ETI ALUMINUM RED MUD CHARACTERIZATION AND PROCESSING

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Abstract

ETI Aluminum has capacity to process 541,000 tons of bauxite, produce 250,000 tons of alumina per year and generate approximately 260,000 tons of red mud. Red mud slurry is disposed at 30 % (w/w) solids and less than 3 g/L Na_2O.

ETI is focusing its efforts in maximizing extraction efficiency in digestion and improving decomposers yield. The red mud area is one of the most important topics that require serious study in terms of handling, recovery and environmental impact.

A study has been initiated to determine red mud characterization, settling performance and separation strategies. XRF, XRD, TG/DTA, IR, SEM/EDX, BET and PSD analysis have been conducted to define red mud physical and chemical characteristics. Many settling tests have been performed to select the most suitable and economic flocculant that provides the best compaction, overflow clarity with an acceptable settling rate and enhanced rheology. Also ETI might face red mud disposal area problems in the following years. ETI has initiated a fast track program towards the improvement of the dewatering of red mud and increase disposal area life time.

Keywords: Red Mud Characterization, Red Mud Dewatering, Red Mud Filterability, Red Mud Settling

Introduction

Red mud handling is one of the most critical issues in an alumina refining process that affects overall economics of a Bayer plant operation, and involves a relevant environmental issue related to the tailings disposal. The first step is to achieve high efficiency in solid liquid separation that can determine plant flow, liquor productivity, product quality and caustic losses. Second, the management of this high quantity of high pH waste product that gives rise to storage and environmental problems.

ETI Aluminum has started development work to characterize red mud in search of recovery and utilization possibilities, considering disposal area lifetime and environmental concerns and then optimize/improve the settling and washing unit accordingly. According to the clarification flow sheet shown in Figure 1, blow off slurry has been fed to two conventional settlers that have approximately 805 m^2 cross sectional area each to separate mud and obtain clean aluminate liquor. The mud is then washed in 6 stages of counter current washing with About 6 tons of hot condensate per ton of red mud wash ratio to keep total soda not higher than 3.0 g/L. Temperature and total soda profile are shown in Figure 2. Last washer underflow has been diluted to 12-14 % solids via red mud lake return water and pumped to lake with centrifugal pumps. Starch has been used as a coagulant for settlers with a performance of 24 % underflow solids, 100 to 200 mg/L overflow suspended solids and about 3 % gibbsite precipitation under 0.2 m/h overflow rising velocity. The performance of settlers has been improved by the selection of a suitable flocculant and doing some modifications.

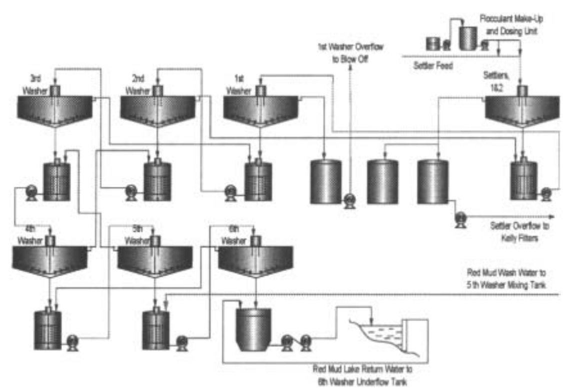


Figure 1.ETI Aluminum Red Mud Clarification Area Flow Sheet

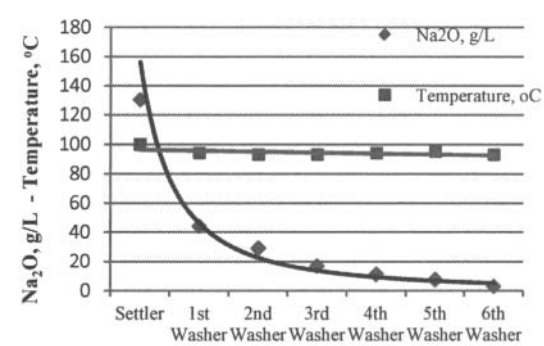


Figure 2. Temperature and Total Soda Profile in Settlers and Washers

ETI Aluminum has disposed about 5,734,288 tons of red mud on dry basis since 1973. The red mud lake which has 10 million m^3capacity has been currently filled up to 88 %. Although 6 millions m^3 extra capacity is available in a second lake, it seems appropriate to consider some investment either for a new dam or a dewatering technology within ten years, considering the same production capacity and climate in this region.

