Mineralogy and glass content of Fe-rich fayalite slag size fractions and their effect on alkali activation and leaching of heavy metals

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Abstract
Fayalite slag (FS) is an Fe-rich nonferrous metallurgy (CaO-MgO-)FeOx-SiO2 slag originating from nickel or copper manufacturing processes, which currently is disposed to landfills or used in low-value applications. This study investigates the mineralogy and glass content of certain sized fractions of FS and how it influences the reactivity, mechanical, and microstructural properties of the alkali-activated materials produced. Water-quenched granular FS was sieved into two size fractions: namely, a fine fraction (FF) with a particle size range of 0–0.5 mm and a coarse fraction (CF) with a particle size range of 1.5–2 mm. It was then milled to a similar median particle size of 10 μm to be used as a binder precursor. The reaction kinetics of each fraction was determined via thermal analysis microcalorimeter, and the microstructural evolution and chemical composition of the binder were studied using a scanning electron microscope coupled with an energy dispersive X-ray spectroscopy. The environmental leaching behavior of both fractions before and after alkali activation was assessed according to the EN 12457-2 standard. The results showed that both fractions consisted of fayalite, magnetite crystalline phases, and MgO-SiO2-FeOx (-CaO-Al2O3) glass phase. However, FF had a higher glass content (63 wt.%) in comparison to CF (39 wt.%), and, consequently, FF was more reactive under alkali activation, as evidenced by faster reaction kinetics, faster strength development, and improved microstructural properties. Alkali-activated samples had differences in the chemical compositions of their binder gels at early stages, though later, their binders became increasingly homogenous and consisted of an Na-K-Fe-Si gel with Mg, Ca, and Al as minor constituents in both samples. Additionally, the leaching behavior of potentially toxic metals and substances from precursors and alkali-activated samples prepared was below the limits set for paved structures as specified by Finnish legislation.

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1 | INTRODUCTION

Portland cement (PC) is the most widely used cementitious material in the construction industry; however, its production and continuous usage results in adverse environmental problems in terms of energy consumption and CO₂ emissions.¹ Thus, there is an increasing demand for an alternative binding material with a lower carbon footprint than PC. One alternative is to utilize inorganic industrial residues as precursors for alkali-activated materials (AAMs).²,³

AAMs are emerging as eco-friendly and sustainable alternatives to PC concrete and mortars. Numerous aluminosilicate supplementary cementitious materials (SCMs) have been identified and studied as precursors for AAMs, including metallurgical slags, fly ashes, calcined clays, mineral wools, and natural pozzolans.⁴,⁵ These precursors are mixed with alkali activators (such as alkali hydroxides and alkali silicates) either as one-part systems (i.e., a blend of solid precursor and solid activator, mixed with water), or two-part systems (solid precursor mixed with a liquid-activating solution) to produce mortars and concretes with superior or comparable properties to PC.⁶,⁷ The development of AAMs using industrial residues has been reported to have numerous economic and environmental benefits, and this development would also comply with the European Union directive on waste management.⁸

Blast furnace slag (BFS) is a type of inorganic industrial residue from metallurgical processes that have been extensively studied; it is frequently used in alkali-activated cements and concretes.⁵ BFS is a calcium-rich aluminosilicate material that can be subjected to alkali activation—its chemical composition, properties, and activation synthesis parameters (choice and content of activator, hydration process, and curing regimes) have been reported in the literature.¹,³,⁹ However, BFS is almost completely utilized as an SCM with cement; thus, other slag types to act as AAM precursors should be investigated.

Fayalite slag (FS) is an Fe-rich nonferrous metallurgical waste generated during the extraction of nickel and copper, which is most often stored at dumping grounds; this causes serious environmental impacts and higher economic costs for industries.¹⁰ The molten slag forms as byproduct during smelting, and can either be rapidly quenched by water, or slowly quenched by air.¹¹ Rapid quenching of FS by water results in a partly glassy or amorphous slag, whereas slow quenching by air produces mostly crystalline slags.¹² The average production of water-quenched FS in Finland was estimated at 200,000 tons per annum, with 90% of it landfilled.¹³,¹⁴ In addition to FS, other Fe-rich materials can include lead and zinc slags, laterite soils, bauxite residue slags, ferronickel slags, and Fe-silicate glasses.¹⁵-¹⁹

