An overview of the utilisation of Fe-rich residues in alkali-activated binders: Mechanical properties and state of iron

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A B S T R A C T

Iron-rich alkali-activated materials (Fe-AAM) are considered potential alternatives to ordinary Portland cement (OPC) to limit CO$_2$ emissions and convert several metallurgical wastes into useful products. Unlike conventional aluminosilicate alkali-activated systems in which the role of the precursor’s main constituents and the reaction products are well defined to some extent, the limited knowledge of the role and state of iron in AAMs restricts its utilisation in the construction sector. Nevertheless, several studies have shown the ability of iron to participate in the formation of alkali-activation reaction products, which induces high compressive strength (over 100 MPa) and provides both environmental and material performance benefits. In this study, we critically evaluate existing data on Fe-rich raw materials, activators, co-binders, mechanical properties, curing types and the reactivity and role of iron in Fe-AAMs.

1. Introduction to alkali-activated materials

The production of Portland cement accounts for 5–9% of global anthropogenic carbon dioxide emissions (Lloyd et al., 2009). In searching for alternative cementitious materials to decrease the carbon dioxide footprint, alkali-activated materials (AAMs) have received broad attention. The reaction of aluminosilicate materials – such as metakaolin (Rovnak, 2010) and calcined clays or their mixtures (PruD’homme et al., 2011), industrial residues, such as granulated blast furnace slag (GBFS) (Collins and Sanjayan, 1999; Fernández-Jiménez et al., 1999; Nath and Kumar, 2013; Wang et al., 1994) and coal combustion fly ash (FA) (Bakharev, 2005; Criado et al., 2010; Fernández-Jiménez et al., 2005) – with an alkaline solution (or alkaline activator) yields a solid and strong material (alkali-activated binder). Compared to Portland cement, AAMs do not rely on calcium carbonate as a key ingredient, thus resulting in reductions of CO$_2$ emissions ranging from 40% to 80–90% (Davidovits, 1993).

Along with reducing CO$_2$ emissions, minimising resource consumption is another major concern of the EU. The United Nations estimates that construction accounts for about 50% of raw material consumption (Sommer and Drees, 2016). Therefore, using industrial waste materials and residues in construction materials is a promising approach to reducing the environmental impact and energy consumption caused by the extraction of primary materials (United Nations Environment Programme, 2020).

AAMs with a high iron content are imperative due to the widespread distribution of Fe-containing residues and their constant accumulation, thereby prompting metallurgical companies to seek alternative end uses for their residues. These residues are mainly ferrous metallurgical slags (FMS) and non-ferrous metallurgical slags (NFMS), but they can also include some type of bauxite residues (BR) and mine tailings (MTs), in which a significant proportion of iron is observed in their chemical composition.

A conservative estimation is that approximately 50 million tonnes of NFMS (Wang, 2016a), 150 million tonnes of BR (Hertel and Pontikes, 2020) and about 200 million tonnes of steel-furnace slag (Wang, 2016b) are produced each year in the world. Only in Finland, NFMS is produced 600 000 tons per year (Kebe et al., 2011). In comparison, Portland cement consumption in Finland is 2 000 000 tons per year, and thus, NFMS-based AAMs could replace more than 25% of this demand (Kebe et al., 2011). An estimated 5–7 billion tons of MTs is generated each year worldwide (Xu et al., 2019), but the amount of Fe-rich tailings is difficult to estimate due to variable composition of the residues. According to statistics, the annual emission of iron ore tailings (IOTs) in China is about 130 million tons (Li et al., 2010).

Adding to the possible ability to utilise several metallurgical wastes and decrease CO$_2$ emissions, Fe-rich AAMs also have some benefits in locations with low production of conventional Portland cement.
This review’s aim is to critically evaluate the state-of-the-art in developing Fe-rich AAMs and to define the areas that need investigation based on the gaps in the current knowledge. Many review articles can be found discussing various aspects and applications of conventional Fe-poor aluminosilicate AAMs (Arbi et al., 2016; Hertel and Pontikes, 2020; Luukkonen et al., 2018, 2019; Pacheco-Torgal et al., 2008a, 2008b; Rakhimova and Rakhimov, 2019; Shi et al., 2011), but no similar reviews about Fe-rich AAMs currently exist. Therefore, we discuss the employed Fe-rich precursors, co-binders, activators, curing conditions, effects of various parameters on the mechanical properties (Fig. 1) and current knowledge of the chemical role and state of iron in Fe-rich AAMs. This study focuses mainly on Fe-rich materials, such as NFMS, FMS and RM, but several other materials, such as GBFS and FA, are mentioned as co-binders. Furthermore, as high crystalline and low reactive materials, Fe-rich MTs are partly discussed here, as mechanical or high-temperature treatment can make them suitable for utilisation in AAMs (Kiventerä et al., 2020).

2. Methods

Scopus and Web of Science databases were used to support the literature search because they are well known and the largest bibliometric information sources of peer-reviewed studies. Several keywords were used to search for the appropriate literature. During the screening process, the terms ‘alkali-activated material’ or ‘alkaline activation’ were used with one of the following words: ‘slag’, ‘red mud’, ‘Fe-silicate glass’ and ‘iron ore tailings’. Together with these words, the following specific classifications of Fe-rich residues were used: non-ferrous metallurgical slag, ferrous metallurgical slag, red mud or bauxite residue and mine tailings, and their abbreviations: NFMS, FMS, RM or BR, MTs, correspondingly. The search also used terms synonymous with and related to AAMs, such as geopolymers and inorganic polymers (IP). In addition, we used a chemistry search of the material to find all possible studies on the alkali activation of Fe-rich materials, even in studies that did not discuss the role of iron and the chemistry of the precursors.

3. Types of precursors: the application of co-binders and pre-treatment techniques

Studies on iron role in the reaction of AAMs have induced some contradictions, which are probably related to the nature of the starting precursors. These precursors can be divided into the following: natural materials (i.e. rocks), slags (including Fe-silicate glasses, FMS and NFMS), FA, BR or red mud (RM) and MTs (Fig. 2). This section discusses the influence of the type, chemistry and mineralogy of the precursors, pre-treatment techniques and addition of co-binders on the mechanical properties of AAMs.

3.1. Natural materials

The alkali activation of natural Fe-rich materials has been studied using volcanic ashes (Lemougna et al., 2013), laterites (Obonyo et al., 2014) and bauxites (Hairi et al., 2015) as precursors. These materials differ in chemistry and mineralogy due to their different origins (Table 1), thus providing different compressive strength values (Table 2).

For example, Lemougna et al. (2013) investigated the formation of AAMs from volcanic ash in Cameroon. The authors obtained mortars with excellent compressive strength from the ash, in which iron was present in the crystalline minerals, i.e. ferroan forsterite (\((\text{Mg}, \text{Fe}^{2+})_2\text{SiO}_4)\) and augite (\((\text{Ca},\text{Mg},\text{Fe}^{2+})_2\text{Si}_2\text{O}_6)\). However, no estimation of the amorphous fraction, which was probably provided with high reactivity, was conducted in this work. Moreover, the authors obtained significantly different compressive strength values for two ashes with similar compositions (12 wt% and 14 wt% of Fe\(_2\text{O}_3\)). This was explained by the greater reactivity of one ash, which resulted from the higher content of small particles. However, this effect may also be explained by
the different amorphous contents in the samples.

Obonyo et al. (2014) studied two Fe-rich laterites (9.68 wt% and 35.2 wt% of Fe$_2$O$_3$) for their suitability as solid precursors for alkali-activated materials. The resulting AAMs revealed good stability in water and low porosity. No compressive strength measurements were conducted, but flexural strength was about 15 MPa, comparable with standard concretes. However, 15–35 wt% of the amorphous fraction obtained by laterite calcination at 700 °C for 4 h was used to increase the reactivity by providing nucleation sites.

Hairi et al. (2015) used bauxite (the primary ore of alumina) to obtain alkali-activated mortars. The alkali activation with sodium silicate solution yields good compressive strength (up to 28 MPa). However, the binder’s composition was modified to an optimal SiO$_2$/Al$_2$O$_3$ ratio of about 3 with silica fume to improve its reactivity.

Many other potential natural iron silicate precursors exist, such as ultramafic igneous rocks, i.e. peridotites and dunites or calcined iron phyllosilicates (Machiels et al., 2014). However, the high hardness and low amorphous content can make these materials challenging to use in AAM.

### 3.2. Slags and glasses

Millions of tons of slag from ferrous and non-ferrous metallurgy are produced worldwide. The slags from ferrous metallurgy are divided into iron slag, such as GBFS, steel-furnace slag (basic oxygen furnace slag (BOFS), electric arc furnace slag (EAFS) and ladle slag (LS) (Yıldırım and Prezzi, 2011), whereas the non-ferrous metallurgy slags are divided into lead, nickel, zinc, cadmium, tin and copper slag (also called fayalite slag due to its mineralogical composition), etc. (Piatak et al., 2015).

#### 3.2.1. Ferrous metallurgical slag (FMS)

Among FMS, the alkali activation of GBFS has been well studied. This material has a very low iron content but is rather rich in calcium, alumina and silica. Granulated corex slag has similar chemical and mineralogical compositions (Nath and Kumar, 2013). Studies on the alkali activation of Fe-rich slags from ferrous metallurgy are usually limited to EAFS (Cristelo et al., 2019; Nikolić et al., 2020; Ozturk et al., 2019), which usually exhibit high contents of iron, silica, alumina and calcium (Table 3, Fig. 3). The mineralogical composition of EAFS is partly amorphous, with crystalline phases of wüstite (FeO), magnetite (Fe$_3$O$_4$), ilmenite (FeTiO$_3$) and goethite (FeOOH).

In Ozturk et al.’s (2019) study, EAFSs (33.42 wt% of Fe$_2$O$_3$) were activated with sodium hydroxide and sodium silicate solutions, and mortar specimens were produced. Using optimal conditions, the authors obtained a maximum compressive strength value of about 41 MPa, which is the highest value obtained for this type of slag in the literature without co-binders.