The present paper describes the physical, chemical and mineralogical characteristics of ETI Aluminum red mud. Flocculant screening, mud rheology and filterability tests will also be discussed.

Red Mud Physical and Chemical Analyses

Red mud semi quantitative elemental analysis done via ARL Advant'x 2098 Quantas are shown in Table 1.

Table 1. Red Mud Elemental Analysis (w/w %)

Element	(w/w) %	Component	(w/w) %
Al	9.870	Al_2O_3	18.650
Ca	2.710	CaO	3.800
Cl	0.047	Cl	0.047
Cr	0.058	Cr_2O_3	0.086
Fe	25.220	Fe_2O_3	36.030
K	0.337	K_2O	0.406
Mg	0.168	MgO	0.279
Mn	0.008	MnO_2	0.013
Na	6.620	Na_2O	8.920
Nb	0.004	Nb_2O_5	0.006
Ni	0.038	NiO	0.049
P	0.015	P_2O_5	0.035
Pb	0.005	PbO	0.006
S	0.041	SO_3	0.102
Sc	0.009	Sc_2O_3	0.015
Si	7.580	SiO_2	16.240
Sr	0.003	SrO	0.004
Ti	3.030	TiO_2	5.050
Y	0.010	Y_2O_3	0.014
Zr	0.046	ZrO_2	0.062

Red mud XRD analyses have been performed at 1.5406 Å wavelengths with Cu Kα radiation via using D 5000 Siemens XRD diffractometer. The values obtained from XRD pattern is shown in Figure 3 have been measured as 2θ between 5-75° and shown at Table 2. The main phases found are hematite and silica containing minerals. XRD analyses are supported with XRF analyses.

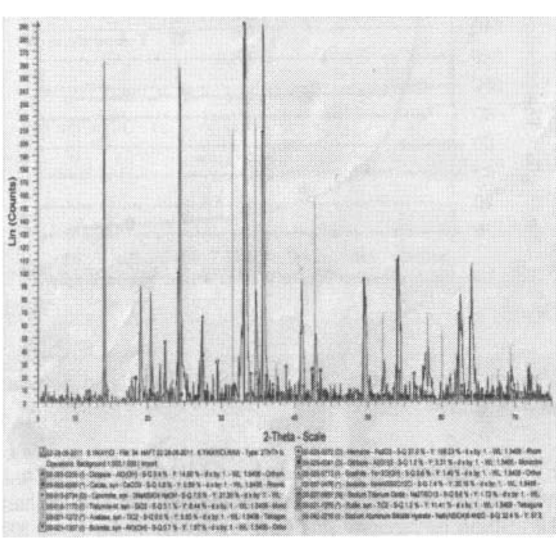


Figure 3. Red Mud XRD Pattern

Table 2. Mineral Phases in Red Mud

Mineral Phases in Red Mud	(w/w) %
Hematite, Fe_2O_3	35.54
Sodalite, $Na_4Al_3SiO_3O_{12}Cl$	6.08
Cancrinite, $3NaAlSiO_4.NaOH$	6.45
Sodium Aluminosilicate hydrate, $Na_6(AlSiO_4)_6.4H_2O$	26.54
Calcite, $CaCO_3$	1.34
Gibbsite, $Al(OH)_3$	1.09
Boehmite, AlO(OH)	0.62
Diaspore, AlO(OH)	4.64
Goethite, FeO(OH)	0.54
Sodium Titanate, $Na_2Ti_6O_{13}$	1.06
Rutile, TiO_2	2.55
Anatas, TiO_2	1.34
Tridimite, SiO_2	2.34
Amorphous	4.42

The micro structure, surface morphology and EDX analyses of red mud have been examined using aJeol JSM 6335F Scanning Electron Microscopy (SEM). Micro structure images of SEM are shown in Figure 4.

