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Vladić Kancir, Ivana; Serdar, Marijana

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# Synergy of red mud, calcined clay and limestone in cementitious binders

Ivana Vladić Kancir<sup>1</sup>, Asst. Prof. Marijana Serdar<sup>2</sup>

<sup>1</sup> University of Zagreb, Faculty of Civil Engineering, Department of Materials, ivana.vladic.kancir@grad.unizg.hr

<sup>2</sup> University of Zagreb, Faculty of Civil Engineering, Department of Materials, marijana.serdar@grad.unizg.hr

## Abstract

Previous research has shown that the reuse of bauxite residues from alumina production, also known as red mud, has potential for use as a cement substitute, especially when combined with other supplementary cementitious materials. The idea behind this research was to investigate the synergy between locally available red mud, clay, and limestone. The synergy study included measurements of heat of hydration at paste level and compressive strength on mortar samples. The mineralogical composition of the mixed binder was analysed by thermogravimetric analysis, which is an indirect method for the confirmation of mineral phases. The investigations revealed that there is a positive synergy between the red mud, clay and limestone and that, with good optimization, a higher cement replacement can be achieved without affecting mechanical properties of mortar.

*Key words: red mud, synergy, clay, limestone, heat of hydration, compressive strength*

# Sinergija crvenog mulja, kalcinirane gline i vapnenca u cementnim vezivima

## Sažetak

Prijašnja istraživanja su pokazala da uporaba boksitnog ostataka prilikom proizvodnje aluminija, također poznatog i kao crveni mulj, ima velik potencijal za korištenje kao zamjenski materijal za cement, posebno u kombinaciji s drugim mineralnim dodatcima. Ideja ovog istraživanja bila je detektirati sinergiju između lokalno dostupnog crvenog mulja, gline i vapnenca. Sinergija navedenih materijala istražena je mjerenjem topline hidratacije na razini paste kao i tlačne čvrstoće na uzorcima morta. Mineraloški sastav miješanog veziva analiziran je termogravimetrijskom analizom koja je indirektna metoda za potvrđivanje mineralnih faza. Istraživanje je pokazalo da postoji sinergija između crvenog mulja, gline i vapnenca te da se uz dobru optimizaciju može postići veća zamjena cementa bez narušavanja mehaničkih svojstava morta.

*Ključne riječi: crveni mulj, sinergija, glina, vapnenac, topline hidratacije, tlačna čvrstoća*

## 1 Introduction

Cement industry is nowadays making great efforts to reduce environmental impact of cement production by using, for instance, waste materials from different industries in blended cements. Large quantities of supplementary cementitious materials (SCM) such as fly ash, granulated blast furnace slag, silica fume, and natural pozzolans have been used in cement industry for many years [1], [2]. On the other hand, availability of commonly used SCMs is decreasing. For example, due to coal exit strategy in Europe, the amount of fly ash is declining [3]. For that reason, other waste materials, that could be used as partial replacement for cement, are being researched.

Over the last few decades, a lot of attention has been attributed to bauxite residue also known as red mud [4, 5]. Red mud is a by-product from aluminium industry, and it is generated from the bauxite ore refining in the scope of the Bayer process. In the Bayer process, after bauxite digestion with sodium hydroxide, the insoluble product is called red mud. This material is widely available and it is produced in great quantities. Between 0.8-1.5 tons of bauxite residue are produced per one ton of alumina produced, [6] resulting in reserves of approximately in excess of 2.7 billion tones worldwide [7]. Chemical composition of red mud is rather complex. Since bauxite ore is washed with the high alkaline sodium hydroxide, it is not surprising that red mud is a highly alkaline slurry of pH 10-13.5 and is therefore considered a great environmental threat [8].

The application of red mud is limited because of the presence of alkalis, high iron content, and very fine particle size distribution, [9]. However, many studies conducted so far have proven the utility of using red mud as construction material [5, 10, 11]. Even though red mud has a lower quantity of reactive silica and calcium than usual SCMs, the idea of its use in concrete is still present. High alkali content in red mud can help achieve a synergic effect between the usual SCMs like slag, fly ash, clay, or limestone [12]. Furthermore, researchers have established that a highly alkaline environment, which is characteristic of red mud, can promote hydration of Portland cement [13]. According to studies, red mud can achieve good synergic effect in cement blends with hydrated lime, fly ash, and silica fume, due to its high alkalinity [11].

