Comparison of advanced hydraulic properties between treated and untreated bauxite residue

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Abstract. Advanced hydraulic characteristics of treated and untreated Bauxite Residue (Red Mud) are studied and compared using a Steady-State Centrifugation (SSC) Unsaturated Flow Apparatus (UFA). Red Mud is the by-product waste from the Bayer process during aluminum production that has shown the potential of being reused as fill material in embankment construction, which can reduce the energy consumption of disposing the mining waste and producing fill materials. There is a limited number of documented studies on unsaturated hydraulic characteristics of RM. Furthermore, the high alkalinity ($\text{pH} > 12$) of the bauxite slurry is a challenge for reusing the material. Past studies have shown two effective and economic neutralization methods: (i) mixing with seawater and (ii) addition of gypsum. This study utilizes Cal State LA centrifuge facilities to characterize the unsaturated hydraulic properties of the treated and untreated Red Mud. The experimental results are used to develop the Soil Water Retention Curve (SWRC) for the three types of Bauxite Residue: untreated, treated with saline solution, and treated with gypsum. The results show that adding gypsum is more effective than mixing with saline solution in reducing the pH value of RM, and the samples treated with saline solution provide the lowest range of unsaturated hydraulic conductivity values compared with the other two types.

1 Introduction

Bauxite Residue, also called Red Mud (RM) is a slurry by-product waste generated during the Bayer Process, a common technique for alumina production [1] that uses a high quantity of oxides, creating an alkaline material with very high pH value (>12). This fact creates an environmental concern since only a small proportion of the slurry is reused, and it is commonly disposed near to the alumina plants into clay-lined impoundments, levees, or dry stacking [1]. Previous studies have shown the potential of reusing relatively large volumes of waste for different industries like transportation, iron production, construction, and fill for levees [2]. Reusing RM can create a win-win scenario in reducing energy consumption: the cost of mining waste disposal and fill material production. However, to reuse Red Mud, reducing the pH value is paramount. Experimental studies were conducted in the past trying to reduce the pH of bauxite residue, by mixing it with different types of solutions (e.g., strong acids, seawater, gypsum, and carbon dioxide) [3]. Two techniques were identified to be more economical and effective: (i) mixing RM with seawater and (ii) addition of gypsum.

Coastal companies use seawater neutralization to precipitate carbonates and hydroxides in RM to reduce the pH value before transporting and storing the materials [4].

Since the seawater is widely available, it's an economical option [3]. Laboratory neutralization tests were performed with seawater at different ratios of red mud to seawater (e.g., 1:2, 1:10, 1:20, and 1:50 by volume) to prepare RM to be used as a soil amendment for agriculture [5]. Seawater was irrigated through RM, resulting in a reduced pH level range of 8 to 8.5 after several weeks, with the benefit of adding plant nutrients (e.g., Ca, Mg). A study comparing different techniques of bauxite residue neutralization, [4], concluded that the utilization of 20 liters of seawater for each gram of the waste is the most effective rate for a better pH reduction.

Gypsum is a material commonly used as a fertilizer, and because of its chemical composition, it is seen as a good option for pH and alkalinity reduction [4]. Utilizing gypsum waste from fertilizer manufacture, Glenister [6] investigated the ability of Gypsum to the decrease in RM alkalinity. Research results show that 50 to 60 g of gypsum per kg of red mud are needed to reduce the alkalinity. The effectiveness of this material to lower the pH of RM from 12.5 to 8 was investigated by Courtney and Kirwan [8].

The basic geotechnical characterization of untreated RM was determined in several research projects. Most of the results point to the Bauxite Residue behaving similarly to inorganic silt or silty clay with low plasticity, according to the Unified Soil Classification System (USCS).