Nikolić et al. (2020) studied the synthesis and characterisation of alkali-activated materials based on EAFS by adding 1%–7% zinc-rich electric arc furnace dust (EAFD). This replacement induced the development of porosity, which resulted in a decrease in compressive strength from 21.04 MPa for pure slag to 8.4 MPa for slag doped with 7% of...
conditions.
The relationship between the types of initial material, iron content and maximum compressive strength obtained in the literature using optimal treatments.

| Initial materials (treatments) | Total FeO, wt.% | Compressive strength under optimal conditions, MPa | Reference |
|-------------------------------|-----------------|-----------------------------------------------|-----------|
| Natural materials             |                 |                                               |           |
| Volcanic ash                  | 12.5            | 60                                            |           |
| bauxite 61.7% + SF 38.3%      | 18.37           | 28.5                                          |           |
| Ferrous metallurgical slags (FMS) |           |                                               |           |
| EAFS 93% + FA 50%             | 20.5            | 27                                            |           |
| EAFS                          | 14.02           | 22                                            |           |
| EAFS                          | 26.1            | 21                                            |           |
| EAFS                          | 32              | 15                                            |           |
| EAFS 93% + EAFD 7%            | 31.03           | 8.4                                           |           |
| Non-ferrous metallurgical slags (NFMS) and Fe-silicate glasses |               |                                               |           |
| Fe–Ni slag                    | 38.6            | 120                                           |           |
| Fe–Ni slag                    | 41.89           | 120                                           |           |
| Cu–Ni slag (CO2 activated)    | 37.01           | 119                                           |           |
| Fe-silicate glass             | 19.9            | 112                                           |           |
| Cu–Ni slag (O2 activated)     | 37.01           | 89.5                                          |           |
| 30% Fe-rich slag + 70% OPC a  | 9.75            | 70                                            |           |
| Fe-silicate glass             | 28.2            | 63                                            |           |
| Fe-silicate glass             | 32.1            | 57                                            |           |
| Fe-silicate glass             | 32.1            | 53                                            |           |
| Fe-silicate glass             | 50              | 53                                            |           |
| Fe–Ni slag                    | 43.83           | 50                                            |           |
| Fayalite slag (FS) 70% + 30% FA | 24.4           | 47                                            |           |
| FS                            | 55.5            | 40                                            |           |
| FS 90% + FA 10%               | 29.2            | 35                                            |           |
| FS                            | 63.8            | 31                                            |           |
| 70% Fe-rich slag + 30% OPC a  | 22.75           | 20                                            |           |
| Red mud (RM)                  |                 |                                               |           |
| RM (calculated) 83.3% + SF 16.66% | 38.92         | 58.13                                         |           |
| RM 50% and GIBFS 50%          | 17.31           | 54                                            |           |
| RM (calculated) 50% + GIBFS 50% | 5.02          | 49.2                                          |           |
| RM (calculated) 88.56% + carbon 1.44% + silica 10% | 48            | 43.5                                          |           |
| RM (mechanical activation) 30% + FA 70% | 20.3        | 40                                            |           |
| RM 75% + SF 25%               | 7.4             | 31.5                                          |           |
| RM 10% + FA 90%               | 6.98            | 28                                            |           |
| RM 25% + cullet soda-glass 75% | 13.5           | 25                                            |           |
| RM 33% + RHA 66%              | 10.2            | 20.5                                          |           |

| Initial materials (treatments) | Total FeO, wt.% | Compressive strength under optimal conditions, MPa | Reference |
|-------------------------------|-----------------|-----------------------------------------------|-----------|
| RM 80% + metakaolin (MK) 20%  | 33.5            | 20                                            |           |
| RM 70% + FA 30%               | 23.2            | 12.75                                          |           |
| RM (calcinated) 85% + NaOH (calcinated) 15% | 9.5          | 10                                            |           |
| Mine tailings (MTs)           |                 |                                               |           |
| Antigorite residue (mechanically activated) | 20.5 | 49                                            |           |
| Phylite residue (mechanically activated) | 11.4 | 25                                            |           |

| Reference |
|-----------|
| Dimas et al. (2009) |
| Li et al. (2019)  |
| Ke et al. (2015)  |
| Kalinkina et al. (2018) |
| Adesanya et al. (2020b) |

a) Not alkali-activated material.

EAFD. However, alkali-activated slag doped with 7% EAFD showed a compressive strength of 13.82 MPa, which could be suitable for construction applications.

Cristelo et al. (2019) used EAFS both as a precursor (milled fraction) and as an aggregate (as a received fraction without milling). To evaluate the potential of EAFS as a precursor, the authors mixed slag with FA using different mass ratios. The uniaxial compressive strength was higher for the combined FA and steel slag, reaching a maximum of 27 MPa with the 50/50 blend, then for either of these two components alone (15 MPa for the slag and 19 MPa for the FA). Also, the replacement of standard sand with the raw EAFS for FA-based mortars provided an increase in compressive strength from 16 to 26 MPa. This better performance was explained by the reaction between the slag particles and the FA-based binder, resulting in the absence of a well-defined binder–particle interface.

The alkali activation of other types of FMS, such as ladle slag (LS) and basic oxygen furnace slag (BOFS), is poorly studied in the literature taking into account the content and state of iron in these materials. However, several studies have shown the potential of LS (Adesanya et al., 2017; Bignozzi et al., 2013) and BOFS (Lopez Gonzalez et al., 2019; Mashifana et al., 2021) for binder formation.

3.2.2. Non-ferrous metallurgical slag (NFMS)

In studies in which iron phases were present in NFMS, promising results were obtained for Fe–Mg slags (Zosin et al., 1998), Fe–Ni slags (Komnitsas et al., 2009; Sakkas et al., 2014), Pb slags (Guo et al., 2017; Onisei et al., 2012) and secondary copper slags (Jacobescu et al., 2017; Onisei et al., 2015, 2018). Alkali-activated NFMS usually exhibits high compressive strength (Fig. 4) and is clearly the most interesting solution for slag utilisation in Fe-AAMs.

Table 3 summarises the chemical and mineralogical peculiarities of NFMS used in the literature to obtain alkali-activated binders. Most slags are highly amorphous. The typical crystalline phases are mainly represented by iron oxides and silicates (wustite, magnetite and fayalite \([Fe_2SiO_4])\) and other silicates (quartz \([SiO_2]\) meltie group minerals, merwinite \([Ca_3Mg(SiO_3)]_2\)\), forsterite \([Mg_2SiO_3]\) \(\) (Table 3). Iron minerals contain \(Fe^2+\), except magnetite, which contains both \(Fe^{2+}\) and \(Fe^{3+}\). The chemical composition is different, usually revealing high silicon and iron contents and variable magnesium, calcium and aluminium contents. The highest iron content is usually observed in fayalite slag (FS) (about 60 wt% of \(FeO\)), followed by Fe–Ni slag, with \(Fe_2O_3\) content of 39–44 wt%. Other types of NFMS, including Cu, Cu–Ni and Pb slags, also contain a high portion of \(Fe_2O_3\).

Notably, the comparison of compressive strength values of alkali-activated slags indicates that the highest values are typical for Fe-rich NFMS: 120 MPa for Fe–Ni slag (Maragkos et al., 2009), 120 MPa for Fe–Ni slag (Sakkas et al., 2014) and 119 MPa for Cu–Ni slag (Kalinkina et al., 2012). Interestingly, there was no correlation between the
concentration of iron in the precursor and the compressive strength of the final product (Table 2). This statement was also confirmed by Yamaguchi et al. (2013), who used various urban waste-incinerated Fe-rich and Fe-poor slags to synthesise AAMs. However, the resulting flexural strength was independent of the content of iron. The authors suggested that the main factor influencing strength was the content of metallic alumina in the initial slag samples, leading to hydrogen generation during alkali activation. This process induced a high degree of foaming and swelling, resulting in a lower density of mortars and, consequently, lower flexural strength values.

The compressive strength of the AAMs obtained from Fe–Ni or Cu–Ni slag prominently exceeded that from FS. Using different curing conditions, Iacobescu et al. (2017) obtained alkali-activated mortars made from FS with a maximum compressive strength value of 31 MPa. The lower value of the compressive strength of FS compared with those of Fe–Ni and Cu–Ni slag is attributed to the lower content of the amorphous phase. Moreover, a significant portion of silica and iron is in the form of crystalline minerals in the forsterite-fayalite solid solution.

Co-binders can increase the mechanical performance of Fe-rich NFMS, and they usually occur as high-Ca-Al-Si precursors. The mixtures of slags with FA are probably the most interesting solutions for combining precursors from different industrial wastes (Nath and Kumar, 2013; Onisei et al., 2012; Zhang et al., 2017). Onisei et al. (2012) reported the synthesis and properties of AAMs made from 100% FA by combusting lignite, 100% primary lead slag and the combination of these two residues. The compressive strength of the mixtures increased up to 47 MPa when lead slag addition was increased to 70 wt%. However, the higher content of lead slag induced a decrease in compressive strength from 47 MPa to approximately 35 MPa.

The use of FA and local high-magnesium nickel slag (HMNS) as solid materials to manufacture alkali-activated cement under room-temperature conditions has been reported (Yang et al., 2014; Zhang et al., 2017). The results showed that using the optimal quantities of an alkali activator (Ms = 1.4) and HMNS (20 wt%) increased the compressive strength of AAMs to 60 MPa, which parallels that of hardened Portland cement.

Komnitsas et al. (2009) studied the alkali activation of electric arc ferronickel slag (FNS) synergistically with kaolin and metakaolin using sodium silicate and sodium/potassium hydroxide solutions. The presence of kaolin in the paste decreased the compressive strength from 45 to 15 MPa as the addition of metakaolin was raised to 12 wt%. When metakaolin (12 wt%) was used instead of kaolin, the final compressive strength decreased to 3 MPa. The authors attributed the lower
Table 3  
Chemistry and mineralogy of Fe-rich slags and glasses used for alkali activation.

| Group                                      | Type                     | Amorphous content | Crystalline phases                                                                 | Essential chemistry | References                     |
|--------------------------------------------|--------------------------|-------------------|------------------------------------------------------------------------------------|---------------------|---------------------------------|
| **FERROUS METALLURGICAL SLAGS (FMS)**     | EAFS                     | n/a               | melilite, magnetite, and wüstite, akermanite, merwinite                           | 8.91                | Cristelo et al. (2019)          |
| Granulated corex slag (GCS) EAFS           | 94%                      | melilite, magnetite, wüstite, akermanite, merwinite                            | 18.36                | Nath and Kumar (2013)           |
| EAFS                                       | no amorphous phase       | larinite, gehlenite, akermanite, magnetite                                     | 11.57                | Oztürk et al. (2019)            |
| Electric arc furnace dust (EAFD) ladle slag (LS) | 58.8                  | larinite, wüstite, gehlenite, montecellite, spinel phase, calcite                | 7.2                 | Nikolić et al. (2020)           |
| Basic oxygen furnace slag (BOFS)           | 55.6                     | franklinite, magnetite, zincite, magnetite                                    | 0.5                 | Nikolić et al. (2020)           |
| **FE-SILICATE GLASSES**                    | Fe-silicate glass        | >97%               |                                                                                   |                     |                                 |
|                                           | Fe-silicate glass        | 67.9–94.4%        |                                                                                   |                     |                                 |
|                                           | Fe-silicate glass        | 93.5              |                                                                                   |                     |                                 |
|                                           | Fe-silicate glass        | 98%               |                                                                                   |                     |                                 |
|                                           | Fe-silicate glass        | >98%              |                                                                                   |                     |                                 |
| **NON-FERROUS METALLURGICAL SLAGS (NFMS)** | Fe-Ni slag               | >50%               |                                                                                   |                     |                                 |
|                                           | Fe-Ni slag high          | 10.11             |                                                                                   |                     |                                 |
|                                           | Fe-Ni slag high          | 13.79             |                                                                                   |                     |                                 |
|                                           | Fe-Ni slag high          | 5.98              |                                                                                   |                     |                                 |
|                                           | Fe-Ni slag high forsterite | 2.67           |                                                                                   |                     |                                 |
|                                           | Fe-Ni slag high forsterite | 6.2                |                                                                                   |                     |                                 |
| **Secondary copper slags – fayalite slag (FS)** | FS                     | 64%               | 26% fayalite, 9% wüstite, 1% spinel, fayalite, ferrite-spinels                   | 2.55                | Onisi et al. (2015)             |
|                                           | FS 80%                   | 5.5               |                                                                                   |                     | Onisi et al. (2018)             |
|                                           | FS 73%                   | 3.4               |                                                                                   |                     | Jacobescu et al. (2017)         |
|                                           | FS 55.5%                 | 2.4               |                                                                                   |                     | Adediran et al. (2021)          |
| **Other non-ferrous metallurgical slags**  | Cu-Ni slag high          | olivine            |                                                                                   | 7.44                | Kalinkin et al. (2012)          |

(continued on next page)
compressive strength to the increased porosity of the new structure after the thermal treatment of metakaolin. Attanasio et al. (2018) suggested that the mechanical performance of metakaolin usually surpasses that of the increased porosity of the new structure after the thermal treatment of metakaolin. Attanasio et al. (2018) suggested mainly determine the final compressive strength, which can reach over 2018 or 60 MPa (Rovnaník, 2010) are excellent for metakaolin-based NFMS. The values of 50 MPa (Attanasio et al., 2018) or 60 MPa (Rovnaník, 2010) are excellent for metakaolin-based AAMs. Therefore, the final compressive strength mainly depends on the specific starting material.

