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The effects of red mud on clay compounds

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Abstract. Recent study focused on the mixing properties of the clay and red mud compounds and the effects of red mud addition on clays with and without earth alkali carbonate content. Raw materials were added to compounds in natural form. Raw materials were applied as received in order to examine how mixing is possible in natural form without drying and grinding the red mud into powder. Highest amount of red mud content (50 wt%) was determined by mixing experiment. Compounds were prepared in pan mill and samples were extruded and analysed. Results indicated that red mud behaved in different way in carbonate and carbonate free clay but it is applicable for manufacturing of heavy clay products. It also revealed that the adequate mixing of red mud into the clay body is one of the most important question of the industrial application.

1. Introduction

Utilization of industrial by-products (e.g. fly ash, red mud etc.) and handle them as secondary raw material becomes more relevant as their volume grow constantly causing increasing dumping cost. Beside economical side they also may cause environmental problems. During Bayer-process in aluminium production, highly alkaline red mud is generated from the reaction of mineral bauxite and sodium-hydroxide. The production of 1 ton aluminium results 0.5-1.5 tons of red mud as waste material. There are several patents and studies dealing with the re-use of red mud in several industrial branch [1-3]. Among them the heavy-clay ceramic industry seems to be one of the possible field where huge volume of it may be consumed. In the production of fired ceramic building blocks beside red mud other organic waste material or by-product are also applied such as rice hull, paper sludge or marble powder [4-8]. In recent years, researchers studied the red mud in clay matrix, for example the change of microstructure in composition during heat treatment, physical and chemical properties of the manufactured samples were also analysed [9-17]. Based on researches above it can be said that the reuse of the red mud in brick clay resulted suitable products which fulfil the technological requirements. In these earlier studies [9-17] there is a uniformity: the raw materials were dried and ground in order to set the proper water content and to help the better mixing of the materials. However, in the heavy clay industrial practise it does not have the technical background for handling a huge volume additive material (i.e. red mud) at the present time. Beside drying, the grinding of red mud would demand also large energy consumption and introduction of the red mud into the production also requires to build up a technological line for raw materials preparation (i.e. special dryers and mills with powder technology system). Maybe that is why the one of the reasons why the red mud consumption is reported mainly in scientific articles. On the other hand, the utilization of red mud consumption in the heavy-clay industry has another aspect as well. Red mud has significant amount of natural radionuclide content of bauxite as residual from the Bayer-process. These materials

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are the naturally occurring radioactive materials (NORM) like ^{226}Ra, ^{232}Th or ^{40}K [18,19,22]. A study on raw materials found that the addition of Hungarian red mud is not proposed over a limit in order to fulfil EU recommendations on activity concentration index (I) of the mix (i.e. clays + red mud). Analysing 27 of hungarian brick clays [20], the maximal mixing ratio of red mud was calculated between 12-39 wt%. However, heat-treatment of the samples can reduce the risk originating from exhaled radon [21] which may elevate the volume of used secondary materials.

Based on the above considerations, we applied the raw materials as received in order to examine how mixing is possible in natural form without drying and grinding the red mud into powder. For brick and roof tiles, the earth alkali carbonate content of the clay affects the colour, water absorption and porosity of the fired products determining the frost-resistance. Clays with and without earth alkali carbonate content were selected to examine the effects of red mud addition on the properties of the products.

2. Materials and methods

2.1. Materials

For the purpose of examining clay and red mud compounds, three clays were obtained from two Hungarian brickworks. Two of them, which will be mixed later, consist considerable weight percentage of carbonates while third clay is carbonate free. The clays were named as follows: Grey clay – carbonate clay: GCC; Yellow clay – carbonate clay: YCC and the carbonate free clay: CFC. The red mud (RM) was obtained from the upper surface of an old Hungarian dump. Before the preparation of the compounds, the mineral composition of the raw materials was analysed by X-ray Powder Diffraction (Rigaku Miniflex II, Cu Kα, 2θ range from 3 to 90°). The quantitative results were calculated by Rietveld full-profile refinement analysis. The XRD patterns and the results are presented in Figure 1. and Table 1. respectively. After sampling, the water content of the raw materials was measured by RADWAG MA50 moisture analyser. Results are also included in Table 1.