The presence of glassy phase in water-quenched FS presents a possibility for its utilization as a precursor for AAMs.²¹-²⁴ Glassy phase is a phase with significant reactivity in FS, as the glass structure is more disordered in comparison to crystalline phases. This makes the phase more susceptible than crystalline phases to dissolution in alkali-activating solutions (such as sodium hydroxide and sodium silicate).²⁵,²⁶

The standard procedure for FS utilization as an AAM precursor is to mill it to a fine particle size (d₅₀ ≈ 10 microns), and to mix it with the alkali activator.²²,²⁵ This approach has been used to increase the reactivity of FS in alkaline solution; the results have been shown to be promising.²²,²³,²⁷ During alkali activation, FS undergoes dissolution, then experiences complex reaction pathways, leading ultimately to the formation of two reaction products; that is, precipitation of Fe²⁺, arranged in trioctahedral layers, while the tetrahedral Fe³⁺ charges are likely to be located in the silicate network, with Na⁺ performing the charge balancing role.²⁸,²⁹ From the results of various studies on alkali activation of FS, it is obvious that the reactivity of FS is largely controlled by the glass content, glass chemistry, and surface area of the FS.²²,²³ Other factors, such as particle size of the precursor, liquid to solid ratio, and curing conditions, could also play a part in its overall reactivity.³⁰,³¹

Compared to BFS, FS is a poor glass-forming material, as it contains fewer glass network-modifying ions, such as Ca and Mg.³² Thus, in industrial cooling processes, major portions of the MgO-FeOx-SiO₂ slag melt crystallize into fayalite mineral and magnetite, which consequently decreases the glass content of FS.¹⁰,¹² The extent of crystallization depends on the cooling rate of molten slag, which is further affected by the size of molten slag droplets.³³ Thus, different sizes of FS particles may have different mineralogy depending on the crystallization/cooling process used, as the process can influence their reactivity in the alkali activation process.

In this study, we investigated the reactivity of certain size fractions of FS under alkali activation. The granule sizes of water-quenched FS are between 0 and 2 mm. The original material was sieved into two size fractions—of 0–0.5 mm.

KEYWORDS
alkali activation, environmental leaching, Fe-rich fayalite slag, glass content, mineralogy, reactivity, size fractions
and 1.5–2 mm—to examine whether those two size range extremes have differences in their mineralogical phases, and how that influences their reactivity, mechanical, and microstructural properties during the alkali activation process. Both fractions were milled to the same final particle size, and the specific surface areas of both were assessed. The reaction kinetics of each fraction when activated with an alkaline solution were determined by isothermal calorimetry. The chemical and mineralogical compositions of each FS fraction were analyzed using X-ray fluorescence (XRF) and X-ray diffraction analysis (XRD) with the Rietveld method. The environmental leaching behavior of each fraction before and after activation was investigated in accordance with EN 12457-2 recommendations, and their microstructure development was analyzed with a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). This information will provide a valuable insight into the reactivity of different fractions of FS.

2 | EXPERIMENTAL WORK

2.1 | Materials and methods

Water-quenched FS used in this study was obtained from Boliden Harjavalta Oy (Finland). The slag is a form of industrial waste originating from nickel-smelting operations. The FS was moist when received and was dried overnight at a temperature of 60°C in order to remove moisture prior to sieving. The FS with a particle size distribution of 0–2 mm was separated into two fractions of particle sizes; 0–0.5 mm (named as “FF”) and 1.5–2 mm (named as “CF”) by a vibratory sieve shaker (Fritsch, Germany), at an amplitude of 1.5 for 10 min (Figure 1). The relative proportions of FF and CF after sieving were 14% and 18% of the total FS, respectively. To enhance the dissolution of the chemical components of slag, and to increase their reactivity, FF and CF were milled for 150 and 180 min, respectively, in order to achieve similar median particle sizes ($d_{50}$ ~10 microns) using a laboratory ball mill (Germatec, Germany) with 150 stainless steel balls of various sizes (45 balls of 40 mm Ø, 45 balls of 30 mm Ø, and 60 balls of 25 mm Ø). The ratio of stainless-steel balls (kg) to FS (kg) was 10:1. The particle size distribution of the milled FF and CF was analyzed by a laser diffraction particle size analyzer (Beckman Coulter 13320, Brea, CA, USA), using the Fraunhofer model. The particle volume distribution (cumulative and differential volume) of the milled FF and CF is presented in Figure S1 (Supplementary Information).

