Current Status of an Industrial Waste: Red Mud an Overview

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Abstract: - **Red mud is a solid residue Produced during the alumina production by the bayer process from bauxite. The red mud generated by this process is highly alkaline with pH usually ranging from 10 to 13. Due to its hazardous corrosive nature its posing a very serious and alarming environmental problem. Globally there are approximately 90 million tonnes of red mud being produced every year. More than 4 million tons of red mud is generated annually in India only. The amount of the red mud generated per ton of the alumina processed, varies greatly with the type of the bauxite ore used. Due to its hazardous nature it is a great challange to researcher to develop new methods for the application of red mud. Various research work going on for the storage, disposal and utilization of the red mud in all over the world. This paper reviews the current status and future trend of the red mud characterization, disposal, various neutralization methods and utilization in world as well as in Indian context.**

Key words: - Bauxite, alumina, Red mud, characterization, neutralization and utilization.

I. INTRODUCTION

Aluminium is the third most abundant element in the earth's crust which constitutes about 7.3% by mass. The first commercial production process of aluminium was started from the year 1854 **[73]**. Since then it has become the world's second most used metal after steel. The aluminium metal has play very important role in the social progress because its contribution to the society is too high. Now-a day the demand for aluminium products is increasing year by year because it has various benefits which make it unique from all. It can provide strength of steel when forming alloys, durability, flexibility, impermeability, lightweight, corrosion-resistant, recyclable and many other benefits. Metallic aluminium is not found in nature, it occurs in the form of hydrated oxides or silicates (clays) with combination of various mixture of silica, iron oxide titania, aluminium silicates and other impurities in minor or trace amounts. Primary aluminium is hot molten metal (as opposed to secondary, or recycled, aluminium) in the smelter. Secondary aluminium is a used aluminium part or used finished goods into a new usable form. The primary aluminium production occurs from bauxite through two steps. In the first step alumina is produced by wet chemical, caustic leach method (Bayer process). In the second step aluminium is produced from alumina by Hall-Heroult process. The alumina production is a chemical enrichment process where alumina is separated from the undesirable components like oxides of iron, titanium, silicon, calcium, vanadium, manganese etc from bauxite ore. In the bayer production of alumina red bauxite sludge or residue is produced as a by-product called red mud.

Red mud is a by-product of the production of alumina from bauxite in the Bayer process which involves reaction with NaOH at high temperature and pressure. Its derive its colour and name from its iron oxide content which can make up upto 60% of the mass of the red mud. Globally, there are approximately 90 million tonnes of red mud being produced every year **[75]**. The amount of the red mud generated, per ton of the alumina processed, varies greatly with the type of the bauxite ore used from 0.3 ton to 2.5 tons for high and very low grade bauxites respectively **[13].** It has been estimated that the world production of bauxite was at 248 million tonnes in 2012 and in India the production of bauxite was at 12,877 thousand tonnes in 2012-13 increased marginally as compared to the previous year **[52]**. As because it generated after the alkaline reaction during alumina process, red mud is highly alkaline with a pH usually ranging from10 to13. Due to its hazardous corrosive nature it posing a very serious and alarming environmental problem which makes a great challange to researcher to develop new methods for the application of red mud. Various research works going on for the storage, disposal and utilization of red mud in all over the world. This paper reviews the current status and future trend of red mud characterization, disposal, various neutralization methods and utilization in world as well as in Indian aspect.

II. ORIGIN OF BAUXITE

Bauxite is not a mineral. It is a rock formed from a laterite soil that has been severely leached of silica and other soluble materials in a wet tropical or subtropical climate **[9]**. Bauxite was named by the French geologist Pierre Berthier in 1821 after the village of Les Baux in Provence, southern France, where he discovered it and was the first to recognize that it contained aluminium **[10]**. Almost all of the aluminum that has ever been produced has been extracted from bauxite.

Bauxite doesn't have specific composition. It is a mixture of hydrous aluminum oxides, aluminum hydroxides, clay minerals and insoluble materials such as quartz, hematite, magnetite, siderite and goethite. Bauxite is typically a soft structure (H: 1-3) light material with specific gravity 2.6 to 3.5. the usual color of bauxite is pink but if of low iron content it may tend to become whitish in color and with increase in iron it is reddish brown in color with pistolic structure which is given in fig: 1 **[9]** .

Fig: 1 Bauxite from little rock exhibiting a pistolic structure and characteristic red iron staining

I) Production and classification of Bauxite

Bauxite resources are estimated to be 55 to 75 billion tons, in Africa (32%), Oceania (23%), South America and the Caribbean (21%), Asia (18%), and elsewhere (6%) while the estimated reserves of bauxite of the world of all categories are placed at 28 billion tonnes **[91]**. Country-wise distribution of bauxite reserves have been revised based on new information available through Government reports and other sources i.e. given in Table I.

TABLE I

COUNTRY WISE BAUXITE PRODUCTION

Country	Mine production (X1000 tonne)		Reserves
	2013	2014	
Australia	81,100	81,000	6500,000
Brazil	32,500	32,500	2,600,000
China	46,000	47,000	830,000
Greece	2,100	2,100	600,000
Guinea	18,800	19,300	7,400,000
Guyana	1,710	1,800	850,000
India	15,400	19000	540,000
Indonesia	55,700	500	1,000,000
Jamaica	9,440	9,800	2,000,000
Kazakhstan	5,440	5,500	160,000
Russia	5,320	5,300	200,000
Suriname	2,700	2,700	580,000
Venezuela	2,160	2,200	320,000
Vietnam	250	1,000	2100,000
Other countries	4,570	4,760	2400,000
World total	283,000	234,000	28,000,000

***Source: - Mineral commodity summaries 2015*[91]**

Globally primary aluminium production has increased marginally to 47 million tonnes from 45.2 million tonnes in 2011 **[51].** According to the report of the International Aluminium Institute, the aluminium production increased gradually to about 2.48 million tons at the end of August from about 2.17 million tons at yearend 2013 **[91**]. The major producers of bauxite are Australia, china, brazil, India, guinea and Jamaica. Australia alone accounts for 33% of the world production **[35].**

We can classify bauxite into 3 ore type basing on the phases of alumina occur. Those are gibbsitic (γ-$Al(OH)_3$), boehmitic (γAlO(OH)) and diasporic (α-AlO(OH)). These are crystallographically different and their occurrence in various countries is given in Table II**. [64]**

TABLE II

BAUXITE ORE TYPE OF DIFFERENT COUNTRY

Gibbsitic	Australia, Brazil, Ghana, Guyana, India (eastern coast), Indonesia, Jamaica, Malaysia, Sierra leone, Suriname, Venezuela
Boehmitic	Australia, Guinea, Hungary, USSR, Yogoslavia, India (Central part)
Diasporic	China, Greece, Guinea, Romania,Turkey