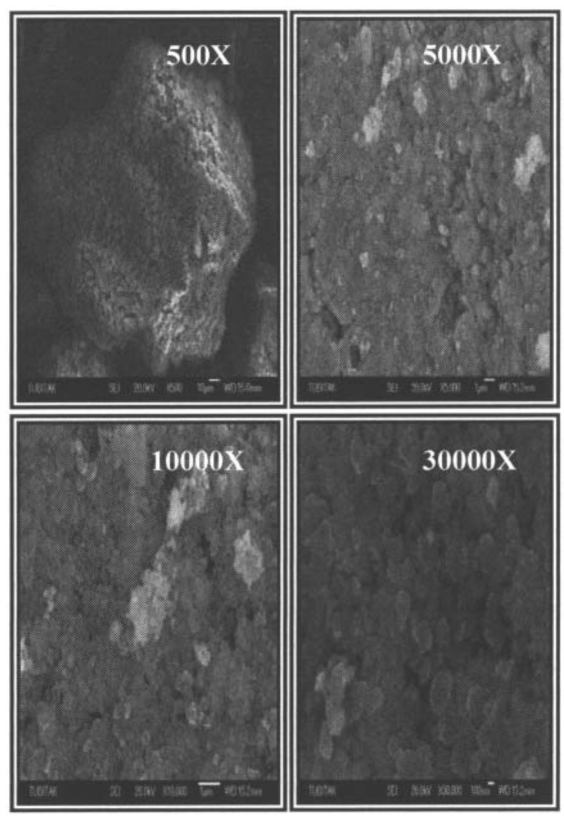
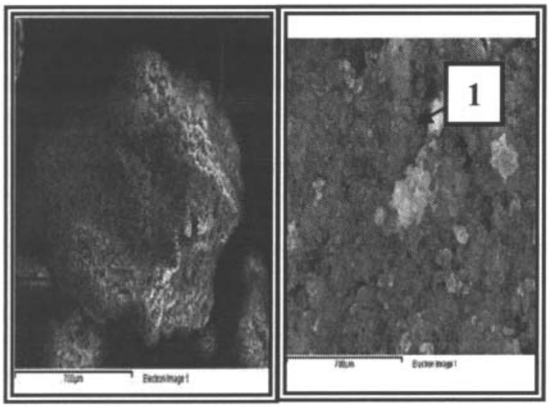


Figure 4. Micro Structure Images of Mud SEM Analyses



Element	(w/w) %
C	9.79
O	44.37
Na	6.15
Al	9.58
Si	5.78
K	0.39
Ca	1.22
Ti	2.08
Fe	19.67
Cu	0.59
Zn	0.39
TOTAL	100.00

Region 1 Analyses	
Element	(w/w) %
C	4.85
O	34.39
Na	4.85
Al	3.41
Si	2.73
Ca	0.43
Ti	2.15
Fe	47.19
TOTAL	100.00

Figure 5. Red Mud EDX Analyses

Particle size distribution of red mud has been analyzed via using Malvern Mastersizer and is shown at Figure 6. It has been found that 90 % of red mud is finer than 9.85 µm. Water was used as a dispersant during analyses.

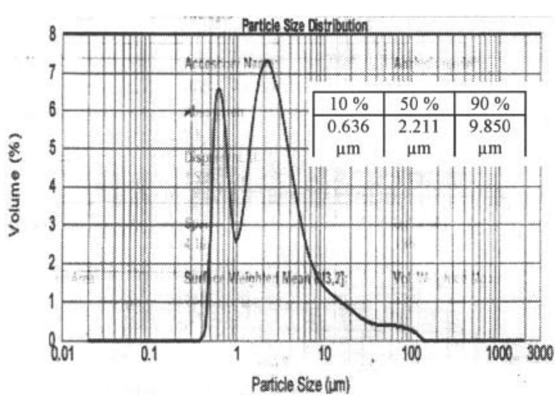


Figure 6. Red Mud Particle Size Distribution

Specific surface area of red mud has been defined as 28.378 m^2/g with N_2 BET method using a Quantachrome Nova 4000E unit.

