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Characterization of red mud and its effects on environment due to its traditional methods of disposal

PS DeshpandeDOI: <https://doi.org/10.22271/chemi.2020.v8.i6s.10949>**Abstract**

Red mud is a by product produced in the process of extraction of alumina from bauxite. The process is called Bayers Process. It is an insoluble product and is generated after bauxite digestion with sodium hydroxide at elevated temperature and pressure is known as red mud. Large quantity of red mud is generated worldwide every year posing a very serious and alarming environmental problem.

This paper describes the production and characterization of red mud in view of World and Indian context. It reviews comprehensively the disposal and neutralization methods of red mud and gives the detailed assessment of the work carried until now for the utilization of red mud, pollution control, metal recovery, coagulant, adsorbent, catalyst and in soil remediation. It also reviews the work carried out for rehabilitation of red mud ponds. This paper is an effort to analyze pollution and ecological considerations in the context of environmental concerns for disposal and utilization of red mud.

Keywords: Bauxite residue, red mud, characterization, disposal, neutralization, utilization

Introduction

In the Bayer process, the insoluble product generated after bauxite digestion with sodium hydroxide at elevated temperature and pressure to produce alumina is known as red mud or bauxite residue. The waste product derives its color and name from its iron oxide content. Red mud is a mixture of compounds originally present in the parent mineral, bauxite and the compounds formed during the Bayer process. Red mud is highly caustic with a pH in the range of 10.5 to 12.5.

The large generation of red mud posing a very serious and alarming environmental problem. Considerable research and development work for the storage, disposal and utilization of red mud is being carried out all over the world.

Aluminium and alumina - a global perspective

Aluminium is electrochemically produced from alumina using the Hall-Heroult process. Alumina in turns produced from the ore bauxite using the Bayer's process. The range of properties offered by aluminium alloy, combined with its inherent light weight, have resulted in the wide spread use of aluminium on a global scale.

Most alumina produced is used for the production of aluminium, however, alumina does have several other uses, the majority of which take advantage of its chemical inertness, and/or large surface area. Alumina is, for example, used in chromatography and catalysis, in the formation of refractory materials, and as dehydrating agent.

Alumina and aluminium are valuable commodities worldwide. The worldwide alumina production is around 58 million tonnes, in which India counts for 2.7 million tonnes. Bauxite ore mined globally amounts to be around 205 million tonnes per year for 2008, posing a very serious and alarming environmental problem.

Output of Bauxite Residue

About 1 ton of alumina is produce from 3 ton of bauxite and about 1 ton of aluminium is produce from 2 ton of alumina. Depending upon raw material processed, 1to1.5 ton of red mud is generated per tonne of alumina produced.

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Chemical and Mineral Composition of Red Mud

Chemical analysis shows that red mud contains silica, 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, ^[5, 8, 9] etc. The variation in chemical composition between red mud worldwide is high. Typical composition of red mud is given in table ^[1].

Table 1: Typical composition of red mud

Composition	Percentage
Fe ₂ O ₃	30-60%
Al ₂ O ₃	10-20%
SiO ₂	3-50%
Na ₂ O	2-10%
CaO	2-8%
TiO ₂	2-8%

Chemical composition of Indian red mud produced by various Indian aluminium manufacturing companies is given in table. ^[2].

Table 2: Chemical composition of Indian red mud

Company	Al ₂ O ₃ %	Fe ₂ O ₃ %	SiO ₂ %	TiO ₂ %	Na ₂ O%	CaO%	LOI%
Balco, Korba	18.10-21.0	35.0-37.0	6.0-6.5	17.0-19.0	5.2-5.5	1.7-2.2	11.8-14.0
Hindalco, Renukoot	17.5-19.0	35.5-36.2	7.0-8.5	16.3-14.5	5.0-6.0	3.2-4.5	10.7-12.0
Hindalco, Muri	19.0-20.5	44.0-46.0	5.5-6.5	17.0-18.9	3.3-3.8	1.5-2.0	12.0-14.0
Hindalco, Belgaum	17.8-20.1	44.0-47.0	7.5-8.5	8.2-10.4	3.5-4.6	1.0-3.0	10.8-14.0
Malco, Metturdam	18.0-22.0	40.0-26.0	12.0-16.0	2.5-3.5	4.0-4.5	1.5-2.5	11.0-15.0
Nalco, Damanjodi	17.7-19.8	48.2-53.8	4.8-5.7	3.6-4.1	3.8-4.6	0.8-1.2	10.8-13.5

Mineralogically, red mud has a very high number of compounds present ^[2, 6, 7], are given in table ^[3].

