

Progress of Red Mud Utilization: An Overview

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ABSTRACT

Red mud is a solid waste residue of the digestion of bauxite ores with caustic soda for alumina production. Its disposal remains a worldwide issue in terms of environmental concerns. During the past decades, extensive work has been done by a lot of researchers to develop various economic ways for the utilization of red mud. This paper provides a review on the comprehensive utilization of red mud globally. The research progress of safe stockpiling of red mud is summarized. Enormous 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 in different fields. The chemical and mineralogical characteristics of red mud are summarized with their environmental concerns.

Keywords: Red mud; characterization; disposal; neutralization; comprehensive utilization

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INTRODUCTION

Red mud is the solid waste residue of the digestion of bauxite ores with caustic soda for alumina (Al_2O_3) production. Approximately 35–40% of the processed bauxite ore goes into the waste as alkaline red mud slurry which consists of 15–40% solids and 0.8–1.5 tons of red mud is generated per ton of alumina produced [1]. It is estimated that annually 70 million tons of red mud is produced all over the world, with 0.7 million tons in Greece [2], 2 million tons in India [3], 30 million tons in Australia [4] and nearly 30 million tons in

China. As a solid waste, red mud is usually disposed in mud lakes in the form of slurry

impoundment or stack in ponds as dry mud near alumina plants or directly discharged through a pipeline into a nearby sea. Due to the characteristics of fine particles, high alkalinity (pH 10–12.5) and trace metal content, the disposal of large quantities of red mud has caused serious environmental problems including soil contamination, groundwater pollution and fine particles' suspension in the sea. Moreover, the storage

of red mud in lakes or ponds occupies huge areas of land, and the storage of dry red mud can also lead to dust pollution which is a serious health problem for the people living near the red mud storage ponds. The cost of red mud disposal is expensive, accounting for about 2% of the alumina price [5]. For example, the alumina price is about US\$439 per ton in China, so the disposal cost of red mud would be nearly US\$9 per ton of alumina production. Over the years, extensive work has been done by researchers worldwide to develop various economic ways for the utilization of red mud. The various applications that have been investigated include: (i) as a stabilization material for the preparation of liners [6]; (ii) as adsorbents for the removal of heavy metals, dyes, phosphate, nitrate and fluoride [7]; (iii) preparation of catalysts; (iv) recovery of iron, aluminum, titanium and other trace metals [8]; (v) production of radiopaque materials [9]; (vi) preparation of ceramics [10]; (vii) production of construction bricks [11]; (viii) development of pigments and paints [12] and (ix) preparation of cements [13].

Considerable research and development work for the storage, disposal and utilization of red mud is being carried out all over the world [14]. The paper reviews the World and Indian aspects of production of bauxite and generation of red mud. It describes the characterization, disposal, various neutralization methods and utilization of red mud. It gives the detailed appraisal of the work being carried out for making use of red mud in building, pollution control and metal recovery. This paper reviews matters in the context of environmental concerns of disposal of red mud and its utilization.

1.ORIGIN OF BAUXITE

The name bauxite was derived from the French province Les Baux and is widely used to describe aluminium ore containing high amounts of aluminum hydroxides. Bauxite is a member of the family of lateritic rocks. It is characterized by a particular enrichment of aluminum-hydroxide minerals, such as gibbsite, boehmite and/or diaspore. Bauxite forms by weathering of aluminous silicate rock (lateritic bauxite) and less commonly of carbonate rock (karst bauxite) mainly in tropical and sub-tropical climate. Bauxite forms by weathering under conditions favorable for the retention of alumina and the leaching of other constituents of the parent rock. Bauxite rock has a specific gravity between 2.6 to 3.5 kg/m³. It is usually, an amorphous or clay like substance which is however, not plastic. The usual color of bauxite is pink but if of lower iron content it may tend to become whitish in color and with increase in iron it is reddish brown in color [15].

