Effects of red mud on the properties of fresh and hardened alkali-activated slag paste and mortar

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HIGHLIGHTS

- AAS shows high potential for incorporation of RM.
- RM and RM thermally treated at 550 °C reduce the rate of consistency loss of AASR.
- Replacement of slag with 20% RM gives optimum mechanical strength.
- RM treated at 550 °C leads to better mechanical strength than neat RM.
- Kaolinite is a major clay mineral in RM that dissolves in alkaline environments.

ARTICLE INFO

ABSTRACT

Alkali-activated slag (AAS) suffers from severe performance issues, such as uncontrolled and rapid setting, unstable rheological behaviour and considerable drying shrinkage. The main objective of this study was to ameliorate these problems by incorporating raw red mud (RM) (at contents of 10, 20, 30, and 40% by weight) and RM thermally treated at 550 and 750 °C (at 40%) into an AAS system. The fresh paste properties (measured by using the flow cone method, the mini-slump cone test and a Vicat apparatus), hardened paste properties (measured by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric-differential thermal analysis (TG/DTA), XRD and scanning electron microscopy (SEM) techniques), and the mechanical strength and dimensional stability of the mortar were measured. The results indicated that incorporating RM decreased the fluidity but led to a more cohesive fresh paste with a lower consistency loss rate. With increasing RM content, both the initial and final setting times of the paste increased. The hardened paste analysis showed that the main hydration products of all the mixtures after 28 days were dominated by a C–A–S–H-type gel with a higher Al incorporation. The drying shrinkage could be explained by the cumulative pore volume in the gel pores and was larger in most samples with low RM content than that in the samples without RM.

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1. Introduction

Red mud (RM) is a by-product of the Bayer process in extracting alumina from bauxite ore in the aluminium industry. In this process, a high-concentration NaOH solution at high pressures and elevated temperatures is used to digest bauxite ore [1–3]. After alumina extraction, residue in the form of slurry is discarded and dried in large landfills. Unlike other industrial by-products, such as fly ash and slag, RM has a high alkalinity (pH between 10 and 12), which renders it a hazardous waste material [4,5]. In Iran, each ton of alumina produced yields 1.5–2 tons of RM, requiring large

disposal areas. These environmental concerns have drawn considerable attention to investigating the feasibility of using RM in various civil engineering fields [6,7].

The presence of silica, alumina, and iron oxides in RM and the alkalinity of RM indicate that this by-product may be used as an aluminosilicate source for materials in new and environmentally friendly binders, such as alkali-activated slag (AAS). As a sustainable binder, AAS is more technically advantageous than ordinary Portland cement (OPC) [8–16] and can be used with RM in the form of binary combinations [17–20]. The hydration products of alkali-activated slag-RM (AASR) were studied by Pan et al. [18] using an alkali activator composed of water glass with a 1.2 modulus and sodium aluminate clinker at concentrations of 8% and 6% of the slag content. The mixture was based on a slag/RM ratio of

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70:30 and a water/cement ratio of 0.46. An analysis of the hardened paste of the mixture showed that the hydration product is primarily C-S-H gel with a low Ca/Si ratio. Other hydration products of hardened PC, such as ettringite mineral, are absent.

Pan et al. [19] also investigated the physical properties and microstructure of the hardened AASR paste and mortar with an alkali activator and a mixture identical to those used in the aforementioned research [18]. After curing for 28 days, the AASR mortar was found to possess high compressive and bending strengths of 56.0 MPa and 8.4 MPa, respectively, which are similar to those of OPC mortar. The AASR paste exhibits better durability characteristics, such as greater resistance to carbonation, chemical attacks, and freeze-thaw cycles, than the OPC paste.

Ye et al. studied the effect of thermal treatment (from 200 to 1000 °C in the range of 100 °C) on the dissolution efficiencies of alumina and silica of RM in alkaline solution to promote its geopolymerization capability [21]. Based on the highest solubility in alkaline leaching tests, the investigators selected RM treated at 800 °C. The treated RM was applied in binary combination with slag at equal contents (50/50) and was activated by sodium silicate with a molar ratio of 1.7 in the form of AASR. The 28-d compressive strength of the paste reached 49.2 MPa. In addition, the XRD, Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM) results showed dense matrices constructed from accumulation of nanosized particulates formed from the coexistence of poorly crystalline C–(A)–S–H and amorphous geopolymeric materials.

Kang and Kwon studied the effects of replacing OPC or alkaline activator with RM at 0, 5, 10, 20 and 30% on the efflorescence in mortars with a binder-to-sand ratio of 1:3 and a water-to-binder (W/B) ratio of 0.75 [20]. They showed that with increasing RM, the compressive strength of the AASR and OPC mortar decreased. Moreover, based on the water absorption and pore size distribution of the mortars, these researchers concluded that the capillary pores increased due to RM replacement, accelerating the salt efflorescence and the consequent damage to the mortar.

