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6 **Thermal behavior of ladle slag mortars containing ferrochrome slag aggregates.**

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46 **Abstract**

47

48 Concretes, depending on their application, may be exposed to elevated temperatures during their  
49 lifetime, especially when placed near or in a furnace or during an accidental fire. We studied the  
50 thermal stability of alkali-activated mortars and hydrated mortars prepared using ladle slag and two  
51 different aggregates. A commercial calcium aluminate cement was used as a comparison for the  
52 properties after exposure to temperatures up to 1000°C. All samples were characterised and  
53 analysed through a strength test, dilatometric analysis, thermogravimetric analysis, ultrasonic pulse  
54 velocity, and scanning electron microscopy. The hydrated ladle slag mortars exhibited properties  
55 similar to or better than the commercial calcium aluminate cement, while the alkali-activated ladle  
56 slag's thermal properties were inferior to the hydrated ladle slag mortars. The tests also showed that  
57 the use of ferrochrome slag aggregates in hydrated ladle slag mortars exhibited similar properties to  
58 those using sand aggregate mortars, but are not suitable as an aggregate in alkali-activated ladle  
59 slag due to the reaction of ferrochrome slag aggregates with the alkali binder. The damage behaviors  
60 of the mortars were dependent on the temperature-induced dehydration, dehydroxylation, and  
61 thermal incompatibility between the paste and aggregates. The results from this study specify the  
62 possibilities of using 100% industrial by-product based mortar and near zero carbon dioxide  
63 emissions as a fire-resistant material in furnaces, buildings and fireplaces.

64

65 Keywords: · High-alumina cement; Thermal behaviour; Alkali-activated cements

66

67 **Notations**

68  $V_p$  pulse velocity

69  $D$  distance between the transducers

70  $t$  time taken for the pulse to reach the receiver

71

## 72 **1. Introduction**

73 Concretes, depending on their application, may be exposed to elevated temperatures during their  
74 lifetime, especially when placed near or in a furnace or during an accidental fire. The performance  
75 of the structure may degrade, inducing irreversible changes to its strength, modulus of elasticity, and  
76 volume stability, and altering the concrete microstructures during these exposures (Arioz, 2007; Yim  
77 et al., 2014). In ordinary Portland cement (OPC), the strength-giving hydration products are calcium-  
78 silicate-hydrate (CSH) and calcium hydroxide (CH). CSH starts dehydrating at temperature above  
79 100°C and further decomposes towards 1000°C, while calcium hydroxide CH dehydrates from  
80 400°C to 550°C (Hertz, 2005; Zhang and Ye, 2012). The decomposition of the cement microstructure  
81 and the evaporation of capillary water due to elevated temperature result in the deterioration of the  
82 concrete.

83

84 Calcium aluminate cement (CAC) and high-alumina cements have better high temperature  
85 properties than OPC due to their hydration products. However, they are four to five times more  
86 expensive than Portland cement (Scrivener et al., 1999). Several grades of CAC are produced, with  
87 alumina contents varying between 40-80%, offering different levels of refractoriness. These cements  
88 are also used in other applications, such as a shotcrete in fire training structures, industrial flooring,  
89 sewer applications, and as co-binders with Portland cement (Ewais et al., 2009; Karen, 2003). Alkali-  
90 activated materials (AAMs), due to their ceramic-like properties, have also shown a high degree of  
91 fire resistance when exposed to elevated temperatures (Bakharev et al., 1999; Cheng and Chiu,  
92 2003; Wang et al., 2014; Ye et al., 2014). They may possess superior fire resistance to OPC.

