Abstract—Red mud or bauxite residue, a waste of alumina refinery has a high pH of 10.5-12.5 due to caustic soda solution used in extraction of alumina from bauxite ore by Bayer process. Red mud poses several environmental problems such as alkali seepage in ground water and alkaline dust generation and cannot be reused without any proper treatment. The paper demonstrates a comparative study on the potential of using coal dust and mixture of coal dust and superphosphate as amenders /neutralizing agents to ameliorate red mud for reducing these problems by lowering the pH of red mud. Contamination related to water is studied and results have been expressed in terms of pH of the slurry, acid required to neutralize the caustic soda leached out and quantity of soda released in stage-wise manner from 0-96 hrs. Superphosphate and coal dust mixed together are found to be the best amenders for red mud. The pH of about 8.0 can be achieved with amenders as compared to the value of above 10.0 obtained without using them. Red mud mixed with amenders releases about 50-80% less caustic soda and decreases the acid quantity required to neutralize it by 65-90%. The red mud mixed with amenders can be used for vegetation and hence better waste management can be carried out.

Keywords: bauxite residue; red mud; caustic seepage; amenders; neutralizers; pH

1.0 INTRODUCTION

In Bayer process, bauxite ore is digested with sodium hydroxide at elevated temperature and pressure to produce alumina. The waste generated in the process is known as ‘red mud’ or ‘bauxite residue’ which is a mixture of compounds originally present in the bauxite ore and of compounds formed during the Bayer cycle. Red mud is disposed of as slurry having a high solid concentration of 30-60%. The main reaction that occurs in the Bayer process can be schematized as follows:

$$2NaOH + Al_2O_3.3H_2O \rightarrow Na_2O.Al_2O_3 + 4H_2O + \text{Red Mud} \qquad (1)$$

Red mud has a muddy and colloidal in consistency and is disposed as dry or semi dry material in red mud pond or abandoned bauxite mines which are engineered disposal areas. The disposal of the red mud represents a major loss of valuable soda. Red mud has a high pH value in the range of 10.5 -12.5 as a result of the entrained soda. Up to 2 tons of liquor with a significant alkalinity of 5- 20 g L^{-1} caustic (as Na_2CO_3) accompanies every ton of dry mud (Paramguru et al. 2005). Worldwide generation of red mud is estimated to be 75 million tones per year. The red mud generation is 1.3-2 times the alumina production depending upon the quality of bauxite used.

Stored bauxite residue represents a long term environmental liability for aluminum manufacturers. Safe storage of these materials requires engineered impoundments with leachate collection and treatment to prevent contamination of soil and groundwater. The storage impoundments typically occupy hundreds of acres of land at processing sites. Poor drainage and water logging during the wet season, and salt scalding during the dry season (Wehr et al. 2006) are problems associated with red mud disposal. The dust (predominantly Na_2CO_3) formed on the dry residue surface can pose a health risk to wildlife or humans when dispersed by wind (Ayres et al. 2001). The physical and chemical properties of the residues, especially the high pH and large fraction of fine, silt-sized particles, are the major constraints limiting reclamation efforts on residue storage areas (Thomann and Portier 1991). Revegetation cannot be done due to the high pH, exchangeable sodium, and fine-grained characteristics of red mud which result in a low hydraulic conductivity and a high impedance to the penetration of roots (Gupta et al 1984; Wong and Ho 1991). Hence caustic properties of red mud must be ameliorated to avoid the ground water contamination, air pollution and also for its utilization. This will help to reduce its environmental impact and will also open opportunities for its re-use. Acid neutralization, seawater neutralization, CO_2 treatment, bioleaching and sintering are some of the processes for its neutralization/treatment. A detailed review of the neutralization processes and red mud utilization is stated by researchers (Rai et al. 2012).