Source: - **[64]**

II) Bauxite Diposits of India

Resources of bauxite in the country as on 1.4.2010, as per UNFC system are placed at 3,480 million tonnes. These resources include 593 million tonnes reserves and 2,887 million tonnes remaining resources. By grades, about 84% resources are of metallurgical grade. By States, Odisha alone accounts for 52% of country's resources of bauxite followed by Andhra Pradesh (18%), Gujarat (7%), Chhattisgarh and Maharashtra (5% each) and Madhya Pradesh and Jharkhand (4% each). Major bauxite resources are concentrated in the East Coast bauxite deposits in Odisha and Andhra Pradesh. **[52**]. India occupies 6th place in the world with a share of 3.19% of world reserves. Odisha and Andhra Pradesh account for more than 90% of country's metallurgical grade resources. The production of bauxite in India in 2008-09 represents about 7.3% of world production placing India in 5^{th} position in the world in bauxite production. The bauxite production is likely to be 30 million tonnes out of which about 24 million tones will be by primary aluminium producers during the 12th Plan period. Though there are about 190 mines operating in the country, most of these are small, and manually operated in open cast method. 46 major deposits account for 88% of the country‟s production. The Panchpatmali bauxite mine of NALCO in Odisha alone accounts for about 30% of the country‟s production. In bauxite production. Odisha ranks the top which is followed by Gujarat, Maharashtra and Chhattisgarh. With the abundance of resources , Eastern Ghats region of Odisha and Andhra Pradesh would be the area of major bauxite mining activities in future. The large deposits of these areas are with reserves of more than 50 million tonnes can be reserved for the Greenfield alumina refineries. Additional bauxite resources are required for the brown field expansion of the existing alumina refineries **[35].**

In india bauxite is found in Gujarat, the Kutch Jamnagar belt, in the east coast bauxite belt covering Andhra Pradesh and Orissa, Ratnagiri in Maharashtra, the Madhya Pradesh bauxite belt covering Amarkantak-Phutkapahar, Jamirapat-Mainpat etc. besides this, bauxite mines are also found in the Satna-Rewa belt (Madhya Pradesh), the Netarhat plateau and adjoining areas in Gumla and the Lohardaga district of Bihar. (**64**). The India map showing the bauxite distribution across the India in fig: 2.

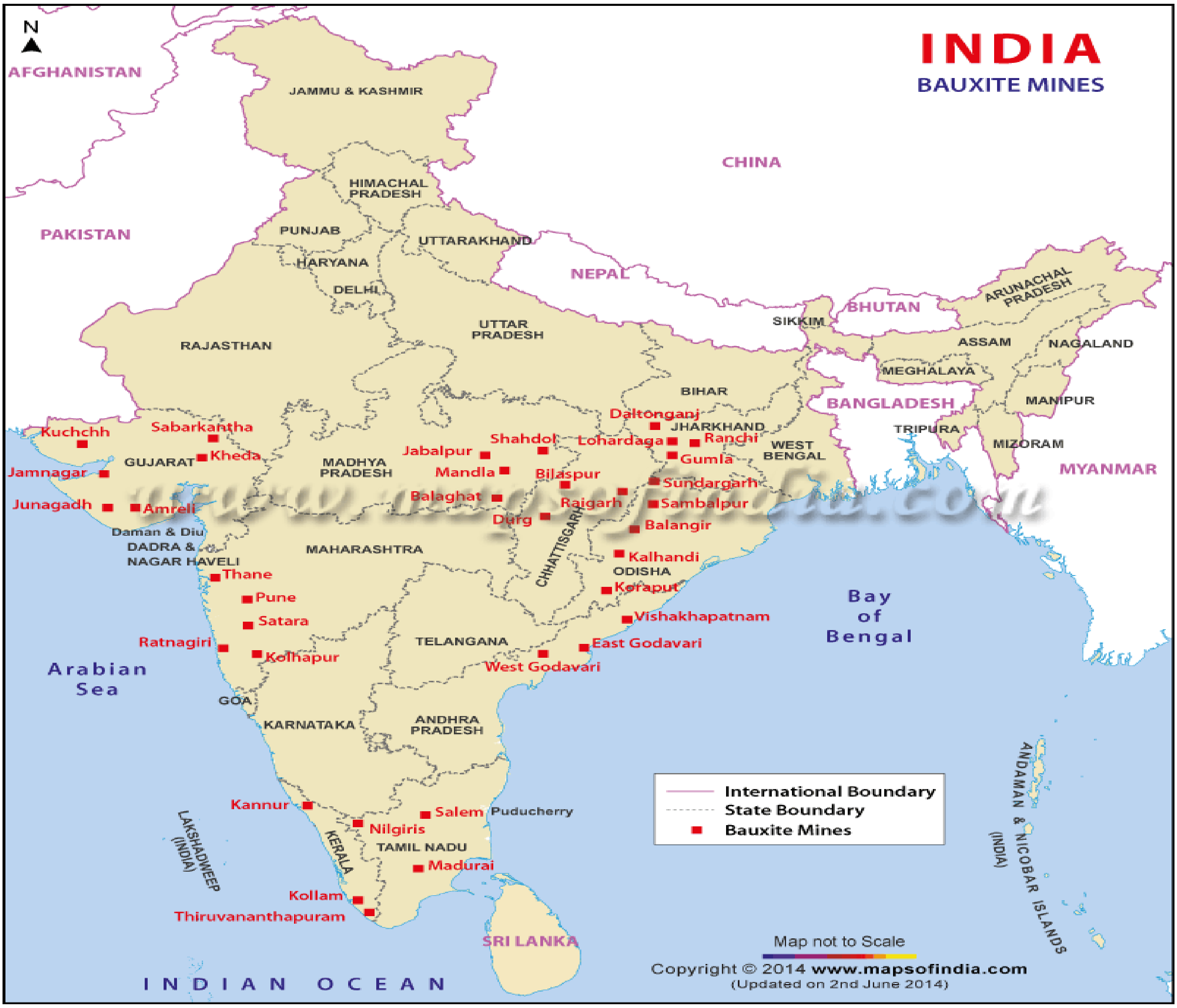

Fig.2. Provinces showing the bauxite mines in India. **[34]**

III) Distribution of Bauxite in India:-

Indian bauxite deposits are grouped into five major geological-geographical areas; they are as follows: Eastern Ghats, Central India, West Coast, Gujarat, Jammu & Kashmir. Based on the mineralogy and order of preference, Indian bauxite can be divided into 4 types:

- Gibbsitic bauxite (Eastern ghats, Gujarat and coastal deposits of western India)
- Mixed gibbsitic- boehmitic bauxite (boehmite < 10%, diaspore < 2%; parts of Western Ghats and Gujarat deposits
- Boehmitic bauxites (boehmite > 10 and diaspore < 2%; Central Indian bauxite

- Diasporic bauxites (diaspore > 5%; J&K and some part of Central Indian and Gujarat deposits **(64)**

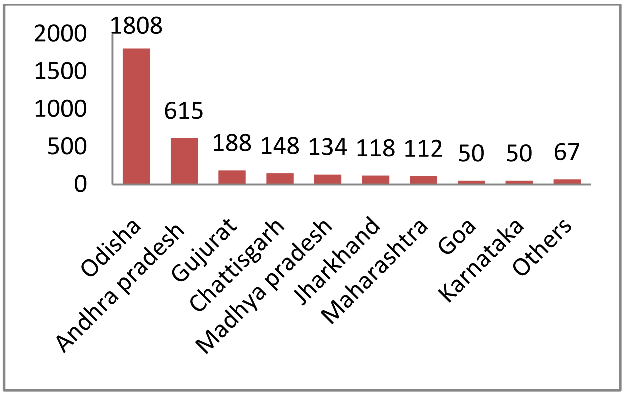

Fig.3. The state-wise distribution of bauxite resources. (Figure in million tons) **[36], [86]**

TABLE III

TYPICAL CHEMICAL COMPOSITION OF BAUXITE

Composition	Percentage (%)
Alumina(Al_2O_3)	33.2–76.9
Water(H_2O)	8.6–31.4
Iron oxide(Fe_2O_3)	0.1–48.8
Silica(SiO_2)	0.3–37.8
Titania(TiO_2)	Up to 4

Source: [73]

III. ALUMINA PRODUCTION IN INDIA

The world production of alumina has increased from 36.7 million tonnes in 2005 to about 52.7 million tonnes in 2010 **[35].** The top global companies in primary aluminium are ALOCA, RUSAL, ALCAN, HYDRO, BHP Billiton, CHALCO, DUBALCO.

