Characterization and stabilization of Red Mud and Ash – Solid Industrial Waste from Aluminum Industry

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Abstract. Ore processing and metal manufacturing industries generates huge quantity of residual wastes. Emphasis has been laid on the residual products of aluminium industries e.g. Red Mud. The industry utilizes bauxite as raw material to extract aluminium out of it. Extraction of aluminium being power intensive, all the aluminium industries have captive power plants which generates huge quantity of Ash as waste product in addition to Red Mud which comes out through the process of Alumina (Al_2O_3) extraction. In the absence of any effective technology that can utilize Red Mud, industries have to incur heavy expenses in terms of land and space for storing Red Mud resulting increased cost of aluminium production. Such a situation calls for an effective, economic and environment friendly method to combat the challenges of disposal of the waste produced by such industries. One of the most common and feasible way to utilize Red Mud in bulk is to utilise the wastes for civil construction e.g. construction of embankments, roads etc utilising the waste material.

This paper aims at characterization of the waste material i.e. Red Mud and Ash through laboratory experiments. Analysing the various aspects of their geotechnical parameter attempt has been made to characterise the mix of Ash and Red Mud as well as Cement and Red Mud. Result obtained through laboratory experiments have been discussed.

Keywords: Red Mud; Characterization; Industrial waste.

1 Introduction

One of the major challenges before the processing and manufacturing industries is disposal of the residual waste products. Out of the various production industries, the ore dressing and mineral processing industries are the major contributors towards disposal of toxic waste products. Present emphasis has been laid on the residual products of aluminum industries (Pond Ash and Red Mud). The industry utilizes bauxite as raw material to extract aluminum out of it. Out of total aluminum production, India contributes only about 5% of the total world‘s production. The major aluminum producers in India are HINDALCO, NALCO, BALCO and MALCO. In the absence of any technology that can utilize the industrial wastes like ash and red mud, the industries have to incur heavy expenses in terms of land and space. This calls for an effective, economic and environment friendly method to combat the utilization and disposal problems of the waste produced by these industries. One of the most common and feasible way to utilize the Ash and Red Mud is to go for civil construction e.g. construction of embankments, roads etc with the waste materials. This paper aims at characterization of the materials through laboratory experiments, analyzing the various aspects of their geotechnical behavior so that material can be used in bulk for civil construction like embankments, roads etc.

For the study, samples are obtained from ash ponds and red mud ponds of HINDALCO(U.P), BALCO(CHATTISHGRAH) and NALCO(ORISSA). However in this paper results of only the Red Mud and Ash collected from HINDALCO ponds are reported. Both the Ash and Red Mud are collected from Thick Slurry Disposal System. This system has the advantage over conventional thin slurry disposal system that the rate of consolidation of disposed materials in the ponds is quite faster. It takes maximum of 24 hours to consolidate and the deposit hardens to the extent that one is able to walk over the surface on account of lesser water content and certain chemical treatment undergone before the disposal.

2 Chemical analysis

Chemical analysis reveals that Red Mud (RM) contains silica, aluminium, iron, calcium, titanium, as well as an array of minor constituents, namely Na, K, Cr, V, Ni, Ba, Cu, Mn, Pb, Zn etc. The variation in chemical composition between different RMs worldwide is high. RM has a very high number of compounds present. The more frequently available compounds are:

Hematite (Fe_2O_3), goethite Fe(1-x)AlxOOH (X=0-0.33), gibbsite $Al(OH)_3$, boehmite AlO(OH), diaspore AlO(OH), calcite ($CaCO_3$), calcium aluminum hydrate ($x.CaO.yAl_2O_3.zH_2O$), quartz (SiO_2), rutile (TiO_2), anatase (TiO_2), $CaTiO_3$, Na_2TiO_3, kaolinite ($Al_2O_3.2SiO_2.2H_2O$), sodalites, aluminium silicates, cancrinite hydroxycancrinite, chantalite, hydrogarnet. A wide variety of oxides are also present.

Typical values are given in Table 1.

Table 1. Oxides present in Bauxite ore

Oxides	Contents
Fe_2O_3	33-35%
$Al_2\ O_3$	10-20%
SiO_2	6.5 – 8.0%
$Na_2\ O$	5 - 6%
CaO	4 - 5%
TiO_2	18 – 20%

XRD was carried out with Red Mud sample. The XRD plot is shown in Fig.1. Some of the important minerals identified on the plot are: Rutile (TiO_2), Boehmite ($AlHO_2$), Quartz (SiO_2), Hematite (Fe_2O_3), Aragonite ($CaCO_3$) etc.

