

Dissolution Behaviour of Alkali-activated Fe-rich Non-ferrous Metallurgy Slag in Acetic Acid

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Abstract. *The application of Fe-rich non-ferrous metallurgy slag (NFS, within a $FeO_x-SiO_2-Al_2O_3-CaO$ system) in alkali-activated materials requires detailed information on the durability performance. The present study investigates the durability of alkali activated NFS (AA-NFS) exposed to acetic acid to simulate the attack of a concrete by organic acids present in animal manure or sewage systems. The dissolution behavior of NFS and alkali-activated NFS (AA-NFS) was assessed by immersing NFS and AA-NFS in a 3 wt. % acetic acid solution at a liquid to solid weight ratio of 1000. The dissolved ions in the acetic solution from NFS and AA-NFS were measured at different time intervals over 7 days. Through the comparison of NFS with AA-NFS, the dissolution behavior of unreacted slag and binder in AA-NFS could be evaluated separately, considering a calculated amount of 47.7 wt.% of unreacted slag was present in the AA-NFS. The results demonstrated that the binder dissolves slightly faster than slag in the first 4 hours. Over half of the dissolution rate of the Ca, Fe and Al in AA-NFS was due to binder. While for Si, 41% total dissolution rate in AA-NFS was from binder and the other 59% was from unreacted slag. After 7 days however, the dissolved fraction of slag was higher than binder. About 90% Ca, 79% Fe and 71% Al in slag was ended up in the acetic acid solution, which is higher than that in binder (74%, 62% and 56%, respectively). A significantly higher difference was found for the total dissolved fraction of Si in slag (86%) compared to that in binder (43%). The highly connected silicate network in the binder remains largely intact as silica gel, while due to the low connectivity of the silicate species in the slag the silicate dissolves after the other elements have left the structure. Overall these results suggest that Ca has the lowest dissolution resistance in binder, followed by Fe, Al and Si.*

Keywords: *Non-ferrous metallurgy slag; Alkali-activated materials; Acetic acid resistance; Dissolution; Si-Al-Fe matrix.*

1 Introduction

As the impact of global warming and the depletion of natural resources in cement production continue to threaten the environment, the need for sustainable alternatives in the construction industry is becoming increasingly important. Alkali activated materials (AAMs) have emerged as a promising alternative to traditional cement binders due to the substantial reduction in CO₂ emissions compared to cement (Provis, 2018). The precursors for AAM synthesis, mainly (calcium) aluminosilicates, such as fly ash, ground granulated blast furnace slag, and metakaolin, have been extensively studied in the literature and been identified as suitable candidates (Lemougna et al., 2016; Provis, 2018). However, another family of materials that has gained recent attention are Fe-silicates, such as non-ferrous metallurgy slags (NFS) (Peys et al., 2022; Ponomar et al., 2022). This novel material has shown great potential for alkali

activation and has demonstrated adequate compressive strength and thermal resistivity for cementitious materials (Adediran et al., 2023; Van De Sande et al., 2020). Despite its promising properties, there is limited knowledge about the durability performance of alkali-activated NFS (AA-NFS). The durability of cementitious materials can vary depending on the environment they are exposed to. While some materials may perform well in regular environments, they may not be able to withstand harsh environments. It's important to note that the definition of a harsh environment can differ based on the chemistry of the binder used in the cementitious material (Bernal et al., 2014). For example, alkali activated materials may have a different threshold for what is considered a harsh environment compared to traditional cement due to differences in their chemistry (Provis and Van Deventer, 2013). Thus, further research is necessary to fully understand the durability of this material as a new binder.

To comprehensively evaluate the durability performance of AA-NFS as a sustainable binder, it is necessary to conduct a range of tests that simulate various harsh conditions that the material may encounter in real-world applications. One such environment that poses a significant challenge for binders is the agricultural sector, which is a vital component of the global economy (Oki and A. L. Anawe, 2015). Organic acids, such as acetic, propionic, butyric, isobutyric and lactic acid, are commonly found in sewer systems and agricultural effluents like liquid manure and ensilage effluent, and their concentration rapidly increases due to bacterial activity. These acids can cause significant damage to binders, leading to deterioration and reduced lifespan. Thus, it is crucial to determine the resistance of AA-NFS to organic acids prevalent in the agricultural environment. Previous research (Oueslati and Duchesne, 2012) has shown that binders rich in Si, Al, and Fe are more resistant to acidic solutions, and this has been demonstrated by the effect of different supplementary cementitious materials (SCMs) on blended cement resistance to acetic acid. This makes that AA-NFS might be a promising candidate for agricultural applications. Moreover, the attack of acetic acid alone is equivalent to the mixture of various acids found in animal manure (Bertron et al., 2005). Therefore, this study aimed to investigate the resistance of AA-NFS to acetic acid to determine its durability for use in organic acid-rich agricultural environments. By conducting such tests, we can gain a better understanding of how AA-NFS performs in harsh environments and determine its potential as a sustainable binder for agricultural applications.