Treatment of red mud with acidic industrial wastes or low cost acidic materials can also be an alternative method for red mud neutralization. Vegetation is one of the areas where bulk utilization of red mud can be carried out after its neutralization with these materials. Vegetation cover will prevent deterioration of soil erosion and act as method of suppressing dust generation due to the dried red mud.

The effectiveness of gypsum, sewage sludge, ferrous sulfate, ammonium sulphate, ammonium nitrate and calcium phosphate as ameliorants for red mud to develop and maintain a low cost, self sustaining vegetation cover has been studied by Xenidis et al. 2005. Gypsum amendments in red mud have been studied by (Wong and Ho, 1993, Woodard et al. 2008; Chauhan and Silori, 2010 for growing different plant species. The potential of using acidic fly ash to neutralize red mud slurry was studied by Khaitan et al (2009).

Red mud is a highly complex material and contains silicon, aluminium, iron, calcium, titanium, sodium as well as an array of minor elements namely K, Cr, V, Ba, Cu, Mn, Pb, Zn, P, F, S, As, and etc. Mineralogically, in general, the red muds from different alumina refineries have phases of undigested alumina, aluminosilicates, phases of iron and titania. Sodium is present in red mud in free and bound form. Free sodium in the form of NaOH, Na_2CO_3, $NaAlO_2$ etc is the caustic soda in the entrained liquor of red mud slurry which gets incorporated during digestion process and remains with red mud in spite of repeated washings. The pH of the red mud is due to the presence of these alkaline solids in red mud. Inclusion of caustic soda in bound form in the red mud is due to the desilication step carried out in the Bayer process for removal of kaolinitic silica in bauxite. It is in the form of sodalite complex which can be stated as “NAS” phases: $3(Na_2OAl_2O_32SiO_2)Na_2X$ ($X=CO_2^{2-}$, $2OH^-$, SO_4^{2-}, $2Cl^-$) (Kurdowski and Sorrentino, 1997). In red mud, about 20-25% is the free sodium while the rest is in the form of sodalite complex. Average particle size of red mud is less than 10 microns. The specific surface area (BET) of red mud is between 10 and 30 m^2/g, depending on the degree of grinding of bauxite.

Gypsum amendments with red mud have been studied till date but use of other amenders has hardly been investigated. Hence the present study is focused on amending red mud with other materials such as coal dust and superphosphate. A comparative study has been made with and without using these neutralizers. Caustic soda released in water has been investigated to study alkali seepage in underground water.

2.0 EXPERIMENTAL WORK

Materials and Methods

2.1 Materials:

Red mud from Indian alumina plant situated on the eastern coast, coal dust, superphosphate, 0.1 N HCl (MERCK make), distilled water were used for the study. Coal dust from Khaparkheda Thermal power plant, Nagpur, India was used. Red mud has a chemical composition as Al_2O_3:16-18%, Fe_2O_3: 54-57%, SiO_2: 6.0-7.0%, TiO_2: 5.0-6.0%, Na_2O: 4.0-5.0% and CaO: 2.0-3.0% with a BET surface area of 20.26 m^2/g. Coal is a combustible carbonaceous rock, formed from accumulated vegetable matter that has been altered by decay and various amounts of heat and pressure over millions of years. It has hydrogen, sulfur, oxygen and nitrogen. The humus mass and other materials get oxidized to acids when exposed to atmosphere. 10 g coal dust boiled with 100 mL of distilled water has a pH value of 9.30. Table 1 shows the chemical composition of coal dust. Superphosphate is a fertilizer produced by the action of concentrated sulfuric acid on powdered phosphate rock. It is highly acidic in nature as 5 g of superphosphate when boiled in 50 mL of distilled water has a pH value of 2.17.

