

Potential of red mud as raw material for alternative binders in concrete

Ivana Vladić Kancir¹, Asst. Prof. Marijana Serdar²

¹Sveučilište u Zagrebu, Građevinski fakultet, Zavod za materijale, ivana.vladic.kancir@grad.unizg.hr

²Sveučilište u Zagrebu, Građevinski fakultet, Zavod za materijale, marijana.serdar@grad.unizg.hr

Abstract

Storage of large quantities of industrial by-products can pose a serious environmental problem. There is a growing need to recycle these industrial by-products, including red mud, in the construction industry, which is one of the largest consumers of raw materials. A preliminary study of the potential of red mud as a raw material for concrete is presented in this paper. Chemical composition of red mud, determined by X-ray fluorescence and particle size distribution by laser diffraction, is tested as part of its initial evaluation. The reactivity of red mud is evaluated by the R3 test method with isothermal calorimetry. The compressive strength test is carried out on a mortar sample in which 30% by weight of cement is replaced by red mud. Preliminary tests indicate that red mud can be used as raw material in alternative binders.

Key words: red mud, compressive strength, R3 test, supplementary cementitious material, concrete

Potencijal crvenog mulja kao sirovine za alternativna veziva za beton

Sažetak

Skladištenje velikih količina industrijskih nusproizvoda može predstavljati ozbiljan ekološki problem. Sve je veća potreba za recikliranjem tih industrijskih nusproizvoda, uključujući crveni mulj, u građevinskoj industriji koja je jedan od najvećih potrošača sirovina. Ovaj rad pokazuje preliminarno istraživanje potencijala crvenog mulja kao sirovine za beton. Kao dio početne procjene crvenog mulja prikazan je njegov kemijski sastav, određen rendgenskom fluorescencijom, i raspodjela veličine čestica, određena laserskom difrakcijom. Reaktivnost crvenog mulja procijenjena je metodom R3 baziranom na izotermalnoj kalorimetriji. Ispitivanje tlačne čvrstoće provedeno je na uzorku morta u kojem je 30% mase cementa zamijenjeno crvenim muljem. Preliminarni rezultati pokazuju da se crveni mulj može koristiti kao sirovina u alternativnim vezivima.

Ključne riječi: crveni mulj, tlačna čvrstoća, R3 ispitivanje, mineralni dodatci, beton

1 Introduction

Due to an increased demand for housing caused by population growth, concrete consumption has increased to such an extent that it has become the second most frequently used material in the world after water [1]. It is estimated that the cement industry alone will be responsible for 24 % of total global CO₂ emissions by 2050 [2]. In order to meet people's need for urbanisation, while meeting European targets for protecting natural resources and reducing emissions, there is a strong motivation to develop more sustainable construction solutions with lower environmental impact, and in line with the seventh basic requirement for construction - the sustainable use of natural resources [3].

CO₂ is emitted during production of Portland cement clinker in two ways, namely a) through the energy input required to heat the cement kiln and b) through the decarbonization of calcium carbonate (CaCO₃) [4]. The first case accounts for 40-50 % of emissions during production, while the chemical reaction of calcium carbonate releases accounts for the rest. Considering that the raw material in Ordinary Portland cement (OPC) consists mainly of CaCO₃ (75 to 79 %) [4], the above-mentioned emissions can significantly be reduced by large-scale replacement of clinker with cement-like additives (SCM). Alternative materials that can be used in sustainable concrete structures are mainly industrial by-products in the form of finely crushed material that is added to the cement as partial replacement in order to improve certain properties and/or create some special properties [5].

Disposal of non-ferrous industrial and municipal solid waste has always been an important environmental issue. Red mud (RM) is a typical non-ferrous industrial solid waste [6]. RM is a bauxite residue from the Bayer process, which is used in alumina production. The Bayer process is the most important industrial process for refining bauxite to produce alumina (aluminium oxide). Bauxite, the main aluminium ore, contains only 30-54 % alumina (alumina), Al₂O₃, while the rest is silica, iron oxides and titanium dioxide. Alumina must be purified before it can be refined into aluminium. In the Bayer process, bauxite is decomposed by washing with warm sodium hydroxide solution, NaOH, at a temperature of 175°C. This converts the alumina in the ore to sodium aluminate, 2NaAl(OH)₄, according to equation (1):



Other bauxite components can not be dissolved. The solution is cleaned by filtration to remove solid impurities. The mixture of solid impurities is called red mud (RM) and is a problem for disposal [7]. In addition, open land disposal of RM contaminates the environment, causing ecological imbalance. Annual emissions of red mud are estimated at more than 70 million tons worldwide [8].