The chemical composition of both fractions was measured using XRF (PANanalytical Omnian Axiosmas, UK), and the loss on ignition (LOI) was determined using a thermogravimeter (prepASH; Precisa). The XRF analysis was carried out on both fractions to check if there is any variation in bulk chemical compositions between FF and CF. The XRF results presented in Table 1 showed that there was no difference in the chemical compositions of FF and CF, with the major oxides present in both being Fe$_2$O$_3$, SiO$_2$, and MgO, together with other minor oxides. This presents some oxide similarities with copper production-based FS. The iron content in both fractions was reported as Fe$_2$O$_3$, due to the oxidation of Fe$^{2+}$ to Fe$^{3+}$ during XRF sample pretreatment, using a thermogravimetric analysis at 950°C. This is represented by negative LOI in Table 1.

The mineralogical phases of FF and CF were analyzed by XRD using a Rigaku Smartlab diffractometer, with Cu K-beta radiation, and a scanning rate of 0.02°2θ/step from 5 to 80°, operated at 135 mA and 40 kV. The quantification of the crystalline content in both fractions was done using analytical grade titanium oxide (10 wt.%) as the internal standard. The crystalline titanium oxide was added to the milled FF and CF and was homogenized together in an agate mortar for 5 min. The quantitative results were obtained using the Rietveld refinement method.  

![Figure 1](https://example.com/figure1.png)

**Figure 1** Schematic representation of the experimental procedure

<table>
<thead>
<tr>
<th>Name</th>
<th>FF</th>
<th>CF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>54.3</td>
<td>54.3</td>
</tr>
<tr>
<td>MgO</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>33.0</td>
<td>33.0</td>
</tr>
<tr>
<td>CaO</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Others</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>LOI at 950°C</td>
<td>−5.3</td>
<td>−5.2</td>
</tr>
</tbody>
</table>
The density of each fraction was analyzed using helium gas pycnometer (Micrometrics, Norcross, GA, USA). An average of five consecutive measurements were taken for each fraction in order to obtain the average density value. The specific surface area of the fractions after milling was measured using an accelerated surface area and porosimetry system (ASAP 2020 Plus physisorption, Micrometrics). Measurements were based on the physical adsorption of N$_2$ gas on a solid surface, and the results were reported as a Brunauer–Emmett–Teller (BET) isotherm.

The environmental analysis was carried out on the precursor and alkali-activated paste samples in accordance to European standard EN 12457-2. After 28 days of curing, paste samples were crushed and sieved to particle sizes below 4 mm prior to determining the water content of the samples. The sieved samples were mixed with pure water using a liquid/solid weight ratio of 10 and were rotated for 24 h at 30 rpm in a rotary tumbler (Retsch, Germany). After rotation, the mixture was filtered through a 0.45 μm membrane filter under vacuum, and the filtrate was collected into a conical flask. The pH and conductivity of the filtrate were measured. The filtrate was acidified with HNO$_3$, and the concentration of the leached elements was determined by the use of an inductively coupled plasma mass spectrometer analysis.

### 2.2 Preparation of alkali activators

The alkaline-activating solution used for the synthesis was a mix of 10 M of sodium hydroxide (NaOH) solution and commercial potassium silicate solution (50:50 mass ratio of 10 M NaOH and potassium silicate). The choice of potassium silicate solution was due to its lower viscosity, by using a mix of NaOH and potassium silicate, the amount of liquid phase in the system is reduced, which results in a AAM with lower porosity, less shrinkage, and greater strength. The commercial potassium silicate solution (Betol K35 T, Woellner Austria GmbH) was composed of 10.92 wt.% of K$_2$O, 23.9 wt.% of SiO$_2$, and 65.18 wt.% of water by mass. NaOH solution was prepared by dissolving analytical grade NaOH pellets (VWR, Chemicals, Germany) of ≥ 99% purity in deionized water. The final molar ratio of the activating solution was (SiO$_2$/Na$_2$O+K$_2$O = 1.0) and (H$_2$O/Na$_2$O+K$_2$O = 15.7). The activating solution was prepared 24 h prior to activating the precursors.

