non-linear behavior.
248 Sulphate immobilization was reduced in a mostly linear manner in both sample series. Based on these

249 results it seems clear that incorporation of Se and SO₄ into ettringite was not successful. Therefore, making
250 any major comparison between the behavior of the different selenium oxyanions was not reasonable.

251 Binder structure

252 Such as with the FS samples, ettringite formation was observed, and its amount in the binder declined as
253 gypsum was substituted with the selenium salts and calcium hydroxide (Fig. 8, 9). This development was
254 observed with all used analysis methods. The ettringite crystals observed with FESEM were significantly
255 smaller in all the samples, as they were in the reference sample (Fig. 10, 11). This implies that the hydration
256 reaction has been disrupted compared to the reference sample. There were also major further differences
257 in the matrix structures in the samples, especially in series SS4.

258 XRD and TGA showed ettringite to remain more abundant in the SS4-samples compared to SS3. From EDS it
259 was observed that both selenite (SS3) and selenate (SS4) were observed to be distributed into the binder
260 matrix, with selenite also showing occasional cumulation on certain small areas in series SS3 (Fig. 12.).
261 Similarly, sodium was distributed into the binder matrix and showed signs of accumulation in SS4-samples.

262 The crystalline compositions of the hydrated samples observed with XRD were highly complicated.
263 Remnants of unreacted ye'elimite and belite remained, while the reaction products contained CaSeO₃
264 (nestolaite) in some of the SS3-samples, and katoite (Ca₃Al₂(OH)₁₂) and thenardite (Na₂SO₄) in both series of
265 samples. In addition, both sample series contained several crystalline phases that remained unidentified in
266 this study. TGA suggested the presence of amorphous aluminum hydroxide in most samples, and
267 monosulphate in the SS4 series samples.

268 Since ettringite formation depleted as gypsum was replaced, it is safe to claim that major selenium
269 ettringite formation was not achieved. A major reason for the failing of these samples was most likely the
270 high contents of sodium from the selenium salts, since sodium can disrupt the hydration process and
271 ettringite formation (Cody et al. 2004; Hekal and Kishar 1999). Furthermore, sodium selenium salts are
272 highly soluble in water, and therefore any salt remnants in the sample would give rise to the observed

273 leaching. The hydration of the SS3-samples was also negatively affected by the unideal L/S-ratio during the
274 mixing of the paste.

275 Conclusions

276 The Se and SO₄ in the industrial filter sludge are effectively immobilized with CSAB cement, as the amount
277 of gypsum in the hydration is reduced. The result is in line with the hypothesis of an excessive gypsum
278 content preventing the anionic components from incorporating into the ettringite matrix. Analysis of the
279 results show both encapsulation and incorporation into the binder as immobilization mechanisms, but
280 simultaneously the ettringite formation is observed to decline. As a result, it can be stated that the
281 immobilizing phase in the matrix is not ettringite, but Se and SO₄ incorporate into some different phase,
282 such as monosulphate.

283 On the other hand, the incorporation of Se from sodium salts is not successful with CSAB. Se and Na are
284 observed to be spread and mixed into the binder matrix, but the leaching results determine that efficient
285 incorporation does not take place. Furthermore, ettringite formation depletes as gypsum is replaced,
286 clearly stating that major selenium ettringite formation is not achieved. It is suspected that the high sodium
287 content of the samples may have disrupted the hydration process.

288 This study gives a clear example that calcium sulfoaluminate belite (CSAB) cement is an effective binder for
289 immobilizing Se and SO₄. The exact chemical compositions of the clinker, and the immobilized components
290 play a major role in defining, if the desired reactions are happening or not. This sensitivity is however
291 balanced by immobilization via encapsulation and incorporation into other hydration products than
292 ettringite. CSAB hydration based ettringite incorporation of Se and SO₄ produces a complicated and highly
293 heterogenous matrix, with several different parameters affecting the outcome of the hydration. In our
294 future research we will focus on reducing the sulphate content of the binder even further.

295 Data availability statement

296 All data, models, or code that support the findings of this study are available from the corresponding
297 author upon reasonable request.

298 Acknowledgements

299 The authors would like to thank Elisa Wirkkala, Jarno Karvonen and Jani Österlund for their assistance with
300 the laboratory experiments.

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368

369

370 Tables

371

372 **Table 1.** The chemical composition of the clinker.

Component	Amount (w-%)
CaO	46.3
Al ₂ O ₃	31.2
SiO ₂	10.5
SO ₃	8.8
Fe ₂ O ₃	3.3
Total	100

373

374 **Table 2.** The target phase composition and the measured final phase composition of the prepared clinker
 375 (XRD).

Phases	Formula	Target (w-%)	Measured (w-%)
Ye'elimite	Ca ₄ Al ₆ (SO ₄)O ₁₂	58	56.5 ± 0.1

Belite	Ca_2SiO_4	30	36.9 ± 0.8
Brownmillerite	$\text{Ca}_2(\text{Al, Fe})_2\text{O}_5$	10	5.4 ± 0.3
Anhydrite	CaSO_4	2	1.5 ± 0.1

376

377 **Table 3.** The main chemical components of FS based on XRF.

Component	Component content (wt%)
Pb	24.6
Hg	21.7
O	21.3
Se	9.00
S	6.84
Br	6.11
Ni	3.45
Fe	3.25

378

379 **Table 4.** Compositions of the FS samples.

Sample name	FS1	FS2	FS3	FS4
Assumed reactivity (%)	20	40	80	100
Gypsum replacement rate (%)	16.2	32.4	64.4	80.5
FS (g)	30	30	30	30
CSAB clinker (g)	51.0	52.8	56.7	58.9
Gypsum (g)	17.6	14.3	7.5	4.1

Calcium hydroxide (g)	1.5	2.9	5.8	7.3
Water (g)	60	60	60	60

380

381 **Table 5.** Compositions of the studied samples presented with the amount of CSAB remaining constant.

Sample name	Reference	SS3-1	SS3-2	SS3-3	SS3-4	SS4-1	SS4-2	SS4-3	SS4-4
Gypsum replaced (%)	0	25	50	75	100	25	50	75	100
CSAB (g)	70	70	70	70	70	70	70	70	70
Gypsum (g)	30	22.5	15	7.5	0	22.5	15	7.5	0
Selenite (g)	0	9.5	19	29	38	0	0	0	0
Selenate (g)	0	0	0	0	0	10	21	31	42
Calcium hydroxide (g)	0	4.1	8.2	12	16	4.1	8.2	12	16
Total solids (g)	100	106	112	118	12	107	114	121	128
Water (g)	55	58	85	79	97	59	63	67	70
L/S-ratio	0.55	0.55	0.76	0.67	0.78	0.55	0.55	0.55	0.55

382