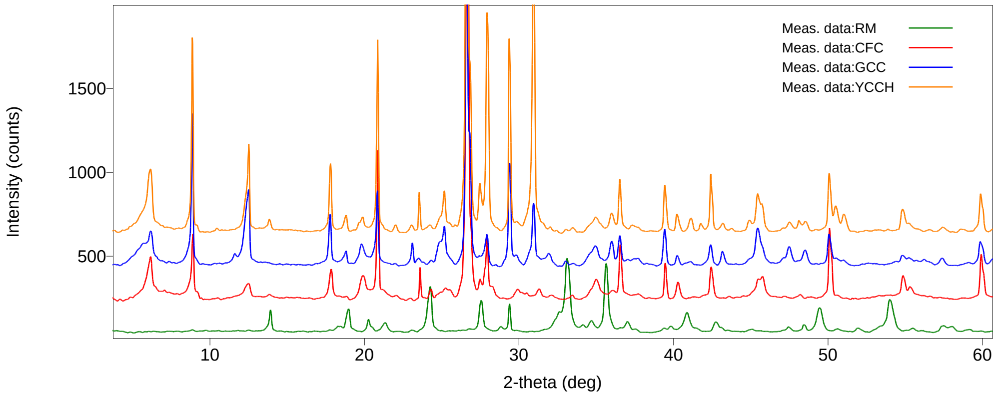

Figure 1. XRD patters of raw materials

Table 1. Mineral composition of raw materials

Raw mat.	Q	I	M	A	SM	G	K	M	C	D	CH	AM	WC
GCC	43.2	13.7	5.3	6.7	4.5	1.1	0.3	6.9	6.3	11.1	0.8	8	12.7
YCC	29.7	25.1	6.8	3.2	7.1	0.5	6.1	1.9	13.4	3.6	2.7	0	14.3
CFC	41.1	24.2	5.0	5.5	6.1	3.3	6.7	4.4	-	-	2.3	10	12.5
	Q	GI	C	H	CA	G	KI						
RM	1.0	7.2	5.5	44.2	32.9	4.5	4.7					0	33.1

(Q: quartz; I: illite; M: muscovite; SM: smectite; A: albite; G: goethite; K: kaolinite; M: microcline; C: calcite; D: dolomite; CH: chabazite; AM: amorphous content; WC: water content – H: hematite; GI: gibbsite; CA: cancrinite; KI: kimzeyite;)

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GCC and YCC contain high amount of calcite and dolomite. The quantity of clay minerals was similar for YCC and CFC while the lowest was at GCC. In red mud hematite and cancrinite were the main phases.

2.2. Methods

2.2.1 Mixing and sample preparation

As raw materials were added to compounds in natural form without drying and grinding, it was necessary to take the nature of clays into account. Adequate mixing of two plastic materials having different water content required more experiment, as paste with higher plasticity could flow around the less plastic material. Red mud was received in soil wet form with around 33 % water content, so it behaved as a paste. The YCC and CFC were soft clays. GCC had very stiff nature so according to industrial practice a pre-grinding was applied. GCC and YCC clays were blended together in the ratio 1:3 and 2:3 to form a carbonate clay mix.

During preliminary mixing experiments, taking the original moisture content of the raw materials (Table 1.) into account, moisture content of the compounds was set to 22 wt% which was most suitable to produce samples by extrusion.This determined the maximal amount of RM that is incorporated into the compound. Both carbonate (CC) and carbonate free clay (CFC) were mixed with different amounts of red mud ranging from 0 to 50 wt% (Table 2.). The masses were homogenized by laboratory pan mill (Figure 2.) and the technical water was also added at this stage gradually. Mixing period was 5 minutes for each compounds. For CFC, increasing amount of red mud, the mass showed an improved consistency. Homogenized mass was illustrated in Figure 3.