### 2.3 Preparation of test samples

Alkali-activated paste samples were prepared for mechanical and microstructural analyses. A liquid to solid ratio of 0.25 was held constant for the paste samples of FF and CF. The choice of the 0.25 ratio was based on the preliminary test, which showed the possibility of obtaining a workable and homogenous paste. The specimens were prepared by mixing each milled fraction with the alkali activator in a mixer (Hobart, Lake County, IN, USA) for 5 min to achieve a homogenous paste. The alkali activator temperature at the time of mixing was 23 ± 1°C. The resulting pastes were casted into oiled rectangular molds with dimensions of 20 × 20 × 80 mm$^3$ and were compacted using a jolting machine (60 shocks; 1 shock per second) to remove entrapped air. All the samples were placed in a tightly sealed plastic bag to prevent water loss and were cured for 24 h at room temperature (approximately 23 ± 1°C). The samples were then demolded after 24 h, and further cured in a sealed plastic bag at room temperature prior to testing after 3, 7, and 28 days of curing.

Isothermal calorimetry analysis was undertaken at a constant temperature of 23°C for 96 h in order to study the reaction kinetics of prepared paste samples. Heat flow data were integrated to obtain the total heat evolution over time and were analyzed to determine the reaction kinetics of the fractions during the alkali activation process. The mixing of the samples was carried out outside the instrument, and approximately 7 g of the mixed pastes was introduced into the instrument for measurement. The instrument used for analysis was a thermal analysis microcalorimeter air micro calorimeter (TA Instruments, New Castle, DE, USA). The heat evolution data obtained in the first 45 min for each paste mix were not used, as the data might have been influenced by the introduction of the ampoules into the instrument.

### 2.4 Sample characterization

SEM and EDS analyses were carried out using a Zeiss Ultra Plus instrument (Zeiss, Germany). Immediately after being sieved into two fractions, FF and CF were impregnated with epoxy resin, and were polished using ethanol as lubricant prior to analysis. The SEM images of the fractions after sieving are shown in the Supplementary Information. For the activated samples, samples for SEM analysis were prepared by impregnating the carefully cut samples (3 and 28 days old) in epoxy; they were then polished. All the samples were carbon coated so as to create a conductive layer over the surface prior to measurement. The elemental composition of the samples was quantified by measuring at least 50 separate points from a representative section of the glass phase of raw slag, as well as from the binder phase formed. An accelerating voltage of 15 keV, coupled with a working distance of 8.4 mm, was used.

The compressive strength was performed using a Zwick testing machine (Zwick Roell Group, Ulm, Germany) with
**FIGURE 2** XRD patterns of FS fractions (FF and CF). Abbreviations: F, fayalite; M, magnetite; R, rutile

**TABLE 2** Mineralogical composition and density of FF and CF

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Fayalite (wt.%)</th>
<th>Magnetite (wt.%)</th>
<th>Glass (wt.%)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FF</td>
<td>35</td>
<td>2</td>
<td>63</td>
<td>3.82 ± 0.2</td>
</tr>
<tr>
<td>CF</td>
<td>57</td>
<td>4</td>
<td>39</td>
<td>3.95 ± 0.3</td>
</tr>
</tbody>
</table>

a maximum load of 100 kN and a loading force of 2.4 kN/s. Four replicate samples of each mix were tested, reporting their average as the compressive strength. The error bars added to the strength graphs indicate double standard deviations of the crushed sample strengths.

### 3 RESULTS AND DISCUSSIONS

**3.1 XRD analysis of the fractions**

The XRD patterns shown in Figure 2 revealed that both fractions consisted of fayalite [(Fe₂SiO₄), pdf. 04-007-9022] and magnetite [(Fe₃O₄), pdf. 04-008-8145] as the crystalline components, whereas the rutile [(TiO₂), pdf. 04-008-7847] signals originate from its use as an internal standard. Particle size fractioning of FS was observed to affect the mineralogical compositions of FF and CF, as shown in Table 2. Differences were observed between FF and CF in the weight percentages of crystalline (fayalite and magnetite) and glass phases. It was observed that the crystalline content of FF was lower than that of CF, and, consequently, the glass content of FF (63 wt.%)) was higher than that of CF (39 wt.%).

The BET analysis results showed that there was a difference in the total specific surface area of the two fractions. Despite a similar particle size distribution, the BET surface areas were 0.88 and 0.77 m²/g for FF and CF, respectively.