Thermal behavior of red mud has been conducted within a temperature range between 25 to 900°C and 10°C dk^{-1} heating rate using a SEIKO ExStar 6300 TG/DTA and shown at Figure 7. The total weight loses between 25 to 900°C is 12 %. The weight loss has been started with increasing temperature. First loses up to 220°C are related to the evaporation of physical water content in the red mud. Depending on gibbsite decomposition, an endothermic peak has been seen at 263.9°C between 220-400°C and 3.9 % of weight loss has been obtained. The small endothermic peak between 500-600°C is boehmite and diaspore dehydration. The peak around 700°C could be related to the decomposition of calcite phase in the sample. Any observed weight loses above 800°C could be explained by decomposition of silica containing phases in the red mud sample. The small endothermic peaks can be explained with the loose of water form or any volatile content of the mineral phases.

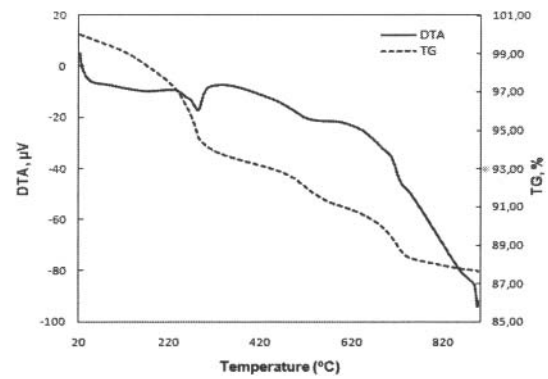


Figure 7.DTA/TG Curve of Red Mud

The molecular structure of red mud has been identified in the infrared region with Infrared Spectroscopy analysis. According to the given IR spectrum in Figure 8, the peak at 3426 cm^{-1} wavelength shows hydroxyl bonds of gibbsite. Free H_2O peaks at 1642.88 and 1454.36 cm^{-1} wavelengths states CaO component in calcite. The peaks at 999.3 cm^{-1} wavelength shows Si-O bond, at 874.66, 712.21 and 628.25 cm^{-1} wavelengths show the Al^{3+}-O^{-2} bonds and at 559.40 and 479.01 cm^{-1}wavelenghts show Fe^{3+}-O^{2-} bonds.

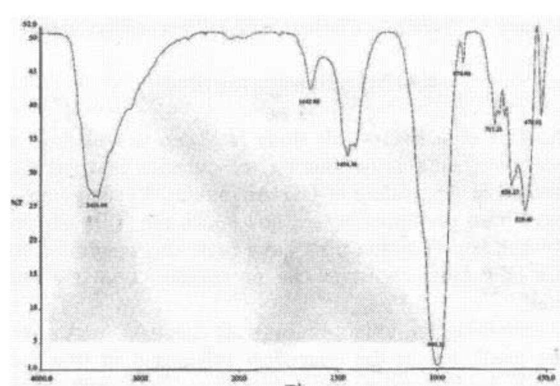


Figure 8.IR Analysis of Red Mud

The density of red mud has been measured as 3.0346 g/cm^3 using a Quantachrome Ultrapycnometer.

Red Mud Settling Tests

Many feedwell and feedline simulated settling tests have been carried out to determine the most suitable flocculant in a water bath at 95°C temperature. Starch, polyacrylate (PA), hydroximated polyacrylamids (HXPAM) and a combination of polyacrylate with starch has been tested. As seen in Figure 9 all synthetic flocculants have provided high settling rates. The combination of HXPAM and starch show good overflow clarity as shown in Figure 10. Although HXPAM has good performance in terms of settling rate and overflow clarity, the same performance at a lower cost has been obtained with the combination of lower dosage of PAs with 270 g/t starch.

