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Properties, Utilization, and Characterization of Red Mud In Terms of Its Environmental Effects

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ABSTRACT
Red mud is a by product produced in the process of extraction of alumina from bauxite. The process is called Bayers Process. It 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 bauxite and 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 these developments and progress made which would be very useful in the context of environmental concerns for disposal and utilization of red mud.

Keywords: Bauxite Residue, Red Mud, Characterization, Disposal, Neutralization, Utilization.

INTRODUCTION

Red mud is the solid waste material which is produced during the production of alumina (Al_2O_3) in the bauxite industry. Red mud is generated by Bayer's process. Quality and processing of ores containing aluminium defines the amount of red mud produced. One to fifteen tonnes of dry red mud is generated during production of 1tones of alumina. There is no other economic method which generates red mud during production of aluminium from bauxite. In India 1.892 million tons per year aluminium is produced by aluminium industry. Metal production of 6×105 tonnes/ year generates nearly 2×106 tonnes of red mud every year. Globally 9×107 tonnes of red mud is produced. The red mud has high alkalinity (pH 11-12.5). It contains Fe_2O_3, Al_2O_3, SiO_2, Na_2O and CaO. The other elements like Zr, Y, Th, U are also present in trace amount. It has reddish-brown colour. [1, 2, 10, 12, 15]

The expenses involved in the transportation and pollution abatement are serious problems faced by industry of aluminium in dumping of Red mud. A 30%-50% Fe_2O_3 and remaining Al_2O_3 and SiO_2 is the typical composition for red mud. Trace amount of metallic elements such as Vanadium, chromium, magnesium and Zirconium are also present in red mud. Haematite, goethite, Anatase, Rutile, Quartz and sodalite are their major components. So, red mud is a potential source of many metals.India is rich in mineral resources and has a long history of mining, is a well known body in mineral producing countries of the world. The Indian economy to a great extent depends on the value of the mineral produced. They represent a major portion of raw materials for country's industrial activities.The lack of finance solutions to the problem of red mud allows room for major progression with the current price of metals at record highs. For most important metals, the climate for advancements has never been better. As shown in table below, composition of generated red mud compound and bauxite. Red mud is a concentration of many elements, aluminium mainly. Composition of bauxite and the generated red mud compound as shown in table.

Origin of Bauxite

Bauxite is an abbreviation applied to a naturally occurring mixture of minerals which are rich in hydrated aluminium oxides. Oxides of iron, silicon, and titanium are major impurities while such elements as zinc, phosphorous, nickel and vanadium are found in trace amount. The type of process needed for alumina production is defined by mineralogical characteristics of the bauxite ore. For the case of aluminium containing minerals, it is important to note whether gibbsite, Boehmite, diasporic mineralogy is dominant. This determines the type of leaching operation to be used. The world's metallurgical bauxite production, as per this mineralogy is listed in presence of silica, usually called active. Since, the active silica determines the process required in the same. Because, the production of aluminium is also continuously rising, it can be concluded that production of bauxite is continuously on a high. Bauxite ore refers to a deposit of the material that contains high levels of aluminium oxide and low levels of hematite (Fe_2O_3) and silica (SiO_2). Bauxite's composition is such that it makes the ore economically mineable in a variety of locations across the globe. Other rich sources of aluminium include a variety of rocks and minerals which includes aluminous shale and slate, aluminium phosphate rock and Kaolites (high alumina clays), etc. [2]. Bauxite deposits are frequently extremely extensive this is due to their method of formation over the geological timeline, and therefore, they are found on almost all continents of the world. Although, bauxite is found worldwide. The countries with the largest economically mineable deposits, in order of production are Jamaica, Australia, Brazil, Guinea, and India. The largest consumers of aluminium of year 2002 are The United States of America, Japan and Germany. All the three countries do not possess any or very little, bauxite deposits [2].

The only ore currently being used for the production of aluminium is bauxite. Bauxite consists of many hydrous aluminium oxide phases in combination with iron, silicon, titanium oxides and other trace impurities. Main mineral present in bauxite, Gibbsite ($Al(OH)_3$), boehmite (-AlO (OH)), and diaspore (-AlO (OH)) a form of boehmite that exhibits a more dense state. Actual hardness of the ore depends on location on the globe where it is found. As friable compacted earth, re- cemented compacted earth, pisolites (small balls), tublules (twig like hollow material) have been reported across the globe. [10].