From the results of a density analysis depicted in Table 2, it is revealed that the density of CF is slightly higher than that of FF. The difference in density may be due to the difference in mineralogical composition. A correlation between slag density, chemical composition, and phase assemblage was reported in one noteworthy study. In said study, a synthetic FeOx-SiO₂ slag with high crystalline content was reported to have higher density than a second slag with lower crystalline phase content. Thus, their own findings, paired with our own findings regarding the higher crystallinity of CF, suggest a higher density may be yielded from this material.

**3.2 Reaction kinetics of the fractions**

FF had a higher heat evolution rate and cumulative heat release in comparison to CF (Figures 3 and 4). A well-defined peak (3.26 mW/g) appeared for FF after about 1.5 h; this peak may be related to the precipitation and formation of the reaction products. A lower peak intensity (0.52 mW/g) was noticeable in CF, even after 96 h. This suggests that less reaction products were formed.
FF had higher reactivity and precipitation of reaction products, as evidenced by a faster exothermic reaction and a higher exothermic peak. This may be attributed to its higher glass content in comparison to CF. Similar observations have been reported in a previous study on alkali activation of volcanic ashes with different glass content. In said study, volcanic ashes with higher glass content exhibited faster exothermic reactions than those with lower glass content.37

Similarly, in another study, three synthetic FeOx-SiO2 slags with different amorphous content, activated with the same alkali activator quantity, were observed to react differently in an alkaline environment. It was reported that FeOx-SiO2 slag with the highest amorphous content undergoes a faster dissolution and polymerization reaction when activated with an alkaline solution.32 Thus, it is fair to say that the higher the glass content, the higher the exothermic peak formed on contact with the alkali activator; as glass phase is the most reactive phase in FS.25,38 The high-intensity peaks formed during reactions in FF are comparable with other reported studies of FS.23,32

The cumulative heat released by FF was higher than that of CF after 96 h of reaction, as shown in Figure 4. There was a steady rise in the heat released by both fractions. Ultimately, the cumulative heat released by FF was five times higher than CF after 24 h. However, at the later stage (96 h), the difference in cumulative heat released between FF and CF had reduced. This indicates that the heat released in CF paste is slower, but the rate of release increases gradually over a long period of time, thereby extending the formation of reaction products. It is additionally worth noting, the differences in the specific surface area of both fractions, as reported in Section 3.1, may influence the heat released. FF has a slightly higher specific surface area than CF, and hence, can influence the reaction process. In other words, the greater the surface area, the higher the reaction ability of the precursors on contact with an alkali activator. This leads to a more fast and complete reaction process.

The cumulative heat released after 96 h of reaction was measured as 81.4 and 25.7 J/g for FF and CF, respectively. This measurement of heat released by FF is consistent with other iron-rich slags activated with similar alkaline solutions, as reported in the literature.32,39,40 In both paste samples, the reaction continues after 96 h, as by this point, the cumulative heat released is still increasing. The continuation of the reaction was found to induce microstructural evolution at the later ages. This was reflected in the strength development, more evidently so in CF. This shall be further discussed in Section 3.3.

### 3.3 Compressive strength

During the first 3 days of curing, FF samples achieved a considerable strength of 25 MPa, compared to CF, with 3 MPa (Figure 5). The heat evolution (Figure 3) correlates with the early age strength gained by FF samples, due to the increased rates of reaction, the higher dissolution kinetics of its glass phase, the evident precipitation of reaction products, and hence, the faster binder structure development. Meanwhile, there was no significant increase in strength of alkali-activated FF samples at 7 days of curing, which indicates that a major part of the compressive strength is already achieved at 3 days of curing. However, significant strength development in CF samples occurred between 7 and 28 days. The strength gained between 7 and 28 days in CF suggested that, even though the matrix development of the paste samples during the curing period
Compressive strength development of alkali-activated FF and CF was slow at an early age, more binder gel was formed and the matrix became denser at a later age, as showcased by the 28-day strength. The final compressive strength of FF (37 MPa) was higher than CF (29 MPa), which indicates that the strength values of both samples are linked to their mineralogical compositions. The higher glass content in FF means that more iron silicate glass is readily dissolved in alkali solution, resulting in more intense reactions and more binder formation. Furthermore, since both samples were cured at room temperature, there was no excessive loss of moisture required for the geopolymerization process to continue in the samples, or to achieve sufficient strength after 28 days. The compressive strengths achieved in FF and CF are relatively impressive and can be considered suitable for specific applications.