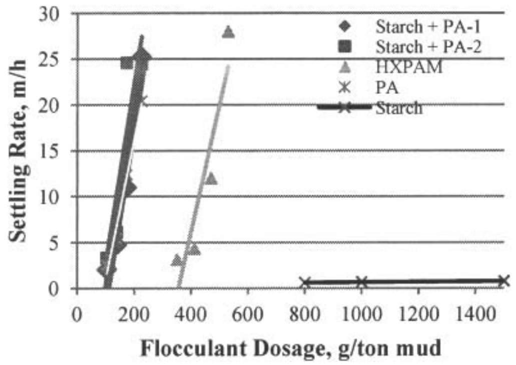


Figure 9. Settling Rates with Different Flocculants

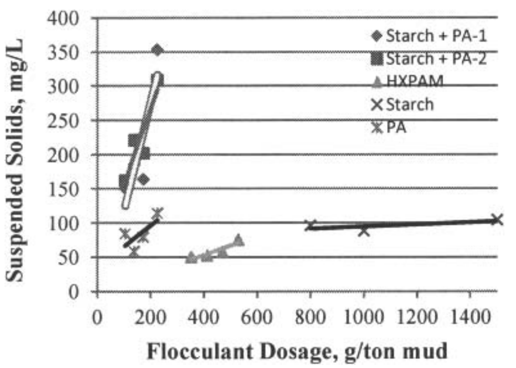


Figure 10. Overflow Clarities with Different Flocculants

Red Mud Dewatering Studies

Another objective of this study has been to undertake a review of tailings dewatering technologies that will be needed in near future at ETI Aluminum. Rheology tests have been performed to see how much the red mud can thicken and filtration tests have been also conducted to see how much moisture can be released from the red mud.

Determining the mud's rheological character allows for the prediction of the underflow solids and in turn the solids loading of a paste thickener. The yield stress measurements expressed in Pa. are initially performed on paste with solids content greater than what can be produced in a thickener and then incrementally reduced to a solids content lower than what a paste thickener is expected to produce. This is accomplished by first filtering or centrifuging the slurry to produce clear filtrate and a dense solid paste. Viscometer measurements are then taken and a small sample of the paste is collected for wt% solids measurement. The paste is then diluted multiple times with a small portion of the filtrate to incrementally lower the solids content. Each time the paste is diluted, viscometer and wt % solids data is collected to create a yield stress curve. This dilution procedure is repeated until a lower yield stress paste is produced for a series of different solids concentrations. Same procedure applied to either starch or starch plus PA flocculated mud samples. These data are used to establish a yield stress curve as shown in Figure 11 and 12. A Haake VT 550 viscometer was used for this study.

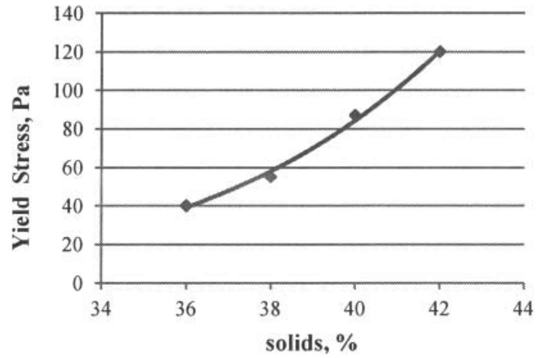


Figure 11. Mud Rheology Flocculated with Starch

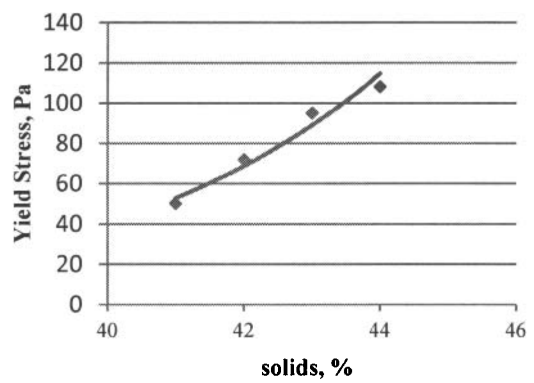


Figure 12. Mud Rheology Flocculated with Starch + PA

The yield stress is affected by many parameters; for example, the solids concentration, particle size distribution, mineralogy, water chemistry, flocculant, temperature, the age (duration of time after processing) and shear history. The yield stress versus weight percent solids relationship curve is a summation of the effects of all these parameters. The tests have been carried out to identify measures to improve current plant performance by using synthetic flocculants. More solids can be achieved with flocculants with the same yield stress.