The objective of this study was to investigate the effects of using RM and thermally treated RM as a replacement for iron slag in AAS paste and mortar. Various quantities of RM were incorporated into the AAS, and the fresh properties were assessed, with a particular focus on the problems commonly associated with AAS, such as poor fluidity behaviour and short setting times. The hardened pastes were analysed using FTIR, DTA/TGA, XRD, BJH and SEM techniques. Furthermore, the mechanical strength and dimensional stability of the AASR mortar were subsequently studied experimentally.

2. Materials

2.1. Slag

Ground granulated blast furnace slag (GGBS) was supplied by Sepahan Cement Co. The chemical compositions and physicochemical properties of the slag are given in Tables 1 and 2, respectively. The slag activity index of the GGBS was 62% and 108% at 7 and 28 days, respectively. Based on ASTM C989 [22], this slag was classified as grade 100. The percentage ratio of the sum of CaO, MgO and SiO_2 to slag was 81. The $(CaO + MgO)/(SiO_2)$ ratio by mass was 1.35, which exceeds the minimum value of 1.0 specified in BS EN: 15167-1 [23]. The XRD pattern of the slag in Fig. 1 exhibited a broad diffuse hump at 23–37° (2θ), indicating a high amorphous content with a glass content of 93%. The minor crystalline phases in the slag were gehlenite ($Ca_2Al(AlSiO_7)$) and akermanite ($Ca_2Mg(Si_2O_7)$).

The strong band at ~977 cm^{-1} and broad, weak band at ~714 cm^{-1} in the FTIR spectra of the slag in Fig. 2 are related to the asymmetric and symmetric stretching vibrations of the Si—O—Si and Al—O—Si bonds, respectively. The bonds at ~501 cm^{-1} (bending vibrations of the O—Si—O bands) imply the presence of orthosilicate units $[Si_2O_7]^{6-}$ with partial substitution of Si^{4+} by Al^{3+} in tetrahedral positions [24–26]. The band at ~1437 cm^{-1} belongs to the asymmetric stretching vibrations of the O—C—O bonds of CO_3^{2-}, indicating the partial carbonation of the slag [26]. The broad band centred at ~977 cm^{-1} indicates a high content of glassy phase in the structure of the raw slag [24].

2.2. Red mud (RM)

RM samples were obtained from the air-dried waste landfill of the Jajarm Alumina Plant (Iranian Alumina Co.). The XRD pattern showed that haematite (Fe_2O_3), calcite ($CaCO_3$), kaolinite ($Al_2Si_2O_5(OH)_4$), cancrinite ($Na_6Ca(Al_6Si_6O_{24})(CO_3)$), katoite ($Ca_{2.93}Al_{1.97}Si_{0.64}O_{2.56}(OH)_{9.44}$) and perovskite ($CaTiO_3$) were the main phases of the RM at room temperature. The physicochemical properties in Table 2 show that the RM is a high fineness modulus material with a low plasticity index (PI) and is classified as a natural-artificial soil. The particle size distribution of the RM was obtained by laser diffraction, as shown in Fig. 3, and by SEM, as shown in Fig. 4; the results indicate that the particle size of the RM is lower than that of the slag.

The infrared spectrum of the RM, as shown in Fig. 2, is mainly affected by the calcite and cancrinite minerals. The absorption bands at ~430 and ~460 cm^{-1} correspond to the bending vibrations of the O—Si—O bands in the SiO_4 tetrahedron; the bands at ~575 and ~620 cm^{-1} are assigned to 4- or 6-membered ring vibrations; several weak bands at ~650–700 cm^{-1} are attributed to the symmetric stretching vibrations of the Si—O—Si and Al—O—Si bridges; and the strong band between 900 and 1060 cm^{-1} and the weaker band at ~1114 cm^{-1} are associated with the asymmetric stretching vibrations of the Si—O—Si and Al—O—Si bonds [27–31]. All the abovementioned bonds are characteristic of the mineral cancrinite [32]; however, the strong band at ~995 cm^{-1} could also be affected by other minerals, such as katoite, clay minerals and other aluminosilicate minerals, that could be present in RM [29]. The strong band at 1425 cm^{-1} and the weaker band at 875 cm^{-1} are related to the stretching vibrations of the O—C—O bonds of the CO_3^{2-} groups [30] and correspond to the vibration modes of calcite [32]. The band at 1622 cm^{-1} is related to the bending vibrations of H—OH and corresponds to the water molecules inside the cancrinite cavities [33]. Additionally, the broad band between 3100 and 3700 cm^{-1} is caused by the O—H stretching vibrations related to the chemically absorbed H_2O [30].

Table 1
Chemical compositions of the ground slag, RM and cement (%).

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	MnO	LOI
GGBFS	34.25	10.75	0.45	38.57	7.75	3.16	0.59	0.96	1.75	1.49	0.02
RM	13.26	15.41	20.54	19.87	1.50	0.54	5.87	0.73	4.97	–	16.32
PC	19.98	3.50	4.11	64.73	2.07	3.79	0.15	0.63	0.27	0.20	0.35