The Indian aluminium sector is characterised by large integrated players like Hindalcoand National Aluminium Company (Nalco). The other producers of primary aluminium include Indian Aluminium (Indal), now merged with Hindalco, Bharat Aluminium (Balco) and Madras Aluminium (Malco) the erstwhile PSUs, which have been acquired by SterliteIndustries. Consequently, there are only three main primary metal producers in the sector namely Balco (Vedanta), National Aluminium Company (Nalco) and Hindalco (Aditya Birla Group) **[73].**

TABLE IV

THE PRODUCTION OF ALUMINA IN 2010-11 IN INDIA IS AS FOLLOWS

Company	Alumina (million tonnes)
HINDALCO	1.35
NALCO	1.55
Vedanta	0.70
Total	3.60

Source: - **[35]**

I) Bayer process of alumina production:-

Alumina refining comprises the conversion of bauxite to alu minum oxide Al_2O_3 (alumina) using the Bayer process. The production of alumina is a complex chemical process. The Bayer

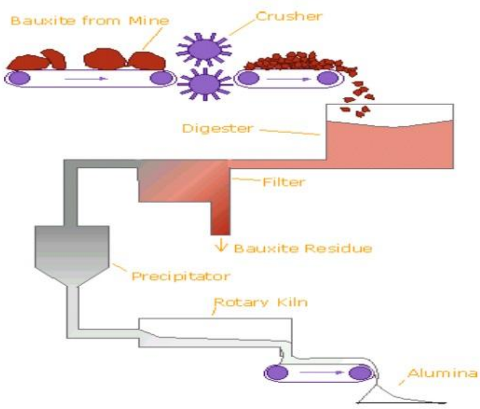

Fig: 4 Bayer process of alumina production

Process is the most economic means of obtaining alumina from bauxite. Other processes for obtaining alumina from metal ores are also in use in some refineries, particularly in China and Russia, although these make up a relatively small percentage of global production. The alumina content of bauxite ores varies from one deposit to another and methods of treatment accordingly. This means that each aluminium plant is different for each particular bauxite. The process is generally same. The bauxite from the mine is crushed and ground. It is then mixed with a solution of caustic soda and pumped into large claves. There, under at 1-6 atm pressure and at a temperature of 110–270°C, the alumina contained in the ore is dissolved to form sodium aluminate. The silica (present in kaolinite) in the bauxite reacts and precipitates from solution as sodium-aluminum-silicate. Iron and titanium oxide and other impurities are not affected chemically, and being solid, settle out of solution. This waste material, known as red mud, is separated from the sodium aluminate solution, washed to recover the caustic soda, and then pumped to disposal areas. After that the hydroxide solution is diluted and cools it to about 100^0C. With stirring and cooling to 60°C, the dissolved aluminum hydroxide $Al(OH)_3$ (hydrargillite) precipitates as a white, fluffy solid. When heated in rotary kilns or in fluidized beds at t 1100°C to 1300°C (calcined), the aluminium hydroxide decomposes to alumina, giving off water vapor in the process which converts the hydroxide to a dry, white powder. This powder is technical purity alumina, containing as impurities at most 0.01–0.02% SiO_2, 0.01–0.03% Fe_2O_3, and 0.3–0.6% NaO_2. Like this a large amount of the alumina so produced is then subsequently smelted in the Hall Heroult process in order to produce aluminium. **[53],[17],[64]**