2.PRODUCTION AND CLASSIFICATION OF BAUXITE

Bauxite resources are estimated to be 55 to 75 billion tons, located in Africa (33%), Oceania (24%), South America and the Caribbean (22%), Asia (15%), and elsewhere (6%) [16]. The worldwide metallurgical bauxite production for the year 2008 and 2009 is given in Table 1. Based on the production, data collected from the International Aluminum Institute, world alumina production during the first two quarters of 2008 increased by 4% as compared to the

same period in 2007. Expansions of bauxite mines in Australia, Brazil, China and India accounted for most of the increase in worldwide production of bauxite in 2008 [16]. Reduced output from bauxite mines in Guinea, Guyana, Jamaica, Russia and Suriname was partially offset by increases in production from new and expanded mines in Australia, China, Brazil and India and accounted for most of the slight decrease in worldwide production of bauxite in 2009 as compared to 2008.

Table 1. Worldwide metallurgical bauxite production, source [16]

Country	Mine production×1000 tone	
2008	2009	
Australia	61400	63000
China	35000	37000
Brazil	22000	28000
India	21200	22300
Guinea	18500	16800
Jamaica	14000	8000
Russia	6300	3300
Venezuela	5500	4800
Suriname	5200	4000
Kazakhstan	4900	4900
Greece	2200	2200
Guyana	2100	1200

Vietnam	30	30
Other Countries	6550	5410
World Total	205000	201000

Bauxites can be classified in function of the ore type. Alumina occurs in 3 phases defining ore type: gibbsitic ($\gamma\text{-Al}(\text{OH})_3$), boehmitic ($\gamma\text{-AlO}(\text{OH})$) and diasporic ($\alpha\text{-AlO}(\text{OH})$). These are crystallographically different and their occurrence in various countries is given in Table 2. The mineralogical characteristics of the bauxite ore determine the type of process needed for alumina production.

India has confirmed 3 billion tones of bauxite reserves out of the global reserve of 65 billion tones [17]. India is self-sufficient in bauxite. Bauxite deposits are mostly associated with

laterite and occur as blankets or as capping on the high plateaus in peninsular India. India has the fifth largest bauxite reserves which are 7% of world deposits.

India's share in world aluminum capacity rests at about 3%. India has large resources of high-grade bauxite deposits of the order of 3037 million tons (proved + probable + possible). The recoverable reserves are placed at 2525 million tones. The proved and probable reserves are 1218 million tones, placing the country 5th in rank in the world, next only to Australia, Guinea, Brazil and Jamaica [18]. About 89% of the recoverable reserves of bauxite are of metallurgical grade. Orissa is the largest bauxite producer (43.6 per cent of total production in 1998-99) followed by Jharkhand (19.2 %), Maharashtra (13.3 %) and Madhya Pradesh/Chhattisgarh (11.4%). Production from Gujarat, Andhra Pradesh and Tamil Nadu is also worth mentioning [15].

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.

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:

1. Gibbsite bauxite (Eastern ghats, Gujarat and coastal deposits of western India)
2. Mixed gibbsite-boehmite bauxite (boehmite < 10%, diasporite < 2%; parts of Western Ghats and Gujarat deposits.)
3. Boehmite bauxites (boehmite > 10 and diasporite < 2%; Central Indian bauxite).
4. Diasporic bauxites (diasporite > 5%; J & K and some part of Central Indian and Gujarat deposits).

Typical compositions of industrially used bauxite are Al_2O_3 (40-60%), combined H_2O (12- 30%), Fe_2O_3 (7-30%), SiO_2 free and combined (1-15%), TiO_2 (3-4%), F, P_2O_5 , V_2O_5 and others (0.05-0.2%) [19].

3. PRODUCTION OF ALUMINA IN INDIA

The worldwide alumina production is around 58 million tones in which India counts for 2.7

million tones [17]. The Indian aluminum sector is characterized by large integrated players like Hindalco and National Aluminum Company (Nalco, Alumina plant at Damanjodi, Orissa), and the newly started Vedanta Alumina Ltd (Alumina plant at Lanjigarh, Orissa). The other producers of alumina include Indian Aluminum Company (Indal having two plants at Belgaum, Karnataka and Muri, Jharkhand), now merged with Hindustan Aluminum Company (Hindalco, Renukoot, Uttar Pradesh), Bharat Aluminum (Balco) and Madras Aluminum (Malco) the erstwhile PSUs, which have been acquired by Sterlite Industries. Consequently, there are only three main primary metal producers in the sector namely Balco (Vedanta), National Aluminum Company (Nalco) and Hindalco (Aditya Birla Group) [17].