Table 3: Mineralogical Composition of Indian Red Mud

Name of Mineral	Formulation of Mineral
Hematite	Fe ₂ O ₃
Goethite	Fe _(1-x) Al _x OOH (X=0.33)
Gibbsite	Al(OH) ₃
Boehmite	AlO(OH)
Diaspore	AlO(OH)
Calcite	CaCO ₃
Calcium-aluminium-hydrate	(_x CaO _y Al ₂ O _{3z} H ₂ O)
Quartz	SiO ₂
Rutile	TiO ₂
Anatase	(TiO ₂), CaTiO ₃ , Na ₂ TiO ₃
Kaolinite	Al ₂ O ₃ 2SiO ₂ 2H ₂ O
Sodalite, aluminium- silicates, cancrinite	(NaAlSiO ₄) ₆ NaOH.H ₂ O
Hydroxycancrinite	(NaAlSiO ₄) ₆ NaOH.H ₂ O
Chantalite	CaO.Al ₂ O ₃ .SiO ₂ .2H ₂ O
Hydrogarnet	Ca ₃ Al ₂ (SiO ₄) _n (OH) _{12-4n}

Environmental Concerns of Red Mud

Red mud is disposed as dry or semidry material in red mud pond or abandoned bauxite mines and as slurry having a high solid concentration of 30 to 60% and with high ionic strength. The environmental concern related to two aspects: very large quantity of red mud generated and causticity. Problems associated with the disposal of red mud waste include:

- Its high pH (10.5 to 12.5).
- Alkali seepage into underground water.
- Instability of storage.
- Alkaline air borne dust impact on plant life.
- Vast area of land consumed.

Up to 2 ton of liquid with a significant alkalinity of 5 to 20 g/l caustic (as Na₂CO₃) accompany every ton of red mud solids ^[3].

Disposal methods for red mud

Red mud disposal methods include traditional closed cycle disposal (CCD) methods and modified closed cycle disposal (MCCD). A new class of dry stacking (DS) technology has requires much less land. Safe treatment and storage of high volume industrial waste streams pose unique waste

management challenges. Seawater discharge, lagooning, dry stacking and dry disposal are the methods currently in use for the disposal of bauxite residue ^[1].

Seawater discharge

In sea water discharge, after washing and thickening process of red mud, the slurry is disposed directly via a pipeline into the deep sea.

This process reduces environmental impact of land disposal but may release toxic metals to the marine environment and increase the turbidity of the sea due to the fine red mud and the formation of colloidal magnesium and aluminium compounds.

The countries like Japan and France have favoured this process ^[4].



Fig 1: Disposal of Red Mud Into The Sea

Lagooning

Lagooning is the conventional disposal method in which the residue slurry is directly pumped into land-based ponds. This consists of construction clay-lined dams into which the bauxite residue slurry is simply pumped and allowed to dry naturally. This minimizes the liquor leakage to the underlying water.

This process requires lowest capital cost, suppresses dust generation but requires substantial storage land and increases environmental hazards such as contact of humans and wildlife with caustic liquor and contamination of ground water.