Table 2. Composition of prepared compounds in wt%

Carbonate clay/ RM	100/0	90/10	80/20	70/30	60/40	50/50
Carbonate free clay / RM	100/0	90/10	80/20	70/30	60/40	50/50

Figure 2. Laboratory pan mill

Figure 3. Homogenized mass

After preparation, masses were sealed and rested for 48 hours. KEMA, PVP5/s type laboratory vacuum extruder with 50mm screw diameter was used to produce 12 pieces of cylindrical samples for each compounds. The diameter of extruded specimens was 24 mm and the length was 50 and 150mm. After extrusion, samples were dried for 24 hours long at room temperature and for 48 hours long in drying chamber at 90 °C. Sintering was performed in a laboratory furnace at 860 °C, with the heating rate of 150 °C.

2.2.2 Testing methods

For discover cracks, colour differences or other faults, the steps of preparation of the samples were followed by a visual inspection. Considering that, the red mud is strongly alkaline (pH=13) the pH value was also measured in some steps of production. In order to follow the effects of red mud on the most important properties of the produced brick samples, typical brick industry tests were performed on the samples according to the related standards, such as drying and firing shrinkage, compressive strength, bending strength, density, and water absorption. For measuring flexural strength, samples with 150 mm length were applied. Average results obtained from the examination of compounds containing RM are illustrated in Figures 5-10.

3. Results and discussion

3.1 Mixing

During mixing experiments, it was observed that the type and the moisture content of clays determine the way of the mixing RM to clay. It was necessary to find a water content to set the proper consistency of the clays. It was not possible to mix the materials together at any moisture content. Larger pieces of the harder material were flowed around by RM having lower consistency without mixing. If the clay was softer, it was also not possible to press the RM among the clay particles as the two material slipped away on each other.

3.2 PH measurement

The original RM samples was strongly alkaline with the pH value of 13. That is why the condensate from the clay strip after extrusion and the evaporated moisture after drying were analysed by pH measurement. According to this, the condensates were no harmful as it showed a neutral pH. This is beneficial for industrial application of RM.

3.3 Colours

The change in colours can be seen in Figure 4 after drying and firing. The impact of red mud on colours was stronger visibly after drying. Firing caused a decrease in the colours difference. RM balanced the yellow colour of fired CC samples to “brick red” owing to its high iron-oxide content. On surface of CC samples there were lot of lime concretion.

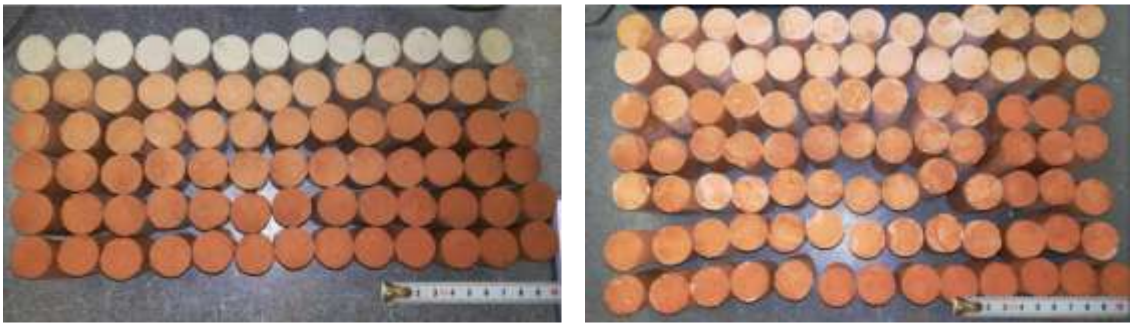

Figure 4. Colour difference after drying and firing

3.4 Drying losses and drying shrinkage

The drying loss in both clay was the same as the percentage of water added. The effect of RM addition on drying shrinkage is illustrated in Figure 5. The shrinkage of carbonate clay (CC) with additional RM slightly increased in all cases while the shrinkage of carbonate free clay (CFC) decreased from 20.41 % to 12.21 %. Overall, CFC samples which content RM showed less shrinkage. The pure CC had 4 % higher shrinkage value as CFC.