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Compaction test results per the ASTM D698 standard have shown the maximum dry unit weight to be 16 kN/m^3 with an optimal moisture content close to 30%. The range of strength characteristic of RM is very wide, with friction angles ranging from $27 - 46^\circ$. For hydraulic properties, Xenidis and Boufonos [10] tested bauxite residue, utilizing a flexible wall permeameter, and found the waste has a saturated hydraulic conductivity ranging from 3×10^{-5} to $4.6 \times 10^{-7} \text{ cm/s}$, depending on the degree of compaction. Gore [3] also conducted tests on RM, using flexible and rigid wall permeameter, following ASTM standards D5084 and D5836, and obtained similar results, for hydraulic conductivity (3×10^{-6} to $7 \times 10^{-7} \text{ cm/s}$). Unsaturated hydraulic characteristics are not as available in the literature as other basic geotechnical properties. This information is essential for utilizing Red Mud in geotechnical applications such as above-ground embankments.

The first goal of this research project is to evaluate and compare the two popular methods used to neutralize bauxite residue: seawater and gypsum. Besides, this research sheds light on the unsaturated hydraulic properties of RM by measuring the unsaturated hydraulic conductivity and matric potential of untreated and treated bauxite residue using the steady-state centrifugation method [11,12].

2 Materials and Methods

Bauxite residue was obtained from Golder Associates Inc. for this study. The waste was collected as part of a project site investigation from a bauxite ore refining facility on the eastern side of India. Bulk samples were collected (in 5-gallon buckets) from one of the red mud ponds located at the facility. Confidentiality with the refinery's owner restricts providing further information.

2.1. Neutralization Process

Brunori et al. [13] and Johnston et al. [4] claim that the desired level for pH is within the range of 7 to 9 for waste storage, transport, and future plant growth. In general, the pH value for the untreated RM is around 12. For this experimental study, the pH goal was set to below 9.

2.1.1 Saline Solution

A saline solution was prepared in the lab mixing tap water (commonly used in levee construction) and non-idolized sodium chloride to create a saline solution with a concentration of 35 g/L (close to seawater) using a mixer device (Fig. 1a). Saline solution was added to RM at a ration of 20L per kilogram of RM. Samples 1 and 2 were prepared with 750 g and 250 g of Red Mud respectively, samples 5, 6, and 7 were all prepared with 500g of RM. After the mixing procedure, pH readings were measured daily with the assistance of a meter (Fisher Scientific, XL 25) which can be seen in Fig. 1b.

Fig. 1. (a) The mixer used to prepare a saline solution and (b) meter used to measure the pH level.

2.1.1 Gypsum Solution

Following Glennister's observation of the optimum utilization of gypsum [7] to neutralize the pH of RM, a mixing ratio of 60 g of gypsum for 1 kg of RM was adopted for this research. For samples 3 and 4, an amount of 2 kg of RM was used. Gypsum was dissolved in tap water to improve the mixing process. Once the solutions reached the desired level (< 9), they were dried using an oven at a temperature of 93°C .

2.2 Sample Preparation

Centrifuge specimens are installed inside the centrifuge within a stainless-steel container, according to the ASTM Standard D6527, and prepared. The preparation consists of two parts: (1) compaction in a standard compaction mold and (2) coring a sample for a centrifuge test at the center of the compaction mold.

Previous compaction data has shown an gravimetric Optimum Moisture Content of 30% [3] for the material tested, however, during the coring procedure, the compacted RM sample undergoes consolidation, causing a significant loss of water during the process. Therefore, after multiple trials, the target water content was changed to 33%. Following ASTM standards D698, RM samples were compacted using standard proctor effort and with a standard compaction mold.

A coring device (Fig. 2) was used to retrieve a centrifuge specimen from a compacted RM sample. The coring device includes a plastic holder, a highly permeable filter paper, and a steel coring capsule.

Fig. 2. Coring assembly used to remove the soil samples.

With the assistance of a hydraulic jack, the coring device was pushed into the compacted RM (Fig 3a). Then the centrifuge specimen (RM inside a cylindrical plastic holder) is removed from the coring device (Fig. 3b). The plastic holders are made explicitly for the SSC-UFA facility with a radius of 3.3 cm and a height of 4.9 cm

Fig. 3 Samples after the coring process (a) and trimming (b).