Figure 1. Red mud landfill [9]

In Southeast Europe, there are several active aluminium processing plants and red mud landfills, which remain at the plant site even after plant closure. In Croatia, the inactive Jadral plant near Obrovac has been closed since 1982, but a 720 000 m³ landfill is still there. In Montenegro, Uniprom KAP is an aluminium plant that produces over 120,000 tons of alumina per year. Its waste is disposed of in two large landfills nearby, each of which contains over four million tons of waste. There are also two red mud landfills in Bosnia and Herzegovina at Birač near Zvornik and at Dobro Selo near Mostar. The landfill in Dobro Selo contains over ten million tons of waste and represents a potential threat to the environment.

Chemical composition of RM depends on the bauxite ore and the refining process. The most important chemical compounds in RM are iron oxide (Fe₂O₃), aluminium oxide (Al₂O₃), sodium oxide (Na₂O), silicon dioxide (SiO₂), titanium oxide (Ti₂O), and calcium oxide (CaO) [10]. RM is also highly alkaline in nature. Conventional methods for the disposal of red mud at a landfill near the factory were simple and inexpensive. However, potential impact on the surrounding groundwater and environment, and difficulties associated with surface remediation, have led to significant changes in waste management practices. The use of RM has been limited due to its high iron content, presence of alkalis, and very small particle size.

Studies have been carried out on the use of RM as raw material in various industries, such as in brick industry, ceramic tile production, chemical industry and in the production of metal absorbents [10]. RM is an alkaline, cement-like material and can be used as a partial substitute for cement to reduce CO₂ emissions and soil pollution through the disposal of RM [11]. In addition, RM has high alumina and silica content [12]. When cement is hydrated, calcium hydroxide reacts with silica in the RM cement, thus increasing the strength of the concrete [13]. The presence of aluminates and ferrites increases the reactivity of silica in cementitious materials [14]. Senff et al [15] and Tang et al [16] prepared cement mortar in which up to 50 % of cement was replaced with RM. They reported that the compressive strength and tensile strength decreased with an increase in RM content. Another study by Ribeiro

et al. [17] revealed that an increase in the amount of RM used to replace cement shortened the setting time and reduced pozzolan reactivity, which in turn reduced the strength of cement mortar. On the other hand, it has been reported in literature that RM can improve resistance of concrete to chloride penetration due to its filling effect and high alkalinity [18]. Iron oxide and aluminium oxide are predominant chemical compounds in RM, and they potentially improve the surface layer that protects reinforcement from carbonation and chloride ion attack [18]. The use of RM in alkali activated materials (AAM) has also been investigated by some researchers [26-29]. In most cases, it was used in combination with other aluminium silicate minerals such as metakaolin and fly ash [19]. It has been observed that the AAM red mud exhibits reasonable compressive strength [19]. In addition, alkali activation makes it possible to significantly increase the quantity of red mud incorporated in cement and concrete without impairing physicommechanical properties of cement and concrete [20].

The aim of this research is to evaluate basic properties of red mud from a land-fill in Bosnia and Herzegovina as part of a more systematic approach to screening by-products and waste streams as potential raw materials in concrete. Previous research has shown that red mud from Dobro Selo, Mostar, Bosnia and Herzegovina, reduces mechanical properties of concrete but improves its durability properties, especially its resistance to chloride diffusion. The same red mud source was used for this research and, as a first step in the research, chemical and physical properties of red mud, as well as its reactivity, were analysed by determining heat development with calorimetry, and strength development.

2 Materials and methods

2.1 Materials

Red mud (RM) from Dobro Selo near Mostar, Bosnia and Herzegovina, was evaluated in this study. In addition, fly ash from Tuzla and cement CEM I 42.5 R were used for comparison purposes. Both red mud and fly ash were first dried in an oven for 24 ± 2 h at $60 \pm 5^\circ\text{C}$ and then ground in a disc mill for 2 minutes.



Figure 2. Dried samples of red mud and fly ash

2.2 Methods

2.2.1 Chemical composition

Chemical composition of the materials was determined by X-ray fluorescence (XRF) in cooperation with the accredited laboratory “HEP-proizvodnja d.o.o.”, Central Chemical-Technological Laboratory, Zagreb. The materials were tested in two conditions: “as received” and after being dried at 110 °C. The difference in the results depends on moisture content of the material. Relevant results presented here are those obtained in dry condition.

2.2.2 Particle size distribution

Particle size distribution (PSD) was tested using the laser diffraction method with the MASTERSIZER instrument (Malvern instruments) at EPFL Federal Institute in Lausanne, Switzerland. The test was performed according to the guidelines [22]. Before the test, the sample was dispersed in a specific solvent. The prepared liquid was dispersed in an ultrasonic bath for 15 minutes and then placed on a magnetic stirrer until the room temperature was reached. A laser diffraction test was then performed.