The idea behind this research was to investigate synergic effect between red mud, calcined clay and limestone, which are considered as SCMs, in cement composites. 20 % of cement by weight was replaced with red mud in all mixtures. Also, in addition to red mud, clay and limestone were added to the mixtures in order to explore the hydration, compressive strength, and hydration products of such composites. All materials used in this study were sourced from different industrial processes such as aluminium production, stone quarry and clay excavation sites, and they all originated from areas close to the cement production plant in Croatia.

## 2 Materials, mix design and methods

### 2.1. Materials

Materials from the region were used in combination with commercial cement, CEM I 42.5 N, produced by Holcim Koromačno, Croatia. The red mud (RM) used in the study is a waste from alumina production in Dobro Selo, Bosnia and Herzegovina. The limestone (LS) sample originates from the quarry in Zvečaj, Arkada, Croatia. The Clay (C) sample, calcined at 800 °C for one hour, originates from brick production in Cerje Tužno, Croatia. Chemical composition of all the materials is given in Table 1. Additionally, the appearance of raw materials and their SEM equivalents is shown in Figure 1.

Table 1. Chemical composition of materials (wt. %)

	CEM I	Red mud	Clay	Limestone
SiO <sub>2</sub>	19.3	21.9	62.4	20.2
Al <sub>2</sub> O <sub>3</sub>	4.9	16.9	21.3	4.3
Fe <sub>2</sub> O <sub>3</sub>	2.9	37.9	7.3	1.4
CaO	64.0	10.0	2.2	71.6
MgO	1.8	0.6	1.8	1.7
SO <sub>3</sub>	2.8	0.2	0.1	0.1
Na <sub>2</sub> O	0.2	7.2	1.5	<0.01
K <sub>2</sub> O	0.8	0.2	2.5	0.1
P <sub>2</sub> O <sub>5</sub>		0.5	0.4	0.4

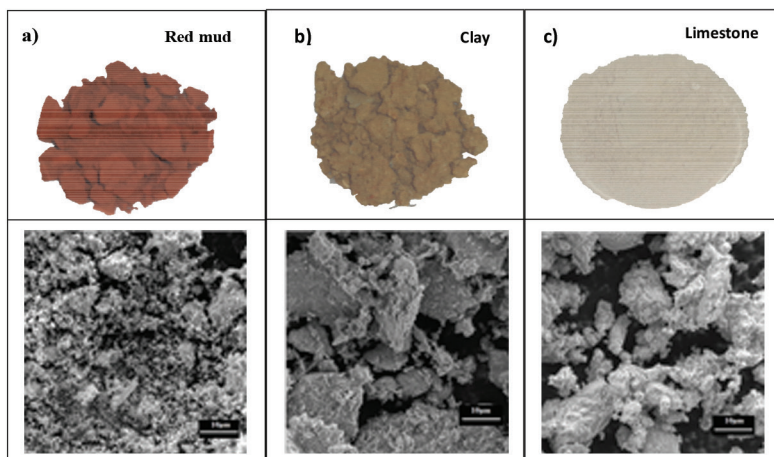


Figure 1. Images of raw materials (top) and their microscopic images (bottom)

## 2.2 Mix design and methods

### 2.2.1 Mix design

Cement was replaced by red mud (RM) in all mixtures in the amount of 20 % by weight, and then additionally by clay (C) also in the amount of 20 % by weight. Furthermore, 5 % of limestone (LS) was added to the mixture. Mixtures were labelled with the amount of cement replacement and abbreviation of the material. For example, in mixture 20RM20C5LS cement was replaced with 20 % of red mud, 20 % of clay, and 5 % of limestone.