Table: Composition of Bauxite and Red Mud.

NO.	Compound	% of Bauxite	% of Red Mud
1	Al_2O_3	56.4	14.7
2	SiO_2	0.7	2.6
3	CaO	1.2	8.8
4	TiO_2	4.3	7.2
5	Fe_2O_3	35.1	60.7
6	Na_2O	0	1.6
7	(P,S,Cr,Hg,Pb,Zn,Cd)	2.3	

Table: Worldwide metallurgical bauxite production

No.	Country	Mine production x 1000 tonne in 2014	Mine production x 1000 tonne in 2015
1	Australia	61,400	63,000
2	China	35,000	37.000
3	Brazil	22,000	28,000
4	India	21,200	22,300
5	Guinea	18500	16800
6	Jamaica	14,000	8,000
7	Russia	6,300	3,300
8	Venezuela	5,500	4,800
9	Suriname	5,200	4,000
10	Kazakhstan	4,900	4,900
11	Greece	2,200	2,200
12	Guyana	2,100	1,200
13	Vietnam	30	30
14	Other Countries	6,550	5,410
15	World Total	205,000	201,000

Bayer process

Bayer process is an economical solution for producing aluminium oxides from bauxite ore using concentrated NaOH solution (caustic soda) at high pressure and temperature. The Bayer process was invented in 1887 by the Austrian chemist Karl Bayer. Russia, to develop a method for supplying alumina to textile industry as alumina was used as a mordant in dyeing cotton. In 1887, Bayer discovered that the aluminium hydroxide, precipitated from alkaline solution was crystalline and could easily filter and washed. The NaOH selectively dissolves Al_2O_3 from bauxite ore; this produces sodium – aluminium solution from which pure alumina Tri- hydrates. Then, Al $(OH)_3$ precipitation is done, which is than calcined to produce Al_2O_3 , from which metal is recovered.[2] A few years earlier, hennery Louis le chatelier in France develop a method for making alumina by heating bauxite in sodium carbonate, Na_2CO_3 at 1200 ºC , leaching the sodium aluminate formed with water. Then, precipitation of Al $(OH)_3$ by CO_2 was done, which was then filtered and dried. This process was abandoned in favour of the Bayer process. Since, the Bayer process is capable of producing huge quantities aluminium oxide and aluminium hydroxide with high – purity aluminium at relatively low – cost. This in fact created opportunity for marketing profitable Bayer plant products outside the aluminium industry. The Bayer process is the principal industrial method of refining bauxite to produce alumina. Bauxite is the most important ore of aluminium. It contains only 30-54% alumina, Al_2O_3. The rest is a mixture of silica, various iron oxides, and titanium dioxide, phosphorous and also zinc, nickel and vanadium, A breakthrough in the quest for a cost-effective production process for aluminium occurred in 1886. With invention of the electrolytic aluminium process invented in 1886, the process began to get importance in metallurgy. The cyanidation process was also invented in 1887. The Bayer process is the birth of the modern field of hydrometallurgy. Today the process is virtually unchanged and it produces nearly all the world's alumina supply. A Bayer process plant is basically, a device for heating and cooling a large recirculating stream of caustic soda solution. Bauxite is added at the high temperature point; red mud is separated at an intermediate temperature. Then, alumina is precipitated at the low temperature point. Bauxite usually consists of two forms of alumina a monohydrate from Tri-hydrate from gibbsite ($Al_2O_3 . 3H_2O$) and boehmite ($Al_2O_3.H_2O$). Boehmite requires elevated temperature (above 200 ºC). To dissolve reading in 10% NaOH solution at temperature below 150 ºC. Alumina is produce by Bayer's process through the continuous four stages which can be stated as:

Digestion of bauxite:

(1) Selective dissolution of alumina from ore.

(a) Grinding: bauxite ore is finely grinded by ball mill to size < 20mm to allow better solid – liquid contact during digestion, then recycled caustic soda solution is added to produce pump-able slurry and lime is introduced for mud condition and phosphate control.