Before alkali activation, different pre-treatment techniques are rarely used for slags because they are already highly reactive materials. Kalinkin et al. (2012) studied the mechanical activation of Cu–Ni slag in a ball mill for 10 min in air and CO₂ atmospheres. The pre-treatment of slag samples in the CO₂ atmosphere induced a higher uniaxial compressive strength, reaching 119 MPa after 150 days of curing. The mechanical activation in air and subsequent alkali activation and 150 days curing induced a compressive strength of 89.5 MPa. The authors explained this difference through the higher reactivity of the slag particles induced by the chemisorption of carbon dioxide molecules.

Despite the high iron content, many non-ferrous slags exhibit high and ultra-high compressive strength values. However, the variability of crystallinity and particle size distribution makes comparing the obtained compressive strength values difficult. So far, iron content and compressive strength are uncorrelated, indicating the variable reactivity of various iron silicate components. The higher reactivity was probably associated with a high amorphous contribution, as the more crystalline Fe-rich slag exhibited variable but high Fe₂O₃ contents, ranging from 20 wt% to 60 wt% at atmospheres. The pre-treatment of slag samples in the CO₂ atmosphere induced a higher uniaxial compressive strength, reaching 119 MPa after 150 days of curing. The mechanical activation in air and subsequent alkali activation and 150 days curing induced a compressive strength of 89.5 MPa. The authors explained this difference through the higher reactivity of the slag particles induced by the chemisorption of carbon dioxide molecules.

Another important question about the reactivity of the slag components, which is usually overlooked in the literature, is the particle size distribution. Usually, slag in its original form, MTs and BR, are represented by coarse-grained particles that must be ground before alkali activation. Consequently, correlating the reactivity of precursors with the particle size distribution and milling regime used with the data presented in the literature is difficult.

### 3.2.3. Fe-silicate glasses

Previous studies have examined laboratory-prepared slags (i.e. Fe-silicate glasses) (Kriskova et al., 2015; Peyes et al., 2019a, 2019b; Sande et al., 2017). These works simulate the composition of Fe-rich NFMS to better understand the reactivity and role of iron in alkali-activated systems. Fe-silicate glasses analysed in the literature exhibit variable but high Fe₂O₃ contents, ranging from 20 wt% to 60 wt%, and high contents of silica and calcium. Due to their high amorphous content (over 90 wt%), the compressive strength of Fe-silicate glasses is high at 50–100 MPa (Table 2).

### 3.3. Red mud (RM)

RM, also called bauxite residue (BR), is a by-product of the Bayer cycle of alumina production from bauxite. Many studies have incorporated BR in solid blends with highly reactive precursor materials, such as metakaolin (Dimas et al., 2009), rice husk ash (RHA) (He et al., 2013), GBFS (Ye et al., 2016), cullet soda-glass (Badanoiu et al., 2015), silica fume (Hairi et al., 2015; Ye et al., 2016), FA (Kumar and Kumar, 2013; Li et al., 2019; Novais et al., 2018), sodium hydroxide (Ke et al., 2015), and carbon and silica (Hertel et al., 2016).

From Table 4, RM contains a high amount of Al₂O₃ (10–25 wt%) and Fe₂O₃ (10–50 wt%) and variable silica, calcium and magnesium contents. RMs are highly crystalline materials that are usually unfavourable for alkali activation without additives or pre-treatment. The mineralogical composition usually includes iron and aluminium oxides and hydroxides, such as haematite (Fe₂O₃), gibbsite (Al(OH)₃), diaspore (AlO(OH)), katoite (Ca₉Al₂(OH)₁₃), goethite (FeOOH) and silicates, such as cancrinite ((Na₉Ca)₉(Al₆Si₆O₂₄)(CO₃)₂S₆O₄)₂H₂O, muscovite (KAl₂(AlSi₃O₁₀)(OH)₂) and quartz (SiO₂).

Analysis of the compressive strength of RM-based AAMs presented in Table 2 shows that additives, such as GBFS (54 MPa for 50% of GBFS) (Lemounga et al., 2017), are needed adding to activation (thermal treatment) (58 MPa for calcined RM with 16.66% silica fume (Hairi et al., 2015) and 49 MPa for calcined RM with 50% GBFS (Ye et al., 2014)). The lack of data on the alkali activation of RM without co-binders suggests that RM is a low-reactive material.

Considering cost efficiency, the most feasible technology for RM utilisation is the application of co-binders without thermal treatment (Dimas et al., 2009; Haire et al., 2015; He et al., 2013; Kumar and Kumar, 2013; Lemounga et al., 2017). The potential use of RM for synthesising AMMs was studied with metakaolin as a co-binder (Dimas et al., 2009). The RM-based AAMs produced in this work had relatively low mechanical properties. Compressive strength was increased from 5 to 20 MPa with an increase in metakaolin content to 20 wt%.

Similar compressive strength values were obtained for the combined RM and RHA at varying mixing ratios of raw materials (He et al., 2013). The alkaline activator was sodium hydroxide, while RHA was used as an amorphous silica supplier. Adding RHA (modifying the nominal Si/Al ratios from 1.68 to 3.35) induced an increase in compressive strength from 3.2 to 20.5 MPa. However, the higher content of RHA negatively affected the mechanical performance of RM-based AAMs.

An alkali-activated system comprising RM and silica fume showed even better mechanical performance (44–58 MPa) (Hairi et al., 2015). X-ray diffraction (XRD) and Mössbauer spectroscopy revealed that high concentrations of haematite in RM did not contribute to the binder formation. Besides, a high compressive strength was obtained for the AAMs from the mixture of RM and GBFS (Lemounga et al., 2017). However, better reactivity and mechanical properties were obtained for
samples with higher contents of slag. The composition of 50% RM and 50% slag achieved a seven-day compressive strength of 54 MPa at 25 °C. Kumar and Kumar (2013) examined the effect of 0–40% RM addition on the reaction, structure and properties of FA-based AAMs. RM addition using the studied range of concentrations improved the intensity of the reaction due to the extra alkalinity provided by RM. The 3-day compressive strength was increased from 26 to 29 MPa with RM up to 20 wt%. The further increase in RM content to 40 wt% induced a decrease in strength to 16 MPa. Another study that combined RM (after partial melting and a subsequent decrease in open porosity. However, a decrease in strength to about 9 MPa due to the opposite effect: an increase in closed porosity) resulted in a higher dissolution rate of silicon and aluminium due to the high alkalinity and partial reactivity of RM. The transformation of the primary silicate and aluminosilicate phases into calcium-rich phases and high alkaline aluminosilicate. The hydration of this product led to the formation of zeolites and an N–A–S–(H) (sodium aluminosilicate hydrate) gel. However, the resulting compressive strength was low, reaching 10 MPa.

One-part AAMs were also synthesised from alkali and thermally activated RM by adding silica fume (SF) to optimise its composition (Ye et al., 2016). The thermal activation was conducted by calcination of RM mixed with NaOH pellets (10 and 15 wt%) at 800 °C. After that, the treated RM was mixed with different quantities of SF. Adding 20–30 wt % SF resulted in a significant improvement in the long-term strength because of the improved polymerisation due to an increase in SiO2/Al2O3 molar ratio from 1.41 to 3.45. The resulting compressive strength reached 31.5 MPa for the sample with 25 wt% SF.

Choo et al. (2016) studied one-part AMMs obtained from a mixture of FA and RM without thermal pre-treatment. FA was used as an aluminosilicate precursor, and RM was the NaOH supplier. Adding RM to FA resulted in a higher dissolution rate of silicon and aluminium due to the increased alkaline environment, but the compressive strength in this study was low (up to 3 MPa).

Even with low reactivity, RM demonstrated the ability to form alkali-activated binders combined with additional reactive binders or after thermal treatment. However, it seems that the heat treatment is less economical than the use of co-binders. The amount of works on the alkali activation of RM indicates considerable practical interest in using this material in the construction sector due to the huge reserves of these residues and the associated environmental concerns. In addition, the high alkalinity and partial reactivity of RM’s components may increase interest in the use of this type of residues.

### 3.4. Fe-rich mine tailings (MTs)

MTs with low reactivity can be utilised as an inert filler in AAMs with a proper binder material (Kiventera et al., 2020), but the range of binders used (e.g. metakaolin, FA, GBFS, etc.) excludes Fe-rich precursors. Several pre-treatment methods have been investigated to enhance the reactivity of different MTs. Mechanical activation, heat treatment or calculation and alkaline fusion have been the most extensively studied for different MTs, but the role and state of iron in these materials remain unexplored (Kiventera et al., 2020).

An overview of the mineralogy and the chemistry of tailings that have been mechanically or thermally treated before alkali activation
shows that they usually have a low iron content. Table 5 summarises the tailings that contain at least 10% of Fe₂O₃. The effect of iron on alkali activation and changes in its mineralogy during mechanochemical activation remain partially discussed. Only the Adesanya et al.’s (2020) study showed that milling minimally affects iron dissolution in phyllite residues. Also, iron was present in the chamotile, which was completely turned into an amorphous material after mechanochemical activation.

Besides some publications dealing with fillers, the studies applying Fe-rich tailings, such as iron ore tailings (IOTs), in alkali-activated systems remains unexplored. The trivial reason is that such tailings usually comprise highly crystalline materials represented by stable minerals, such as haematite, quartz and goethite (Xu et al., 2019). Bezerra et al. (2019) attempted to incorporate IOTs as an aggregate into an alkali-activated binder based on high-calcium ash (HCA), but the resulting compressive strength values did not exceed 5 MPa. This seems to be due to the characteristics of the HCA-based binder, not to the material of the tailings themselves.

Moreover, mechanochemically activated IOTs have been used to prepare concrete as a supplementary cementing material to substitute material of the tailings themselves (Cheng et al., 2016; Yao et al., 2020). Currently, the more common applications of IOTs include metal extraction (Ponomar, 2018; Ponomar et al., 2019; Xu et al., 2019) and clay alternatives for preparing construction bricks (Li et al., 2019; Mendes et al., 2019). Although IOTs are extremely widespread in mining regions, the number of studies on their utilisation in the construction sector is rather scarce.