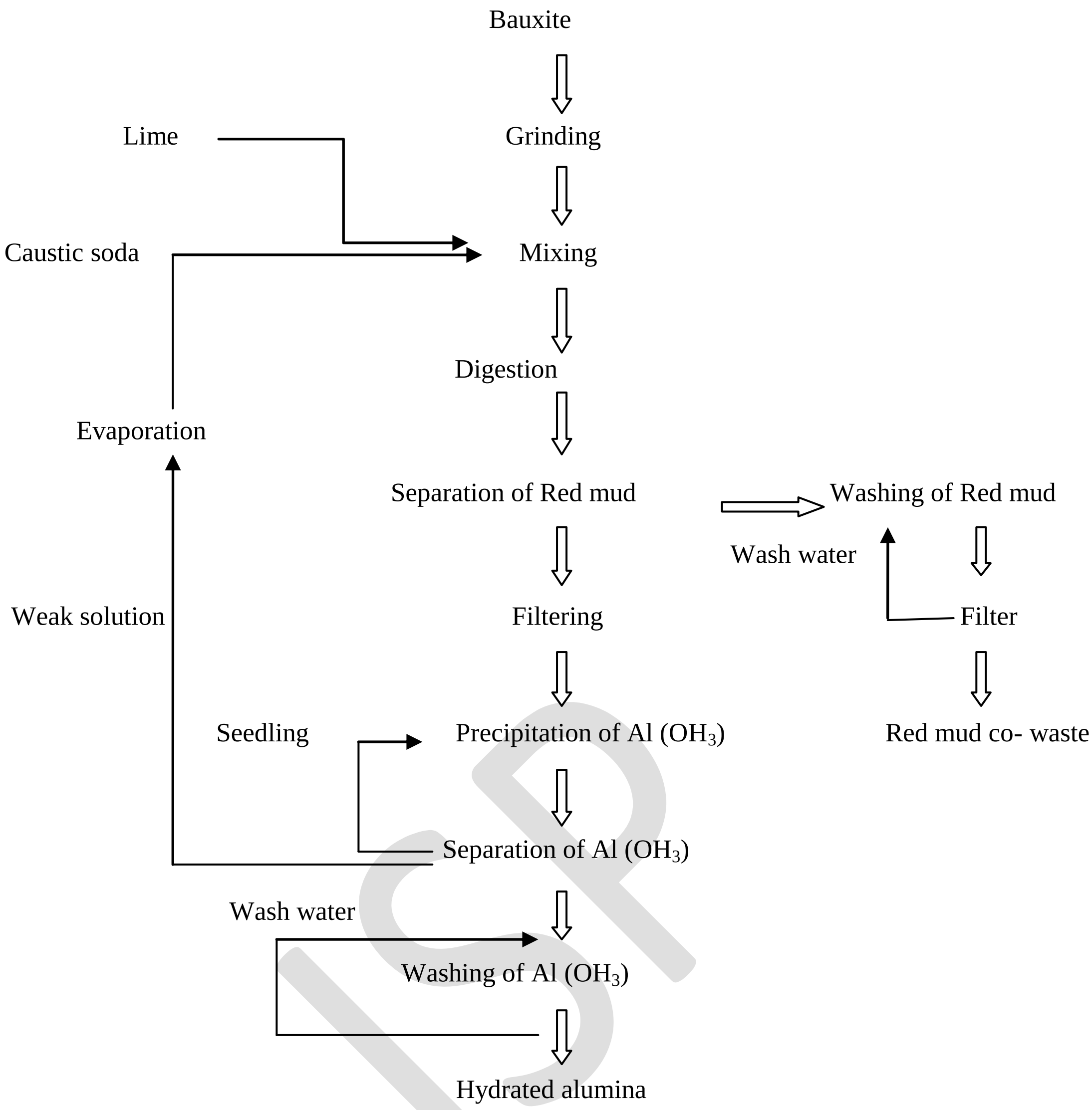

Fig: 5 A schematic representation of a bayer process (Source: - **[74]**)

II) Production and characterisation of red mud:-

Red Mud is produced during the process for alumina production. Depending on the raw material processed, 1–2.5 tons of red mud is generated per ton of alumina produced. In India, about 4.71million tons/annum of red mud is produced which is 6.25% of world's total generation **[67]**.

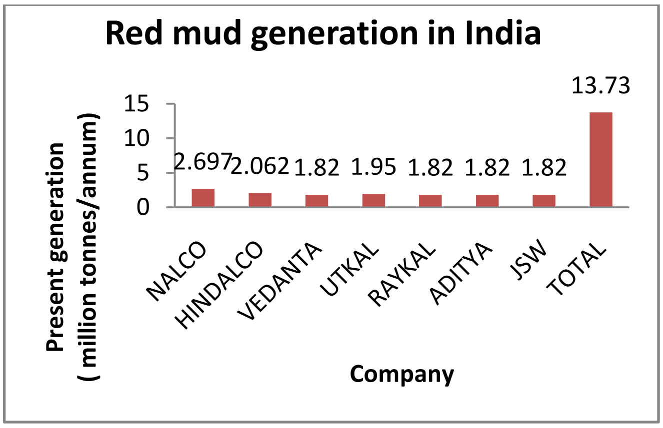

Fig: 6 Red mud generation in India (Source: - **[74]**)

III) Chemical and mineral composition of red mud:-

Chemical analysis shows that red mud 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 etc. the typical composition of red mud generated by Indian alumina plant is given in table V.

TABLE V

TYPICAL COMPOSITION OF RED MUD

Composition	Percentage
Fe_2O_3	30-60%
Al_2O_3	10-20%
SiO_2	10-20%
Na_2O	2-10%
CaO	2-8%
TiO_2	trace-25%

Source: - **[67]**

Mineralogically, these red muds have phases of undigestedalumina, aluminosilicates, phases of iron and titania. These phases are hematite (Fe_2O_3), goethite $Fe_{(1-x)}AlxOOH(x=0.33)$, gibbsite $Al(OH)_3$, boehmite AlO(OH),calcite ($CaCO_3$), calcium aluminium hydrate($x.CaO.yAl_2O_3.zH_2O$), rutile (TiO_2), anatase (TiO_2),$CaTiO_3$, Na_2TiO_3, kaolinite $Al_2O_3.2SiO_2.2H_2O$, sodalites, aluminum silicates, cancrinite ($NaAlSiO_4$)6$CaCO_3$and hydrogarnet $Ca_3Al_2(SiO_4)_n(OH)_{12-4n}$. **[64]**

TABLE VI

CHEMICAL COMPOSITION OF INDIAN RED MUDS **[64, 83].**

Company	Al_2O_3%	Fe_2O_3%	SiO_2%	TiO_2%	Na_2O%	CaO%	LOI%
BALCO Korba	18-21	35-37	6-7	17-19	5-6	2-3	11-14
HINDALCO Renukoot	17-19	35-36	7-9	14-16	5-6	3-5	10-12
HINDALCO Muri	19-21	44-46	5-7	17-19	3-4	1-2	12-14
HINDALCO Belgaum	17-20	44-47	7-9	8-11	3-5	1-3	10-14
MALCO Metturdam	18-22	40-26	12-16	3-4	4-5	1-3	11-15
NALCO Damonjodi	17-20	48-54	4-6	3-4	3-5	1-2	10-14

TABLE VII

MAJOR CHEMICAL COMPOSITION OF RED MUD GENERATED IN ALUMINA PLANTS IN VARIOUS COUNTRIES **[64], [83]**

Country	Plant	Ref.No.	Major Composition (Wt %)					
			Fe_2O_3	Al_2O_3	TiO_2	SiO_2	Na_2O	CaO
Italy	Eurallumina	[77]	35.2	20	9.2	11.6	7.5	6.7
Turkey	Seydisehir	[4]	36.94	20.39	4.98	15.74	10.10	2.23
UK	ALCAN	[81]	46.0	20.0	6.0	5.0	8.0	1.0
France	Aluminum Pechiney	[54]	26.62	15.0	15.76	4.98	1.02	22.21
Canada	ALCAN	[93]	31.60	20.61	6.23	8.89	10.26	1.66
Australia	AWAAK	[80]	28.5	24.0	3.11	18.8	3.4	5.26
Brazil	Alunorte	[80]	45.6	15.1	4.29	15.6	7.5	1.16
Germany	AOSG	[80]	44.8	16.2	12.33	5.4	4.0	5.22
Spain	Alcoa	[80]	37.5	21.2	11.45	4.4	3.6	5.51
USA	RMC	[80]	35.5	18.4	6.31	8.5	6.1	7.73

In red mud sodium is present in two forms: free soda and bound soda form. Free sodium 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. Free sodium is in the form of NaOH, Na_2CO_3, $NaAlO_2$ etc. The pH of the red mud is due to the presence of these alkaline solids in red mud. Bound soda in the red mud is due to the desilication step carried out in the Bayer process for removal of kaolinitic silica in bauxite. Bound soda 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-} ,$2Cl^-$)[7] . In red muds, about 20-25 % is the free sodium while the rest is in the form of sodalite complex. Red mud is a very fine material in terms of particle size distribution. 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^{-1} depending on the degree of grinding of bauxite**.[65],[83]**

IV) Environmental problems of red mud:-

Disposal of red mud is typically problematic for most alumina refineries. Red mud is disposed as dry or semi dry material in red mud pond or abandoned bauxite mines and as slurry having a high solid concentration of 30-60% with a high ionic strength. Untreated red mud has such high pH (typically 11-13) that plant growth is impossible and this posses a very serious and alarming environmental problem. The environmental problems associated with the disposal of red mud are:

- its high pH
- alkali seepage into underground water
- safety storage problem
- alkaline airborne dust emissions
- Vast area of land required for disposal.
- minor and trace amounts of heavy metals and radionuclides seepage into ground water

Up to 2 tonnes of liquor with a significant alkalinity of 5–20 g L−1 caustic soda (as Na_2CO_3) accompanies every tonne of dry mud. **[63].**

IV. STORAGE AND DISPOSAL OF RED MUD

A wide variety of potential uses has been suggested for the residue, and significant research has been done in a number of areas. Despite this, to date there are no economically viable and environmentally acceptable solutions for effective utilization of the high-residue volumes that have developed. Consequently, most of the bauxite residue produced is stored on land for future rehabilitation or use. Current best practice is to contain the material within specially constructed landfill sites, called red mud ponds/stacks or bauxite residue disposal areas (BRDAs). The intention is that, after exhausting the storage capacities, the landfill sites are either used for industrial or civil purposes or re-afforested to ensure merging with the surrounding eco-system.