Table 1: Composition of coal dust

Air dry basis	
Ash %	24.07
VM%	24.11
FC%	39.07
Moisture Content %	12.75
Derived ultimate analysis	
C, %	52.80
H, %	3.0
N, %	1.2
S, %	0.60
O_2, %	7.30
CO_2, %	0.81
Eq. moist %	7.45

VM- Volatile Matter, FC- Fixed Carbon

2.2 Method

Red mud, coal dust and superphosphate were ground to 100 mesh size and used for the study. Magnetic stirrer (Eltek M S 204) was used for stirring red mud slurry and pH was measured on calibrated pH meter (Orion EA940, Thermo Electron Corporation). Analysis of red mud has been carried out by conventional wet chemical method.

Effectiveness of the materials such as coal dust and superphosphate in reducing the pH of red mud slurry was seen by adding them to red mud slurry in different quantities and measuring the pH value. These materials would be henceforth called as neutralizers as their neutralizing effect was very well seen in each of the treatment processes.

Red mud slurry was made with 50 g of red mud and 100 mL distilled water. Coal dust and superphosphate were added to red mud slurry in different quantities, separately as well as in combination of both. pH value was measured and acid required to neutralize the soda released in the liquor was calculated by titrating it with 0.1 N HCl. Each amender was tested in 4 stages for 96 hours with 24 hours of each stage. In all, six set of experiments were carried out with following combinations: (i) Red mud with distilled water (i.e without addition of amenders) (ii) Red mud with distilled water + 10 g coal dust (iii) Red mud with distilled water + 30 g coal dust (iv) Red mud with distilled water + 50 g coal dust (v) Red mud with distilled water + 5 g superphosphate (vi) Red mud with distilled water +5 g superphosphate + 10 g coal dust.

For each set of experiment, red mud slurry was prepared in four beakers. The slurry in all the beakers was stirred thoroughly. The pH in the 1st beaker was measured and the reading was for 0 hrs residence time. After 24 hours i.e the first stage of the experiment, the slurry in 1st beaker was filtered. The pH of the filtrate was measured. The filtrate was titrated with 0.1 N HCl. The endpoint was noted and the volume of acid indicated the amount of acid required to neutralize the caustic soda released within 24 hours. This amount of acid was added in all the remaining three beakers so as to neutralize the caustic soda released within 24 hours and the contents in each beaker were stirred thoroughly. After next 24 hours, i.e in the 2nd stage (after 48 hours), the slurry was filtered from one of the beakers, pH measured. The filtrate was titrated with HCl and the amount of HCl required for titration was added in the remaining 2 beakers. The contents in the beaker were thoroughly stirred and similar procedure was followed for the next 2 stages i.e after 72 hours and 96 hours. The readings were thus taken for 4 consecutive days in stage-wise manner i.e for 0 hrs, 24 hrs, 48 hrs, 72 hrs and 96 hrs. The above procedure was followed for each of the combinations. The neutralizing effect of these was studied in terms of pH, soda release in the solution and acid requirement.

3.0 RESULTS AND DISCUSSION

3.1 Stage-wise change in pH of red mud with different neutralizers

Fig. 1 shows the stage-wise change in pH for the red mud slurry for all the combinations as specified in Section 2.2 for a time range of 0- 96 hours. The study shows that for a mixture of red mud with only water, pH varies from 10.73 to 9.75. With 10 g coal dust, the variation of pH is from 9.96 to 9.64 and with 30 g coal dust, pH varies from 9.70 to 9.35. For red mud with 50 g of coal dust the pH ranges from 9.46 to 9.04. The change in pH is not significant even after 4 days with a use of large quantity of coal dust (50 g) while with the use of a small quantity of superphosphate (5 g), the pH decreases considerably from 9.23 to 8.30. In case of superphosphates being used, there is considerable drop in pH at every stage (24 hrs). But the maximum reduction in pH is observed when red mud is mixed with a mixture of superphosphate and coal dust. The pH reduces from 8.58 to 7.99 within 96 hrs.

The effect of using amenders is precisely seen as its pH gets reduced significantly at each stage as compared to the pH variation in case when red mud is mixed only with water (no use of amenders). This shows that these materials definitely help in neutralizing the caustic soda in red mud to a great extent.