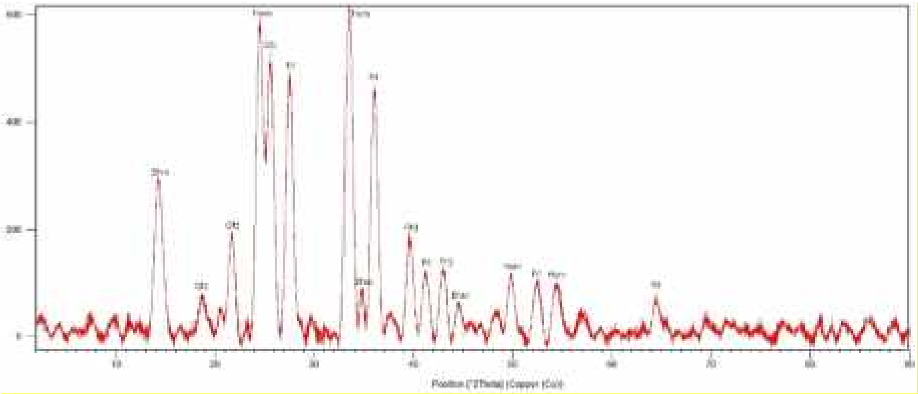

Fig.1. XRD plot of Red Mud Sample

3 State of the art

The disposal of Red Mud is difficult and the reports on this issue in the open literature seem scarce. However information available in the open source has been collected about the disposal as well as common practice in the USA, India, China, Japan, France and Greece.

In a research by Hind et al (1999) it is reported that conventional disposal methods have revolved around the construction of clay lined dams or dykes into which Red Mud slurry is pumped and allowed to dry naturally. The design and construction of such residue impoundments has varied considerably over the years, with disposal practices generally dependent upon the nature of the immediate environment (B. Salopek, J. Strazisar, 1993). However the potential effect on ground water and surrounding environment, and the difficulties associated with the surface rehabilitation forced significant changes in the disposal practices (D.J.Coolong, D.J.Glenister, 1992). This lead to doubly sealed impoundment incorporating a polymeric membrane as well as clay lining.

In another report by Agrawal et al (2004) it is reported that out of the 84 Alumina plants all over the world only seven are still practicing the sea disposal in a planned manner because of scarcity of land.

Ekrem Kalkan (2006), in his investigation with Red Mud for its possible use as stabilization material for clay liners used Red mud and cement. This investigation showed that the addition of RM and Cement improved the compressive strength, the hydraulic conductivity, and the vertical swelling percentage values of compacted composite samples. Also, the results of this study proved that RM and Cement are suitable for utilization in geotechnical applications and that RM can be used for the modification of clay liners. Consequently, it is concluded that Red Mud and Cement materials can be successfully used for the stabilization of clay liners in geotechnical applications. Furthermore, the use of this waste material in clay stabilization could decrease the cost of stabilization and provide a beneficial end use for this by-product material.

Newson et at (2006) described a laboratory program to investigate the mechanical and physicochemical properties of Red Mud at a site in the United Kingdom. The red mud storage facility has been recently decommissioned and has been considered for future rehabilitation and construction activity. Based on a series of laboratory tests conducted on the Red Mud, it is concluded that the material has compression behavior similar to clayey soils, but frictional behavior closer to sandy soils. The red mud appears to be “structured” and has features consistent with sensitive, cemented clay soils. Exposure of the red mud to acidic conditions causes dissolution of the hydroxysodalite and a loss of particle cementation. The shape, size, and electrically charged properties of the hydroxysodalite, goethite, and hematite in the red mud appear to be causing mechanical behavior with features consistent with clay and sand, without the presence of either quartz or clay minerals.

Ram. K. Mohan et al (1997) illustrated a cost-effective method for reclaiming solid waste landfills by capping with clayey dredged material using a closure design developed for bauxite residue landfills in Texas. A research methodology comprised of laboratory cylinder tests, field revegetation tests and computer-based transport modeling was used to evaluate the effectiveness of the various capping alternatives and to select the final design parameters for the landfill. The design developed in this study can be applied to other similar solid waste sites with minor modifications depending upon the waste properties, site characteristics, and closure requirements of the facility.