3.4 | SEM-EDS

The SEM micrographs in Figure 6 reveal a significant difference in the microstructure analyses of FF and CF. Comparing the micrographs of milled raw slag of FF and CF in Figure 6A and D, a large number of crystalline phases were visible in CF compared to FF. This matches the XRD analyses shown in Figure 2.

Alkali-activated FF matrix after 3 days of reaction is presented in Figure 6B. Microcracks were observed to have penetrated through the newly formed binder gel, and this may have occurred during sample cutting and polishing, or when exposed to the vacuum procedure of the SEM. On the other hand, the partially reacted and unreacted FF slag particles acted as a filler and/or aggregate in the matrix, and they are surrounded and bonded together by the binder gel formed during alkali activation. Microstructural examination of the unreacted or undissolved particles in both fractions revealed that they are relics of fayalite and magnetite, which are the predominant crystalline phases observed in the XRD analysis, shown in Figure 2. Conversely, the unreacted slag particles in alkali-activated samples of CF (Figure 6E) after 3 days of reaction were more visible, suggesting lower degrees of formation of the binder gel.

Considering the morphology of FF after 28 days of reaction in Figure 6C, the dissolution of the glass phase was still noticeable, although it was limited. The unreacted FF slag particle became smaller in size when the matrix was denser. The edges of the partially reacted slag particles showed deterioration (white ring), which suggests a continuous dissolution of the glass phase of FF as the activator is present, thereby causing a release of ions. Furthermore, CF showed improved binder formation and a denser matrix with some pores after 28 days of curing.

The EDS point analyses for both fractions of the glass phase of the precursors and binder gel formed after alkali activation are presented in Figure 7. It is worth noting that the EDS analysis is semiquantitative and could thus have some limitations. For instance, when a 15 kV acceleration voltage is used, it is possible that the data points obtained could be a combination of several unreacted particles and/or of binder phases, if they appear on a scale smaller than the depth of X-ray generation. Meanwhile, the average and standard deviations of several data points obtained on a specific phase could provide information regarding the composition of that particular phase. Figure 7 shows that the glass phase of FF contained a slightly higher quantity of Mg, Fe, Al, and Ca, and consequently contains less Si than the glass phase of CF. Mg, Fe, Al, and Ca are glass network-modifying elements, which make the glass more reactive when in contact with the alkali activator. Thus, it may be that FF not only has a higher quantity of glass, but the glass itself is also more reactive than the glass in CF.

Nevertheless, all the elements present in the glass composition of the precursors (FF and CF) were also present in the binder gel formed after 3 and 28 days of reaction (Figure 7). However, the average concentrations of Na, Si, Ca, Al, and K were higher, whereas quantities of Fe and Mg were lower in the binder gel of both FF and CF compared to their glass compositions (Figure 7). The average elemental composition of the binder gel of both FF and CF consisted of substantial amounts of Fe and Si along with minor quantities of Ca, Al, Mg, Na, and K, which shows that Fe-containing glass phases in both fractions dissolve in alkaline media, and is structurally integrated into the binder gel. These results match other reported studies on the alkali activation of FS. 14,21,23
The average elemental concentration of Na and K in the binder gel of CF is higher than in FF after 3 days of curing (Figure 7). An excess amount of Na and K (mostly originating from activating solution) in relation to other elements could be present due to a lower extent of dissolution of CF in comparison to FF, which would consequently decrease the proportion of other elements in the binder gel. This would further influence strength development at early stages by inhibiting binder gel development due to excessive alkali content.41

A closer look at the binder gel composition with the help of Si-(Na+K) - (Fe+Al) ternary diagrams shows that the glass phases of FF and CF appear to be close to one another in content (Figure 8A). After 3 days of curing (Figure 8B), there was a clear difference between the binder gel compositions of FF and CF pastes. At this stage, FF binder gel contained less alkali, and more Fe and Al compared to CF binder gel. However, after 28 days of curing (Figure 8C), the binder gels in both samples held similar compositions; one close to the composition of FF paste after 3 days of curing. These further highlight that the binder gel of FF was relatively mature after only 3 days of curing, whereas the reactions of CF paste continued between 3 and 28 days. This claim is supported by the compressive strength results (Figure 5).