The centrifuge specimen was weighted using a lab-scale to confirm the proximity to the targeted unit weight (98% of maximum dry unit weight). The compaction and sample coring procedures were repeated until the unit weight of the centrifuge specimen is within 5 % of the target. Afterward, the specimens were saturated inside a glass breaker with a water level no higher than 2/3 of the sample height for at least 24 hours. ASTM standard D6527 does not require the specimen being fully submerged during saturation. After saturation, the specimen was weighed again and assembled in the UFA apparatus to start the centrifugation process.

2.3 Steady-State Centrifugation (SSC)

Steady State Centrifugation (SSC) method was implemented utilizing an Unsaturated Flow Apparatus (UFA) to determine the unsaturated hydraulic conductivity (K) and the matric potential (ψ) as functions of the volumetric water content (θ). The major advantage of SSC is that it uses gravity, a whole-body force, and controlled flow rate to impose the hydraulic conductivity. All the tests were performed following ASTM D6527, utilizing Cal State LA SSC UFA facility and a laboratory scale.

2.3.1 Cal State LA SSC-UFA Facility

Cal State LA SSC-UFA facility has an UFA rotor and high-precision infusion pumps (Figure 4). It can achieve a rotational speed up to 4000 rpm, and hydraulic conductivity values as low as 3.7 E-9 cm/s .

Fig. 4. SSC-UFA and infusing pumps at Cal State LA facility.

The rotor scheme is shown in Figure 5.

Fig. 5. SSC - UFA rotor scheme (ASTM D6527).

2.3.3 Hydraulic Conductivity

As discussed in Menezes et al. [14] if the level of saturation is the same across the sample because enough water is pumped into the sample, the effect of matric potential becomes negligible compared to centrifugation forces. If this is the case, Darcy's equation can be solved for hydraulic conductivity of unsaturated soil, $K(\theta)$, as shown in Equation 1 (ASTM D6527).

$$K(\theta) = \frac{q}{\rho \omega^2 r} \quad (1)$$

where $K(\theta)$ is the hydraulic conductivity, [cm/s]; q is the flow rate, [mL/h]; ω is the angular velocity, [rad/min]; r is the distance from the axis of rotation to the middle of the sample, [cm]; and ρ is the fluid density, [g/cm³].

Since fluid density (water) and the axis of rotation are constant, the hydraulic conductivity is a function of pump rate and rotation speed. In other words, the hydraulic conductivity is "imposed" by adjusting the flow rate, q , and the angular velocity, ω , and the volumetric water content, θ , changes in the sample, based on set parameters, until a steady-state condition is achieved. Steady-state condition is determined by monitoring the weight of the sample through a laboratory scale, which is affected by the change of water content. Table 1 shows the runs for the centrifuge testing program in determining the hydraulic conductivity as a function volumetric water content.

Table 1. Imposed hydraulic conductivity values

Pump Rate (mL/h)	Speed (rpm)	Hydraulic Conductivity (cm/s)
50	300	$1.85 \cdot 10^{-4}$
50	600	$4.63 \cdot 10^{-5}$
50	1000	$1.67 \cdot 10^{-5}$
50	1500	$7.41 \cdot 10^{-6}$
40	2000	$3.33 \cdot 10^{-6}$
15	2000	$1.25 \cdot 10^{-6}$
5	2000	$4.17 \cdot 10^{-7}$
1	2000	$8.34 \cdot 10^{-8}$
0.5	2000	$4.17 \cdot 10^{-8}$
0.2	2300	$1.26 \cdot 10^{-8}$
0.1	2500	$5.33 \cdot 10^{-9}$
0.1	3000	$3.70 \cdot 10^{-9}$

2.3.4 Matric Potential

A saturated sample under centrifugation forces, experiences a reduction in water content, until the negative pressure created by matric potential equals the centrifugation forces and the water is unable to flow, creating a steady-state no-flow condition, with constant water content. At that point, the matric potential can be calculated using the equilibrium profile equation [15, 16], shown in equation 2.

$$\psi = \frac{\rho\omega^2}{2g} (r_1^2 - r_0^2) \quad (2)$$

where ψ is the average matric potential, [bar]; g is gravity acceleration, [cm/s^2]; ρ is the fluid density, [g/cm^3]; ω is the angular speed, [rad/s]; r_1 is the average radius of the sample, [cm]; and r_0 is the radius of rotation of outer sample face [cm].