3.5. Hybrid systems

A high molarity alkaline solution is expensive and has a relatively high environmental footprint. A possible way to reduce the amount of alkalis necessary to activate the precursor is by combining iron-rich residues with ordinary Portland cement (OPC) and minor alkalis. Cementitious binders, which use only water as an activator, are not discussed here, but readers can refer to the work of Hallet et al. (2020), who studied the replacement of OPC with NFMS of different fineness. The hydration behaviour of RM–coal gangue-based cementitious materials was examined by Zhang et al. (2016a, 2016b). The hydration of blended cement containing granulated high-magnesium FNS was also analysed (Katsiotis et al., 2015; Lemonis et al., 2015; Rahman et al., 2017).

4. Alkali activation parameters

Adding to the nature, chemistry and mineralogy of Fe-rich precursors, alkali activation and curing parameters also affect the properties of AAMs. The nature of the activator (i.e., potassium hydroxide, sodium hydroxide, sodium silicate, etc.), concentration and composition of activator and water-to-solid ratio are among the most important alkali activation parameters affecting the mechanical strength of AAMs. Temperature, time and humidity of curing have also been proven to affect the mechanical properties of AAMs.

4.1. Dissolution tests of the precursors

Dissolution of the components of precursors is a mandatory stage for obtaining a solid structure through alkali activation of the raw material. Results of the reactivity test of FS have been presented (Iacobescu et al., 2017; Onisei et al., 2015). Onisei et al. (2015) found that significant quantities of alumina and silica were dissolved by shaking 1 g of FS with 40 mL of 10 M NaOH within 24 h at room temperature. However, the values of dissolved iron in the leachate were low. Iacobescu et al. (2017) studied the reactivity of FS in 10 mol/L NaOH found that iron

**Table 5**

Chemistry and mineralogy of Fe-rich tailings used for alkali activation.

| Type (treatment) | Amorphous content | Crystalline phases | Essential chemistry | References |
|-----------------|-------------------|-------------------|---------------------|-----------|
| **Sulphidic tailings (as a filler)** | n/a | pyrite, quartz, calcite and ankerite | Al₂O₃: 4.33, CaO: 2.55, Fe₂O₃: 46.32, MgO: 2.37, SiO₂: 12.78 | Cihangir et al. (2018) |
| **Sulphidic tailings (as a filler)** | n/a | n/a | Al₂O₃: 4.7, CaO: 8.3, Fe₂O₃: 20.8, MgO: 5.2, SiO₂: 17.3 | Sarkkinen et al. (2019) |
| **IOTs (as a filler)** | n/a | quartz, haematite, goethite, gibbsite, kaolinite | Al₂O₃: 4.25, CaO: 0.01, Fe₂O₃: 65.78, MgO: 0.14, SiO₂: 22.30 | Bezerra et al. (2019) |
| **Antigorite residue (mechanical activation)** | n/a | Al₂O₃: 3.29, CaO: 2.16, Fe₂O₃: 20.5, MgO: 25.2, SiO₂: 35.64 | Al₂O₃: 3.29, CaO: 2.16, Fe₂O₃: 20.5, MgO: 25.2, SiO₂: 35.64 | Kalinkina et al. (2018) |
| **Phyllite residue (mechanical activation)** | 27 | muscovite, chamotite, albite, quartz | Al₂O₃: 17.4, CaO: 0.90, Fe₂O₃: 11.4, MgO: 4.2, SiO₂: 57.5 | Adesanya et al. (2020b) |
| **IOTs (mechanical activation)** | n/a | quartz, haematite, albite, endenite | Al₂O₃: 2.64, CaO: 1.47, Fe₂O₃: 11.31, MgO: 2.10, SiO₂: 75.23 | Cheng et al. (2016) |
| **IOTs (mechanical activation)** | n/a | quartz, amphibole, stilpnomelane, muscovite | Al₂O₃: 5.8, CaO: 4.27, Fe₂O₃: 22.06, MgO: 3.4, SiO₂: 62.04 | Yao et al. (2020) |
| **Tungsten tailings (thermal activation)** | low | muscovite and quartz | Al₂O₃: 16.66, CaO: n/a, Fe₂O₃: 12.33, MgO: 1.27, SiO₂: 53.48 | Fernando et al., 2010; Pacheco-Torgal et al., 2007, 2008c; Yu et al. (2017) |
| **Copper tailings (thermal activation)** | low | quartz, albite, chlorite, dolomite | Al₂O₃: 13.3, CaO: 5.4, Fe₂O₃: 10.7, MgO: 1.9, SiO₂: 58.5 | Sreenivasan et al. (2017) |
| **Apatite tailings (thermal activation)** | n/a | phlogopite | Al₂O₃: 9.8, CaO: 1.5, Fe₂O₃: 9.1, MgO: 23.8, SiO₂: 40.9 | Sreenivasan et al. (2017) |

* As a replacement for cementing material.
dissolution was very low and linear with time (Fig. 5). In both works on FS dissolution, the low content of iron in leachate was explained by the possible precipitation of iron oxides and hydroxides under alkaline conditions. However, both works confirmed that iron was found in substantial quantities in the binder phase; thus, the Fe-containing phases in the slag were dissolved. But this seems to contradict the fact that iron was precipitated as hydroxide. Moreover, the iron hydroxides were only suggested and not detected in these works.

Similar conclusions were made by Daux et al. (1997) after studying the dissolution of Fe\(^{3+}\)-rich basaltic glasses under slightly alkaline conditions. The authors indicated that the precipitation of dissolved iron was much faster than that of silicon and alumina. Based on the above, van Deventer et al. (2007) concluded that any reactive iron tends to precipitate very rapidly as hydroxide or oxy-hydroxide phases during alkali activation of FA or slag.

A more detailed study was conducted on the precipitate obtained by the alkaline solubility test of phlogopite-rich apatite tailings using XRD and scanning transmission electron microscopy (STEM) (Sreenivasan et al., 2017). The results showed that magnesium and iron were released, but they were mainly precipitated as secondary minerals rather than remaining in the solution. Using XRD analysis, the authors found a new Mg-rich precipitated phase of meixnerite (Mg\(_6\)Al\(_2\)(OH)\(_{18}\)4H\(_2\)O). However, no crystalline iron phases were detected using XRD in the precipitate. According to STEM measurements, the precipitated phases were rich in iron and magnesium, but no quantification was performed on the initial, dissolved and precipitated iron.

Given the fact that iron in slags is mostly in a divalent state (Piatak et al., 2015; Simon et al., 2018), the chemistry of Fe\(^{2+}\) aqueous system states that soluble Fe\(^{2+}\) oxidises directly or forms green rust complexes or Fe(OH)\(_2\) (Cornell and Schwertmann, 2003). Moreover, the oxidation rate is slow below pH 6 but accelerates rapidly at higher values. The iron in a pure aqueous alkaline system should undergo oxidation, followed by precipitation as oxides and hydroxides. Therefore, it seems that dissolution and precipitation of iron in slag occur differently because Peys et al. (2019c) found divalent iron in the binder, suggesting that oxidation occurs in the binder phase. In alkali-activated systems, not only hydroxides are present, but other anionic components, such as silicates, carbonates and sulphates, are also usually present. Iron can form soluble complexes with these anions and prevent the precipitation of Fe-hydroxides. In addition, the Fe\(^{3+}\) oxidation rate is lowered through the presence of H\(_2\)SiO\(_4\) anions (Tamura et al., 1976).

Thus, the following conclusions can be drawn about the behaviour of iron upon dissolution:

1. Little is known about the precipitated phases during slag dissolution tests, especially the quantities and valence states of precipitated iron. Studies on slag dissolution have shown almost no iron in leachate.
2. A significant quantity of Fe\(^{3+}\) and Fe\(^{2+}\) in the binder phase has been detected in several studies.
3. Iron, such as ferric nitrate solution or ferric hydroxide with metakaolin, does not contribute to the binder phase (Perera et al., 2007).

Therefore, it can be suggested that iron from Fe-rich slag dissolves but forms Fe-silicate or other soluble complexes that prevent the immediate precipitation of Fe-hydroxides, contributing to the binder formation.

4.2. Nature of activators

As shown in Table 6, the most commonly used alkali activators for Fe-rich materials are sodium silicate solutions for all types of precursors, including NFMS, EAFS, RM and tailings. For low-iron FMS, the common activator is sodium or rarely potassium hydroxide. This can be explained by the higher amount of reactive silica in FMS, unlike NFMS; thus, extra soluble silica is usually not required. According to Table 3, the highest compressive strength value of 112–120 MPa (Kalinkin et al., 2012; Krikova et al., 2015; Maragkos et al., 2009) was obtained using sodium silicate solution.

Several authors have studied the influence of different alkali cations on the activation of Fe-rich slags (Komnitas et al., 2009; Onisei et al., 2015). Onisei et al. (2015) used FS activated with three solutions: 10 M sodium hydroxide, sodium silicate solution (SiO\(_2\)/Na\(_2\)O = 3.4) and a 1:1 mixture of the two solutions. The fastest binder formation determined by calorimetry measurements was observed for activation with NaOH, the most alkaline solution. In contrast, the slowest reaction activated sodium silicate solution alone since no exothermic reaction was detected up to 140 h.

Komnitas et al. (2009) showed that using KOH with sodium silicate solution up to 8 M resulted in a much higher compressive strength of alkali-activated Fe–Ni slag, reaching 50 MPa. Using NaOH between 4 M and 8 M with sodium silicate solution resulted in compressive strength not exceeding 25 MPa. The authors suggested that KOH provides a more developed polymer structure than NaOH because of the larger size of potassium ions, which leads to the formation of more-developed silicate oligomers. Also, Simon et al. (2018) demonstrated a slightly higher reactivity of Fe-silicate glass when using K-silicate instead of Na-silicate solution.

Thus, the most successful activator for Fe-rich precursors is sodium or potassium silicate solution with a SiO\(_2\)/M\(_2\)O (M = K, Na) ratio of 1.2–1.6. The application of K-silicate solutions can lead to better reactivity of the slag and higher compressive strength in some cases. However, the difference in compressive strength was moderate, so using Na-silicates is a better option, considering the reagents’ costs. In addition, the role of alkali cations can be minor for Ca-rich systems, like C–S–H gels. The alkali activation of Fe-rich slag with sodium or potassium hydroxide solutions (i.e. without a commercial silicate solution) has not been well described in the literature. However, the ultra-high compressive strength obtained for some NFMS activated with silicate solutions is not needed for most applications in the construction sector. Considering these facts, it may be interesting to study the possibility of obtaining AAM from NFMS using alkaline solutions that do not contain commercial silicate solutions because the use of alkali-silicate solution has some concerns, such as carbon dioxide emissions from high-temperature production. Alternative solution to the problem is using waste materials containing soluble alkaline sources, like Bayer process liquor or paper sludge, which can allow a reduction of up to 60% of the environmental impacts linked with the traditional alkali activators production (Adesanya et al., 2020a; Mellado et al., 2014).