3.5 Burning shrinkage and density

The numerical values of shrinkage and density can be seen in Figure 6 and Figure 7, respectively. The CC had around 29 % of shrinkage value which is relatively high related to CFC. The amount of red mud had no significant effect on the firing shrinkage of the CC. At CFC samples with additional 10 % RM, the shrinkage decreased from 21.2 % to 18.3 %. Lager amounts of RM in CFC had but not tendentious effect on shrinkage value. The maximum is 23.82 % (at 30-40 wt%) RM, which is 10 % change related to pure clay. Compare to CC to CFC the shrinkage was always higher at CC.

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In all cases, samples of CFC had higher density. For the two types of clays, RM behaved in similar way. Density of CC without RM was increased from 1,81 g/cm^3 to 1,91 g/cm^3 up to 30 wt% RM addition. Over this value density began to lower. The effect of RM on CFC was parallel in grow to CC but in this case the density increased up to 40 wt%. For both CC and CFC, the pure clay samples had the lowest density.

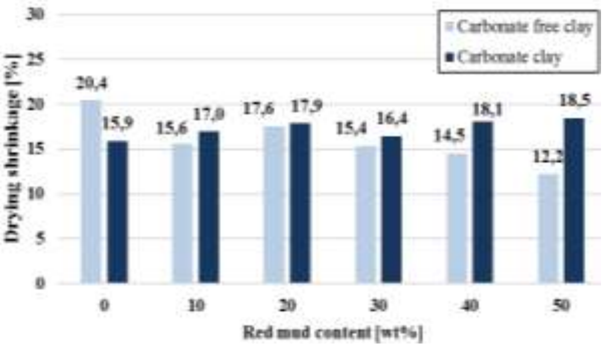

Figure 5. The effect of RM on drying shrinkage

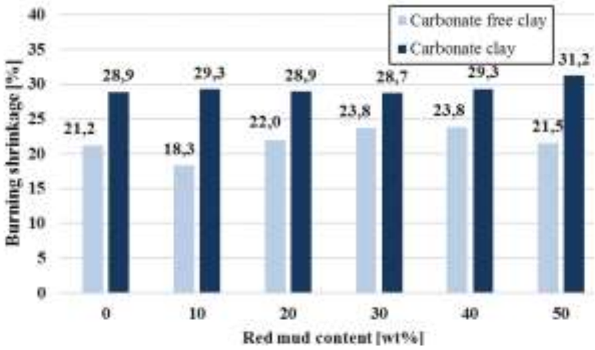

Figure 6. The effect of RM on firing shrinkage

For CC and CFC, RM affected the water absorption similar in tendency (Figure 8). Up 30 wt% RM content in CFC, there was no considerable change, the CFC held its closer structure. Over 30 wt% of RM, absorption capacity raised from about 14.4 % to 21.6 %. Correspondingly, adding over 30 wt% RM to CC, RM facilitated higher water absorption by opening more pores on the surface of the samples.