I) Disposal of red mud:-

Red mud waste is usually managed by discharge into engineered or natural impoundment reservoirs, with subsequent dewatering by gravity-driven consolidation and sometimes followed by capping for closure. 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 also emerged which requires much less land. Due to various problems associated with disposal of red mud, it may cause economical as well as ecological problem in near future. **[64].**

The disposal of RM remains a major problem in different countries like USA, India, China, Japan, Australia, France and Greece.**[1]**, reported that out of 84 alumina plants all over the world, only seven are still practising the sea disposal in a planned manner because of scarcity of land. Currently Seawater discharge,lagooning, dry stacking and dry disposal methods are being used for the disposal of the bauxite residue.

In seawater 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 mud and the formation of colloidal magnesium and aluminium compounds.

Lagooning is the conventional disposal method in which the residue slurry is directly pumped into land- based ponds. This consists of the construction of clay- lined dams into which bauxite residue slurry is simply pumped and allowed to dry naturally. This process requires lowest capital cost, suppresses dust generation but requires substantial storage land and increases environmental hazards such as contact of humans and wild life with caustic liquor and contamination of ground water.

In dry stacking method, the residue slurry is thickened to 48-55% solids and discharged 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. This method has been successfully applied at the MOTIM plant in Hungary **[64].**

Dry disposal is a method in which the residue is filtered to a dry cake (>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.

A) Australia

Quite recently, the Virotec International Ltd. (Australia), announcened a treatment process for RM that renders the material safe for a variety of applications. The method is based on the use of seawater, which allows the conversion of "soluble alkalinity" (above all from sodium hydroxide) into low soluble minerals (essentially Ca and Mg hydroxides, carbonates and hydrocarbonates). The pH of RM is also reduced and can be decreased down to pH < 9. This technology is patented and several products with the name Bauxsol are available**. [26], [27].**

B) United States of America

In the United States of America red and brown muds are precipitated from a caustic suspension of sodium aluminate in 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. The water is then removed treated and either discharged or reused. The muds are not removed, but accumulated and disposed of in place. **[74]**

C) China

In China things appear to be slightly different. it is reported that most of the RM disposal is in landfill, however there is a precentage close to 10% of RM that is being recycled for further metal extraction or as a raw material for brick production. **[23]**

D) Japan

In Japan, majority of RM is deposited into the ocean after neutralization. Aluminum manufacturing companies in Japan have already developed pretreatment techniques for bauxite before the Bayer process to reduce the amount of BR discharged **[39], [40],[41],[42],104].**

E) Greece

There is only one alumina industry in Greece. The situation concerning the disposal method is changing. Up to now (2006) Red Mud is discharged through a pipe line at the sea of Antikyra Bay. A new project, involving high pressure filtering and dry disposal and reuse of Red Mud, is under implementation. **[60], [69], [95]**

F) France

In france the practise used to be sea disposal, at least in some cases, but we speculate that this has changed in view of the new European legislation. **[69]**

G) India

In India there are various disposal practices have been done in different aluminium plants of India. These plants are applying different dumping procedure for their red mud disposal. Those are given in table VII

TABLE VIII

RED MUD DISPOSAL PRACTICES AT THE INDIAN ALUMINA PLANTS. **[1]**

Serial number	Name of the plant	Plant capacity (t)	Red mud (t/t) of alumina	Dumping procedure
1	INDAL, Muri	72,000	1.35-1.45	This refinary adopted the closed cycle (wet slurry) disposal system (CCD). The disposal ponds have not been provided with any liner.
2	INDAL, Belgaum	2,20,000	1.16	The plant switched over to dry disposal mode from wet slurry disposal mode in 1985. The mud after clarification passes through six stage counter current washing and after filtration (65% solids), it is disposed off by dumpers at the pond site. The dry portion of the pond is covered with a 15 cm black cotton soil for promoting green vegetation.
3	HINDALCO, Renukoot	3,50,000	1.4	Traditional CCD method of impoundment was used. In late 1979 dry disposal method was implemented. After five stages counter current washing the solid is filtered (70% solids) and disposed off into the pond.
4	BALCO, Korba	2,00,000	1.3	Residue after settling, counter currently washed in four stages and filtered. The filtered cake is repulped with the pond returned water and dumped in the pond. Uses modified CCD system of disposal. The dykes of the currently used pond have stone masonry and well protected polythene liner and clay layer.
5	NALCO, Damonjodi	8,00,000	1.2	A modified CCD method is used for disposal. Subjected to six stage counter current washing by pond returned water (0.5 g/l Na_2O) and condensate from the evaporators. The washed red mud is repulped and sent to disposal sites. The bottom and sides of the pond are covered by impervious and semi pervious clay with base filters.

CCD: closed cycle disposal; MCCD: modified CCD; DS: dry stacking.

TABLE IX

MERITS AND DEMERITS OF VARIOUS METHODS OF DISPOSAL OF RED MUD **[55],[58],[59],[74].**

Method	Merits	Demerits
Slurry disposal	Return of caustic to plant; cheaper mode of transport; low infrastructure investment; natural surfaces can be used for providing banks	Large space requirements; higher storage cost, high investments for building ponds; potential pollution hazards; continuous need for enlargement of ponds or erection of new ponds; reclamation of area is expensive and time consuming
Dry mud disposal	Environmentally preferred; requires less space; consolidate rapidly	High investment costs on machinery for concentrating the slurry and pumping; higher energy and expensive earth moving equipment.
Sea/lake disposal	No investment on ponds; moderate investment on machinery for transportations; lower energy requirements	No return water and hence less recovery of caustic; harmful to marine organisms in the long run; should be dumped at depths exceeding 3000 m; extensive pipe line requirements
Solar drying	Area required is less than that for slurry disposal but more than that for dry disposal; reduced soluble soda losses.	Requirements stand-by method for use during rainy seasons; large requirements of even surfaces; need for pumping rain water

V. NEUTRALIZATION OF RED MUD

The main problems of storing red mud slurry are as follows: costly maintenance of large red mud pond areas, risk of caustic for all living organisms, leakage of alkaline compounds into the ground water, overflow of materials and dusting of dry surfaces interfere with nearby rehabilitation on plant life **[71].** Neutralization is required to convert the highly caustic state of red mud to a state which is no longer highly caustic and is less hazardous. Neutralization of red mud will help to reduce the environmental impact caused by the adverse storage behaviour of the residue and also significantly lower the effort needed during ongoing management of the deposits after closure. It will also open new opportunities for utilization of the residue which to date have been prevented because of the high pH**. [63]**. But these processes are costly, so hardly any industry takes the major to neutralize the red mud. As per the Guidelines of Australian and New Zealand Environment and Conservation Council (ANZEX) and Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ), the liquor being strongly alkaline with a high pH, requires neutralization to a pH below 9 with an optimum value of 8.5-8.9 before becoming environmentally benign **[63]**. Neutralisation 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 [**64**]. From literature review it was cleared that there are various pH reduction processing steps (neutralizing step) which are based on acid neutralization, CO_2 treatment, seawater neutralization, Ca and Mg rich brines (salt lake brines), fly ash, bioleaching and sintering.