93

94 Ladle slag (LS) is a high-calcium alumina slag generated during the secondary steelmaking process.  
95 2.5-4 Mt of this slag are estimated to be produced annually in Europe (Adesanya et al., 2016; Serjun  
96 et al., 2015). It has been reported that 80% of this slag is either stored or landfilled (Serjun et al.,  
97 2013). The slag may be classified either as a waste material or as a by-product depending on the  
98 steel plant and country in which it is generated. The utilisation of this industrial side-stream as a

99 replacement for conventional cements could potentially reduce the reliance on natural resources,  
100 reduce greenhouse emissions, and reduce economical costs of operating a landfill and purchasing  
101 commercial cement. Few methods of utilising this slag in hydration, alkali activation, and as fillers in  
102 cement composites have been previously published. In previous studies on the alkali activation of  
103 ladle slag and its fiber reinforcement, Hoang et al. (Nguyen et al., 2018) achieved a compressive  
104 strength of 78 MPa after 28 days for plain mortar and 100 MPa after reinforcement with  
105 polypropylene fibers. Sideris et al. (Sideris et al., 2015) used ladle slag as a filler in self-compacting  
106 concretes with enhanced durability properties. Manso et al. (Manso et al., 2011) reported that the  
107 addition of ladle slag to masonry mortars enhanced their durability. Ladle slag has shown similar  
108 hydration properties to CAC due to its high alumina (30-40%) and calcium (40-50%) contents  
109 (Adesanya et al., 2018), and hypothetically it can exhibit similar or comparable refractory properties.  
110 In this study, the refractoriness of LS mortars was studied for the first time.

111

112 During the production of high-carbon ferrochrome, ferrochrome slag (Fs) is generated as a by-  
113 product. Fs is formed as a liquid at 1700°C; through slow-cooling in air, it crystallises to form a stable  
114 MgO-Al<sub>2</sub>O<sub>3</sub>-silicate, which is then crushed and screened to different fractions (Kumar et al., 2014;  
115 Niemelä and Kauppi, 2007; Zelić, 2005). About 1.1 to 1.5 tons of Fs are produced for each ton of  
116 ferrochrome alloy. The global annual production of this slag is estimated to be between 12 and 16  
117 Mt (Kumar et al., 2014; Sahu et al., 2016). Due to its excellent properties, such as good insulation  
118 and lower shrinkage, Fs has been previously used as an aggregate in road construction and brick  
119 production (Gencil et al., 2013; Lind et al., 2000). However, some of the slag is still landfilled (Kumar  
120 et al., 2014; Lind et al., 2000; Zelić, 2005). Therefore, we aim to utilise Fs in high temperature  
121 applications as an alternative to sand aggregates. This will provide more options for recycling and  
122 reduce the cost of producing refractory mortars.

123

124 In this study, we investigated the performance of alkali-activated ladle slag (AALS) and water-  
125 hydrated ladle slag (HLS) mortars when they were exposed to temperatures up to 1000°C. We also

126 investigated the effect of aggregate type (ferrochrome slag aggregates and sand aggregates) on the  
127 residual properties of the mortar. The performances of these ladle slag mortars were compared with  
128 these of a commercial CAC mortar as a reference binder with regard to residual strength, ultrasonic  
129 pulse velocity, and dilatometric properties. Additional tests were conducted to further examine the  
130 microstructure and thermogravimetric properties of the mortars through scanning electron  
131 microscopy (SEM) and thermogravimetric analysis (TGA).

132

## 133 **2. Experimental study**

### 134 2.1. Materials

135 The materials used in this study included commercial calcium aluminate cement, air-cooled ladle  
136 slag (LS), ferrochrome slag (Fs), and commercial sand aggregates (Ss). Their properties and pre-  
137 treatment are described as follows.

#### 138 2.1.1. Cement

139 The CAC (CALIGHT 40) was supplied by CALTRA (Netherlands). The initial setting time as provided  
140 by the producer was 70 min, and it had a compressive strength of 65.8 MPa after 24 h. This cement  
141 is used in high-temperature applications and as a binder for making industrial floors. Ladle slag was  
142 collected from SSAB (Raahe, Finland). The as-received LS was further ball milled for two hours to  
143 achieve a  $d_{10}$ ,  $d_{50}$ , and  $d_{90}$  of 1.2, 12.3, and 64.9  $\mu\text{m}$ , respectively. The particle size distributions for  
144 the ball milled ladle slag (LS\_BM), raw ladle slag (LS\_R), and CAC are shown in Figure 1 (a).