2.2.3 Reactivity by calorimetry

The R3 test [24], developed for the RILEM TC-267 committee, was used to determine reactivity of red mud and fly ash. This was carried out at 40 °C by isothermal calorimetry, and it involved determination of the total release of hydration heat from the paste composed of the SCMs, for 7 days. Before the test, SCMs and dry reagents were weighed, mixed and held at 40 ± 2 °C for 24 h. The formulation of solid blends relies on the ratio of $\text{Ca(OH)}_2/\text{SCM}$ and CaCO_3/SCM of 3 and $\frac{1}{2}$, respectively. In addition, an alkaline solution 3M of K was prepared with KOH and K_2SO_4 . The pastes with red mud and fly ash were prepared in a high shear mixer at 1600 ± 50 rpm and mixed for 2 minutes until a homogeneous paste was obtained. The pastes were immediately poured into a glass vial and placed in the isothermal calorimeter. The cumulative heat release acquired was given per g SCM. The corresponding results are shown in Figure 6.

2.2.4 Evolution of compressive strength

Standard mortars were cast according to HRN EN 196-1 [23] to determine strength development of the blends. Mortar samples were prepared with CEM 1 45.2 R, and 30 % of the cement mass was replaced by red mud and fly ash. The water-binder

ratio was constant, i.e. 0.5. The standardized sand was used as aggregate and there was no need for water adjustment. After casting, 40 x 40 x 160 mm samples were covered with plastic foil and kept for 24 h under laboratory conditions. After demoulding, the samples were cured in a damp chamber until the test time. The compressive strength test was determined on 2 prisms after 2, 7, and 28 days of curing.

3 Results

3.1 Characterization of red mud

Table 1 shows chemical analysis of cement CEM I 42.5 R, red mud (RM), and fly ash (FA). The main RM constituents are Fe_2O_3 , SiO_2 and Al_2O_3 , which account for about 75 % of the total composition. Compared to fly ash, red mud has a lower content of silicon dioxide and a higher content of iron oxides. Furthermore, red mud has a significantly higher content of Na_2O (7.23 % compared to 0.26 % in fly ash) and a lower content of SO_3 (0.24 % compared to 1.48 % in fly ash).

Table 1. Chemical composition of red mud, fly ash and cement

| Constituents | Red mud | Fly ash | CEM I 42,5 R |
|-------------------------|---------|---------|--------------|
| P_2O_5 | 0.47 | 0.36 | |
| Na_2O | 7.23 | 0.26 | |
| K_2O | 0.18 | 1.51 | |
| CaO | 9.96 | 11.52 | 64.04 |
| MgO | 0.61 | 2.78 | 1.83 |
| Al_2O_3 | 16.94 | 19.11 | 4.86 |
| TiO_2 | 4.13 | 0.52 | |
| Fe_2O_3 | 37.88 | 9.05 | 2.94 |
| SiO_2 | 21.95 | 53.28 | 19.32 |
| MnO | 0.43 | 0.13 | |
| SO_3 | 0.24 | 1.48 | 2.75 |

3.2 Particle size distribution

The particle size distribution of RM is shown in Figure 3. Red mud particles range from 0,05 to 65 μm in size. The highest number of particles is in the range of 0,1 – 1 μm . Compared to fly ash samples and Portland cement samples, where most particles are between 1 and 100 μm , RM particles are finer.

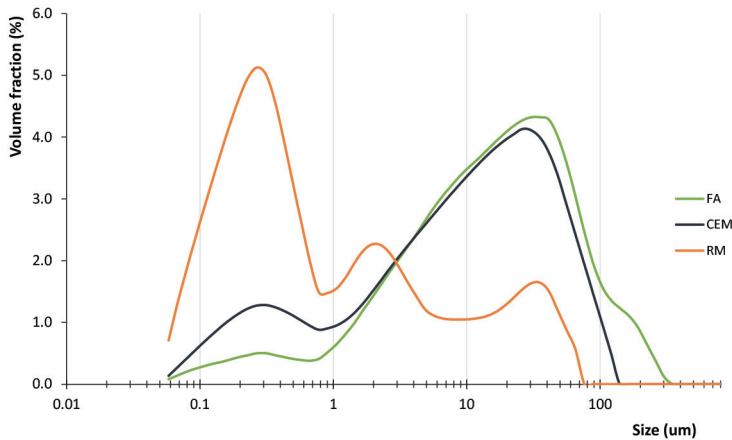


Figure 3. Particle size distribution of red mud (RM), fly ash (FA) and cement (CEM)

3.3 Mechanical properties of mortar samples

Compressive strength results are shown in Figure 4. A mixture with 30 % red mud (RM) showed lower compressive strength results than the OPC mortar after 28 days. However, a rapid increase in strength can be observed after 2 days for the sample with RM. The fly ash sample initially exhibited a lower compressive strength than the RM sample, but the fly ash sample strength was higher after 7 and 28 days.