Cementitious materials like AAM or cement are known to be highly alkaline materials that can become unstable when exposed to acidic environments. In particular, the hardened paste of AA-NFS comprises two solid constituents, namely unreacted slag and reacted binder. To improve the resistance of AA-NFS to acid attack, it is crucial to identify the more vulnerable component between the unreacted slag and the reacted binder. In light of this, a dissolution test was performed on both raw NFS and AA-NFS in an acetic acid solution. The resistance of the reacted binder can be determined by comparing the performance of AA-NFS and NFS under identical test conditions. Such detailed test can provide insight into the mechanism behind the resistance of AA-NFS to organic acids and into pathways to enhance its durability when exposed to harsh environments.

2 Materials and Methods

To prevent the influence of impurities in industrial NFS on the dissolution behaviour of AA-NFS, a synthetic slag that closely mimicked the real NFS chemistry was utilized in this study.

The detailed process for synthesizing the slag was described in previous works (Van De Sande et al., 2020; Wen, et al., 2021; Wen et al., 2021). The chemical composition of the slag was determined using a wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer (Bruker S8) and is presented in Table 1.

Table 1. Chemical composition of the synthetic slag (wt%).

	FeO	SiO ₂	Al ₂ O ₃	CaO
NFS	43	29	11	17

The activation of the NFS was carried out using a sodium silicate solution (Na₂O·1.65 SiO₂, with 65 wt% H₂O) which was prepared by mixing sodium hydroxide pellets, sodium silicate solution (Na₂O·3.3 SiO₂, 63.5 wt% H₂O) and deionized water.

AA-NFS paste samples were prepared by manually mixing NFS and activating solution in a liquid to solid ratio of 0.4 for 2 minutes. After curing in a sealed container for 28 days, the paste was ground by hand until passing through a 60 µm sieve for dissolution test, similar to the size of NFS. The dissolution test was carried out on both raw NFS and AA-NFS paste. 0.3 g NFS and 0.3 g AA-NFS samples were immersed in 300 g of 3 wt.% acetic acid. This high liquid to solid ratio of 1000 was chosen to prevent precipitation. The dissolution testing procedure utilized in this study was modified from a previously published method (Snellings and Jantzen, 2013). During the test, a shaking table was employed and set to operate at a speed of 150 rotations per minute. The samples were immersed for different durations of 5 min, 30 min, 2 h, 4 h, 8 h, 24 h, 48h and 168 h. After each immersion, a 10 mL solution was collected and filtered through a 0.4 µm filter paper. The filtered solution was then diluted 10-fold with 3% HNO₃ and subjected to inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis. The concentrations of Fe, Si, Al, and Ca in the solution were quantified using this analytical technique.

The mineralogy of NFS, AA-NFS and residue AA-NFS after dissolution test was determined by X-ray diffractometry (XRD, Bruker D2). It was equipped with a copper target X-ray tube operated at 30 kV and 10 mA. The XRD patterns were recorded at 2-theta from 5° to 70° with a step rate of 2° /min.

3 Results and Discussion

In this study, the mineralogy of three materials, namely NFS, AA-NFS at 28 days, and AA-NFS after exposure to acetic acid, was investigated and presented in Figure 1. The NFS was found to consist of more than 98% amorphous phase with some minor fayalite (not clear in XRD pattern but detected in microscopy). The amorphous nature of the NFS was confirmed by the absence of clear reflections. Similarly, the AA-NFS at 28 days showed a mainly amorphous character with no significant reflections observed in the XRD pattern. Additionally, subsequent to exposure to acetic acid, no discernible crystalline phases were observed to precipitate in a manner similar to that which occurs in alkali-activated fly ash specimens exposed to acetic acid, as has been reported previously (Aiken et al., 2020). However, owing to the inherent limitations of X-ray diffraction (XRD) analysis with regard to the characterization of amorphous materials, no further information regarding these structural changes could be ascertained.

Figure 2 depicts the dissolved fraction of ions present in NFS and AA-NFS during 7 days exposure in acetic acid, which was obtained by normalizing the amount of the each element leached into acetic solution over the initial amount present in the solid NFS or AA-NFS. During the initial period (up to 2 hours), the dissolution rate of AA-NFS was higher and with a higher dissolved fraction than that of NFS, especially for Ca. However, the final dissolved fraction of slag was slightly higher than that of AA-NFS with a questionable statistical relevance. The total dissolved fraction after 7 days of each element is provided in Table 2. Further analysis, employing unpublished results obtained from backscattered electron image analysis, revealed that 47.7 wt.% of unreacted slag particles remained present in the AA-NFS. This enabled the calculation of the total dissolution of the slag and reacted binder components separately, as delineated in Table 2.