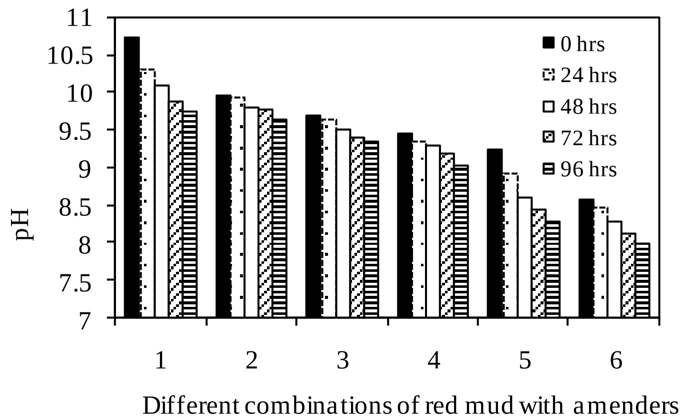

Fig. 1: Comparison of pH attained within 24 hrs for different combinations as specified in Section 2.2.

3.2 Release of sodium with respect to time:

Fig. 2 shows the sodium released in the liquor with respect to time. Release of caustic soda in the solution decreases at each stage. But red mud is substantially alkaline even after 4 days as the pH stabilizes to an average value of about 9.5 with distilled water and 9.04 with a large quantity of coal dust (50 g). But with the use of superphosphate and superphosphate mixed with coal dust, sodium released is quite less and hence the pH value obtained is also quite low which is within disposable limit.

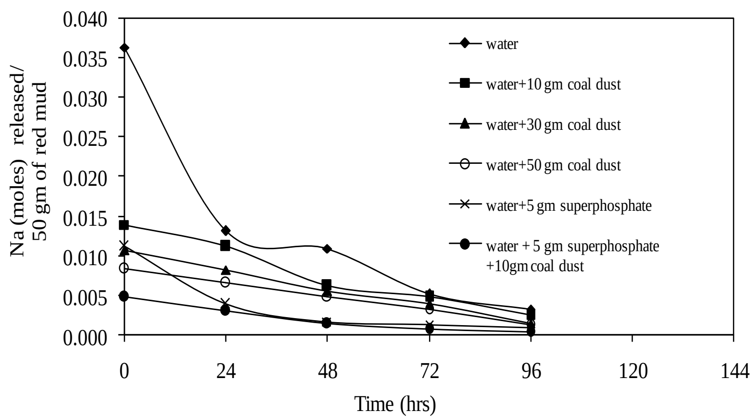

Fig. 2: Stage-wise caustic soda release in red mud slurry with/ without amenders.

3.3 Acid requirement

Figure 3 shows the acid required to neutralize the soda released per 100 ml of the liquor for each treatment process. It can be seen that the acid requirement decreases at each stage. Acid requirement is less with the use of superphosphate as compared to coal dust. Soda leaching is a slow process and the soda released in water reduces with the addition of amenders which is confirmed by the amount of acid required to neutralize it at each stage.