I) Acid neutralization

The feasibility of treating red mud with acid has been studied by researchers. Various aqueous acidic solutions have been considered for this application including acidic industrial wastewater. The use of carbonic acid has also been considered. A number of studies have been done for the feasibility of treating bauxite residue with acid on Kwinana red mud slurry. Treating red mud with acidic spent pickling solutions (SPSs), derived from the steelmaking process, provides a coagulant – a mixture of aluminium and iron salts- for waste water treatment. Neutralization using acids is reasonably cheap if sufficiently large quantities of waste acid are available. **[65]**

II) Carbon dioxide treatment

In carbon dioxide treatment the Gas phase CO_2 or CO_2 -containing flue gas has been bubbled through aqueous slurries to form carbonic acid in the aqueous phase [**85**]. The carbonic acid results with basic components of the red mud, lowering its pH. However, the pH of water exposed to gaseous CO_2 is not likely to drop below 5.5 (approximately), and hence the rate of reaction neutralization of the solids in the aqueous sluny is typically not fast enough to satisfy industrial needs. At the short contact times which industrial process rates demand, only a fraction of the alkaline material in red mud is neutralized using gaseous CO_2. Hence although the pH of the aqueous phase drops rapidly upon exposure to CO_2 gas, it soon rises again to unacceptable levels as additional alkaline material leaches from the mud **[18].**

III) Sea water neutralization

The mud is actively mixed with the seawater for a period of around 30 minutes to enable the reactions to take place. When seawater is added to caustic red mud, the pH of the mixture is reduced causing hydroxide, carbonate or hydroxycarbonate minerals to be precipitated **[50]**. Average seawater contains 965 gm of water and 35 gm of salts (i.e. 3.5% salinity). The concentration of various salt ions in seawater is 55% Chlorine (Cl^-), 30.6% sodium (Na^+), 7.7% sulphate (SO_4^{2-}), 3.65% magnesium (Mg^{2+}), 1.17% calcium (Ca^{2+}), 1.13% potassium (K^+) and 0.7% others**[49].** Seawater is added until the liquid phase of the precipitates can be decanted and reduced in alkalinity from pH 9.5 to 9. Seawater neutralization does not eliminate hydroxide from the system but converts the readily soluble, strongly caustic wastes into less soluble, weakly alkaline solids. To meet marine discharge standards the liquid is treated with acid to bring the pH to below 9 and a total alkalinity less than 200 mg/l (as calcium carbonate equivalent alkalinity). This would normally require 0.05 litres of concentrated sulphuric acid per 1,000 litres of red mud after treating with seawater.

IV) Bioleaching

The microbial remediation of the buxite residue has been tried by some researcher of western Australia by Alcoa of Australia Limited. They added some organic substrate to the red mud which facilitate the growth of organisms, which produce some organic acids and CO_2 to neutralize the red mud. There are commercially many different types of organic substrates used for producing each type of organic acids. The commercial substrate used for acetic acid production are grape wine, fermented apples, barley or cereal malt and rice starch. The substrates used for production of citric acid are glucose, fructose, sucrose and lactose. 12-18% sucrose, whey, 3% 1, 2-propanediol are used as substrate for production of lactic acid. Lactose and glucose is used for production of propionic acid.

V) Sintering

Sintering of residue can be carried out to fix all leachable soda, but the cost would be very high due to the elevated energy consumption required for high temperature sintering of red mud. But the mechanism can be made use of in making bricks and blocks from red mud.[**64]**

VI. UTILIZATION OF RED MUD

Due to unique physical and chemical properties of red mud it can be used in several aspects. The applications which have been in use either in pilot or commercial scale are shortly reviewed here:

- for amendment of acidic soils, for immobilization of heavy metals and/or for retaining of certain nutrients, such as phosphorus in agriculture

- for making crude and fine ceramics, such as tiles, floor tiles
- for making bricks
- in road contruction, first of all the coarse fraction
- as a component in making cement, OPC and special cements, cement mortar
- an an additive in ferrous metallurgy
- as a filler in rubber and plastic industry
- as pigment in production of paints
- as a material used for trapping carbon dioxide and/or sulfur dioxide from flue gases
- as a feedstock for manufacturing adsorbents and catalysts
- as a feedstock for making water and sewage treatment agents **[33]**

But till date red mud has limited commercial utilization in road making, land reclamation and also used as a constituent in making Portland cement. Development of suitable metallurgical process for metal recovery from red mud is important for bulk utilisation, value addition and moving towards zero waste. **[75]**

I) Recovery of metals

Since iron as oxides/oxyhydroxides is usually the largest component of red muds, iron recovery from red mud has attracted major attention. Several reviews have been published on the utilization of metal values present in red mud. Two main approaches which have been generally investigated to recover iron values are based on : (a) solid state reduction of red mud followed by magnetic separation to recover iron; and (b) reduction smelting in a blast/electric/low shaft furnace (with or without pre reduction) to produce pig iron. The former had limited success but the smelting technology appears to have been standardised on bench/pilot scale, for example the work done at McDowel Wellman Engg. Co.,USA, and Giulini GmbH, Germany **[66].**

The fundamental industrial processes used for extraction of single oxides such as iron from red mud demonstrated to be economically unsustainable. The iron oxide content of the red mud cannot be considered as competitive raw material for steel making because of it is lower than commercial iron ore. This kind of single oxide application generates new solid waste again. Therefore, development of a novel economic process to recover valuables from red mud while minimising the disposal of this residue was of much interest. So for that a new aluminothermic process applicable to the Bayer waste in order to recover valuables such as ferro alloys and other raw materials such as ceramic powders while reducing the disposal of this residue. The main advantages of this process upon the other applications are that, it occurs at low processing temperatures and the reaction products can easily be separated by a magnetic method **[8].**

In India, know how for the recovery of Fe, Al_2O_3, V and Cr from red mud has been developed by Regional Research Laboratory (RRL), Bhubaneswar . National Metallurgical Laboratory (NML), Jamshedpur has evaluated technical feasibility of Al_2O_3 extraction, along with vanadium oxide, from Muri red mud by Soda-Lime sinter process. Prasad and co-workers have explored the production of ferrotitanium to utilize both iron and titanium values of Indian red muds. **[57],[12],[19],[66]**

Researchers in Russia, Hungary, America and Japan have carried out iron production experiments from red mud. Researchers from the University of Central South have made steel directly with iron recovered from red mud **[44]**. The Chinese Metallurgical Research Institute has enhanced the iron recovery rate to 86% through making a sponge by red mud-magnetic separation technology. Sun et al. **[84]** researched magnetic separation of iron from Bayer red mud and determined the process parameters of the magnetic roasting-magnetic selecting method to recover concentrated iron ore **[67].**