United States of America

Red and brown muds are precipitated from a caustic suspension of sodium aluminate in a slurry and routed to large on-site surface impoundments known as red and brown mud lakes. In these lakes, the red and brown muds settle to the bottom and the water is removed, treated, and either discharged or reused. The muds are not removed, but are accumulated and disposed in place. The muds dry to a solid with a very fine particle size (sometimes less than 1µm). Red muds contain significant amounts of iron (20 to 50 percent), aluminum (20 to 30 percent), silicon (10 to 20 percent), calcium (10 to 30 percent), and sodium (10 to 20 percent). Red muds may also contain trace amounts of elements such as barium, boron, cadmium, chromium, cobalt, gallium, vanadium, scandium, and lead, as well as radionuclides

China

In China things appear to be slightly different. In a research by Fei Peng et al.(2004), it is reported that most of the RM disposal is in landfill. However close to 10% of RM is being recycled for further metal extraction or as a raw material for brick production.

Japan

J. Hyuna et al., (2004) reports that in Japan, majority of RM is deposited into the ocean after neutralization. However, authors also reported that aluminium manufacturing companies in Japan have developed pretreatment techniques for bauxite before the Bayer process to reduce the amount of RM discharged.

France

Very limited information is available about the disposal practice. The practise used to be sea disposal but it is speculated that this has changed in view of the new European legislation. Recently available satellite pictures show presence of Red Mud pond referred as lagoons.

Greece

Situation concerning the disposal method is changing. Till 2006 Red Mud, was discharged through a pipe line at the sea of Antikyra Bay. Currently high pressure filtering and dry disposal and reuse of Red Mud, is under implementation.

Fotini Kehagia (2008) attempted to utilize Red mud for embankment construction. 8.0m wide, 75.0m long and 3m high embankment was experimentally constructed to establish the feasibility of utilizing Red mud for civil construction works. Encouraging results were obtained.

National status

Hajela et al (1989) worked with Red Mud generated at Hindalco Industries Ltd, Renukut to utilize the same for manufacture of building components. Fly ash was used as admixture to manufacture brick. High water absorption and cracks on the brick prohibited the material to be used for brick manufacturing.

4 Characterisation of Red Mud and Ash

Red Mud (RM) and Ash have been collected from Hindalco, Red Mud Pond. Geotechnical characterisation of RM and Ash were carried out as per BIS code through the following laboratory tests:

- Grain size analysis
- Proctor density test
- Consolidation test
- Direct Shear Test

Table 2. and Table 3. Gives the values of Physical and Geotechnical parameters of Red Mud and Ash collected from Renukutn Hindalco Red Mud pond.

Table 2. Physical and Geotechnical Properties of Ash and Red Mud

Type of Material	Grain Size				Proctor Density	Specific Gravity
	Sand %	Silt %	Clay %	OMC %	Dry Density gm/cc	
Ash	62	38	-	32	1.22	2.36
Red Mud	22	60	18	29	2.04	3.15

Table 3. Direct shear, consolidation and permeability properties of Ash and Red Mud d

Material	Direct Shear Test				Consolidation Test		Permeability cm/sec
	Unsaturated		Saturated		Cv	Cc	
	C kg/cm^2	Φ (deg)	C kg/cm^2	Φ (deg)	cm^2/sec		
Ash	0.07	40	0.05	38	$1.29x10^{-3}$	0.076	$0.38x10^{-4}$
Red Mud	0.26	33	0.06	30	$0.85x10^{-3}$	0.23	$0.43x10^{-5}$

5 Stabilisation of Red Mud

5.1 Red Mud mixed with Ash

Red Mud and Ash were mixed homogeneously with different proportion and samples were prepared for determination of engineering parameters .The following proportions of Red Mud and Ash were evaluated:

- Red Mud + Ash – 30% + 70%
- Red Mud + Ash - 40% + 60%
- Red Mud + Ash - 50% + 50%
- Red Mud + Ash - 60% + 40%
- Red Mud + Ash - 70% + 30%

Table 4. and Table 5. Gives the values of Physical and Geotechnical parameters of Red Mud mixed with Ash in different proportion.

Table 4. Physical and Geotechnical properties of mix composition

Mix Composition (Mud + Ash)	Grain Size			Proctor Density		Specific Gravity
	Sand %	Silt %	Clay %	OMC %	Dry Density gm/cc	
50%+50%	65	28	7	28	1.49	2.74
70%+30%	50	40	10	28	1.56	2.91
30%+70%	70	28	2	29	1.41	2.44
60% + 40%	58	35	7	27	1.54	2.64
40% + 60%	63	32	5	28	1.52	2.68

Table 5. Direct shear, consolidation and permeability properties of mix composition