(b) Desilication: The silica component of the bauxite is chemically reacted with caustic soda this causes alumina and soda losses by combining to solid desilication products. To desilicate the slurry before digestion, it is heated. It is then projected to atmospheric pressure in the pre-treatment tanks. Most desilication products pass out with the mud waste as sodium-aluminium silicate compounds.

(c) Digestion: in digestion bauxite slurry is pumped by high pressure pumps through agitated vertical digester vessels which operate in series. After this, it is mixed with steam and caustic solution. This dissolves the alumina content of the bauxite selectively and then forms a concentrated sodium alumina solution and leaves un-dissolved impurities. Reaction condition to extract the monohydrate alumina are about 250 ºC and a pressure of about 3500 kPa, achieved by steam generated at 5000 kPa in coal fired Boilers. However, for trihydrate alumina temperature of digestion is < 150 ºC.

The chemical reactions can be given as:

$2NaOH+Al_2O_3 . 3H_2O = 2NaAlO_2 + 4H_2O$

$2NaOH + Al_2O_3 . H_2O = 2NaAlO_2 + 2H_2O$

After digestion, about 30% of the bauxite mass remains in suspension as thin red mud as slurry of silicate and oxide of iron and titanium. By flowing through a series of flash vessels, the mud – laden liquor leaving the digestion vessel is flash-cooled to atmospheric boiling point which is then operated at lower pressure.[10]

(2) Clarification of the liquor stream: setting out un-dissolved impurities

(a) Settlers: most red mud waste solids are settled from the liquor stream in single deck settling tanks. To improve the rate of mud settling and achieve good clarity in the overflow liquor stream, flocculants are added to the settler feed.

(b) Washers: Here, the mud is washed with fresh water in counter – current washing process to remove the soda and alumina content in the mud before being pumped to large disposal dams, slacked Lime is also added to remove Na_2CO_3 , which is formed by reaction with compounds in bauxite and also from the atmospheric CO_2. Carbon-di-oxide reduces the effectiveness of liquor to dissolve alumina and lime regenerates caustic soda, allowing the insoluble calcium carbonate in precipitated form, to be removed with the waste red mud. Following reaction can be shown below:

$Na_2CO_3 + Ca (OH)_2= CaCO_3 + 2 NaOH$

(C) Filters: settlers overflow liquor containing traces of fine mud which is filtered in Kelly type constant pressure filters using polypropylene filter cloth.

(3) Precipitation of alumina tri-hydrate:

(a) Crystallization: dissolved alumina is recovered from the liquor by precipitation of crystals. Alumina precipitates as the tri-hydrate (Al_2O_3 $3H_2O$) in a reaction, which is the reverse of the digestion of tri-hydrate:

$2NaAl_2 + 4H_2O = Al_2O_3 .3H_2O + 2NaOH$

The cooled pregnant liquor flows to rows of precipitation tanks which are seeded with previously Precipitated crystalline tri-hydrate alumina. Usually they are of an intermediate or fine particle size to assist crystal growth. The correct particle size is important to smelter operations. So, sizing is carefully controlled. The finished mix of crystal sizes is settled from the liquor stream and separated into their size ranges "gravity" classification tanks.

Caustic liquor which is essentially free from solids overflows from the tertiary classifiers and then it is returned through an evaporation stage where it is re-concentrated, heated and recycled to dissolve more alumina in the digesters. Fresh caustic soda is added to the stream to make up for process losses.

(4) Calcinations of alumina:

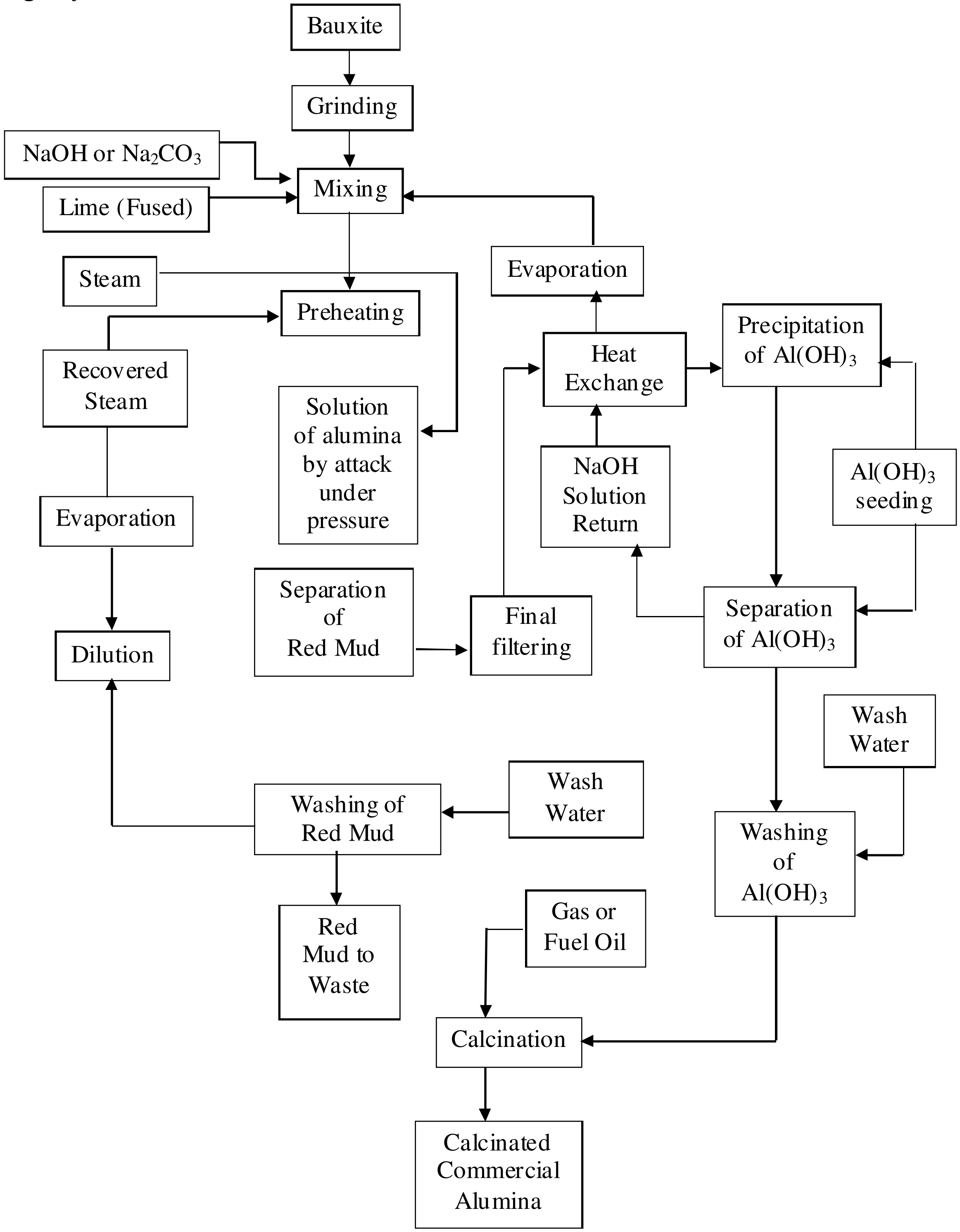
Slurry of $Al_2O_3.3H_2O$ from the primary thickeners is pumped to hydrate storage tanks and then to remove process liquor it is washed on horizontal – table vaccume filters. The resulting filter cake is fed to a series of calcining units and by circulating fluidized bed calciner or rotary kilns the feed material is calcined at 1100 °C to remove both free moisture and chemically combined water.