#### 145 2.1.2. Aggregates

146 CEN standard sand conforming to the EN 196-1 (EN 196-1, 2016) requirements supplied by  
147 Normensand GmbH (Germany) was used. The grain distribution ranged between 0.08 and 2.00 mm  
148 and the sand had a maximum moisture content of 0.2% (provided by the manufacturer). Ferrochrome  
149 slag (Fs) was collected from Outokumpu Chrome Oy (Tornio, Finland). The as-received Fs was dried  
150 in an oven at 100°C for 24 h and then sieved using a 2 mm mesh to remove slag with a >2 mm  
151 particle size. The particle size distribution after sieving ranged between 0 and 2 mm; the distribution  
152 curve is shown in Figure 1 (b). The chemical compositions are listed in Table 1.

153 Table 1. Chemical composition of the cement and slag.

Oxides (%)	Calcium oxide (CaO)	Aluminium oxide (Al <sub>2</sub> O <sub>3</sub> )	Silica (SiO <sub>2</sub> )	Magnesium oxide (MgO)	Iron (III) oxide (Fe <sub>2</sub> O <sub>3</sub> )	Sodium oxide (Na <sub>2</sub> O)	Potassium oxide (K <sub>2</sub> O)	Chromium oxide (Cr <sub>2</sub> O <sub>5</sub> )
LS	45.7	29.8	9.5	6.2	0.8	0.03	0.05	0.02
Fs	1.8	25.1	28.9	22.8	7.5	0.14	0.22	14.9
CAC*	37-39	38-40.5	5-6.5	-	15-18	-	-	-

154 \*provided by the manufacturer

155

156 Figure 1. Particle size distribution of the materials used (a) Particle size distribution of ball  
 157 milled ladle slag, raw ladle slag and CAC (b) Grading curves of ferrochrome slag and sand  
 158 aggregates.

159

160 2.2. Sample preparation

161 The mortars were prepared by mixing the cement with demineralised water in a Kenwood mixer  
 162 according to the EN 196-1 standard. For the alkali-activated slag, sodium silicate (Na-Sil) with  
 163 SiO<sub>2</sub>/Na<sub>2</sub>O = 3.5 (65.5% of H<sub>2</sub>O) and analytical-grade sodium hydroxide (NaOH) pellets were used  
 164 as alkali activators. The solution was prepared 24 h before mixing. 1% citric acid was added to the  
 165 water; this solution was used to retard the fast setting of the slag. In order to achieve a good packing  
 166 for the slag mortar, the LS used in the mix contained equal amounts of milled slag and as-received  
 167 slag, optimised using a modified Andreassen's packing model with a distribution coefficient (q) of  
 168 0.20, a maximum particle size of 2 mm, and slag density of 3.01 g/cm<sup>3</sup>. The water-to-cement (w/c)

169 ratio for all the mortars was 0.35. The mix composition is presented in Table 2. After mixing, the  
 170 slurry was cast into rectangular prism molds with dimensions of 40 x 40 x 160 mm for strength  
 171 analysis and 10 x 10 x 50 mm for dilatometry analysis. The mold was then jolted on a vibration table  
 172 for two minutes and sealed with plastic foil to avoid loss of moisture. The slurry was left to cure at  
 173 room temperature for 24 h, after which the hardened mortars were demolded and kept in an air-tight  
 174 chamber to prevent moisture loss until testing.

175  
 176

Table 2. Mortar mix composition.

Sample name	LS (g)	Na-Sil (g)	NaOH (g)	w/c	CAC (g)	sand (g)	FS (g)
AALS-Ss	500	246	9	0.35	-	500±5	-
HLS-Ss	500	-	-	0.35	-	500±5	-
CAC-Ss	-	-	-	0.35	500	500±5	-
AALS-Fs	500	246	9	0.35	-	-	500±5
HLS-Fs	500	-	-	0.35	-	-	500±5
CAC-Fs	-	-	-	0.35	500	-	500±5

177

### 178 2.3. Thermal treatment

179 At 28 days, the cured mortars were dried at 105°C for 18 h in order remove the capillary water and  
 180 to reduce the spalling tendency of the sample during heat exposure (Maaroufi et al., 2015). After  
 181 drying, the mortars were then exposed to thermal loads of 200, 400, 600, 800, and 1000°C at a  
 182 heating rate of 6°C/min (see Figure 2). A dwell time of 1 h at each temperature was used before the  
 183 mortars were removed from the furnace to cool.