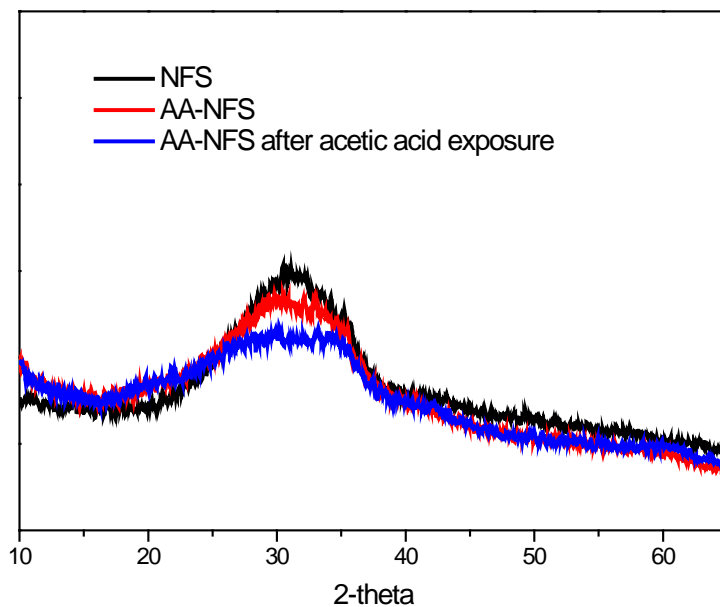


Figure 1. XRD patterns of raw NFS, AA-NFS at 28 days and AA-NFS after acetic acid attack.

Table 2. Total dissolved fraction of each element and calculated dissolution extent for slag and binder separately (%).

	Total dissolved fraction		Dissolution extent	
	NFS	AA-NFS	NFS	Binder
Si	86	67	86	43
Ca	90	89	90	74
Fe	79	76	79	62
Al	71	68	71	56

As shown in Table 2, the dissolved ratios of each element (Fe, Si, Al, and Ca) were found to vary, indicating that the dissolution of each element occurred in a distinct and individual manner, which is also the case for alkali-activated fly ash (Aiken et al., 2020). In the NFS, 90% of Ca ended up in acetic acid, and 86% Si dissolved in solution. While less Fe (79%) and Al (71%)

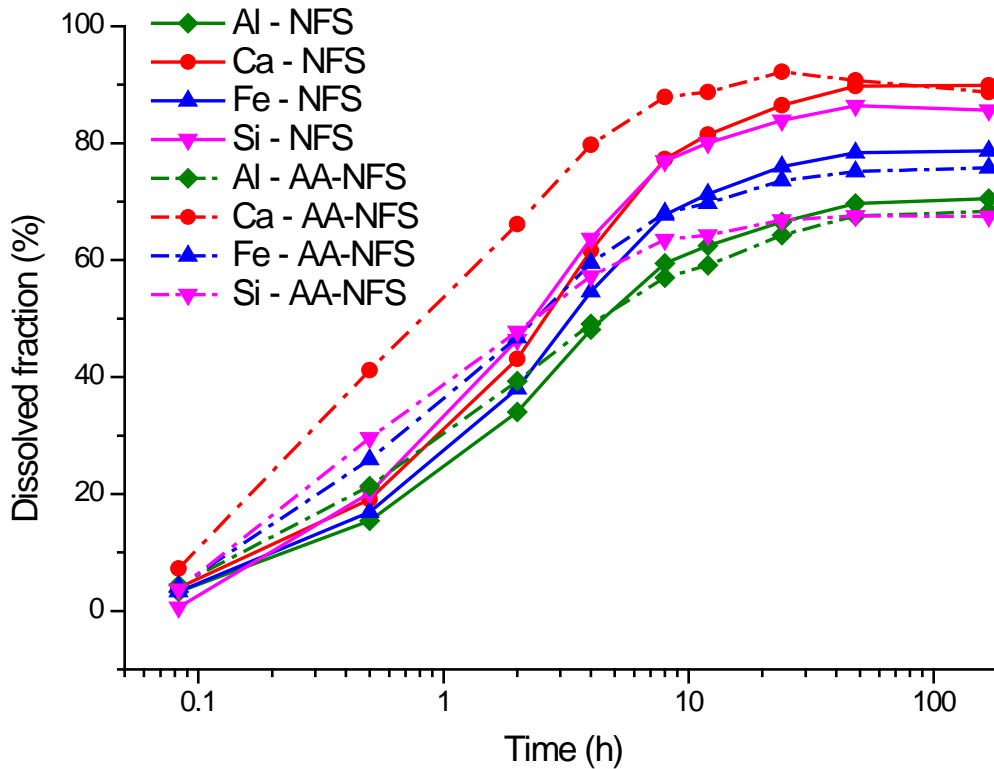


Figure 2. Calculated element dissolved fraction obtained in the dissolution tests and initial NFS and AA-NFS chemical composition.