Fig. 5. Reactivity test of the fayalitic slag in 10 mol/L NaOH showing the dissolution rate of Al, Si, Pb and Zn over time (Iacobescu et al., 2017).
Table 6
The relationship between compressive strength, activator type and liquid-to-solid ratio (L/S) in Fe-rich AAMs.

| Initial material                  | Liquid/Solid ratio | Activator                        | Compressive strength, MPa | Reference               |
|----------------------------------|--------------------|----------------------------------|---------------------------|-------------------------|
| **Natural materials**            |                    |                                  |                           |                         |
| Volcanic ash                     | 0.21               | sodium silicate solution (SiO₂/Na₂O = 0.55) | 60                        | Lemougná et al. (2013)  |
| Bauxite 61.7% + SF 38.3%         | n/a                | sodium silicate solution (SiO₂/Na₂O = 0.48) | 28.5                      | Hairi et al. (2015)     |
| **Ferrous metallurgical slags**  |                    |                                  |                           |                         |
| EAFS 50% + FA 50%                | 0.28               | sodium hydroxide (8M NaOH)        | 27                        | Cristelo et al. (2019)  |
| EAFS n/a                         |                    | sodium silicate solution (SiO₂/Na₂O = 3.19) | 21.04                     | Nikolić et al. (2020)   |
| EAFS 0.25                        |                    | sodium silicate solution (SiO₂/Na₂O = 3.35) | 15                        | Cristelo et al. (2019)  |
| **Non-ferrous metallurgical slags and Fe-silicate glasses** | |                                  |                           |                         |
| Fe-Ni slag (CO₂ activated)       | 0.19               | sodium silicate solution (SiO₂/Na₂O = 3.19) | 120                       | Maragkos et al. (2009)  |
| Cu-Ni slag (CO₂ activated)       | 0.19               | sodium silicate solution (SiO₂/Na₂O = 1.5) | 119                       | Kalinkin et al. (2012)  |
| Fe-silicate glass 0.45           |                    | sodium silicate solution (SiO₂/Na₂O = 1.2) | 112                       | Krisková et al. (2015)  |
| Cu-Ni slag (O₂ activated)        | 0.22               | sodium silicate solution (SiO₂/Na₂O = 1.5) | 89.5                      | Kalinkin et al. (2012)  |
| Fe-silicate glass 0.77           |                    | sodium silicate solution (SiO₂/Na₂O = 1.2) | 88.3                      | Krisková et al. (2015)  |
| Fe-silicate glass n/a            |                    | sodium silicate solution (SiO₂/Na₂O = 1.2) | 63                        | Mast et al. (2021)      |
| Fe-Ni slag                       | 0.19               | sodium silicate solution (SiO₂/Na₂O = 1.2) | 61                        | Maragkos et al. (2009)  |
| Fe-silicate glass 0.45           |                    | sodium silicate solution (SiO₂/Na₂O = 0.28) | 57                        | Machiels et al. (2014)  |
| Fe-silicate glass 0.60           |                    | sodium silicate solution (SiO₂/Na₂O = 0.28) | 53                        | Machiels et al. (2014)  |
| Fe-silicate glass 0.28           |                    | sodium silicate solution (SiO₂/Na₂O = 1.6–2.0) | 53                        | Sande et al. (2017)     |
| Fe-Ni slag                       | 0.19               | sodium silicate solution (SiO₂/Na₂O = 0.19) | 50                        | Maragkos et al. (2009)  |
| Fe-Ni slag (mechanically activated) | n/a                | potassium-sodium silicate solution (7.5M KOH + Na₂SiO₃ 2%) | 50                        | Komnitsas et al. (2009) |
| Fe-silicate glass                | 1.0                | sodium silicate solution (SiO₂/Na₂O = 0.28) | 48                        | Machiels et al. (2014)  |
| Fe-Ni slag                       | 0.19               | sodium silicate solution (SiO₂/Na₂O = 0.25) | 47                        | Maragkos et al. (2009)  |
| FS 70% + 30% FA                  | 0.31               | sodium silicate solution (SiO₂/Na₂O = 2.38) | 47                        | Onisi et al. (2012)     |
| Fe-silicate glass n/a            |                    |                                  | 39                        |                         |

Table 6 (continued)

| Initial material                  | Liquid/Solid ratio | Activator                        | Compressive strength, MPa | Reference               |
|----------------------------------|--------------------|----------------------------------|---------------------------|-------------------------|
| **Natural materials**            |                    |                                  |                           |                         |
| Fe-Ni slag                       | n/a                | sodium silicate solution (SiO₂/Na₂O = 2.0) | 37                        | Komnitsas et al. (2009) |
| Fe-Ni slag                       | n/a                | sodium silicate solution (SiO₂/Na₂O = 1.54) | 31                        | hairi et al. (2015)     |
| Fe-Ni slag                       | n/a                | sodium silicate solution (SiO₂/Na₂O = 0.25) | 28                        | Maragkos et al. (2009)  |
| Fe-silicate glass                | 0.3                | sodium silicate solution (SiO₂/Na₂O = 0.28) | 23                        | Machiels et al. (2014)  |
| Fe-Ni slag                       | n/a                | sodium silicate solution (SiO₂/Na₂O = 1.2) | 18                        | Komnitsas et al. (2009) |
| Bauxite residues (red mud) 50%   | n/a                | sodium silicate solution (SiO₂/Na₂O = 2.0) | 70                        | Lemougná et al. (2017)  |
| RM 50% + GBFS 50%                | n/a                | sodium silicate solution (SiO₂/Na₂O = 1.6) | 65                        | Lemougná et al. (2017)  |
| RM (calcinated)                 | 83.3% + SF 16.66%  | sodium silicate solution (SiO₂/Na₂O = 0.48) | 58.13                     | hairi et al. (2015)     |
| RM (calcinated)                 | 50% + GBFS 50%     | sodium silicate solution (SiO₂/Na₂O = 1.7) | 49.2                      | Ye et al. (2014)        |
| RM (calcinated)                 |                    | potassium silicate solution (SiO₂/K₂O = 1.6) | 43.5                      | Hertel et al. (2016)    |
| RM (calcinated)                 |                    | sodium silicate solution (SiO₂/Na₂O = 1.3) | 37                        | Ye et al. (2014)        |
| RM 80% + MK 20%                  |                    | sodium silicate solution (SiO₂/Na₂O = 0.85) | 20                        | Dimas et al. (2009)     |
| RM                               |                    | sodium hydroxide (10% Na₂O in the powder form) | 10                        | Ke et al. (2015)        |
| **Tailings**                     |                    |                                  |                           |                         |
| Antigorite residue (mechanically activated) | 0.29             | sodium silicate solution (SiO₂/Na₂O = 2.25) | 49                        | Kalinkina et al. (2018) |
| Phyllite residue (mechanically activated) | 0.22             | sodium silicate solution (SiO₂/Na₂O = 3) | 25                        | Adesanya et al. (2020b) |

4.3. Concentration of activators

The influence of the concentration of SiO₂ and alkali cations on the compressive strength of the produced Fe-AAMs has been experimentally studied in several works (Maragkos et al., 2009; Mast et al., 2021; Ozturk et al., 2019; Sakkas et al., 2014). Mast et al. (2021) found that decreasing SiO₂/Na₂O from 2.0 to 1.6 led to an increase in compressive strength from 39 to 63 MPa for Fe-rich
slag-based AAMs. Kriskova et al. (2015) claimed that the molar ratio of SiO$_2$/Na$_2$O of 0.9–1.2 seemed optimum regarding the compressive strength (over 80 MPa) of Fe-rich silicate glass. However, the lower crack formations were observed for SiO$_2$/Na$_2$O ratios of 1.2 and 1.5, but in a later case, the strength decreased to 45 MPa. Conversely, slags activated with SiO$_2$/Na$_2$O solution with a molar ratio of 2.0 revealed a 90-day strength of about 3 MPa. For an RM-slag alkali-activated system, an increase in SiO$_2$/Na$_2$O molar ratio from 1.3 to 1.7 resulted in an increase in compressive strength from 37 to 49 MPa (Ye et al., 2014). For the mixture of FA and high-magnesium nickel slag (Zhang et al., 2017), an increase in modulus from 1.4 to 2.0 led to a substantial decrease in compressive strength, from 60 to 25 MPa.

Maragkos et al. (2009) found that the compressive strength of AAMs based on Fe–Ni slag increased approximately 2.5 times (from 50 to 120 MPa), as the initial silica concentration in the aqueous phase increased from 0.7 M to 4 M (in the presence of 7 M of NaOH). Komnitas et al. (2009) studied the activation of Fe–Ni slag at different concentrations of Na$_2$SiO$_3$, ranging from 0 wt% to 14 wt% when 8 M of KOH or NaOH was used. The results showed that increasing the sodium silicate content up to 8 wt% led to increased compressive strength from about 20 to 55 MPa. Sande et al. (2017) reported that the early strength of the resulting AAMs from FeO$_2$–CaO–SiO$_2$ slags was mainly affected by silica availability. A higher SiO$_2$/Na$_2$O molar ratio in the activating solution and a lower (FeO + CaO)/SiO$_2$ molar ratio led to higher compressive strength after two days of curing.

Alkali activation without a silicate solution has been studied mainly for low-iron FMS, which is well studied and contains more reactive silica in amorphous phases. Table 6 shows that the optimal molarity of NaOH solution for alkali activation is 6–10 M. Using only sodium hydroxide solution (8 M NaOH), Cristelo et al. (2019) obtained mortars from EAFS (32.33 wt% of Fe$_2$O$_3$) with a resulting compressive strength of 15 MPa. For the hybrid system, which mainly comprises NFMS and a small amount of OPC (Arnout et al., 2021), an increase in NaOH content resulted in a further increase in reactivity and strength. Besides, a NaOH content lower than 0.8 wt% resulted in low reactivity.

The compressive strength of the produced AAMs increases as a linear function of the initial silica concentration in the activating solution (Maragkos et al., 2009; Ozturk et al., 2019; Sakkas et al., 2014). Usually, the presence of soluble silicate enhances the formation and poly-condensation of oligomers (Swaddle, 2001). Moreover, the higher silica content in activating solution influences the kinetics and increases the strengths of Fe-silicate glasses at early ages (Van De Sande et al., 2020). However, an excessive amount of SiO$_2$ in the aqueous phase reduces alkalinity due to an increase in SiO$_2$/Na$_2$O ratio and, therefore, de-celerates the alkaline dissolution of the solid phase of the system (Beersaerts et al., 2021; Maragkos et al., 2009). Consequently, there is always an optimal ratio of SiO$_2$/Na$_2$O, partially depending on the chemistry and mineralogy of the binder. As shown in Table 6, the optimal ratios of SiO$_2$/Na$_2$O for Fe-rich NFMS are in the range of 1.2–1.6, consistent with the literature.

### 4.4. Liquid to solid (L/S) ratio

The L/S ratio is a crucial parameter for compressive strength development of AAMs. Maragkos et al. (2009) found that the compressive strength of AAMs synthesised from Fe–Ni slag increased from 28 to 45 MPa, decreasing the L/S ratio from 0.25 to 0.19. However, the L/S ratio has a lower limit value, which is strongly related to the efficiency of the moulding procedure due to its low workability.