184 Figure 2. (a) Heating regime applied to the mortars inside the furnace (b) test furnace for the  
 185 mortar prisms.

### 186 2.4. Hardened concrete testing

187 To determine the physico-mechanical properties and make a comparison between the specimens,  
 188 residual strength, weight loss, and thermal expansion or shrinkage were determined at different  
 189 thermal loadings. The unconfined compressive strength (UCS) and three-point flexural testing were  
 190 done using a Zwick testing machine according to the EN 196-1 standard. The average of four values

191 was then reported as the UCS and the average of two replica samples was reported as the flexural  
192 strength for each temperature. Ultrasonic pulse velocity testing was done using a Matest C369N  
193 tester to ascertain the thermal damage to each specimen. The ultrasonic pulse velocity,  $V_p$  ( $m^{s^{-1}}$ ),  
194 was calculated using the distance ( $d$ ) between the two transducers and the time taken ( $t$ ) for the  
195 pulse to reach the receiver, as shown in equation (1):

$$196 \quad V_p = \frac{d}{t} \quad (1)$$

197 Thermogravimetric analysis (TGA) was conducted using the Precisa Gravimetrics AG prepASH  
198 automatic drying and ashing system. 3.5 g of powdered mortar were heated from room temperature  
199 to 1000°C in an inert nitrogen atmosphere. To investigate the microstructure of the mortars before  
200 and after thermal exposure, the samples were mounted in epoxy resin and polished with diamond  
201 pastes. The polished samples were then coated with platinum before examination with backscattered  
202 scanning electron (BSE) microscopy using a Zeiss Ultra Plus microscope with an accelerating  
203 voltage of 15 keV.

#### 204 2.5. Dilatometry analysis

205 Dilatometry analysis was carried out via NETZSCH DIL 402 Expeditis dilatometer, using samples  
206 sized approximately 8×8×10 mm. Samples were heated to 1000°C at 6°C/min, there was a one-hour  
207 dwell time at the peak temperature, and for the final stage, the furnace was set to a cooling rate of  
208 10°C/min. The heating chamber was open-ended, with a constant flow of nitrogen (40 ml/min) as the  
209 purge gas to prevent unwanted gaseous/evaporated matter from getting into the measurement  
210 chamber, which was separate from the heating chamber and sample holder.

211

### 212 **3. Results and discussion**

#### 213 3.1. Visual observations

214 Visual observation of the mortar structures was used to determine the flaws, deterioration, and  
215 serviceability before and after exposure to elevated temperatures. Visual inspection was performed



216 after removing the cooled specimens from the furnace to evaluate the mortar damage, which  
217 included examining the color change, surface spalling, disintegration, cracks, and swelling. Figure  
218 3, 4, 5, 6, 7 and 8 shows the visible discoloration of the outer structure of HLS\_Fs, HLS\_Ss,  
219 AALS\_Fs, AALS\_Ss, CAC\_Fs and CAC\_Ss respectively with increasing temperatures from 23°C to  
220 1000°C. It has been previously reported that concrete samples containing siliceous aggregates  
221 change color to whitish grey when exposed to temperatures between 600°C and 900°C, and to a  
222 buff color when exposed to temperatures between 900°C and 1000°C (Short et al., 2001). This color  
223 change is attributed to the loss of water, the dehydration of the binder, and the phase transformations  
224 taking place within the aggregates (Hager, 2013; Shang and Lu, 2014).

225 The HLS specimens showed great resistance to thermal damage, with no noticeable cracks or  
226 spalling—except the HLS\_Ss samples, which showed visible microcracks at 1000°C. These cracks  
227 were attributed to the shrinkage resulting from the dehydration of the binders and expansion of the  
228 siliceous aggregates during heating (Duxson et al., 2006). In AALS specimens, thermal cracks were  
229 more apparent with Fs mortars after 400°C and increased in size and propagation up to 1000°C,  
230 while in the mortar containing sand as an aggregate, cracks were evident from 600 to 1000°C. It is  
231 believed that the ferrochrome slag aggregates in AALS experienced an alkali-silica aggregates  
232 reaction, which sped the deterioration of the mortar under elevated temperatures. This limits its use  
233 as an aggregate in alkali-activated systems. Nevertheless, neither the HLS nor the AALS samples  
234 showed any noticeable spalling under these temperature exposures.