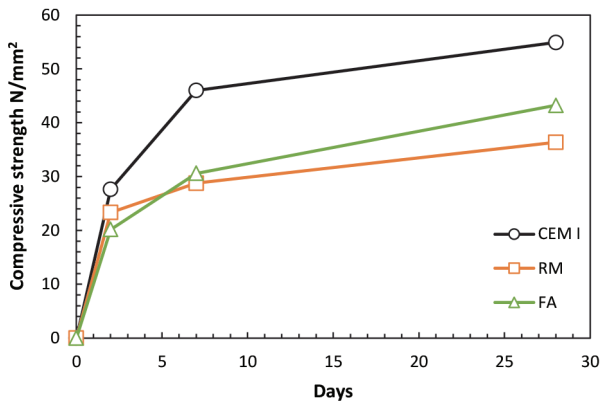


Figure 4. Compressive strength results for mortar samples with cement (CEM I), 30 % of red mud (RM) and 30 % of fly ash (FA)

This difference in strength increase is particularly evident when looking at relative compressive strength values in Figure 5. The relative strength is defined as the ratio

of strength results obtained from the mixtures to compressive strength results of the OPC mortar sample.

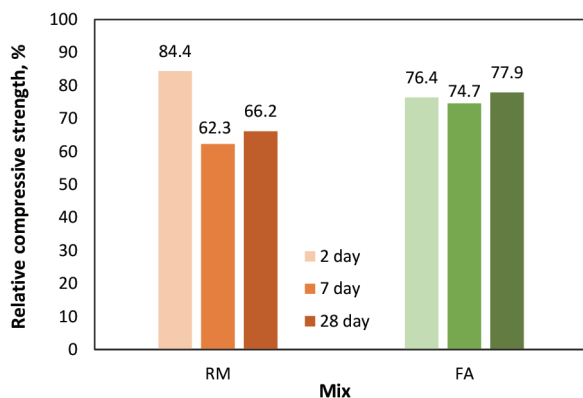


Figure 5. Compressive strength of mortar with 30 % replacement by red mud (RM) and fly ash (FA) relative to mortar with cement

3.4 Pozzolanic reactivity of red mud

Figure 6 shows the total heat release during the R3 test performed on red mud and fly ash. According to the R3 test [23], the amount of heat can be used to assess the reactivity of SCMs. During the first 5 hours, the red mud sample showed a higher heat release, indicating a fast initial reaction. Compared to red mud, fly ash showed a slower initial reaction, but a higher long-term reactivity. These results are in strong agreement with compressive strength results.

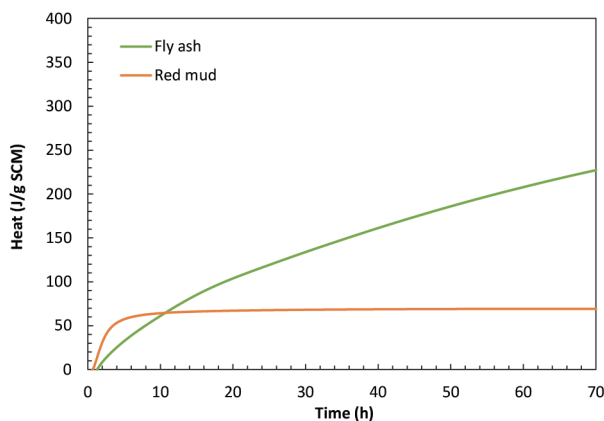


Figure 6. Results obtained by heat release measurement via R3 test using isothermal calorimetry

4 Conclusion and further research

The red mud used in this research is characterised as a very fine powder consisting mainly of Fe_2O_3 , SiO_2 and Al_2O_3 , which account for about 75 % of its total composition. A large amount of alkalis is also characteristic of this waste material. The largest proportion of particles is in the range of 0.1 - 1 μm . Both the heat development and the compressive strength development showed that red mud reacts very quickly during the first few hours, and that later on it has low reactivity, especially compared to fly ash.

Based on the presented analysis, it can be concluded that the red mud used in this research has a potential as a raw material for concrete production. Even though strength tests show lower values, due to the large number of fine particles, red mud could potentially improve durability properties of concrete and ensure the filling of fine pores. Further research, which is to consider high levels of alumina and silica and high alkalinity, will be focused at developing alkali-activated binders based on red mud. In addition to durability aspect, possible radioactivity of red mud will be investigated in further research, which might narrow its potential for use in construction industry.

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