A slightly higher optimal L/S ratio was obtained by Machiels et al. (2014), who analysed the microstructure of AAMs from Fe-silicate glasses while modifying the activating solution to a solid (L/S) mass ratio in the range of 0.3–1.0. The prominent improvements in compressive strength from 23 to 57 MPa occurred when the L/S ratio was decreased from 1.00 to 0.45. Furthermore, the progressive formation of microcracks was observed at higher L/S, lowering the compressive strength to 48 MPa.

Kriskova et al. (2015) found that increasing the water content level (i.e. H$_2$O/Na$_2$O) increased the reaction heat. Thus, the mechanical strength of the activated slag increased from 88 to 112 MPa by decreasing H$_2$O/Na$_2$O molar ratio from 54.5 to 22.0. Mast et al. (2021) found that decreasing the relative water content (H$_2$O/Na$_2$O molar ratio) from 29 to 20 increased the strength from 40 to 73 MPa.

To conclude, decreasing water content generally leads to an increase in compressive strength. However, there is a lower limit of water concentration that defines the development of the polymer structure and its optimal hardening. It seems that for Fe-rich precursors the L/S ratio plays an important role by influencing the workability that is usually lower compared to conventional geopolymers.

### 5. Curing conditions

The effect of curing conditions on the mechanical strength of AAMs has been analysed (Cristelo et al., 2019; Iacobescu et al., 2017; Kalinkin et al., 2012; Komnitas et al., 2009). Three basic parameters of curing include time, temperature and relative humidity (RH).

Table 7 shows that the curing temperature is almost irrelevant, depending on the nature of the precursors. For example, Maragkos et al. (2009) and Kalinkin et al. (2010) observed increased compressive strength of AAMs at curing temperatures of 40°C over one week of alkali-activated GBFS with 50% of RM, Lemounga et al. (2017) found that the optimum curing temperature was 40°C. Conversely, Iacobescu et al. (2017) found that decreasing the curing temperature of FS-based alkali-activated mortars resulted in lower compressive strength. In particular, the resulting strength varied between 19 MPa for the sample cured at 20°C and RH of 50% and 31 MPa cured at 20°C and RH ≥ 90%. The lower mechanical performance of FS-based AAMs at lower temperatures was explained by more extensive crack formation. In the experimental study of Komnitas et al. (2009), AAMs were synthesised from low-Ca electric arc FMS with precuring treatment both at 80°C and room temperature, followed by seven days curing at room temperature for both modes. The results showed that the compressive strength was only slightly higher for samples cured at 80°C (~39 MPa) than at room temperature (~32 MPa).

The curing time can also have some effects on the properties of AAMs. Note that the highest compressive strength values (over 100 MPa) presented in Table 7 were obtained for a curing time of 48–360 days. Cristelo et al. (2019) showed that the uniaxial compressive strength of the pastes made from EAFS and FA after two days of curing was only slightly lower than the samples after 28 days of curing. Using a curing time of 1–360 days, Kalinkin et al. (2012) found a more pronounced increase in compressive strength from 50.5 to 89.5 MPa for Fe–Ni slag mechanically activated in air and from 53.8 to 119 MPa for in the slag mechanically activated in CO$_2$.

For less reactive materials, such as RM, curing time can significantly improve mechanical performance. Lemounga et al. (2017) found that a long curing time is required to achieve good strength for GBFS samples containing the highest amount of RM (75%). For these samples, the compressive strength increased from 10 MPa at seven days of curing at 25°C to 30 MPa after 28 days. Therefore, RM is less reactive than slag at an ambient temperature (25°C) and contributes more to strength development in the system only at a higher temperature. He et al. (2013) confirmed that a longer curing time is important for BR-based AAMs: the compressive strength increased from 3.40 to 11.70 MPa, as the curing time was prolonged from 21 to 49 days. Also, similar results were obtained by Ye et al. (2014), who studied BR-based AAMs with GBFS as a co-binder. The resulting compressive strength of the AAMs was increased from 25 to 49 MPa as the curing time increased from three to
Table 7

The effect of curing conditions on the compressive strength of different Fe-rich AAMs.

| Initial material | Time, days | T, °C | RH, % | Compressive strength, MPa | Reference |
|------------------|-----------|-------|-------|---------------------------|-----------|
| Natural materials |           |       |       |                           |           |
| Volcanic ash     | 7         | 40    | n/a   | 60                        | Lemounga et al. (2013) |
|                  | 1         | 60    | n/a   | 28.5                      | Hizri et al. (2015)   |
| Bauxite residues (red mud) | 28       | 85    | 99    | 27                        | Cristelo et al. (2019) |
|                  | 0.5       | 80    | bath  | 22                        | Orturturk et al. (2019) |
|                  | 2         | 65    | n/a   | 21.04                     | Nikolic et al. (2020)  |
|                  | 28        | 85    | 99    | 15                        | Cristelo et al. (2019) |
| Non-ferrous metallurgical slags and Fe-silicate glasses |           |       |       |                           |           |
| Fe-Ni slag       | 48        | 60    | 70    | 120                       | Maragkos et al. (2009) |
| Cu-Ni slag (CO$_2$ activated) | 360     | 20    | 95    | 119                       | Kalinkin et al. (2012) |
| Fe-silicate glass| 90        | room  | n/a   | 112                       | Krikovkova et al. (2015) |
| Fe-silicate glass| 100       | room  | n/a   | 57                        | Machieis et al. (2014) |
| Cu-Ni slag (CO$_2$ activated) | 1       | 20    | 95    | 53.8                      | Kalinkin et al. (2012) |
| Fe-silicate glass| 28        | room  | n/a   | 53                        | Machieis et al. (2014) |
| Fe-silicate glass| 28        | room  | n/a   | 53                        | Sande et al. (2017)   |
| Fe-Ni slag       | 9         | 80    | n/a   | 50                        | Kommitas et al. (2009) |
| FS 70% + 30% FA  | 28        | 20    | n/a   | 47                        | Onisei et al. (2012)   |
| Fe-silicate glass| 7         | room  | n/a   | 35.1                      | Krikovkova et al. (2015) |
| Fe-silicate glass| 28        | room  | n/a   | 34                        | Machieis et al. (2014) |
| FS               | 28        | 20    | 90    | 31                        | Iacobescu et al. (2017) |
| FS               | 28        | 60    | 20    | 21                        | Iacobescu et al. (2017) |
| FS               | 28        | 20    | 50    | 19                        | Iacobescu et al. (2017) |
| Bauxite residues (red mud) |           |       |       |                           |           |
| RM (calcinated)  | 1         | 60    | n/a   | 58.13                     | Hairi et al. (2015)   |
|                  | 28        | 20    | 95    | 49.2                      | Ye et al. (2014)      |
|                  | 3         | 60    | n/a   | 43.5                      | Hertel et al. (2016)  |
|                  | 28        | 20    | n/a   | 31.5                      | Ye et al. (2016)      |
|                  | 28        | 25    | n/a   | 10                        | Lemounga et al. (2017) |
|                  | 3         | 20    | 95    | 25                        | Ye et al. (2014)      |
|                  | 3         | 60    | n/a   | 20                        | Dimas et al. (2009)   |
|                  | 28        | room  | n/a   | 12.75                     | Li et al. (2019)      |
|                  | 7         | 25    | n/a   | 10                        | Lemounga et al. (2017) |
|                  | 7         | 20    | 95    | 10                        | Ke et al. (2015)      |
| Tailings         | 28        | 20    | ± 65  | 49                        | Kalinkin et al. (2018) |
|                  |           | 2     | ± 5   | 25                        |                       |

Table 7 (continued)

| Initial material | Time, days | T, °C | RH, % | Compressive strength, MPa | Reference |
|------------------|------------|-------|-------|---------------------------|-----------|
| Phyllite residue (mechanically activated) | 23 ± 2 | Adesanya et al. (2020b) |
| Phyllite residue (mechanically activated) | 28 ± 60 | n/a | 20 | Adesanya et al. (2020b) |
| Phyllite residue (mechanically activated) | 7 ± 23 | n/a | 15 | Adesanya et al. (2020b) |
| Antiporite residue (mechanically activated) | 28 ± 20 | 95 | 15 | Kalinkin et al. (2018) |
| Phyllite residue (mechanically activated) | 7 ± 60 | n/a | 7 | Adesanya et al. (2020b) |

Moreover, long-term curing is important when silica fume is used as a co-binder for RM-based one-part ‘just add water’ AAMs due to the slower dissolution rate of SF (Ye et al., 2016). The addition of 25 wt% SF considerably improved the long-term strength of the binders. Conversely, a decrease in compressive strength over time has been reported for one-part binders synthesised through the alkali-thermal activation of the RM (Ke et al., 2015). The authors observed a clear decrease in compressive strength from 10 to 1.8 MPa as the curing period was prolonged from seven to 28 days. The degradation of the matrix explained this effect through processes such as dehydration, carbonation and efflorescence.

The curing conditions can be even more variable for Fe-based alkali-activated systems than for conventional systems regarding the possible oxidation of divalent iron into the trivalent form. Peys et al. (2019) showed that the oxidation reactions of slag-based Fe-silicate AAMs during the first days after mixing were the same in the air and N$_2$ atmosphere, suggesting that it was not driven by atmospheric oxygen. However, the mechanism of this oxidation and its connection with the resulting compressive strength are still questionable. Mast et al. (2020) found a twofold increase in compressive strength for gamma-irradiated specimens. Moreover, the prominent increase in strength was only attributed to the samples after a short curing period (i.e. 1 h and 24 h). The authors suggested that this effect could be related to the irradiation-induced oxidation of Fe$^{2+}$ to Fe$^{3+}$.

Several recent studies examined the effect of Ca/Fe and Si/Fe ratios on curing characteristics of Fe-silicate glasses (Siakati et al., 2021; Simon et al., 2018; Van De Sande et al., 2020). It was shown that higher Si content results in higher compressive strength at an early age (Van De Sande et al., 2020), whereas higher calcium content (i.e. CaO/FeO molar ratios) enhances compressive strength at later ages (Siakati et al., 2021). In addition, when the CaO content was reduced to 5 wt%, the strength after 28 days was lower (Wen et al., 2021) and the reaction rate was very slow (Simon et al., 2018). Thus, curing conditions of Fe-AAMs seem to depend more on the chemical composition of precursors and less on the composition of activating solutions. However, it is still difficult to exclude the influence of iron content on the curing properties of Fe-AAMs. High compressive strength of Fe-silicates at an early age implies fast-setting properties of Fe-rich precursors. In addition, the higher content of calcium has a positive effect on the reaction rate and compressive strength of Fe-AAMs.

6. Analytical challenges of iron-rich binder characterisations

The characterisation of Fe-rich binders faces many challenges due to the presence of magnetic phases and iron minerals in the starting material and the stronger signals from silica components. Conventional methods such as XRD, FTIR and SEM have provided insufficient data for...
determining the chemical role of iron in alkali-activated materials. Moreover, nuclear magnetic resonance (NMR) was not applicable for Fe-AAMs since magnetic particles are always present in the starting material. However, the use of advanced or unconventional physical techniques, such as total X-ray scattering and subsequent pair distribution function analysis or Mössbauer spectroscopy, provides clear data on the reactivity of iron during alkali activation.