235 Surface cracking and spalling was noticeable in the CAC specimens with both aggregates, starting  
236 from 600 °C to 1000 °C. Spalling in concrete is attributed to the gradual accumulation of pore  
237 pressure in the specimen during heating (Kodur V.K.R, 2018). Dense concretes have been reported  
238 to be susceptible to spalling under fire even if they were dried before exposure (Hertz, 2003, 1992;  
239 Sanjayan et al., 1993). CAC mortar is thought to be susceptible to this pressure buildup because of  
240 its higher density compared to HLS specimens. The heated capillary water in the binder vaporises  
241 during fire exposure; due to the low permeability of the concrete, it causes an increase in internal  
242 pressure, resulting in the rapid loss of the mortar surface layers (Kodur V.K.R, 1999).

243 Figure 3. Visual appearances of HLS\_Fs before and after exposure to elevated temperatures (a)  
244 before exposure (b) at 400 °C (c) at 600 °C (d) 800 °C and (e) at 1000 °C.

245 Figure 4. Visual appearances of HLS\_Ss before and after exposure to elevated temperatures (a)  
246 before exposure (b) at 400 °C (c) at 600 °C (d) 800 °C and (e) at 1000 °C.

247 Figure 5. Visual appearances of AALS\_Fs before and after exposure to elevated temperatures (a)  
248 before exposure (b) at 400 °C (c) at 600 °C (d) 800 °C and (e) at 1000 °C.

249 Figure 6. Visual appearances of AALS\_Ss before and after exposure to elevated temperatures (a)  
250 before exposure (b) at 400 °C (c) at 600 °C (d) 800 °C and (e) at 1000 °C.

251 Figure 7. Visual appearances of CAC\_Fs before and after exposure to elevated temperatures (a)  
252 before exposure (b) at 400 °C (c) at 600 °C (d) 800 °C and (e) at 1000 °C.

253 Figure 8. Visual appearances of CAC\_Ss before and after exposure to elevated temperatures (a)  
254 before exposure (b) at 400 °C (c) at 600 °C (d) 800 °C and (e) at 1000 °C.

255

### 256 3.2. Mechanical properties after thermal treatment

257 HLS\_Ss mortar samples showed an increment in compressive strength of 60% after the mortars  
258 were exposed to 110 °C compared to the reference (see Figure 9) which had similar strength  
259 properties at the same condition. The gain in strength continued for HLS\_Ss mortars at 200 °C  
260 attaining UCS of 65 MPa compared to CAC\_Ss strength of 58 MPa. Similar trend at this condition  
261 have been reported earlier (Aydın et al., 2008; Netinger et al., 2013). The gain in strength in this  
262 temperature range is consistent with the effect of lower temperature drying on cement mortars before  
263 elevated thermal exposures. The drying at lower temperature relaxes the pressure internally,  
264 creating van der Waals forces that results in a closer configuration of capillary pores and gain in  
265 strength (Aydın et al., 2008). While AALS mortar sample lost 71% of its strength after 110 °C  
266 exposure. This significant loss of strength at 110°C for AALS specimens is understood to be due to

267 the dehydration of the calcium aluminate silicate hydrate phase (C-A-S-H) (Abdel-Gawwad and Abo-  
268 El-Enein, 2016; Zhang et al., 2016).

269 From 400 °C, HLS\_Ss and CAC\_Ss mortar samples exhibited similar residual strength up to 1000  
270 °C, while AALS mortars exhibited different thermal behaviour in comparison. Notably, after 800 °C  
271 AALS exhibited an increment in strength from 10 MPa at 800 °C to 20 MPa at 1000 °C. This increase  
272 in strength is credited to the densification of the sample by the viscous sintering of the binder, which  
273 fills in the voids and closes the micro cracks (See Figure 14). Similar strength increments at high  
274 temperatures have been reported of alkali-activated materials (Lemougna et al., 2011; Rickard et  
275 al., 2010; Ye et al., 2014).