Fig 2: Disposal of red mud into the ponds

Dry stacking

In dry stacking method, the residue slurry is thickened to 48-55% solids and discharge in thin layers, dewatered and air dried before discharge of next layer on it. After the consolidation of paste to about 65% it can be safely stacked. This reduces the area of disposal but may increase dust generation and requires funds for its long term closure. The original wet disposal method at NALCO, India has been replaced by thickened tailing disposal (TTD) system. Dry disposal is a method in which the residue is filtered to a dry cake (more than 65% solids) and the material is washed on the filter with water or steam to recover soda and minimize the alkalinity of residue. Without further treatment, the dry residue is carried by truck or conveyor to the disposal site. This reduces the storage area but requires installation and operation of filtration plant.



Fig 3: Disposal of red mud by dry stacking method.

Neutralization

Neutralization of red mud will help to reduce the environmental impact caused due to its storage and also less significant for the ongoing management of the deposits after closure. It will also open opportunities for re-use of the residue which to date have been prevented because of the high pH. Neutralization of red mud to pH around 8.0 is optimal because the chemically adsorbed Na is released, alkaline buffer minerals are neutralized and toxic metals are insoluble at this pH.

Efforts are being carried out to study the amelioration of red mud by possibly incorporating a pH-reduction processing step during disposal of red mud and include studies on processes based on acid neutralization, CO₂ treatment^[14], seawater neutralization, bioleaching and sintering.

Pollution and ecological considerations

Till today red mud is disposed off from the plant in two conventional ways, depending upon facility available and surrounding conditions. Where – ever real estate is available, red mud is disposed off to nearby pools or lagoons made for this purpose where slurry is left open for drying and overflowing water is taken back into the plant depending upon conditions. The main reasons for popularity of this method are low cost and easy implementation. This practice is followed by all Indian plants producing alumina from bauxite.

Whatever way this waste is disposed, it causes pollution to surrounding. Unfortunately certain areas of pollution are not investigated at all. The environmental chemistry and toxicity of aluminium in red mud may be significant under such alkaline conditions. Red mud of similar composition may create different types of pollution under different environmental conditions. The conditions are available sunshine, annual rainfall, average temperature, wind velocity, soil permeability and so on for the land disposal while for the sea disposal it depends on specific zone, length of inlet pipe, and depth of the area at that point, variety of fish culture and under – currents if any.

Halsband and Halsband^[10] studied the physiological effect of red mud on marine organisms. It was observed in North sea that fish was getting affected faster as compared to algae. Paffenhoefer^[11] also studied the effect of red mud on sea organisms. It was noticed that iron hydroxide part of red mud was particularly responsible for growth inhibiting effect on phytoplankton. Red mud was found harmful to fish or shell fish, will similarly affect other organisms also. This kind of sea pollution study is categorized under four subheads,

1. Killing of fish or shellfish at any stage in their life cycle, i.e., as larvae, juvenile or adults;
2. Interference in biological process such as growth physiology, breeding, etc.
3. Contaminations with persistent toxic substances so that fish and shell fish become unsafe to eat; and
4. Tainting so that fish and shell fish were rendered unpalatable and temporarily unsalable.

The above said effects are directly due to red mud. However, indirect effect also takes place, i.e., the environment of sea water or sea bed is altered so that its capacity to sustain fish is impaired. Another way of pollution is that certain metals may accumulate in fish at all but render the fish quite unsafe for human consumption.

According to Blackman and Wilson^[12] toxicity of red mud to marine animals depends on source of bauxite and process conditions of the alumina production. It was suggested that before dumping red mud to the sea physico-chemical and toxic characteristics of the red mud should be studied and correlated to the features of hydrographic and biotic features of the disposal site.

Nauke^[13] investigated geological aspects of red mud dumping site. In North sea at an experimental site 15000 tonnes of red mud were dumped and after several months it was observed that waste spread to 250 square km. High iron contents were observed at dumping area, grey colour of sand had changed to brown indicating that red mud changed to brown iron hydroxide which was found on the surface of sand grains. It was observed that dumping the red mud into river increased silt content, concentration of the heavy minerals and limited the downstream uses of water.

It was observed from the red mud ponds that the pollutants like sodium, iron-hydroxide and organic substances make way to ground water table. This polluted water becomes unfit for domestic, agricultural as well as for industrial uses.