### 6.1. X-ray diffraction analysis

X-ray diffraction was commonly used to confirm that alkali activation did not result in new crystalline minerals or the transformation and dissolution of minerals present in the original composition. In some cases, the formation of calcite due to carbonation (Ozturk et al., 2019) or crystallisation of sodium (Lemougna et al., 2013) and calcium (Ozturk et al., 2019) aluminosilicates because of slag alkali activation, but the formation of iron phases was not found. In addition, the reactivity of the crystalline phases of iron has not been confirmed by XRD. For example, fayalite (Onisei et al., 2015), magnetite (Maragkos et al., 2009) and haematite (Hairi et al., 2015) were stable under alkaline conditions.

For conventional aluminosilicate geopolymers, the hump in the X-ray diffraction patterns generated by the amorphous phases is usually observed with alkali activation of Fe-rich slag. Iacobescu et al. (2017) suggested that the shift was not visible because the range of the hump was large, so the resulting hump from the reaction product overlapped with the original one.

### 6.2. Scanning electron microscopy: microstructure and microchemistry

The microstructure of alkali-activated Fe-rich slag is usually dense, with low porosity and minor crack formation. It usually contains undissolved particles of irregularly shaped slag of various sizes, surrounded by a gel-like (amorphous) inorganic binder (Maragkos et al., 2009). However, a decrease in the SiO₂/Na₂O ratio leads to more pronounced cracking caused by drying shrinkage and possibly chemical and/or autogenous shrinkage during curing (Kriskova et al., 2015). At higher magnification in the secondary electron (SE) mode, one can observe the morphology of the matrix comprising spherical aggregates 50–100 nm in size, a typical morphology that was also found in aluminosilicate geopolymers (Machiels et al., 2014). No noticeable differences in electron microscope images were observed between AAMs obtained from different slags and slags with different iron content (Van De Sande et al., 2020). In addition, no relationship was found between electron microscope images and compressive strength (Van De Sande et al., 2020).

SEM micrographs with elemental mapping indicated a relatively uniform distribution of iron in alkali-activated samples, with only a few small regions having a higher iron content corresponding to less well-reacted iron minerals (Iacobescu et al., 2017; Lemougna et al., 2017). For some materials, aluminium and calcium appeared to be more uniformly distributed in the binder phase (Fig. 6), while iron was present throughout the binder and in certain areas. The latter may mean precipitation of an Fe-rich phase, possibly in the form of hydroxide or oxhydroxide (Kriskova et al., 2015). However, one more possibility of nonuniform iron distribution is the aggregation of non-reactive crystalline iron phases during the alkali activation in a more reactive matrix.

### 6.3. FTIR spectroscopy

As for conventional aluminosilicate geopolymers, Fe-rich AAMs exhibit the development of a bending vibration band of molecular H₂O at ~1660 cm⁻¹ and ~3600 cm⁻¹, which indicates the formation of hydrated phases (Garcia Lodeiro et al., 2010; Mostafa et al., 2009; Wang et al., 2014). In addition, the stretching vibrations of C-O at ~1405 cm⁻¹ and 1460-1470 cm⁻¹ indicate the presence of CO₃²⁻ groups (Garcia Lodeiro et al., 2010; Mostafa et al., 2009; Wang et al., 2014) due to atmospheric carbonation as a result of alkali activation and subsequent sample preparation (Mostafa et al., 2009).

The position of the main band corresponding to the stretching vibrations of Si-O in the spectra of both AAM and Fe-AAM usually shifts towards higher wavelengths compared to the precursors. Possibly, this indicates the presence of a smaller amount of non-bridging oxygen due to the elongation of the T-O-Si bonds, reducing the bond angle and, consequently, a decrease in the constant molecular vibrational force (Komnitas et al., 2009). In addition, the shift towards higher wavelengths can also be associated with the oxidation of Fe³⁺ in the slag to Fe⁵⁺ in the binder (Onisei et al., 2015) and nanoscale clustering of iron, which leads to more Si-O-Si and Fe-O-Fe bonds and fewer Si-O-Fe bonds (Van De Sande et al., 2020). In fact, the role of iron remains unclear since no Fe-O bonds expected around 590 cm⁻¹ or Fe³⁺-O-Si bonds at around 1000 cm⁻¹ have been found; all conclusions are drawn from the Si-O-T shift that several reasons can cause. Although considering the data of Mössbauer spectroscopy, this shift can be explained by the oxidation of iron with the subsequent formation of Si-O-Si and Fe-O-Fe bonds. However, the connection between these components and the general picture of the framework remains in question, and the structural parameters require quantitative assessment.

### 6.4. Mössbauer spectroscopy

The authors (Lemougna et al., 2017; Onisei et al., 2018) clearly observed iron oxidation during alkali activation using ⁵⁷Fe Mössbauer spectroscopy. For example, Lemougna et al. (2013) found a 38% decrease in the intensity of the Fe²⁺ band with a simultaneous 30% increase in Fe³⁺ (Fig. 7). Both works suggested that the new regions of ferric iron have Mössbauer parameters similar to distorted tetrahedral or five-coordinated sites, which can be in the gel phase. Peys et al. (2019a) later disclosed a more detailed information on the
structure of Fe-rich AAM using Mössbauer spectroscopy. The authors found that a new \( \text{Fe}^{3+} \) occurred after 6 h of the reaction at 20 °C, and the most intensive oxidation took place during the first 24 h. It is assumed that this \( \text{Fe}^{3+} \) is in tetrahedral coordination in the silicate framework. Also, it was found that a new octahedral \( \text{Fe}^{2+} \) component is formed in the binder phase with Mössbauer parameters similar to clay minerals, which approximately follows the same formation kinetics as the \( \text{Fe}^{3+} \) state (Peys et al., 2019a).

### 6.5. X-ray absorption near-edge structure (XANES) spectroscopy at the Fe K-edge

XANES spectroscopy at the Fe K-edge (Simon et al., 2018) also showed a significant increase in \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratio, thus implying the oxidation of \( \text{Fe}^{3+} \) from the original amorphous fraction to \( \text{Fe}^{3+} \) of the reaction product. The iron in the resulting AAM was about fivefold coordinated on average, matching the coordination number of iron in the initial slag.

XANES spectroscopy also allowed the authors to calculate the degree of reaction using the \( \text{Fe}^{3+}/\Sigma\text{Fe} \) ratios of the initial slags and the activated slags (Simon et al., 2018). Thus, the following conclusions were drawn:

1. The degree of reaction increased with an increase in the amorphous fraction of slags.
2. The reaction with Na-silicate solution results in a slightly lower reaction degree than activation with K-silicate solution.
3. The degree of reaction was very low (~0.12–0.18) if there was no CaO in the initial composition.

### 6.6. X-ray total scattering and subsequent pair distribution function analysis

The alkali activation of CaO-FeO-SiO\( _2 \) slag as a precursor has been studied using in situ X-ray total scattering and PDF analysis (Peys et al., 2019c). It has been shown that the dissolution of Fe-rich slag determines the reaction during the first few hours. In addition, the atomic structure of iron silicate particles entering the solution depends on the type of alkaline cation. In particular, the use of sodium silicate keeps the atomic correlations of the intermediate particles unchanged. In contrast, a solution of potassium silicate leads to an increase in the coordination number of iron. Thus, the curing of the binder begins with the formation of two new phases with different degrees of iron oxidation.

The silicate network containing \( \text{Fe}^{3+} \) did not explicitly reveal its structural details in PDF, except for its glassy nature. However, the total scattering data and PDF do show the appearance of \( \text{V}^{\text{VI}}\text{Fe}^{\text{III}} \) trioctahedral layers, especially for the low calcium alkali-activated slag. The insert of Fig. 8 shows a shift of the maximum intensity of Fe-O toward higher \( r \) values, suggesting the emergence of \( \text{V}^{\text{VI}}\text{Fe}^{\text{III}}+ \) species. These layers are typical of Fe(OH)\( _2 \) and layered double hydroxides (LDH) and are observed in clay minerals such as smectites or micas.

### 7. The role and state of iron: proposed mechanisms

Despite the attractiveness of using Fe-rich residues in the construction sector, studies on the role and state of iron in AAMs have emerged only during the past few years. Earlier works (Bell and Kriven, 2010; Perera et al., 2007) attempted to use pure chemical precursors to obtain alkali-activated binders, and the results were unsuccessful. For example, Perera et al. (2007) used metakaolin as a binder with the addition of both ferric nitrate (Fe(NO\( _3 \))\( _3 \cdot 9\text{H}_2\text{O} \) solution and two-line ferrihydrite (Fe(OH)\( _2 \)) as a source of Fe\( ^{3+} \). The authors claimed that iron was not included in the polymer structure but occupied octahedral sites as isolated ions or oxy-hydroxide aggregates. Bell and Kriven (2010) attempted to obtain AAMs from Fe\( _2\text{O}_3 \cdot 2\text{SiO}_2 \) powder with potassium silicate solution. The resulting material was ductile and water-soluble. The partial solidification of the resulting material was observed only after one year of curing. However, in this case, the powder was partly crystalline and contained some portions of haematite and magnetite. Bernal et al. (2014) observed metallic iron particles in an alkali-activated slag binder. But the starting material was represented by GBFS with a low iron content (2.35 wt% of Fe\( _2\text{O}_3 \). As shown below, the process proceeds differently during the alkaline activation of Fe-rich slags.

The participation of iron in forming a polymeric binder structure has been examined in the literature (Lemougna et al., 2013; Onisei et al., 2018; Peys et al., 2019a, 2019c). Using analytical methods, such as Mössbauer spectroscopy, in situ total X-ray scattering and subsequent pair distribution function analysis, X-ray absorption near-edge structure (XANES) spectroscopy at the Fe K-edge, Fourier-transform infrared spectroscopy (FTIR), iron from FS, Fe-rich glasses or volcanic ashes could be incorporated into the binder structure.

The disadvantage of AAMs with a high iron content compared with aluminium or calcium silicates is the system’s complexity due to the existence of several oxidation states (Fe\( ^{3+} \), Fe\( ^{2+} \)) and coordination numbers (4,5,6) of iron. Slags from non-ferrous metallurgy dominantly contain Fe\( ^{3+} \) in its amorphous fraction, often with a small content of Fe\( ^{2+} \) (Piatak et al., 2015; Simon et al., 2018). The alkaline-activated binder is believed to contain mainly Fe\( ^{3+} \) (Onisei et al., 2018; Simon et al., 2018). Peys et al. (2019a) used \( ^{57}\text{Fe} \) Mössbauer analyses to show that oxidation reactions coincide with polymerisation reactions. The large FTIR shift of the slags to AAMs can be attributed to the oxidation of iron (Fe\( ^{2+} \) to Fe\( ^{3+} \)). The oxidation of iron from slag to the final binder phase was also observed using Mössbauer spectroscopy (Onisei et al., 2018) and XANES spectroscopy at the Fe K-edge (Simon et al., 2018). It is commonly suggested that all reactive iron is in the amorphous fraction.
of the slag, but Lemougna et al. (2013) observed the reaction of augite \(((\text{Ca, Mg, Fe}^{2+})_2\text{SiO}_6)\) from volcanic ashes, in which the iron is in divalent form during alkali activation and formation of new Fe\(^{3+}\) site. But, it seems that the dissolution rate of augite is rather low under alkaline conditions (Xu and Van Deventer, 2000); thus, the general contribution of crystalline silicate minerals to binder development is usually low.