276 On the use of ferrochrome slag as aggregates in the binder, generally it can be observed from Fig.  
277 9b that the mortars exhibited almost similar residual strength compared with sand aggregates  
278 mortars. HLS\_Fs similarly displayed an increment in strength (65 MPa) at 110 °C from 38 MPa at  
279 23 °C. However, the strength began reducing at 200 °C unlike with HLS\_Ss; which had a continuous  
280 strength increment at this temperature. CAC\_Fs showed similar residual strength trend with  
281 CAC\_Ss. Though at 1000 °C, CAC\_Fs strength was 5 MPa lower than CAC\_Ss.

282 AALS\_Fs displayed the highest compressive strength (93 MPa) before heat exposure but suffered  
283 a 57% loss of strength after exposure to 110°C (Figure 9b). It is suggested that the initial high  
284 strength exhibited by AALS\_Fs may be due to the reaction of some fraction of the ferrochrome  
285 aggregate with the AALS binder. This means that the ferrochrome worked as an aggregate as well  
286 as a binder. This is consistent with a previous study of alkali-activated mortars with ferrochrome and  
287 natural aggregates by Elibol and Sengul (Elibol and Sengul, 2016). Overall, the gradual loss of  
288 strength in all the specimens was attributed to the thermal shrinkage of the binders and thermal  
289 expansion of the aggregates. Altogether, replacing the sand aggregate with a ferrochrome aggregate  
290 showed comparable properties in all specimens except with AALS binder. Similar strength  
291 progression was observed during the flexural strength test shown in Figure 10, showing the  
292 dependence of flexural strength gain or loss on temperature.

293

294 Figure 9. Compressive strength of (a) sand aggregate mortars and (b) ferrochrome aggregate  
295 mortars at different temperatures.

296

297 Figure 10. Flexural strength of (a) sand aggregate mortars and (b) ferrochrome aggregate mortars  
298 at different temperatures.

### 299 3.3. Ultrasonic pulse velocity

300 The effect of elevated temperatures on the microstructural uniformity and compactness of the  
301 mortars was observed through ultrasonic pulse velocity (UPV) analysis. This non-destructive  
302 technique can be used to predict the mechanical performance and microstructure of concrete. The  
303 higher the rate of velocities, the fewer the internal pores and defects. Figure. 11((a) and (b)) show  
304 that mortars with sand aggregates displayed a greater decline in pulse velocity than ferrochrome  
305 aggregate-based mortars across the temperature range (110°C -1000°C), most noticeably for  
306 temperatures between 400°C and 1000°C. This is partly attributed to the irregular surface texture of  
307 ferrochrome aggregates, which helped the packing of the mortar through superior mechanical  
308 bonding between the aggregates and the binder compared to sand aggregates (Elibol and Sengul,  
309 2016).

310 The pulse velocities for both the AALS\_Ss and AALS\_Fs specimens decreases by 60% and 55%,  
311 respectively, at 110°C, which is consistent with the loss of strength described earlier. While the  
312 AALS\_Fs pulse velocity stayed constant between 110°C and 1000°C, the AALS\_Ss pulse velocity  
313 decreased further, with the lowest UPV ( $1697 \text{ ms}^{-1}$ ) recorded at 600°C, and increased from 800°C  
314 to 1000°C. This increase in the UPV correlates with the strength gain due to the densification of the  
315 sample mentioned earlier.

316

317 Figure 11. Ultrasonic pulse velocities for the specimens before and after temperature exposure (a)  
318 for sand mortars and (b) for ferrochrome mortars.