was detected in solution. In reacted binder, similarly, Ca obtained the highest dissolution fraction (74%), followed by Fe (62%), and Al (56%). Si, on the other hand, had the lowest dissolution fraction (43%), indicating that it is more likely to remain in the matrix rather than dissolve in solution. After acetic acid attack, the reacted binder exhibits a high concentration of Fe, Si and Al. This observation provides evidence for the durability of AA-NFS in acetic acid as a previous research has reported the presence of Si, Al, and Fe in the binder improve the resistance to acidic solutions (Oueslati & Duchesne, 2012). In the context of cement, this finding can be explained from two aspects : the amount of Ca added and the mobility of the elements present in the system. A lower amount of Ca in the system results in less formation of portlandite and C-S-H, reducing the number of phases that can be consumed or reacted with acid. Additionally, the mobility of elements in the system can play a crucial role, with Ca being highly mobile compared to Fe, Al, and Si. This second perspective is particularly relevant to this work as the absence of portlandite or C-S-H in AA-NFS. Given that the AA-NFS system is characterized by low Ca content and high Fe content, it is possible that this material could offer an attractive option for deployment in organic acid rich situation.

The findings presented in Table 3 show that the initial 4-hour period of dissolution testing yielded a slope for the dissolution fraction, which was designated as the dissolution rate. Analysis of the dissolution rate indicated that slightly over half of the Ca, Fe and Al could be attributed to the reacted binder. Conversely, the dissolution rate of silicon from the reacted binder was higher than that of the unreacted slag (59% versus 41%). Collectively, these results suggest that the reacted binder dissolves at a faster rate in acetic acid than the unreacted slag

during the early stages of the dissolution process.

Table 3. Slope for dissolution rate and calculated dissolution rate source.

	Slope		Dissolution rate distribution (%)	
	NFS	AA-NFS	Unreacted slag part	Binder part
Si	0.16	0.12	59	41
Ca	0.15	0.16	40	60
Fe	0.13	0.13	45	55
Al	0.11	0.10	49	52

Although the current study provides important insights into the dissolution behavior of AA-NFS in acetic acid, it is also important to investigate the behavior of AA-NFS in other acid environments. A related our previous study (Wen, et al., 2023) reported the dissolution behavior of AA-NFS in sulfuric acid, which is another common acid often present in sewer system or agricultural structure. It was observed that both NFS and reacted binder were dissolved in sulfuric acid, but the dissolution of NFS occurred to a greater extent and at a significantly faster rate than that of AA-NFS. The majority of Ca (98%) and Si (99%) present in NFS dissolved in the sulfuric acid solution, while 65% of the Ca and only 20% of the Si in the reacted binder was detected in the acid solution. In contrast, acetic acid induces much less degradation in both NFS and reacted binder than sulfuric acid. Furthermore, the effect of acetic acid on the dissolution of NFS and reacted binder is distinct from that of sulfuric acid. Notably, the reacted binder dissolves more quickly than NFS, but to a lesser extent. All the results indicate that the behavior of AA-NFS in different environment is different, which could have implications for its use in acidic environments

4 Conclusion

In this study, we investigated the dissolution behavior of both unreacted NFS and AA-NFS in acetic acid. Our findings indicate that the reacted binder in AA-NFS dissolves more rapidly than that of NFS at the beginning, although the extent of dissolution is lower. Ca from both NFS and reacted slag is highly soluble in acetic acid, while Si dissolution shows distinct characteristics in NFS and reacted binder. Specifically, Si in unreacted NFS is relatively soluble (86%), but Si in reacted binder is more likely to remain in the matrix. The dissolution of Fe and Al in both NFS and AA-NFS is similar. This phenomenon indicated the formation of a stable matrix that is rich in Fe-Si-Al of AA-NFS after the acetic acid attack, which could prevent further acetic acid attack and contributes to its durability in acetic acid environments. Overall, the results indicate that AA-NFS has the potential as a sustainable and durable binder in organic acid environments. However, to fully understand the resistance of AA-NFS under various exposure conditions, further studies are needed. These studies could include investigating the effects of different acids or the combination of different acids, varying exposure times, and exploring the long-term durability of AA-NFS in real-world applications.

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