Corresponding matric potential values for each centrifugation speed value are summarized in Table 2.

Table 2. Matric potential correspondent values

Rotation Speed (rpm)	Matric Potential (kPa)	Rotation Speed (rpm)	Matric Potential (kPa)
50	0.1	1500	106
150	1.0	1800	153
300	4	2100	208
600	17	2500	295
800	30	3000	425
1000	47	3500	579
1200	68	4000	756

3 Results

3.1. Red Mud Neutralization

The pH reduction was performed by mixing RM with two different solutions: (i) a saline solution of NaCl (35g/L) and (ii) gypsum solution. Multiple buckets were needed to prepare enough treated samples for soil compaction.

Fig. 6 shows the changes in pH value during the neutralization process for the saltwater and gypsum treated samples in the slurry state (before drying). In general, the gypsum solution was more effective (pH reduction rate at 0.047 per day) than a saline solution (0.024 per day) for neutralizing RM. The pH values were also measured after drying in the oven, and before the centrifugation process. After oven-dry, the pH values were further reduced by 0.65 for the gypsum sample #4 and overall by 0.5 for the saline solution samples. Table 3 summarizes the information of centrifuge specimens before testing in the SSC-UFA setup.

Fig. 6. pH measurements of treated samples in the slurry states (S = saline solution; G = Gypsum). Masses of RM for mixing are indicated in the round brackets.

Table 3: Sample Information. The w.c. and pH values were measured before the centrifuge test.

Test	Neutralizer	Density (g/cm^3)	w.c. (%)	pH
1A	-	2.05	33	12
1B	-	2.01	33	12
2A	Gypsum	2.10	30	8.5
2B	Gypsum	2.10	30	8.4
3A	Saline Solution	2.20	33	8.4
3B	Saline Solution	2.17	33	8.4

3.1. Hydraulic Conductivity

The data generated from the SSC-UFA resulted in the hydraulic conductivity plot and soil water retention curve (SWRC), which are very helpful for geotechnical engineering designs. After being neutralized using gypsum (pH reduced from 12 to 9), the unsaturated hydraulic conductivity values have decreased across the range of measured volumetric water contents (Fig. 7). The decreases in hydraulic conductivity may be caused by the active participation of gypsum (calcium sulfate, CaSO_4) reacting with red mud. Further studies in the chemical reactions between gypsum and red mud affecting the hydraulic performance of treated residue will be performed in the future. For the specimens that were treated with saline solution, the results show that the saturated hydraulic conductivity is about the same for all samples, and in the loam to clay loam range. There was a change, however, in the saturated water content, indicating a change in the porosity of the samples. That led the values of unsaturated hydraulic conductivity to be lower for treated samples (Gypsum and saline) than for untreated at the same saturation levels.

Fig. 7. Hydraulic Conductivity of untreated and treated RM.

3.2. Matric Potential

The results for untreated red mud samples show matric potential magnitude close to silty soil (Fig. 8), which agrees with the previous findings that the basic geotechnical engineering properties of the residue are silt-like. For comparison purposes, average values for clay, silt and sand soils [17]. However, the shape of the SWRC is closer to that of clay, but a little steeper, indicating higher relative water retention potential than clay. Also, similarly to the K plots, SWRC also shows initial saturation is low for untreated RM, compared to treated samples, indicating a reduction in porosity. The tested RM samples were prepared by compacting to a dense configuration, 98% relative compaction, so less volume change is expected as soil suction increase [18].