### 319 3.4. Thermal expansion/shrinkage of the mortars

320 Dilatometrical analysis was conducted on the specimens to investigate their linear thermal expansion  
321 or shrinkage. The shrinkage/expansion of the mortars was dependent on the aggregate type used.  
322 For mortars with sand aggregates (Figure 12(a)), no significant expansion/shrinkage occurred until  
323 100°C—except for the AALS\_Ss sample, which displayed shrinkage after 80°C. The shrinkage  
324 below 100°C can be attributed to the loss of free water from the mortar. As previously reported for  
325 alkali-activated materials (Duxson et al., 2006; Provis et al., 2009; Rickard et al., 2012; Zhang et al.,  
326 2016), the AALS\_Ss sample continued shrinking in the 100-230°C range, which corresponds to the  
327 loss of structural water. After the capillary strain, resulting from the loss of water from the pores, is  
328 increased, the pores collapse and the sample began to shrink. This results in the loss of strength  
329 experienced by the AALS specimens. Between 230°C and 570°C, a gradual expansion of the  
330 AALS\_Ss mortar was observed. This was not due to the swelling of the AALS gel because of the  
331 low Si/Al ratio of 1.30 used in this study. Previously, the swelling of alkali activated material gels with  
332 high Si/Al ratios under elevated temperatures has been reported (Fletcher et al., 2005; Provis et al.,  
333 2009; Rickard et al., 2012). Therefore, the expansion in this range was attributed to the expansion  
334 of the quartz sand towards its phase transformation at 573°C; the net expansion of the quartz  
335 dominated the contraction of the binder gel. The specimen was stable in the 570-650°C range and  
336 then shrank further until 750°C. At this range, the densification of some alkali-activated materials  
337 have been reported earlier; this may have contributed to the strength and UPV gain (Mohd et al.,  
338 2015). The AALS\_Ss remained constant between 750-1000°C, with no further shrinkage or  
339 expansion.

340 HLS\_Ss and CAC\_Ss experienced similar expansion starting from 100°C, with an initial peak at  
341 250°C, but both exhibited slight shrinkage in the 250- 320°C range. This was then followed by further  
342 expansion, with a final peak at 570°C. After that, the samples stabilise toward 1000°C. The  
343 expansion as seen with the HLS\_Ss specimen is due to the aggregates' expansion at high

344 temperatures, which also leads to the cracking of the matrix. The slight shrinkage at 250-320°C is  
345 attributed to the loss of pore water and pores collapse. Figure 12(b) also shows the dilatometric  
346 curves for mortars with a ferrochrome aggregate.

347 AALS\_Fs samples experienced shrinkage from 70°C to 200°C, mainly due to loss of water from the  
348 matrix (Figure 12(b)). This stayed constant until 620°C, when a second sharp shrinkage was  
349 observed as a result of densification, with the highest shrinkage value recorded at 750°C. The  
350 sample continued to expand until the end of the test, which may be a result of cracking. Figure 12(b)  
351 also shows the linear thermal behavior of CAC\_Fs and HLS\_Fs—similar to their corresponding sand  
352 mortars, both samples shrank slightly in the 250-320°C range. Thereafter, CAC\_Fs exhibited a  
353 marginal expansion and shrinkage until 1000°C, while HLS\_Fs expanded slightly and then  
354 experienced a steep shrinkage at 700-900°C and stabilised until 1000°C.

355

356 Figure 12. Dilatometric curves showing the expansion and shrinkage of (a) mortars with sand (b)  
357 mortars with ferrochrome aggregates after temperature exposure.

### 358 3.5. Thermogravimetric analysis

359 Thermogravimetric analysis (TGA) was used to measure the loss of mass of the specimens ranging  
360 from 24°C to 1000°C after 28 days of curing. The TGA for AALS\_Fs and AALS\_Ss in Fig. 13 showed  
361 a rapid loss in weight of the mortars between 85-350°C due to the excessive loss of structural and  
362 free water in the binder. Also weight loss in this range is attributed to decomposition of gels, most  
363 likely a calcium aluminate silicate hydrate (C-A-S-H) and/or dicalcium aluminate octahydrate (C<sub>2</sub>AH<sub>8</sub>)  
364 (Adesanya et al., 2017; Lothenbach and Gruskovnjak, 2007). This rapid loss and migration of water  
365 out of the mortar initiated the appearance of micro cracks in the structure of the AALS mortar. This  
366 also may explain the substantial deterioration in compressive strength in both AALS mortars in this  
367 range and consistent with the shrinkage observed in the dilatometry analysis. After this initial decline  
368 in mass, the loss eased significantly from 500°C with lower loss of mass recorded thereafter. At the  
369 end of the analysis, about 6% loss of mass was recorded for both samples.