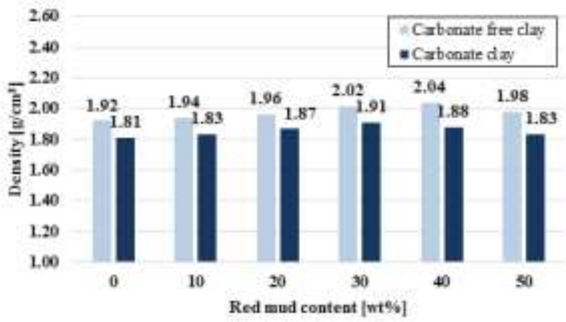

Figure 7. The effect of RM on density

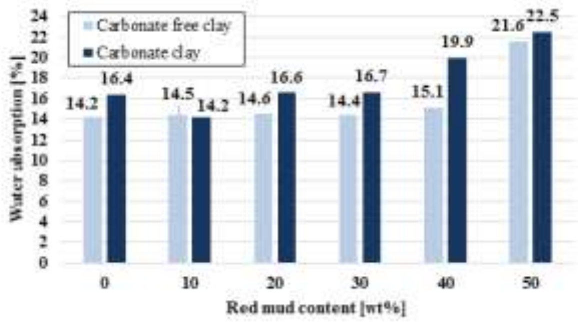

Figure 8. The effect of RM on water absorption

Adding RM to CFC had good effect on compressive strength (Figure 9.) since pure clay has the lowest strength value. Up to 40 wt% RM content the strength increased constantly from 23.8 to 36.8 MPa. It represented an 54% increase in strength. Other researchers experienced the same but at higher sintering temperature [12]. For CC, the use of RM caused lower compressive strength than the pure clay except at 30 wt% RM addition where it was higher. The more RM added to clays, the more it contained calcite which resulted in more open pores. It caused higher water absorption and lower strength.

For CFC samples, RM addition up to 20 wt% had no significant effect on flexural strength (Figure 10.). Similar to compressive strength at 30-40 wt% RM content in CFC resulted the highest strength value. Adding RM to CC, flexural strength decreased in tendency. Higher strength value at 10 wt% of RM content was only obtained.

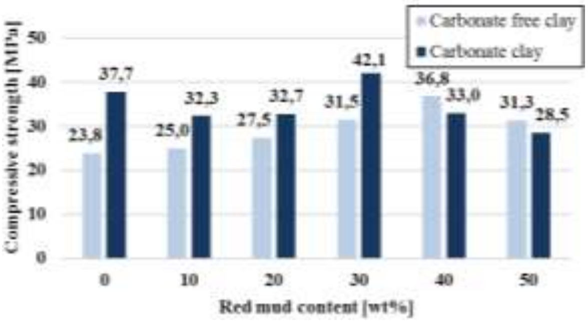

Figure 9. The effect of RM on compressive strength

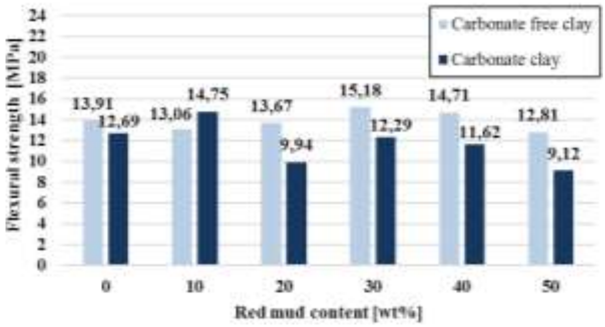

Figure 10. The effect of RM on flexural strength

4. Conclusions

Clays and RM were added to compounds in natural form without drying and grinding. The moisture content of clays determined the maximal amount of RM (50 wt%) that can be mixed into compounds. Adequate mixing of two plastic materials having different water content required more experiment, as paste with higher plasticity could flow around the less plastic material. It was observed that if the red mud content was higher than 50 wt%, than the compound became more plastic and the extrusion was not possible. The type and the moisture content of clays determined the way of the mixing RM to clay. It was not possible to mix the materials together at any moisture content. We controlled and set the proper water content for mixing to had the adequate plasticity of the compounds.

The test results of extruded and fired products showed that firing shrinkage of CC and RM compounds were always higher than that for CFC. In all cases, samples of CC had lower density owing to the high carbonate content.