Space requirements for storage of red mud are one of the largest constant problems facing the aluminium industry to date. There are two current methods of storage. The first is to simply pump the red mud into holding ponds. However, this method takes up a considerable amount of land.

The other way to store the mud is to first dry it and then dry stack it upon a special liner. Once there is sufficient red mud the dry stack is then covered with topsoil. This method still alleviates some of the issue of land use however; the land

cannot be used for farming or to live on. Farming cannot occur due to the fact that red mud is extremely basic in chemical nature due to the large amounts of sodium used in the original processing of aluminium that is left in the byproducts. Although there have not been any reports of leaching from the red mud through the liners there is still the risk of caustic soda leaching into groundwater. Another risk is leaching of heavy metal into the groundwater such as lead, cadmium and mercury.

Perhaps one of the most well documented tragedies associated with red mud occurred on October 4, 2010 in Hungary. The

dam wall of the Ajka refinery collapsed and approximately one million cubic meters of red mud flowed into the surrounding countryside. Nine people were killed in the disaster, 122 people were injured and the contamination included 40 square kilometres. The nearby Marcal River was reported to have suffered a loss of all living organisms, and within days the contamination had reached the Danube River as well. This is hardly the only incident of contamination caused by red mud. Table given below discusses 11 other incidents in the past 10 years.

Table 4: Incidents in the last 10 years

No.	Date	Company	Country	Incident
1	1966	Rio tinto	France	Red mud discharge into sea.
2	06/5/2012	Alcoa	Australia	Disposal of red mud on to local farm land.
3	14/5/2006	Alcoa	Australia	Poisonous dust emission.
4	06/4/2007	Rio tinto	Canada	49 tonnes released into Saguenay river.
5	21/2/2008	KAP Aluminium	Montenegro	Fine dust contamination.
6	20/8/2008	Rio tinto	Canada	Red mud disposal into river.
7	27/4/2009	Norsk Hydro	Brazil	Red mud discharge into Murucupi river.
8	01/2/2010	Rusal	Jamaica	Clouds of toxic dust.
9	27/6/2010	Vedanta	India	Fine dust contamination.
10	16/5/2011	Vedanta	India	Pollution after heavy rain.
11	26/5/2012	Gaungxi Huayin	China	Leaking of disposal pond.

Utilization of Red mud

A considerable research has been done on the utilization of red mud as a raw material for production of a range of products. It can be used as a construction/building material in bricks, blocks, light weight aggregates, in cement industry as cements and special cements and in concrete industry. Bauxite residues can be used for soil remediation, as geopolymers and as a clay material. It can also be used as an additive to cements, mortars and concretes, construction of dykes and as ceramic/refractory product. In iron and steel industry it can be used after recovery of iron and titania. In environmental field, it can be utilized in pollution control by acting as adsorbent for cleaning of industrial gases, as synthetic coagulants in waste water treatment and as a catalyst especially for coal hydrogenation. Red mud can as well be used in paints and pigments^[15, 16].

Conclusion

It is apparent that red mud is highly complex material that differ due to the different bauxites used and the different process parameter. Therefore red mud should be regarded as a group of materials, having particular characteristics such as,

- Produced during bauxite refining.
- Highly alkaline.
- Mainly composed of iron oxides having a variety of elements and mineralogical phases.
- Relatively high specific surface.
- Fine particle size distribution.

One of the most important ways of reducing the negative environmental impact of the alumina industry is environmentally sustainable discharge and storage of red mud. In the recent years it has been seen that there has been consistent trend away from seawater disposal to land – based disposal and from wet to dry disposal methods. As the high pH is highly lethal to natural ecosystems, disposal of red mud can unquestionably be made safer by neutralizing it and the most significant hazard associated with the residue can thus be removed. Continue research is required by studying residue neutralization technologies to reduce the alkalinity of red mud which is most important barrier for its reuse and

disposal management. A large variety of uses of red mud have been reviewed, yet there is no economically viable and environmentally acceptable solution for the utilization of large volume of red mud.

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