Plasticity of Red Mud and Clay Mixtures

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Abstract. Recent study is focusing on the plasticity properties of clay and red mud (RM) mixtures. Two different clays were examined with (carbonate clay, CC) and without earth alkali carbonate (carbonate free clay, CFC) content. Red mud with 32 wt% moisture content was added for dried and powdered clays. Maximum applicable red mud content (30 wt%) was determined by mixing experiment. The mixtures were prepared by pan mill and samples of 33 mm in diameter and 40 mm in height were pressed. Measurements were obtained with 20, 22, 24 and 26 wt% moisture content in each mixture. Two methods were used for measurement and characterization of the plasticity of clay body. Beside determination of Pfefferkorn plasticity index, deformation curves of different samples were also recorded and analysed. Results indicated that red mud affected the forming behaviour of clays. Addition of red mud may rise the energy consumption of extrusion process.

1. Introduction

Red mud (RM) is highly alkaline by-product of Bayer-process. As a huge volume can be found worldwide of this material, utilization of it generated many research works. Based on lots of scientific studies on several fields of application, RM may be considered as secondary raw material. It seems to be useable in several branch in ceramic and silicate industry, like cement production, glass ceramics, ceramic glazes, concrete and mortar production or geopolymerization. Among them the heavy-clay ceramic industry seems to be one of the possible fields, where huge volume of RM may be consumed [1-17]. The re-use of RM is possible not only in powdered form [5-15], but it can be added to clay in plastic consistency, as well [18]. In latter, there is a restriction in water content of red mud. If it is too high, red mud became very sticky and its dosage became impossible. In deposits, red mud usually has high water content, however its surface level could partly get dry. Dewatering technique are required, like filter press [19] in order to decrease water content to 32-35 wt%. Mixing red mud into clay is only possible under this water content value [18]. For extrusion technique in heavy clay industry, clay mixtures should have sufficient plasticity. Clay minerals, additive materials, water content, particle size distribution effects on the plasticity of a clay or a clay mixture – generally on clay-water system [20,21]. Several practical tests have been developed to determine and describe plastic behaviour with certain figures or indices like Pfefferkorn, Atterberg or cone penetration methods. Beside them, more precise, but time-consuming techniques, like capillary rheometry are also used, which resulted the total flow curve of a plastic material [22,23]. As strength, porosity or wear resistance would be the main behaviour of ceramic materials [24-28], former studies focused mainly on the analysis of products based on raw materials incorporated with red mud [5-15]. The effect of red mud addition on the plasticity of brick clay mixtures is not fully known [29]. As red mud has paste consistency and it consist of mainly fine particles, it would be expected that it behaves like plastic body, so it contains a small amount of clay minerals, so
the flow behaviour and the amount of adsorbed water are caused by the high surface area and not the ions as it is in case of the clays and silts [30,31]. This would be the base for that a rheological analysis of red mud indicated its thixotropic behaviour, so its viscosity changes during forming. Adding RM to clay, plasticity changes, which affects the operation and energy demand of shaping technology. The aim of this study is to examine and describe the effects of RM on the plasticity with the help of the two different measuring method.

2. Materials and Methods

2.1 Raw materials

For the purpose of examining clay and red mud mixtures, three clays were obtained from two Hungarian brickworks. Two of them consist considerable weight percentage of carbonate, 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 mixtures, 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.

| 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 |
| RM | 1.0 | 7.2 | 5.5 | 44.2 | 32.9 | 4.5 | 2.3 | 10 | 12.5 |

(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: kimezeyite)

**Figure 1.** XRD patterns of raw materials
2.2 Mixing and sample preparation
An industrial clay mixture was prepared by mixing GCC and YCC and used as carbonate clays (CC). RM with 32 wt% water content was added for dried and powdered clays. Maximum applicable RM content (30 wt%) was determined by mixing experiment [18]. After that mixtures were prepared by pan mill, cylindrical samples of 33 mm in diameter and 40 mm in height were manually pressed for both measurement method. The moisture contents of mixtures were set to between 20 and 28 wt% in order to get more point to distinguish from each other. Table 2. indicated the composition of mixtures. The mixtures were marked as follows: code for clay (CC or CFC) + RM content - e.g. CC10 means carbonate clay with 10wt% RM content.

Table 2. Composition of prepared mixtures in wt%
| Carbonate clay (CC)/RM | 100/0 | 90/10 | 80/20 | 70/30 |
| Carbonate free clay (CFC)/ RM | 100/0 | 90/10 | 80/20 | 70/30 |

2.3 Testing methods for plasticity
In order to describe the effects of red mud on the clays, numerical values of plasticity (or formability) were determined by applying two methods. For both techniques, three samples were used and average value were represented on figures as a results. Overall 48 samples were prepared for each test, separately.