The new Fe\(^{3+}\) state was believed to be in a silicate network (Lemougna et al., 2013; Peys et al., 2019c; Simon et al., 2018), revealing atomic arrangements similar to the precursor (Onisei et al., 2018; Simon et al., 2018). The new Fe\(^{3+}\) site, which is associated with the amorphous glassy binder, exhibited an average five-fold or tetrahedral O-coordination, while the initial slag had the same average coordination number for iron in the amorphous fraction (Onisei et al., 2018; Simon et al., 2018). The authors (Simon et al., 2018) suggested that both Fe\(^{3+}\)-O-Fe\(^{3+}\) and Si-O-Fe\(^{3+}\) bonds exist in Fe-AAMs, but the arrangement and connectivity of these bonds remains to be clarified in future studies.

To maintain a charge balance, a fixed ratio of Na/Al = 1 should be saved in the binder product of conventional aluminosilicate geopolymers (Davidovits, 2011). Using Mössbauer spectroscopy, Arne Peys et al. (2019a) showed the change in the adsorption area contribution of Fe\(^{3+}\) and Fe\(^{2+}\) during alkali activation of Fe-silicate glass. So, the resulting ratio of Na/Fe\(^{3+}\) in the binder was approximately 1, similar to the typical Na/Al ratio in geopolymers. However, the effect of alkaline cations may be different for C-S-H gels, hydrogarnets and other related Fe-rich cementitious systems. For example, silicate-bridging complexes in C-A-S-H stabilized by hydroxyl ligands are charge balanced by both calcium and iron ions in the interlayer space (Kunhi Mohamed et al., 2020). Also, Siakati et al. (2021) found an excess of Na\(^+\) for the higher CaO/FeO molar ratio, suggesting that both Ca\(^{2+}\) and Na\(^+\) participate in charge balancing of Fe\(^{3+}\) ions, while the rest of the Na\(^+\) is likely to form a separate phase.

In contrast to Fe\(^{2+}\), Fe\(^{3+}\) ions, due to a similar ionic radii and charge, can substitute for aluminium in many compounds and behave similarly during various chemical reactions (Cornell and Schwertmann, 2003). Besides, it is well known that the presence of aluminium in geopolymers plays an important role by accelerating the condensation reactions, resulting in higher compressive strength and faster setting time (Weng et al., 2005). Thus, the early oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) can also control the kinetics of condensation reactions in AAMs, and Fe\(^{3+}\) contributes to the compressive strength and setting behaviour of Fe-rich AAMs. This can also be supported by the results of (Mast et al., 2020), who observed an early-age increase in the compressive strength of AAMs upon gamma irradiation, resulting from the possible oxidation of Fe\(^{2+}\) to Fe\(^{3+}\). The similar role of Fe\(^{3+}\) and aluminium in AAMs, as well as their structural competition, still needs to be clarified, since Fe\(^{3+}\) in AAM often has a fivefold coordination number, in contrast to the always tetrahedrally coordinated aluminium. Thus, Simon et al. (2018) proposed that Fe\(^{3+}\) in AAMs are not simply Fe-analogues of aluminium in conventional aluminosilicate geopolymers but have structural characteristics that are significantly different from the latter.

Recently, Peys et al. (2019c) discovered the formation of a new Fe\(^{3+}\) state in the form of trioctahedral Fe(OH)\(_2\)-like layers during the alkali activation of Fe-silicate glasses. These trioctahedral layers are shown to be hydroxylated and in contact with silicates, in a similar way to phylllosilicate minerals (Siakati et al., 2021). The partial incorporation of calcium ions in these layers resulted in an overall more distorted near neighbour environment of the Fe(OH)\(_2\)-like layers. Also, Peys et al. (2019c) observed the oxidation of iron in these layers during the first days after mixing. The oxidation reactions were the same in the air and N\(_2\) atmosphere, suggesting that it was not driven by atmospheric oxygen. Siakati et al. (2021) indicate that the newly oxidized Fe\(^{3+}\) ions in the binder are unlikely to be present in the tetrahedral configuration in the network, but it is more likely that some layers may now consist of Fe\(^{3+}\) ions in the octahedral configuration.
For precipitated C–S–H gels (Siramantan et al., 2021), it was shown by $^{29}$Si NMR and EXAFS data that, when solvated Fe$^{3+}$ is freely available, Fe$^{3+}$ tend to uptake in octahedral coordination into interlayers of C–S–H phase. Another evidence that iron uptake into interlayered position is that in the presence of Fe$^{3+}$, the Ca/Si ratios of precipitated synthetic C–S–H are generally slightly decreased (Mancini et al., 2020). For tobermorite that is an ordered analogue of C–S–H gel, Mössbauer study showed that the Fe$^{3+}$ replacing interlayered Ca$^{2+}$ ions are surrounded by the both distorted and undistorted oxygen octahedra (Labhasetwar et al., 1991).

The variations of coordination numbers and valence states of iron in the binder phase indicate that the reaction of Fe-silicates is different from that reported for aluminosilicate precursors. There is iron dissolution liberating the Fe-silicate species with the same atomic arrangement as the slag, but after reaching a threshold value for the Fe-silicate species in the solution, a complex mechanism forms two reaction products (Peys et al., 2019c). There is a formation of an Fe$^{3+}$-containing phase, in which the Fe$^{3+}$ is in an octahedral configuration, arranged in triangles similar to ‘brucite-like’ layers. The second reaction product is in the silicate network, which is similar to aluminosilicates, as it contains an Fe$^{3+}$ in a tetrahedral configuration and is presumably charge balanced by Na$^+$ or other interlayered ions (e.g. Ca$^{2+}$ or Fe$^{2+}/3^+$.). The third stage includes the oxidation of the $^{26}$Fe$^{2+}$ trioctahedral layers towards a more Fe$^{3+}$ binder, consisting of Fe$^{3+}$ ions with the same or similar arrangement.

8. Conclusions and further challenges

The development of Fe-AAM is an important step forward in the commercialisation of these alternative low-carbon binders that do not rely on carbonates like Portland cement. The advancement of this system arises due to the necessity of metallurgical and mining companies to seek end uses of their residues, which are constantly accumulating in huge quantities with a negative impact on the environment. As the knowledge of the reactivity and state of iron in this system remains scarce, the current state of Fe-AAM was discussed in this review with a critical evaluation of the data on the initial precursors, mechanical properties, reactivity and role of iron, in addition to analytical challenges associated with the characterisation of Fe-rich binders.

These residues are mainly from the non-ferrous metallurgy sector (NFMS), but they can also include FMS, BR and MT, which contain a significant proportion of iron. Regarding mechanical properties, the highest compressive strength values of about 120 MPa were attributed to highly amorphous NFMS, such as Fe–Ni slag and Cu–Ni slag. These Fe-rich precursors appear to have higher compressive strengths than conventional geopolymers or Portland cement. This indicates that not only environmental but also technical benefits can be attributed to Fe-rich AAMs. However, a decrease in the crystallinity of the components or an increase in the size of the particles can significantly reduce the reactivity of the slag and the resulting compressive strength. Also, the higher crystallinity of MTs and BR results in low reactivity of these residues under alkaline conditions. However, mechanical or thermal activation and the use of more reactive co-binders can make these residues at least partially reactive, and the resulting materials exhibit a good mechanical performance. Interestingly, there was no correlation between the concentration of iron in the precursor and the compressive strength of the final product.

Alkali activation (e.g. nature and concentration of activator and water content) and curing parameters play an important role in forming alkali-activated binders, depending strongly on the chemistry of precursors. The most successful activating solution for Fe-rich precursors is sodium silicate with a SiO$_2$/Na$_2$O ratio of 1.2–1.6. There is insufficient data on studying the possibility of producing AAM from NFMS using alkaline solutions that do not contain commercial silicate solutions, such as alkaline hydroxides or wastes containing soluble alkali sources, such as Bayer’s process solution or paper sludge. In terms of curing behaviour, Fe-rich slags can be classified as a fast-hardening material since high compressive strength is usually observed at early ages. Higher Si/Fe ratio can improve early-age compressive strength, while the better mechanical performance at later ages is attributed to precursors with higher Ca/Fe ratios. Besides, the temperature of curing mainly depends on the composition of both precursors and activating solution, but no correlation with iron content or state was confirmed yet.

It seems that traditional characterisation methods, such as XRD, SEM and FTIR, did not provide sufficient information on the role of iron in AAMs, while NMR could not be applied because of the magnetic iron particles presented in the original precursors. However, Mössbauer spectroscopy and in situ total X-ray scattering and subsequent pair distribution function analysis and X-ray absorption near-edge structure (XANES) spectroscopy at the Fe K-edge provided more valuable information on the reactivity and role of iron in AAMs. These methods have clearly shown the ability of iron in slags and glasses to participate in the formation of the polymer structure, including the partial oxidation of Fe$^{3+}$ to new Fe$^{2+}$ sites. The new Fe$^{3+}$ state has been suggested to be in a silicate network, exhibiting an average five-fold or tetrahedral O-coordination. The amount of these Fe$^{3+}$ sites is probably controlled by the Na$^+$ or other cations (e.g. Ca$^{2+}$ or Fe$^{2+}/3^+$) in the system since it was shown that the Na$_2$/Fe$^{3+}$ ratio in the binder is about 1, similar to Na$_2$/Al$_3$ = 1 ratio in aluminosilicate geopolymers. The remaining unoxidised Fe$^{2+}$ precipitates in the trioctahedral Fe(OH)$_2$ layers, hydroxylated and connected to silicates in a similar way as phyllosilicates. Then, the oxidation of the Fe$^{2+}$ trioctahedral layers towards a more Fe$^{3+}$ binder with a similar configuration occurs. Also, Fe$^{3+}$ that is freely available in the solution tends to uptake in octahedral coordination into the interlayer of the C–S–H phases.

Despite the recent progress, the mechanism of forming Fe-rich binder remains questionable, especially the structural role of iron in the reaction products in relation to other structural components, such as CaO sheets or Al$^{3+}$ tetrahedra, etc. The supposed similar role of tetrahedral Fe$^{3+}$ and Al$^{3+}$ in AAMs, as well as their structural competition, still needs to be clarified, since iron in AAM obtained from slags often has a fivefold coordination number, in contrast to always tetrahedrally coordinated Al. In addition, the charge balancing mechanism should be further explained or thermodynamically modelled in the systems with different chemistry, where silicate-bridging complexes are possibly charge-balanced by interlayered Ca$^{2+}$ and Fe$^{2+}/3^+$ ions.

Thus, upscaling and commercialisation of Fe-rich AAM is a viable option in the nearest future due to its many ecological and technological benefits. The use of different types of hazardous metallurgical and mining residues is an attractive option regarding sustainability, especially in areas where conventional Portland cement is not produced. Moreover, the reduction in Portland cement production in other regions will have a positive environmental impact by decreasing CO$_2$ emissions and minimising the exploration of natural resources. In addition, the construction sector will have benefits regarding material performance, as some AAMs exhibit improved or unique physical properties (e.g. ultra-high compressive strength, high thermal stability, etc.), thus creating new destinations for various by-products.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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