The RM content in CFC and CC up 30 wt% had no considerable change in water absorption. On the contrary, adding over 30 wt% RM to CC, RM facilitated higher water absorption by opening more pores on the surface of the samples.

Adding RM to CFC had good effect on compressive strength. For CC, the use of RM caused lower compressive strength than the pure clay. It raised the compressive strength for CFC since up to 40 wt% RM content the strength increased constantly from 23.8 to 36.8 MPa as but it was decreased for CC. RM affected the values of compressive and flexural strength inordinately.

According to these results it can be said that usage of RM in heavy clay industry is possible without expansive drying and grinding the RM into powder.

5. Acknowledgement

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6. References

[1] C Klauber, M Gräfe and G. Power 2011 *Hydrometallurgy* 108 pp 11–32
[2] R K Paramguru, P C Rath and V N Misra 2005 *Mineral Processing & Extractive Metall. Rev.* **26** pp 1-29
[3] W.Liu, J. Yang and B. Xiao 2009 *Int. J. Miner. Process*. **93** pp 220–231
[4] K Junge 2000 *Ziegelindustrie Internationa*l **12** pp.25-39
[5] Z Xuanye 2003 *Ziegelindustrie International* **4** pp.22-27
[6] V Ducman and T Kopar 2007 *Materials and technology* **41/6** pp. 289–293
[7] I Kocserha and L A Gömze 2010 *Applied Clay Science* **48/3** pp 425-430
[8] F Kristaly, L A Gömze and I Papp 2010 *Materials Science Forum* **659** pp 37-42
[9] V M Sglavo, S Maurina, A Conci, A Salviati, G Carturan and G Cocco 1999 *Journal of the European Ceramic Society,* **20** pp 245-252
[10] Y Pontikes, P Nikolopoulos and G N Angelopoulos 2007 *Journal of the European Ceramic Society,* **27** pp 1645-1649
[11] H He, Q Yue, Y Su, B Gao, Y Gao, J Wang and H Yu 2011 *Journal of Hazardous Materials* **213-214** pp 53-61.
[12] L. Pérez-Villarejo, F.A. Corpas-Iglesias , S. Martínez-Martínez, R. Artiaga, J. Pascual-Cosp 2012 *Construction and Building Materials* **35** pp 656-665.
[13] H He, Q Yue, Y Qi, B Gao, Y Zhao, H Yu, J Li, Q Li and Y Wang 2012 *Applied Clay Science* **70** pp 67-73
[14] S Pişkin, A K Figen, E Özkan and Ü Özçay 2013 *IFAC Proceedings* **46** pp 484-487.
[15] M P Babisk, T P Altoé, H J O Lopes, U S Prado, M C B Gadioli, S N Monteiro and C M F Vieira 2014 *Materials, Science Forum* ***798-799*** pp 509-513
[16] S Liu, X Guan, S Zhang, C Xu, H Li and J Zhang 2016 *Materials Letters* **191** pp 222-224.
[17] C Scribot, W Maherzi, M Benzerzour, Y Mamindy-Pajany and N E Abriak 2018 *Construction and Building Materials* **163** pp 21–31
[18] J Somlai, V Jobbágy, J Kovács, S Tarján and T Kovács 2007 *Journal of Hazardous Materials* **150** pp 541–545
[19] S Landsberger, A Sharp, S Wang , Y Pontikes and A H Tkaczyk 2016 *Journal of Environmental Radioactivity* **173** pp 97-101

[20] Z Sas, J Somlai, G Szeiler and T Kovács 2015 *Journal of Radioanalytical and Nuclear Chemistry* **306** pp 271–275
[21] Z Sas, J Szántó, J Kovács, J Somlai and T Kovács *Journal of Environmental Radioactivity* **148** pp27-32
[22] S S Nenadovic, G Mucsi, L M Kljajevic, M M Mirkovic, M T Nenadovic, F Kristály and I S Vukanac 2017 *Nuclear Technology & Radiation Protection* **32/3** pp 261-266