Pfefferkorn method
Pfefferkorn test was the first method for measuring of plasticity. This is a simple practical method and it is based on the principle of impact deformation. Pfefferkorn’s plasticity number or index shows the percentage water content, at which the sample is pressed to 1/307 ratio. A defined sample with a diameter of 33 mm and an initial height of 40 mm, is deformed by a freefalling plate with a mass of 1.192 kg. The initial height is related to the impact deformation, the result is the ratio of deformation. The ratios of deformations or the impact deformation heights ($H_0$, initial height; $H_f$ final height) are plotted against the water content. [20,21]

Compression test
Compression test was also applied on cylindrical samples to evaluate the plasticity of clay and RM mixtures. Samples were compressed with deformation rate of 60 mm/min on an Instron 5570 Universal Material Tester and stress-deformation curves were recorded (96 curves). Similar to metals, yield stress was obtained from the curves according to Figure. 2. Stress value was the basis of comparison. [20]

Figure 2. Determination of yield stress from stress-strain curve
3. Results and discussion

3.1. Pfefferkorn plasticity

Plasticity curves according to Pfefferkorn can be seen on Figure 3 and Figure 5 for CC and CFC clay and RM mixtures. Figure 4 and Figure 6 show an example for deformation of samples with different water content. Plasticity indices and determination coefficients obtained from curves were summarized in Table 2.

![Figure 3. Pfefferkorn plasticity curves for CC mixes](image)

**Figure 3.** Pfefferkorn plasticity curves for CC mixes

![Figure 4. CC mix samples with 30 wt% RM content](image)

**Figure 4.** CC mix samples with 30 wt% RM content

![Figure 5. Pfefferkorn plasticity curves for CFC mixes](image)

**Figure 5.** Pfefferkorn plasticity curves for CFC mixes

![Figure 6. CFC samples with 30 wt% RM content](image)

**Figure 6.** CFC samples with 30 wt% RM content

| Mixture | RM [wt%] | R²   | m   | b   | Plasticity index | Mixture | R²   | m   | b   | Plasticity index |
|---------|----------|------|-----|-----|-----------------|---------|------|-----|-----|-----------------|
| CC0     | 0        | 0.96 | 1.94| 17.19| 23.49           | CFC0    | 0.99 | 1.15| 18.84| 22.57           |
| CC10    | 10       | 0.95 | 3.54| 16.06| 27.57           | CFC10   | 0.99 | 1.89| 18.05| 24.19           |
| CC20    | 20       | 0.94 | 5.94| 13.05| 32.36           | CFC20   | 0.95 | 1.47| 20.27| 25.04           |
| CC30    | 30       | 0.66 | 5.32| 15.23| 32.50           | CFC30   | 0.98 | 5.70| 14.53| 33.05           |

Table 3. Pfefferkorn plasticity index for CC and CFC clay mixtures

![Table 3](image)
The steeper the curve, the “shorter” the body, i.e. the more intensely the body will react to variations of the water content [21]. Regarding plasticity index of clays without RM, CFC had higher plasticity, than CC i.e. less water was enough to reach to 30% contraction. Adding RM to clay, plasticity index increased for both clays. Increasing the amount of RM from 0% to 30% resulted an increase in index value by 18% for CC and by 32% for CFC mixtures. Results show that the use of RM as clay replacement material made clay mixtures harder, energy demand for processing would be higher.

3.2. Compression test and yield stress determination
Compression test was performed on all mixtures with different RM and water content. Figure 7. and Figure 8. present two typical stress-displacement curves for CC and CFC with 22 w% water content. According to Figure. 2., yield stress values obtained from curves and their average values were illustrated on Figure 9. and Figure 10. as function of RM content. Numerical values were summarized in Table 4.

Analyzing Figure 7. and Figure 8., it can be seen, that higher RM content means steeper curve, so clay-RM mixtures become stiffer. Forming of mixtures with RM require more force and higher energy consumption. This tendency was the same for all CC and CFC compounds.

![Figure 7. Stress-deformation curves of CC and RM mixes (22 wt% water content)](image)

![Figure 8. Stress-deformation curves of CFC and RM mixes (22 wt% water content)](image)

![Figure 9. Yield stress as function of RM content for CC](image)

![Figure 10. Yield stress as function of RM content for CFC](image)

| Table 4. Yield stresses of clay-RM compounds |
|---------------------------------------------|
| **Mixture name**                           |
| Water content [wt%]                        |
| Yield stress σ_{0.2} [MPa]                 |
| CC0  | CC10 | CC20 | CC30 | CFC0 | CFC10 | CFC20 | CFC30 |
|------|------|------|------|------|-------|-------|-------|
| 20   | 0.073| 0.083| 0.103| 0.147| 0.025 | 0.050 | 0.065 | 0.095 |
| 22   | 0.040| 0.063| 0.080| 0.110| 0.020 | 0.030 | 0.065 | 0.070 |
| 24   | 0.033| 0.040| 0.063| 0.057| 0.010 | 0.020 | 0.045 | 0.045 |
| 26   | 0.020| 0.027| 0.043| 0.033| 0.010 | 0.010 | 0.025 | 0.030 |
4. Conclusion
Plasticity of mixtures of carbonate and carbonate free clays with RM were analyzed by Pfefferkorn and compression test methods. Results obtained from both methods proved that RM decreases the plasticity of clay mixtures. Same water content, but lower plasticity means higher forming force and higher energy consumption in processing and forming technology. According to these and former results, the usage of RM in heavy clay industry is possible without expensive drying and grinding of RM up to 30 wt%. However, in heavy clay industry if clay as mined is too 'fat', opening agents (usually natural sand) are added to the mixture in order to decrease the plasticity. Taking into account environmental issues, beside incorporating in clay, primer raw materials, like sand can be replaced with RM.

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