Fig. 8. Soil Water Retention Curves (SWRC) of the RM samples (untreated, treated with saline and Gypsum) and compared with other typical soil types.

Fig. 9 shows the three water retention curves of the RM samples. All three tests show a similar residual value, around 250 kPa, while the experiment with saline solution shows an air-entry value of 8 kPa.

Fig. 9. Water Retention Curves of the three RM samples

4 Conclusion

This research project experimentally evaluated the two popular neutralization solutions: (1) mixing with saline solution and (2) addition of gypsum for bauxite residue (Red Mud) in a laboratory, and have identified adding gypsum is more effective in reducing the alkalinity of the RM, at a rate of two times faster in pH value reduction. Furthermore, the hydraulic characteristic of treated and untreated red mud samples was studied using a steady-state centrifugation (SSC) unsaturated flow apparatus (UFA). The results show that unsaturated hydraulic conductivity values of the treated samples are generally lower than the untreated ones for the same level of saturation, while the K values from the saline samples are further lower than the gypsum samples. For the matric potential, untreated and treated samples of RM demonstrate similar water retention behavior to that of clay soils, which the characteristics of low permeability and high suction range are ideal for the use of fill material in levee construction. At the same time, the water content range of RM samples is more closely similar to silt soils. Furthermore, there was a considerable increase in the water content at saturation, or an increase in porosity. In the future, we will further investigate how treatments after the particle structure of RM and the impact on porosity, hydraulic conductivity, and matric potential.

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References

1. International Aluminium Institute (IAI), *Eur. Alum. Assoc.* (2015)
2. C. Klauber, M. Grafe, G. Power, *Hydrometallurgy*, **108**, 11-32 (2011)

3. M. Gore., *Ph.D. Dissertation* (The University of Texas at Austin), 311 (2015)
4. M. Johnston, M.W. Clark, P. McMahon, N. Ward, *J. of Haz. Mat.*, **182**, 710-715 (2010)
5. I.M. Fulton, N.W. Menzies, W.J. Morell, *J. of Env. Qual.*, **33**, 1877-1884 (2004)
6. A. Xenidis, A.D. Harokopou, E. Mylona, G. Brogas, *JOM*, **57**, 42-46 (2005)
7. D.J. Glennister, M.R. Thomber, *Chemeca*, **85**, 100-113 (1985)
8. R. Courtney, L. Kirwan. *Ecol. Eng.* **42**, 279-282 (2012)
9. T. Newson, T. Dyer, C. Adam, S. Sharp. *J. Geotech. Geoenviron. Eng.*, **132**, 143-151 (2006)
10. A. Xenidis, D. Boufonos, *ASCE GeoCongress: Geotechnics of Waste Management and Remediation*, 40-47 (2008)
11. J.G. Zornberg, J.S. McCartney. *ASCE J. of Geotech. and Geoenv. Eng.* **136**(8), 1051-1063(2010).
12. J.S. McCartney, J.G. Zornberg *ASCE J. of Geotech. and Geoenv. Eng.* **136**(8), 1064-1076 (2010).
13. C. Brunori, C. Cremisini, P. Massanisso, V. Pinto, L. Torricelli, *J. of Haz. Mat.*, **55** (2005)
14. G.B. Menezes, A. Ward, H. K. Moo-Young, *Int. J. Hydrol. Sci. Tech.*, **1**, 147–163, (2011)
15. R. Gardner, *Soil Sci.*, **43**, 277, (1937)
16. F. J.Veihmeyer, O. W. Israelsen, and J.P. Conrad, *Tech. Pap.*, 16, (1924)
17. B. Minasny, A.B. McBratney, *Plant and Soil*, **249**, 253 – 262 (2003)
18. D.G. Fredlund, H. Rahardjo, M.D. Fredlund. *Unsaturated Soil Mechanics in Engineering Practice*. (2012)