370 The HLS mortar samples, on the other hand, exhibited superior resistance to mass loss when  
371 compared with the CAC and AALS mortars. The mass loss curve for HLS for both aggregate mortars  
372 shows a different curve between 85 - 350°C due to a different decomposing temperature for the  
373 hydrating product. Here, the loss of water at this range and decomposition of the hydrating product  
374 (dicalcium aluminate hydrate - katoite) was less significant compared to AALS samples. Overall,  
375 both HLS aggregate mortars recorded approximately 2% loss in weight at the end of the analysis.

376 Similarly, CAC mortars experienced loss of weight between 85 - 350°C caused by the loss of free  
377 water and decomposition of calcium aluminate decahydrate ( $\text{CAH}_{10}$ ) (Collier, 2016). Overall, CAC  
378 mortars suffered between 5.3-7% at the end of the thermogravimetric analysis.

379

380 Figure 13. TGA curves for (a) sand mortars and (b) ferrochrome mortars after 28 days of curing.

### 381 3.6. Morphology and microstructure analysis

382

383 The microstructures of the mortars before and after thermal exposure were investigated through  
384 backscattered scanning electroscopy (BSE-SEM) analysis after 28 days and shown in Figure 14. In  
385 all pre-exposed mortars, there exist microcrack formations with a diameter under 1  $\mu\text{m}$ , induced by  
386 the shrinkage of the mortars and possibly through stress propagation from the cutting of the samples  
387 for epoxy preparation. Subjecting the specimens to a temperature of 1000°C led to a significant  
388 increase in the cracks' formation and size. There was also shrinkage of the binder as a result of  
389 uneven thermal strains between the aggregates and the binder. The binder microstructure became  
390 porous. The sintering effect can also be seen in the microstructure after thermal exposure. The effect  
391 is more pronounced in the AALS sample, which may be due to the alkaline environment (Wang et  
392 al., 2017). The chemical interaction between the alkali paste and the ferrochrome aggregate is  
393 shown in Figure 14(e). The zone marked with a rectangular box shows a diffused layer at the  
394 interfacial zone (ITZ), which indicates the development of chemical bonding between the paste and  
395 the aggregate. This observation is consistent with the high strength of the unexposed AALS\_Fs

396 mortar compared to the AALS\_Ss mortar (see Figures 9 and 10). Therefore, its use as an aggregate  
397 in an alkaline environment may not be suitable.

398

399 Figure 14. BSE-SEM image of the mortars before exposure; (a) HLS\_Fs, (c) HLS\_Ss, (e)  
400 AALS\_Fs and (g) AALS\_Ss and after exposure to 1000 °C; (b) HLS\_Fs, (d) HLS\_Ss, (f) AALS\_Fs  
401 and (h) AALS\_Ss. Fs: Ferrochrome aggregate; B: Binder and LS: Unreacted ladle slag/aggregate.  
402 Red rings show the area of sintering/densification in the mortar and rectangular box shows the  
403 interfacial zone (ITZ) between the alkali binder and the ferrochrome aggregate.

404

#### 405 **4. Conclusion**

406

407 The damage behavior of ladle slag mortars under elevated temperatures were studied and compared  
408 with those of a commercial refractory cement having similar hydration properties and chemical  
409 composition. The use of ferrochrome slag as a potential refractory aggregate substitution for sand  
410 was also investigated. Hydrated ladle slag (HLS) mortars showed properties similar or superior to  
411 the commercial calcium aluminate cement investigated, exhibiting less damage structurally after  
412 exposure to temperatures of up to 1000°C. The use of ferrochrome slag as a refractory aggregate  
413 was promising; it showed similar properties when compared to sand. However, in alkali-activated  
414 mortars, the use of ferrochrome slag as an aggregate was unfavorable due to its reaction with the  
415 alkali binder. The lower thermal damage to HLS mortars suggests that they could be used in high  
416 temperature applications where CAC 40 grade is used, such as in furnaces, building fireplace and  
417 other applications where temperatures reach 1000°C.

418

419

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421



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429

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