Mix Composition (Mud +Ash)	Direct Shear Test: Unsaturated C kg/cm^2	Direct Shear Test: Unsaturated Φ (deg.)	Direct Shear Test: Saturated C kg/cm^2	Direct Shear Test: Saturated Φ (deg)	Consolidation Properties: Cv cm^2/sec x10^{-3}	Consolidation Properties: Cc	Permeability cm/sec x10^{-4}
50%+50%	0.18	36	0.04	33	1.05	0.059	0.14
70%+30%	0.19	37	0.10	35	0.95	0.086	1.25
30%+70%	0.12	39	0.05	38	1.14	0.082	0.42
60% + 40%	0.20	36	0.08	34	1.02	0.078	0.95
40% + 60%	0.17	37	0.06	36	1.08	0.075	0.87

5.2 Red Mud stabilized with Cement

It was decided to stabilize RM with cement commercially available in the market. The decision to use cement as stabilizer was due to its easy availability, quick hardening properties as compared to other stabilizer e.g lime, most economical stabilizing material available in the market etc. Mechanism of improvement in strength when cement is mixed with Red Mud is exactly same as gain in strength when sand is mixed with cement to prepare sand cement mortar. Like in sand cement mortar, cement acts as binding material and sand as filler here too cement binds the Red Mud particles. In both the cases, on hydration, cement gains strength with filler material present in the matrix. The water - cement reaction is well known and beyond the scope of the paper hence it is not described here.

After stabilization experimental program was undertaken to study the effect of cement on RM with respect to the improvement in strength characteristics. The oven dried RM were mixed with cement at liquid limit. The liquid limit of the Red Mud was found to be 32.5%. The cement content varied from 2% to 6% with increment of 2% and the mix was transferred to a specially fabricated air tight perspex mould with inner diameter 38mm and length 76mm maintaining L/d ratio as 2. For every percentage of mix minimum 3 samples were prepared.

After a rest period of 7, 21, 28 and 56 days the samples were taken out from the mould and tested for unconfined compressive strength. Failure patterns are showed in Fig.2. Compressive strength of cement stabilized Red Mud samples with variation of cement content is given in Table 6. Modulus and strain values at 28 days are given in Table 7.

Table 6. Unconfined compressive strength of Cement stabilized red mud (Kg/cm^2)

Rest period	Red mud + 2% cement	Red mud + 4% cement	Red mud + 6% cement
7 days	-	1.92	2.17
21 days	0.67	3.80	5.62
28 days	1.57	4.36	7.07
56 days	1.96	4.70	7.42

Table 7. Modulus and Strain Values at 28 days

RM + % of cement	Initial Tangent Modulus E_i (Kg/cm^2)	Strain at Failure ϵ_f	50% Failure Strain ϵ_{50}	Secant Modulus E_{50} (Kg/cm^2)
2%	38	0.044	0.018	42
4%	185	0.047	0.019	190
6%	200	0.049	0.021	200

Fig. 1. Faliure Pattern Of Cement Stablized Sample By UCS Test

Consolidation tests were carried out on cement stabilized RM samples in odeometers. The coefficient of consolidation (Cv) and compression Index (Cc) were measured after the specified rest period of 7, 21, 28 and 56 days. Table 8. and Table 9. Gives the values of Cv and Cc respectively with variation of cement content and time.

Table 8. Coefficient of consolidation (Cv) of stabilized red mud (cm^2/Sec)x10^{-3}

Rest period	RM + 2% cement	RM + 4% cement	RM + 6% cement
7 days	0.95	1.14	1.37
21 days	1.01	1.21	1.47
28 days	1.04	1.29	1.60
56 days	1.08	1.31	1.65

Table 9. Compression index (Cc) of stabilized red mud

Rest period	RM + 2% cement	RM + 4% Cement	RM + 6% cement
7 days	0.202	0.106	0.056

21 days	0.191	0.087	0.053
28 days	0.118	0.079	0.051
56 days	0.109	0.071	0.048

6 Discussions on the test results

6.1 Red Mud and Ash

Grain size analysis shows that the ash has mostly sand size particles (62%) where as the red mud has only 22% of sand size particle. The total fines in the red mud are 78% as against 38% in ash. Ash does not have clay size particle but in contrast red mud has 18% of clay size particle. The red mud is found to be heavier material as compared to ash because the specific gravity of red mud is nearly 33% more than the ash.

The shear properties of ash show that the friction angle is 40^0 under partially saturated condition and under saturation the value drops down to 38^0. The similar trend is observed in case of red mud for friction angle but the cohesion value of the red mud drops drastically from 0.26 Kg/ cm^2 under partially saturated condition to 0.06 Kg/ cm^2 under saturated condition. This shows that under saturated condition the red mud will loose its strength.