II) Waste water treatment

Red mud presents a promising application in water treatment for removal of toxic heavy metal and metalloid ions, inorganic anions such as nitrate, fluoride, and phosphate, as well as organics including dyes, phenolic compounds and bacteria **[63],[35].** The use of red mud as adsorbent for heavy metals (Cu(II), Pb(II), Cd(II), Cr(V), As(III), As(V), Ni(II), Zn(II)) has been avocated. **[28],[46],[27],[14],[22],[79],[103],[92],[96]**

TABLE X

ADSORPTION CAPACITY OF RED MUD FOR THE REMOVAL OF DIFFERENT METAL IONS FROM WATER **[11].**

Adsorbent	Adsorbate	Amount adsorbed	Reference
Red mud	As(III)	8.86 µmol/g	[5]
Red mud	As(V)	6.86 µmol/g	[5]
Activated red mud	As(III)	11.80 µmol/g	[4]
Activated red mud	As(V)	12.57 µmol/g	[4]
Seawater-neutralized red mud (Bauxsol)	As(V)	6.08–14.43 µmol/g	[26]
Bauxsol-coated sand	As(V)	1.64–3.32 mg/g	[25]

Activated-Bauxsol-coated Sand	As(V)	2.14 mg/g	[25]
FeCl3-coated sand	As(V)	23.2–68.5 mg/g	[101]
CO2-neutralized red mud (ANRM)	As(V)	55.55 mg/g	[72]
Activated red mud	Cr(VI)	30.74 mmol/g	[55]
Red mud	Ni(II)	13.69 mg/g	[33]
Red mud	Cu(II)	2.28 mg/g	[2]
Granular red mud	Cd(II)	38.2–52.1 mg/g	[102]
Red mud	Cu(II)	19.72 mg/g	[43]
Red mud	Zn(II)	12.59 mg/g	[43]
Red mud	Ni(II)	10.95 mg/g	[43]
Red mud	Cd(II)	10.57 mg/g	[43]
Treated red mud	Cd(II)	46.9–66.8 mg/g	[7]
Treated red mud	Cu(II)	35.2–75.2 mg/g	[7]
Treated red mud	Pb(II)	117.3–165.8 mg/g	[7]
Red mud	Pb(II)	64.79 mg/g	[28]
Red mud	Cr(VI)	35.66 mg/g	[28]
Red mud	Cd(II)	1.16 × 104 mol/g	[30]
Red mud	Zn(II)	2.22 × 104 mol/g	[30]
Red mud	Cd(II)	68 mg/g	[92]
Red mud	Zn(II)	133 mg/g	[92]
Calcined red mud	Copper	18.18–65.17 mg/g	[78]
Calcined red mud	Zinc	15.45–99.20 mg/g	[78]
Calcined red mud	Arsenic	18.83–27.51 mg/g	[78]
Neutralized red mud	Boron	30.12 mg/g	[15]

TABLE XI

ADSORPTION CAPACITY OF RED MUD FOR THE REMOVAL OF DIFFERENT DYES FROM WATER. **[11]**

Adsorbent	Adsorbate	Amount adsorbed	Reference
Red mud	Rhodamine B	(1.01–1.16) × 10−5 mol/g	[29]
Red mud	Fast Green	(7.25–9.35) × 10−6 mol/g	[47]
Red mud	Methylene Blue	(4.35–5.23) × 10−5 mol/g	[30]
Red mud	Congo Red	4.05 mg/g	[47]
Red mud	Acid Violet	1.37 mg/g	[48]
Acid-activated red mud	Congo Red	7.08 mg/g	[87]

TABLE XII

ADSORPTION CAPACITY OF RED MUD FOR THE REMOVAL OF PHENOLIC POLLUTANTS FROM WATER. **[11]**

Adsorbent	Adsorbate	Amount adsorbed	Reference
Red mud	Phenol	0.63–0.74 mol/g	[24]
Red mud	2-chlorophenol	0.72–0.79 mol/g	[24]
Red mud	4-chlorophenol	0.78–0.82 mol/g	[24]
Red mud	2,4-dichlorophenol	0.80–0.85 mol/g	[24]
Neutralized red mud	Phenol	4.12 mg/g	[88]
Acid-activated red mud	Phenol	8.16 mg/g	[89]

TABLE XIII

ADSORPTION CAPACITY OF RED MUD FOR THE REMOVAL OF DIFFERENT ANIONS FROM WATER. **[11]**

Adsorbent	Adsorbate	Amount adsorbed	Reference
Heat-activated red mud	Phosphate	155.2 mg/g	[45]
Acid-heat-activated red mud	Phosphate	202.9 mg/g	[45]
HCl-treated red mud	Phosphate	0.58 mg/g	[37]
Bauxsol	Phosphate	0.21–0.48 mmol/g	[3]
Red mud	Fluoride	13.46 mg/g	[98]
Red mud modified with AlC13 (MRMA)	Fluoride	68.07 mg/g	[98]
Red mud modified with heat activation (MRMAH)	Fluoride	91.28 mg/g	[98]
Red mud	Nitrate	1.859 mmol/g	[16]
Activated red mud	Nitrate	5.858 mmol/g	[16]

III) Construction

A) Red Mud in Cement Replacement

Dicalcium silicate in red mud is also one of the main phases in cement clinker, and red mud can play the role of crystallization in the production of cement clinker. Fly ash is mainly composed of SiO_2 and Al_2O_3, thus can be used to absorb the water contained in the red mud and improve the reactive silica content of the cement. Scientists conducted a series of studies into the production of cement using red mud, fly ash, lime and gypsum as raw materials. Use of red mud cement not only reduces the energy consumption of cement production, but also improves the early strength of cement and resistance to sulfate attack. **[62],[20],[67]**

Red mud from HINDALCO (Hindustan Aluminum Corporation) Industries Limited, Renukoot, India, contains significant quantities of alumina, iron oxide and silica. Preparation of these varieties of cements was namely

- Aluminoferrite (C_4 AF)–belite (β-C 2S) using lime +red mud+ fly ash
- Aluminoferrite-ferrite (C_2 F)–aluminates (C_3 AandC$_{12}$ A_7) utilising lime+ red mud+ bauxite
- Sulfoaluminate (C_4 A_3 "S)-aluminoferrite-ferrite using lime +red mud+ bauxite gypsum

Cements made from lime+ red mud+ bauxite or lime+ red mud+ bauxite +gypsum exhibit strengths comparable or superior to ordinary Portland cement. The most promising proportions seem to be30–35% of the HINDALCO redmud+15–20%bauxite+7.5–10% gypsum+45– 50% lime depending on the type of cement desired **[74]**