Vacuum filtration tests have been performed with last washer samples with approximately 30 % solids and thickened samples with about 42 % solids using 70.6 cm^2 filtration test leaf. This leaf was first placed in position on a vacuum flask and the vacuum set to approximately 0.65 bars by ensuring good joint seals in the vacuum system. In quick succession, the slurry was poured onto the test leaf, the drain valve was opened to apply vacuum and a timer was started. Cake formation (form time) was considered complete when all of the free liquid had disappeared from the surface of the cake. The cake was then allowed to dry for a period of time. At the end of the drying period the vacuum was turned off and the cake was measured for thickness weighed and analyzed for moisture content by drying to a constant weight in a +150°C oven. The data for each test is shown in Table 3.

Table 3. Test Results of Filtration Tests

Test Conditions	Filtration Parameters	
~30 wt % 6th Washer Underflow Sample Cloth: 10 scfm	Vacuum – bar abs	0.65
	Cake Thickness. mm	6.4
	Cake Weight. kg/m^2	5.86
	Form Time. min	1.25
	Dry Time. min	< 0.5
	Drum Cycle Time. min	3.5
	Filtration Rate. kg/m^2 h	82.3
	Cake Solids. %	54
	Cake Moisture. %	46
~42 wt % thickened underflow Cloth: 10 scfm	Vacuum – bar	0.65
	Cake Thickness. mm	6.4
	Cake Weight. kg/m^2	5.86
	Form Time. min	0.75
	Dry Time. min	< 0.5
	Drum Cycle Time. min	2.1
	Filtration Rate. kg/m^2 h	137.2
	Cake Solids. %	54
	Cake Moisture. %	46

Testing showed that the slurry was relatively good to dewater. Cakes 6.4 mm thick needed 80 - 90 seconds to form. The filter cake has the tendency to crack. For a 6.4 mm cake the crack would appear after 15-20 seconds. Because of the crack formation there was little benefit of long drying cycles. As soon as the crack would form the air would short circuit through the cake and drying would stop. The filter cake moisture after form only (with no drying time) was 48 wt %. The cake moisture was only reduced to 46 wt % after 20 seconds of drying and did not reduce with longer drying times.

Conclusions

The chemical and physical characterization of ETI red mud samples have been done in this work by different methods. Samples contain considerable amount of valuable oxides such as unrecovered alumina. iron and titanium oxides. While iron oxide is the dominant phase in red mud sample, silica containing minerals can be seen due to high efficiency in the desilication stage. Calcium containing minerals are also found because of different purposes of lime application in process. The characteristics of current produced red mud make it difficult to be treated and utilized. The current high water content and alkalinity contribute to disposal and reuseability issues of this residue.

Despite having high specific surface, it has good density and settles well due to the high iron content.

In the light of flocculant screening tests, the combination of PA synthetic flocculants with starch show a better performance and it is more economical compared to HXPAM flocculants. This combination is being used at the settlers with underflow solids of 27 %, suspended solids below 100 mg/L and 1.5 % gibbsite at 0.23 m/h overflow velocity.

Rheology tests show that Turkish red mud can be thickened to 37-41 % solids when flocculated with starch only and to 41-44 % solids when a combination of starch and synthetic flocculant is used resulting in yield stress between 50-100 Pa depending on the operating conditions. Use of a paste thickener as the final stage of the counter current washing circuit could significantly reduce soda losses and wash water consumption for the circuit.

Vacuum filtration tests showed that the plant tailing can be filtered and dewatered to 46 % moisture. Vacuum filtration rate is affected by the feed slurry weight percent solids. While 82.3 kg/m^{2}h filtration rate was obtained with 30 % feed slurry solids. 137.2 kg/m^{2}h filtration rate can be achieved 42 % feed slurry solids.

Current red mud product can be dewatered with the mentioned paste thickening or vacuum filtration technologies. Then the use of this product; which will have low moisture and leachable soda content, can be evaluated. Furthermore beneficiation of red mud can be considered to recover valuable elements.

Acknowledgements

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