**Table 2. Mix proportions of cement composites**

Mix label	Mass ratio within the binder (%)			
	CEM I	RM	C	LS
CEM	100	0	0	0
20RM	80	20	0	0
20RM20C	60	20	20	0
20RM20C5LS	55	20	20	5

### 2.2.2 Methods

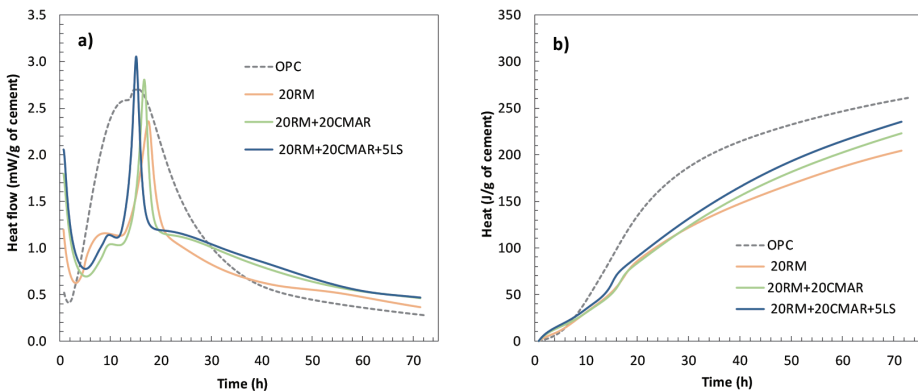
In order to evaluate the synergy between red mud, clay and limestone, the heat of hydration of the reference and blended pastes, with different binder compositions, was determined using the 8-channel TAM Air isothermal calorimeter. For each mix, 10 g of fresh paste with 0.5 w/b ratio was prepared, mixed outside the calorimeter, cast into glass vials, and then placed into the calorimeter. The heat of hydration was measured for 3 days at 20 °C.

The thermogravimetric analysis (TGA) was performed with TGA 55, TA instruments on mortar samples after 2, 7, and 28 days. 50±5 mg samples were heated from 40 °C to 1000 °C, at a constant heating rate of 20 °C and a nitrogen flow of 40mL/min. The compressive strength test was performed on mortar samples. The samples were cast in 40 x 40 x 160 mm moulds, all according to EN 196-1. The samples were demoulded after 24 hours and cured in moisture chamber (20 °C and 95 % RH) until testing time. The compressive strength was tested after 2, 7 and 28 days, according to EN 196-1.

### 3 Results

The heat of hydration of the OPC, red mud only system and red mud + clay + (limestone) are shown in Figure 2. Generally, the first peak corresponds to the hydration silicate phases in the isothermal calorimetry curve of the OPC, while the second peak is associated with the reaction of the aluminate phases [14]. When red mud is added to the system, the second peak becomes more pronounced in blended systems.

The red mud sample contains a relatively high amount of alumina compared to the OPC sample, as shown in Table 1. The presence of alumina affects the second or shoulder peak of hydration in calorimetry by increasing it [5], [15]. Moreover, the percentage of alkalis in the red mud system is higher than in the OPC system, which are present due to the origin of red mud, and alkalis could advance the second peak of hydration because the presence of alkalis affects hydration of aluminates [16]. Hydration curves change further once the calcined clay is added to the system. The second peak is more pronounced when clay has been added, probably due to the synergy with red mud, where the alkalis from red mud enhance the aluminate reaction, and alumina content is even higher with clay in the system. The activation of aluminate phases seems to improve with the addition of limestone. With 5 % of limestone, the second peak occurs earlier and is even more pronounced. Additionally, the total heat released per gram of cement is higher with limestone addition, compared to binder with red mud and calcined clay only.



**Figure 2.** Heat flow a) and cumulative heat b) curves of the systems with red mud and clay (without and with the addition of limestone) obtained by isothermal calorimetry for 72 hours

The differences in hydration products occurring in OPC sample and blended mixes were analysed using TGA on 28-day-old mortar samples. The corresponding results are shown in Figure 3. The amount of portlandite decreased in the mixes with ce-

ment substitution, which is indicated by the peak between 400 °C - 500 °C [17]. This peak is higher in the mixture with limestone than in the mixture with red mud and clay only.