B) Red mud in the brick industry

D.Dodoo- Arhin, et al [2013] have been investigated bauxite red mud-Tetegbu clay composites for their applicability in the ceramic brick construction industry as a means of recycling the bauxite waste. The initial raw samples were characterized by X-ray diffraction (XRD) and thermo gravimetric (TG) analysis. The red mud-clay composites have been formulated as 80%-20%, 70%-30%, 60%-40%, 50%-50% and fired at sintering temperatures of 800ºC, 900ºC and 1100ºC. Generally, mechanical strengths (modulus of rupture) increased with higher sintering temperature. The results obtained for various characterization analyses such as bulk densities of 1.59 g/cm^3 and 1.51 g/cm^3 compare very well with literature and hold potential in bauxite residue eco-friendly application for low-cost recyclable constructional materials. Considering the physical and mechanical properties of the fabricated brick samples, the batch formulation which contained 50% each of the red mud and Tetegbu clay is considered the best combination with optimal properties for the construction bricks application and it could be employed in lighter weight structural applications. **[67]**

Stabilized red mud blocks have been prepared by Banaras Hindu University (BHU) using HINDALCO red mud. From a mixture of red mud, fly ash, lime grit and ordinary port land cement, blocks of high strength 60 kg/cm^2 were produced after sun drying (curing). CBRI, Roorke has developed stabilized blocks whose strength is between that of grades II/III bricks. They have developed red mud+ clay and red mud+ fly ash bricks of high strength comparing to grade I bricks. BHU has prepared low density/hollow bricks and blocks of red mud with low density 1.1–1.2 g/cm^3 . These hollow/foamed bricks have varying crushing strength of 50–260 kg/cm^2 . They have also used a mixture of red mud, fly ash and additive with firing at 1000 °C producing bricks with crushing strength of 130–160 kg/cm^2 and 14% water absorption capacity. Central Glass Ceramic Research Institute (CGCRI), Jadhavpur has also prepared hollow bricks using red mud and a proprietary foaming agent. They developed red mud+ clay and red mud + fly ash bricks of high strength comparing to grade I bricks **[58], [74].**

BHU has used red mud as additive for production of cement and mortars (Project Sponsored by HINDALCO). The crushing strength was found to be optimum at a minimum of 10 % red mud addition. The crushing strength and bond stress of the mortar has been found to improve with 5–10% red mud addition. MALCO red mud has been used by orient cements (2–4%) and certain parameters of the cement showed improvement while using red mud **[58],[75].**

C) Concrete industry

Red mud from Birac Alumina Industry, Serbia was tested as a pigment for use in the building material industry for standard concrete mixtures. Red mud was added as a pigment in various proportions (dried, not ground, ground, calcinated) to concrete mixes of standard test blocks (ground limestone, cement and water) **[13]**. The idea to use red mud as pigment was based on extremely fine particles of red mud (upon sieving: 0.147 mm up to 4 wt%, 0.058 mm up to 25 wt% and the majority smaller than 10 microns) and a characteristic red colour. Compressive strengths from 14.83 to 27.77 MPa of the blocks that contained red mud between 1 and 32% were considered satisfactory. The reported tests have shown that neutralized, dried, calcined and ground red mud is usable as pigment in the building materials industry. Red oxide pigment containing about 70 % iron oxide was prepared from NALCO red mud by **[76]** after hot water leaching filtration, drying and sieving. **[67]**

D) Used as filling Material

1) *Road base material*: High-grade road base material using red mud from the sintering process is promising, that may lead to large-scale consumption of red mud. Qi JZ [2005] suggest using red mud as road material. Based on the work of Qi, a 15 m wide and 4 km long highway using red mud as a base material was constructed in Zibo, Shandong Province. A relevant department had tested the sub grade stability and the strength of road and concluded that the red mud base road meets the strength requirements of the highway **[100],[67]**
2) *Mining:* Yang et al. [Yang LG et al 1996], from the Institute of Changsha Mining Research, have studied the properties, preparation and pump pressure transmission process of red mud paste binder backfill material. Based on this study, a new technology named "pumped red mud paste cemented filling mining" has been developed by the Institute of Changsha Mining Research, in cooperation with the Shandong Aluminum Company. They mixed red mud, fly ash, lime and water in a ratio of 2:1:0.5:2.43, and then pumped the mixture into the mine to prevent ground subsidence during bauxite mining. The tested 28-day strength can reach to 3.24 MPa. This technology is a new way not only for the use of red mud, but also for non-cement cemented filling, successfully resolving the problem of mining methods in the Hutian bauxite stop. Underground exploitation practice on the bauxite has proved that cemented filling technology is reliable and can effectively reduce the filling costs, increase the safety factor of the stop and increase the comprehensive benefits of mining **[97],[67]**
3) *Smelting of red mud:* The recent trend in the development of cleaner processes for iron making is to reduce the number of steps involved in the conventional process. The newly emerging smelting reduction (SR) processes use non-coking coal as fuel and reductant and burden preparation steps such as sintering. Hence, the environmental performance of a smelting reduction-based steel plant is expected to be significantly superior as compared to a blast furnace-based steel plant **[59],[74].**

The National Mineral Development Corporation (NMDC), is setting up a 0.3 mtpa iron plant at Dantewada district of Chhattisgarh, India, to utilize the fines and slimes generated from their mines. It has been proposed to convert all the red mud into pig iron and slag. A laboratory study was conducted to investigate the ability of neutralization of red mud using carbon dioxide gas sequestration cycle at ambient conditions **[71].** Red mud can also be used for the sequestration of green house gases with reference to carbon dioxide. A red mud sample was separated into three different size fractions of varying densities (1.5–2.2 g cm − 3). Carbonation of each fraction of red mud was carried out separately at room temperature using a stainless steel reaction chamber at a fixed pressure of 3.5 bar. The effects of reaction time (0.5–12 h) were studied as well as the liquid to solid ratio (0.2–0.6). Characterization studies revealed the presence of boehmite, cancrinite, chantalite, hematite, gibbsite, anatase, rutile and quartz **[81]** Calcium bearing mineral phases were responsible for carbonation of red mud. The carbonation capacity was evaluated to be 5.3 g of CO_2 /100 g of red mud. Red mud has been utilized for making X-ray shielding materials. A novel method for making radiation shielding materials utilizing red mud and barium compounds has been developed by ceramic processing routes using phosphate bonding **[63].** The study confirmed the presence of celasian, bafertise and iron titanium oxide as the major shielding phases. It can be preferably be used for the construction of X-ray diagnostic and CT scanners room to provide adequate shielding against X-ray photons **[97]**. Recently red mud played a significant role in the preparation of TiO_2 nano powders **[87],[74]**

VII. SUMMARY AND CONCLUSION

In this review article it was shown that the Red mud is a highly complex material having group of materials due to different bauxites used and the different process parameter. The red mud has a very wide range of application from building material to metal recovery. The economic evaluation of a specific process to recover metal of significant value depends on the red mud composition. Considerable effort has been expended in finding application for bauxite residue but a number of key factors affect the feasibility and economics of its adoption. One of the most important ways of reducing the negative environmental impacts of the alumina industry is environmentally sustainable discharge and storage of digestion residue. It has been seen that there are various neutralizing method has been adopted to reduce the alkalinity hazard of red mud which is a significant hazard associated with this. The developments in dry disposal methods will certainly lead to better management of residue but neutralization of red mud will be an essential ingredient of any permanent solution. There still a continuous research is required by studying its residue neutralization technologies which is an important barrier for its use and management practice. Depending upon the 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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