FIGURE 6 Backscattered electron images of (A) milled FF in epoxy; (B) alkali-activated FF sample at 3 days of curing; (C) alkali-activated FF sample at 28 days of curing; (D) milled CF in epoxy; (E) alkali-activated CF sample at 3 days of curing; and (F) alkali-activated CF sample at 28 days of curing at room temperature

4 | ENVIRONMENTAL LEACHING BEHAVIOR

The leaching test results of the precursors and alkali-activated samples are presented in Table 3. The results revealed that the elements released from both fractions prior to alkali activation were below the regulatory limits for covered and paved structures specified by Finnish government legislation.42 After alkali activation, pH and
conductivity values were higher compared to those of the precursors. This is attributed to the highly alkaline activator used in the production of the binder. Alkali-activated FF showed a slightly higher release of elements compared to alkali-activated CF, with the exception of Na. The higher release of elements in alkali-activated FF may be due to its higher glass content (Table 2) and greater reaction kinetics (Figures 3 and 4). This is because leaching mostly occurs during the dissolution of the glassy components of the slag and the binder phase, since most of elements released are concentrated in either of them.43 Furthermore, the leaching values of Cr, Mo, Ni, and Se in alkali-activated FF slightly exceeded the limit specified by Finnish legislation for covered structures, whereas in alkali-activated CF, only Mo exceeded the limit. The leaching of other substances (such as Na and K) was determined, but no limit is specified for these substances. The increased leaching of elements, such as Cr, Mo, Ni, and Se, has also been previously observed in AAMs made from coal fly ashes, fluidized bed combustion fly ashes, and ferronickel slag, with leaching test being done according to EN 12457 or similar procedures.44–46 This is due to the alkaline conditions that occur in such leaching tests.47 The leaching of basic elements or unreacted alkali activator from AAMs increases the pH of the water of the leaching test. Elements, such as Cr, Ni, Se, and Mo, are soluble in such high pH conditions. They consequently show increased leaching compared to raw materials.

5 | DISCUSSION

The differences in mineralogical composition of the two fractions are likely related to the different cooling rates on the different slag size droplet. It has been previously reported that the amount of glassy content formed in the slag is related to the slag's chemistry and the cooling conditions.10,12,32 Meanwhile, since both fractions were water-quenched, the differences in mineralogy can, therefore, be ascribed to the impact of cooling on different slag size droplets. One possible explanation for such a phenomenon could be that the surface cooling rate of the small slag droplet (FF) was higher than that of the large particle fractions (CF), resulting in rapid solidification and lower formation of crystalline phase, and hence, lower crystal content. This hypothesis is supported by prior studies on the crystallization behavior of molten BFS droplets, as the model used for crystallization behavior in this mentioned study revealed that smaller slag droplets have higher surface cooling rates and lower crystal content in comparison to larger slag droplets.33 However, the influence of cooling rates on the different size fractions of FS was not fully investigated in the present study.
TABLE 3 Leaching test of precursors and crushed samples determined in accordance with EN 12457-2, and limits specified by Finnish legislation (843/2017)42

<table>
<thead>
<tr>
<th>Hazardous elements</th>
<th>Element concentration (mg/kg)</th>
<th>Alkali-activated FF</th>
<th>Alkali-activated CF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Covered structure</td>
<td>Paved structure</td>
<td>FF(powder)</td>
</tr>
<tr>
<td>pH</td>
<td>N/A</td>
<td>N/A</td>
<td>9.59</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>N/A</td>
<td>N/A</td>
<td>0.05</td>
</tr>
<tr>
<td>As</td>
<td>0.5</td>
<td>1.5</td>
<td>0.005</td>
</tr>
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<td>Ba</td>
<td>20</td>
<td>60</td>
<td>0.036</td>
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<tr>
<td>Cd</td>
<td>0.04</td>
<td>0.06</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Cr</td>
<td>0.5</td>
<td>5</td>
<td>0.009</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>10</td>
<td>0.05</td>
</tr>
<tr>
<td>Hg</td>
<td>0.01</td>
<td>0.03</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Mo</td>
<td>0.5</td>
<td>6</td>
<td>0.007</td>
</tr>
<tr>
<td>Ni</td>
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<td>1.2</td>
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</tr>
<tr>
<td>Pb</td>
<td>0.5</td>
<td>2</td>
<td>0.003</td>
</tr>
<tr>
<td>Sb</td>
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<td>0.7</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Se</td>
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<td>1</td>
<td>0.021</td>
</tr>
<tr>
<td>Zn</td>
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<td>12</td>
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</tr>
<tr>
<td>Cl</td>
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<td>2400</td>
<td>25</td>
</tr>
<tr>
<td>F</td>
<td>10</td>
<td>50</td>
<td>&lt;5</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1200</td>
<td>10000</td>
<td>120</td>
</tr>
<tr>
<td>V</td>
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<td>3</td>
<td>&lt;0.005</td>
</tr>
<tr>
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<td>0.013</td>
<td>6.3</td>
</tr>
<tr>
<td>K</td>
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<td>0.15</td>
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FF had a higher glass content and lower crystalline content than CF, with higher glass content being the predominant factors influencing their reactivity in alkali activation. This is not surprising, as previous works have revealed that it is only the glass phase that undergoes dissolution in alkaline environment, whereas the dissolution of the crystalline phase in alkaline media is often insignificant.48 Therefore, the percentage of glass content in a slag is of interest when it is to be used as a precursor in AAMs. In addition, there was a slight difference in the chemical compositions of the glass phases of FF and CF (shown in Figure 8), which could further affect their reactivity. Glass phase of FF contained more network-modifying elements, which could make the glass more reactive.