From the permeability values it is observed that both ash and red mud is free draining material though red mud has large quantity of total fines (78%). However uniformity could not be observed in the permeability value of the mixed material

6.2 Red Mud mixed with Ash

Under homogenous mix of different proportions, the properties get changed as per expectations. The density of the mixed material decreases as different proportions of ash are mixed. The range of specific gravity obtained is 2.44 to 2.91 for the mix composition Red Mud + Ash – (30%+70%) and (70%+30%) respectively. The specific gravity obtained for Red Mud + Ash (50%+50%) is 2.74. Similarly the shear test results also showed change in cohesion and friction value when red mud and ash were mixed in different proportions. While friction angle for the mixed material decreases marginally the cohesion value increases as compared to ash.

6.3 Red Mud stabilized with Cement

Red mud was mixed with ordinary Portland cement to form a homogenous mix. The quantity of cement varied from 2% to 6% with increment of 2%. The rest period was varied from 7days to 56 days. 2% cement after 7days failed to stabilize the red mud.

The sample was unable to retain its shape. Hence UCS could not be carried out. Unconfined compression tests were conducted to establish a general trend for gain in strength with different percentage of cement. However, after a rest period of 21 days the same sample got stabilised and marginal strength development took place. When the cement content increased to 4% after 7days, the sample got stabilised and UCS value obtained was 1.92 Kg / cm^2 and the same value was increased to 4.70Kg/cm^2 for the rest period of 56days ie 145% increase in UCS value could be recorded. The UCS value was increased from 2.17Kg/cm^2 to 7.42 Kg/cm^2 when 6% cement was added as stabilizer and rest period was increased from 7days to 56 days, i.e. 240% increase in UCS value could be recorded in this case.

The value of initial tangent modulus E_i increased from 38Kg/cm^2 to 200Kg/cm^2 for 2% cement to 6% cement added as stabilizer. Thus more than 425% increase in E_i value could be observed when 2% cement to 6% cement added as stabilizer. However it is interesting to note that the value of the failure strain and the Strain at 50% failure remains almost same.

The value of coefficient of consolidation Cv increased to $0.95x10^{-3}$ cm^2/sec for a rest period of 7days and same value was increased to $1.08x10^{-3}$ cm^2/sec for the rest period of 56days with 2% cement added as stabilizer which show 14% increase between 7days to 56 days. The value of compression index Cc decreased to 0.202 for rest period of 7 days with 2 % of cement and further the same value decreased to 0.109 for a rest period of 56 days. This shows 46 % decrease. As the value of compression index Cc decreased, settlement will also decrease.

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References

1. Hind, A. R., Bhargava, S. K., Stephen C. Grocott. :The surface chemistry of Bayer process solids: a review, Colloids and Surfaces **146,** 359–374 (1999).
2. Salopek, B., Strazisar,J. : The influence of red mud impoundments on the environment. Light Metals, Warrendale, PA, United States 4-41, (1993).
3. Cooling, D.J., Glenister, D.J.: Practical aspects of dry residue disposal, Light Metals 25-31,(1992), In: Proceedings of the 121st TMS Annual Meeting, Published by Minerals, Metals & Materials Society, San Diego, CA, USA.
4. Agrawal, A., Sahu,, K.K., Pandey, B.D. : Solid waste management in non-ferrous industries in India, In: Resources, Conservation and Recycling **42,** 99–120, (2004).
5. Peng, F., Liang, K., Shao,H., Hu,A. : Nano-crystal glass-ceramics obtained by crystallization of vitrified red mud, Chemosphere (2004)
6. Hyuna, J., Endoha, S., Masudaa, K., Shinb, H., Ohyaa, H.,: Reduction of chlorine in bauxite residue by fine particle separation, International Journal of Mineral Processing (2004)

7. Ekrem Kalkan**,:** Utilization of red mud as a stabilization material for the preparation of clay liners , Engineering Geology, 87, 220–229 (2006)
8. Newson, Tim., Dyer, Tom., Adam. Chris., Sandra Sharp,: Effect of Structure on the Geotechnical Properties of Bauxite Residue, Journal of Geotechnical and Geoenvironmental Engineering, American Society of Civil Engineers, 143 – 151 (2006)
9. Ram K. Mohan., John, B., Herbich, B., Lloyd, R., Hossner, Fred S., Williams, D.,: Reclamation of solid waste landfills by capping with dredged material, Journal of hazardous material, 53, 141 – 164, (1997)
10. Hajela. R. B., Gupta. R.G., Goel. R.K., : Disposal of solid wastes – Red mud and flyash in the production of heavy clay products, International Journal of Environmental studies, 33, 125- 132, (1989)
11. Fotini Kehagia, : An innovative geotechnical application of bauxite residue, Electronic Journal of Geotechnical Engineering, 13, 1-10, (2008)