A smaller peak, present in mixed systems in the range between 110 °C and 160°, proves formation of Afm phases [18]. This peak has not been observed in the OPC system. The appearance of the peak between 60 °C and 100 °C is usually caused by the decomposition of ettringite, CSH and CAH gel.

In the system with limestone, the curve changes and both the first and second peaks seem to decrease, which is probably related to the differences in the Afm phase where monocarboaluminate forms instead of monosulphate. This change can explain an increase in compressive strength [19].

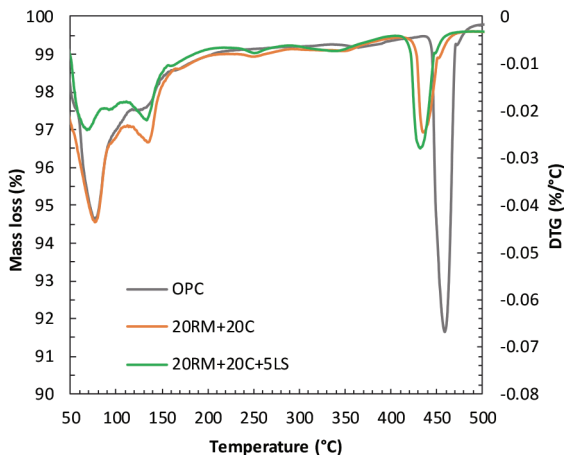


Figure 3. Derivative of mass loss (DTG curve) for mortar mixtures after 28 days of curing

Compressive strength results for mortar prepared with red mud, clay, and limestone are presented per mass of cement in Figure 4. These results reveal that the addition of clay causes decrease in early strength, compared to mix with red mud only. The synergy between red mud and clay is evident after 7 and 28 days of curing when higher strength is reached. On the other hand, when 5 % of limestone is added, both early and later strength increase, especially after 28 days. It can be observed that even small content of limestone improved synergy between red mud and clay, due to its filling effect and the additional amount of calcium interacting with alumina hydrates [19]. Compressive strength results are in good correlation with the heat of hydration.

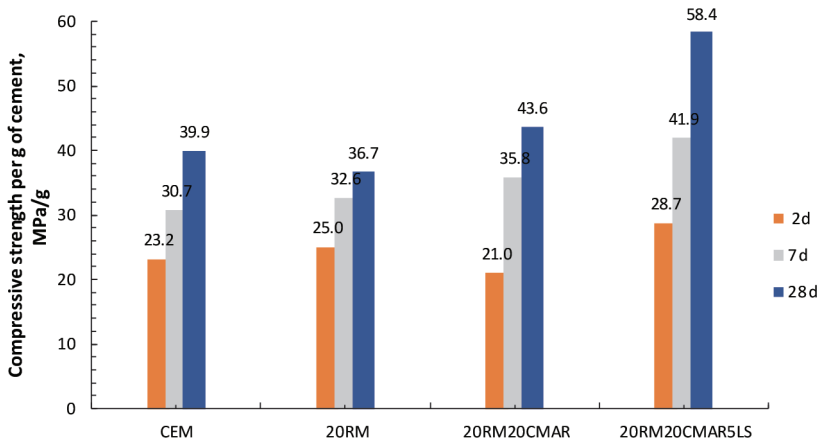


Figure 4. Compressive strength of mortar per gram of cement after 2, 7 and 28 days

## 4 Conclusion

The synergy between red mud, clay and limestone was investigated in this study. The heat of hydration of the pastes was measured and compared with compressive strength to determine if the synergy exists. Thermogravimetric analysis was also carried out to determine if the microstructure was altered by the addition of red mud, clay, and limestone. The results show that there is an interaction between clay and red mud, and that this interaction improved with the addition of limestone. The addition of limestone improved the reactivity of the alumina based mixtures and resulted in higher compressive strength. Moreover, with the addition of limestone, the (dTG) curve also changed, indicating a change in the phases where monosulphoaluminate was converted to monocarboaluminate. This change can explain the increase in compressive strength. This study showed that, with a good combination of materials and favourable optimization, a higher amount of cement can be substituted with SCM providing satisfactory mortar properties.

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