$2Al(OH)_3 + heat = Al_2O_3 + 3H_2O$

The circulating fluidized bed calciner is more energy efficient than the rotary kiln. Finally it produces 90% sandy alumina particles of size +45 micron. To cool the calcined alumina from the rotary kiln, Rotary or satellite coolers are used. Further Fluidised–bed coolers reduce alumina temperature to less than 90c, before it is discharged into conveyer belts, which carry it into storage buildings.[30] Alumina (aluminium oxide, Al_2O_3) is a fine white material and is the main component of bauxite. The largest manufactures in the world of alumina are ALCAN, ALCOA, RUCAL, NALCO, Queensland Alumina Limited (QAL) etc. The residue also contains alumina which is undisclosed during the alumina extraction from bauxite. Other components of bauxite Fe_2O_3 ,SiO_2 ,TiO_2 etc do not dissolve in the basic medium. Some SiO2 dissolve as silicate Si (OH)6-2 and are then filtered from the solution as solid impurities (clarification) for various reasons. Most alumina producer adds lime at some point in the process and the lime forms a number of compounds that end up with the bauxite residue. The red mud is the solid impurities remained. The red mud, due to its caustic nature causes disposal problem.A large amount of the alumina produced is then subsequently smelted in the hall-heroult process, in order to produce aluminium. Metallic aluminium is very reactive with atmospheric oxygen, and then thin passive layer of alumina quickly forms on any exposed aluminium surface. This layer protects the metal from further oxidation due to its passive nature. Through anodizing thickness and properties of this oxide layer can be enhanced. A number of alloys, such as aluminium, magnalum, bronzes are prepared to enhance corrosion resistance. One metal whose growth in the past century has been very fast is aluminium. Its strength and light weight guarantees its demand, especially in transportation where fuel efficiency is of apex importance. Annual world production of alumina is approximately 45 million tons, over 90% of which is used in the manufacture of aluminium metal. Due to high melting point Al_2O_3 is a refractory material. The major uses of aluminium oxides are in refractory, polishing, ceramics and abrasive applications.

An aluminium oxide is an electrical insulator, but still has a relatively high thermal conductivity. The is α-Al_2O_3 called corundum, most commonly occurring crystal line alumina. Its hardness makes it suitable for use as an abrasive and also as a component in cutting tools. Bauxite residue (also known as "red mud") is a by-product of the Bayer process (shown in fig. below) [12]. Its colour is red, due to presence of iron oxides. The amount of residue generated, per ton of alumina produced varies greatly. It depends on the type of bauxite used i.e. from 0.3 tons for high grade bauxite to 2.5 tons for very low grade. The chemical and physical properties of red mud depends primarily on the bauxite used and to a lesser extent the manner in which it is processed. The main solid waste product of alumina industry is Red mud. The world wide annual production of red mud is 70 million tons. Its disposal remains an issue of great importance.

Fig: Bayer Process



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 tonnes of liquid with a significant alkalinity of 5 to 20 g/l caustic (as Na_2CO_3) accompany every tonne of red mud solids[5]

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. . [6]

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.

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.

Neutralization:

Even with excellent washing of red mud by water/steam, significant alkalinity remains associated with the solids because of the complex nature of red mud Hence these hazards associated with alkalinity may be further reduced by employing suitable methods of neutralizing the red mud slurry. The 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. The process is carried out by acid neutralization, CO_2 treatment, sea water 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. Bayer's process save a few who have adopted dry disposal only. The other methods of disposal into sea/bay is practice by countries like France, England, Germany, Japan, etc. Where availability of land for dumping is scarce and the sea is nearby. Red mud is piped directly into the sea at the disposal site. [2]

Whatever way this waste is disposed, is 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, depth of the area at that point, variety of fish culture and under – currents if any.

Halsband and Halsband [12] 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 [13] 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 C. helgolendices cultured 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 categorised under four subheads,

(i) Killing of fish or shellfish at any stage in their life cycle, i.e., as larvae, juvenile or adults;

(ii) Interference in biological process such as growth physiology or breeding etc.

(iii) Contaminations with persistent toxic substances so that fish and shell fish become unsafe to eat; and

(iv) Tainting so that fish and shell fish were rendered unpalatable and temporarily unsalable.

The above said effect are directly due to red mud. However, indirect effect also take 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 [14] 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 hydro graphic and biotic features of the disposal site.

Nauke [15] 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 slit 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 few industrial uses.

Application of red mud in present work:

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 important way of reducing the negative environmental impact of the aluminium industry is environmentally sustainable discharge and storage of digestion residue.

Depending upon the red mud characteristics, a systematic strategy should be taken up by each alumina plant and a zero waste alumina refinery may be realized by developing a universal technique of disposal, management and full utilization of red mud.

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