From the assessment of the isothermal calorimetry results, it is clear that the differences in mineralogy between the two fractions are what mainly influenced their reactivity rates. This is clearer when considering that both FF and CF have similar particle size distributions (Supplementary Information), bulk chemical compositions, and are activated with similar alkaline solution. Thus, the differences in the initial heat released between both fractions are mainly attributed to the differences in glass content. FF had a higher heat evolution rate and greater cumulative heat release, which had a positive influence on the compressive strength of alkali-activated FF. This can, therefore, be used as a significant indicator of the reactivity of FF (Figure 5). This effect was more pronounced in the early stages of the samples, as FF had a higher early age strength after 3 days of curing. Again, the differences of early age strength were ascribed to the higher glass content of FF, which favors a higher extent of dissolution when activated with an alkaline solution. As a result, more binder gel was formed, resulting in a denser matrix and higher compressive strength, particularly during early stages. From these results, it can be deduced that in FF, the dissolution and precipitation of reaction products occur mainly during the early stages, whereas the dissolution of CF occurs over longer periods of time due to the lower glass content. CF consequently shows slower reaction product formation and strength development. However, the differences between the fractions diminished gradually over time, and the final strength values for both samples after 28 days of curing were quite high, in comparison to previously reported study on alkali-activated synthetic slag of an FeOₓ-SiO₂ system.32 In the mentioned study, two out of
The experimental results revealed that different size fractions of FS from nickel-smelting operations can behave differently when used as a precursor in AAMs. In this study, FS was sieved into two size fractions: namely, “FF,” with a particle size range of 0–0.5 mm, and “CF,” with a particle size range of 1.5–2 mm. The glass content of FF was found to be higher than that of CF (63 vs. 39 wt.%), even though the bulk chemical compositions of the samples were the same.

Higher glass content of the FF resulted in faster reaction kinetics, a higher early age strength, and a denser microstructure. CF can achieve a similar mechanical performance to that of FF, but the hardening reactions and compressive strength develop at a slower pace. The final strength achieved in FF and CF was 37 and 29 MPa, respectively.
respectively. These suit both EN 196-1 and ASTM C62-10 specifications. The final binder phase formed in both fractions was a Na-K-Fe-Si gel with minor quantities of Mg, Al, and Ca. The leaching values of potentially hazardous elements and substances of the precursors and alkali-activated binders prepared were below the limit values for paved structures specified by Finnish regulation. These findings provide a basis for understanding the mineralogy and glass content of different size fractions of FS, and how these values control the reactivity, as well as the mechanical and microstructural properties of these materials. This gives new insight into the valorization of different fractions of FS and provides a sustainable pathway for its use in construction and other allied industries.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest whatsoever.

**AUTHOR CONTRIBUTIONS**

Adeolu Adediran: Conceptualization, methodology, validation, formal analysis, investigation, visualization, writing—original draft, writing—review and editing.

Juho Yliniemi: Conceptualization, methodology, validation, writing—review and editing, funding acquisition, project administration.

Mirja Illikainen: Conceptualization, writing—review and editing, funding acquisition, project administration.

**REFERENCES**


SUPPORTING INFORMATION
Additional supporting information may be found in the online version of the article at the publisher’s website.

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