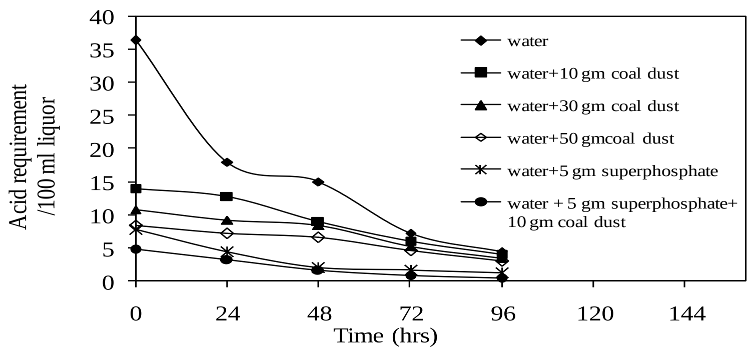

Fig. 3: Stage-wise acid requirement

The overall study shows that the pH of red mud can be reduced to a great extent when mixed with coal dust and superphosphates. The coal dust contains humus mass and sulphur which oxidize to humic acid and sulphur dioxide and neutralize the free caustic soda in red mud. Though the amount of coal dust required is quite large, it is very effective when used along with superphosphate as the optimum results are obtained with the combination of the two. Also the quantity of coal dust required is very less when used with superphosphate. The study shows that the release of caustic soda in water reduces by 50-80% by using these neutralizers i.e the caustic seepage in underground water will decrease by this percentage thus avoiding the water contamination to a large extent. This is confirmed by the reduction of acid requirement to neutralize the caustic soda in all the stages. The acid requirement has decreased by about 65-90% in all the cases. This shows that if only acid is used to neutralize the caustic soda in red mud, its quantity can be substantially reduced if red mud is amended with these neutralizers.

4.0 CONCLUSIONS

Red mud is dominated by presence of alkaline solids (hydroxides, carbonates and aluminates) formed during the Bayer process wherein caustic soda is reacted with bauxite leading to a high pH. Here we have shown that red mud can be ameliorated with amenders such as coal dust and superphosphate in suitable proportions which results in lowering the pH and reduced caustic soda seepage in underground water. This would help in preventing the water pollution in the vicinity of alumina refinery. The acid required to neutralize the released caustic soda decreases by about 65-90% with the use of neutralizers indicating reduction of caustic soda leaching in water by 50-80%. After treatment of red mud with these materials, it certainly becomes a much less hazardous material for disposal and a reuse of red mud can be made for vegetation.

References

Paramguru K, Rath PC, Misra VN (2005) Trends in red mud utilisation- A review. Mineral Processing & Extractive Metall. Rev., 26: 1-29

Wehr BJ, Fulton I, Menzies NW (2006) Revegetation strategies for bauxite refinery residue: a case study of Alcan Gove in Northern Territory, Australia. Environmental Management 37(3): 297-306

Ayres RU, Holmberg J, Anderson B (2001) Materials and the global environment : Waste mining in the 21st century. MRS Bull , 26 : 477-480

Thomann CH, Portier J (1981) Research into the recovery of red mud by the introduction of vegetation. UNEP Ind. Environ., p 6

Gupta RK, Bhumbla DK, Abrol IP, (1984) Effect of sodicity, pH, organic matter and calcium carbonate on dispersion behavior of soils. Soil Sci., 137: 245-251

Wong JWC, Ho GE,(1991) Effects of gypsum and sewage sludge amendment on physical properties of fine bauxite refining residue. Soil Sci., 152: 326-332.

Rai S, Wasewar K, Mukhopadhaya J , Chang K, Uslu H (2012) Neutralization and Utilization of red mud for its better waste management. Arch. Environ. Sci. 6: 13-33.

Xenidis A, Harokopou AD, Mylona E, Brofas (2005) Modifying Alumina Red Mud to Support a Revegetation Cover. JOM 57 (2): 42-46

Wong WC, Ho GE (1993) Use of Waste Gypsum in the Revegetation on Red Mud Deposits: A Greenhouse Study. Waste Management & Research 11(3): 249-25.

Woodard HJ, Hossner L, Bush J (2008) Ameliorating caustic properties of aluminium extraction residue to establish a vegetative cover. J Environ Sci Health A Tox Hazard Subst Environ Eng. 43 (10): 1157-1166

Chauhan S, Silori CS (2010) Rehabilitation of Red Mud Bauxite Wasteland in India (Belgaum, Karnataka). Ecological Restoration 28 (1): 12-14

Khaitan S, Dzombak D, Lowry G (2009). Neutralization of bauxite residue with acidic fly ash. Environ. Eng. Sci., 26(2): 431-440

Kurdowski W, Sorrentino F (1997) Waste materials used in concrete manufacturing. Satish C (ed), William Andrew Publishing/ Noyes, pp290-308