4. BAYER'S AND SINTERING PROCESS

The production of caustic red mud makes the Bayer process an environmentally challenging process. Red mud, which derives its name from the color of iron oxides in the substance, comprises up to 60% of the bauxite material, depending on the ore. For each tone of alumina produced, up to two tones of red mud are generated. The exponential growth rate of the quantity of red mud in the world, driven by global consumption of aluminum, is a major environmental concern for the aluminum industry and a hazard for the communities and ecosystems near production facilities.

Though alumina can be produced from bauxite under alkaline conditions using lime

(Lime Sinter process) [20], sodium carbonate (Deville Pechiney process) [21], at high temperature in reducing environment with presence of coke and nitrogen (Serpeck process) [22], the alkalisation by the use of sodium hydroxide (Bayer process) [23] is the most economical process which is employed for purification of bauxite if it contains considerable amount of Fe_2O_3 .

The production process of alumina is shown in Fig. 1. In the Bayer process, bauxite is digested by leaching it with a hot solution of sodium hydroxide, NaOH , at $106\text{--}240^\circ\text{C}$ and at 1-6 atm pressure. This converts the aluminum minerals into tetrahydroxoaluminate $\text{Al}(\text{OH})_4^-$, while dissolving in the hydroxide solution. The other components of bauxite except silica (present in kaolinite) do not dissolve [14]. The insoluble compounds are separated by settling and the decant solution is further clarified by filtering off remaining solid impurities [24]. The waste solid is washed and filter pressed to regenerate caustic soda and is called red mud presenting a disposal problem. Next, the hydroxide solution is cooled and the dissolved aluminum hydroxide precipitates as a white, fluffy solid. When heated to 1050°C (calcined), the aluminum hydroxide decomposes to alumina, giving off water vapor in the process. A large amount of the alumina so produced is then subsequently smelted in the Hall Heroult process in order to produce aluminum.

In the sintering process, the crushed bauxite ores are usually mixed with limestone and caustic soda and the mixture is sintered at a high temperature of about 1200°C to form soluble sodium aluminate upon addition of water or diluted alkaline solution. The sintering process is suitable for refining bauxite ore with $\text{Al}_2\text{O}_3/\text{SiO}_2$, (A/S) values of 3–6. In addition, the combination of Bayer process and sintering process is also used in some of the Chinese alumina plants with large productions such as Zhengzhou Aluminum Plant, Guizhou Aluminum Plant and Shanxi Aluminum Plant. The combination process is used for refining bauxite ores with $\text{A/S} > 4.5$.

5. CHEMICAL AND MINERALOGICAL CHARACTERISTICS OF RED MUD

No matter what the production process is, the chemical composition of red mud contains six major constituents. Chemical analysis shows that red mud contains silicium, aluminium, iron, calcium, titanium, sodium as well as an array of minor elements namely K, Cr, V, Ba, Cu, Mn, Pb, Zn, P, F, S, As and etc. The variation in chemical composition between red mud worldwide is high. Typical composition of red mud is given in Table 3 [25]. Typical chemical composition of red mud generated by Indian alumina plants is as given in Table 4 [26], whereas calcium oxide and silica are the most major constituents for red mud from the sintering process. The major chemical composition of red mud for selected countries over the world is presented in Table 5.

Fig. 1. Production process for Alumina;
Source: [University of West Indies]

Table 3. Typical composition of red mud

Composition	Weight %
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	Trace-25 %

Table 4. Chemical composition of Indian red muds

Company	Al ₂ O ₃ %	Fe ₂ O ₃ %	SiO ₂ %	TiO ₂ %	Na ₂ O%	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		

Generally, the major mineralogical phases of red mud from the Bayer process are gibbsite (Al(OH)₃), boehmite (γ -AlOOH), hematite (Fe₂O₃), goethite (FeO(OH)), quartz (SiO₂), anatase (TiO₂), rutile (TiO₂) and calcite (CaCO₃), and the principal mineralogical constituents of red mud from the sintering process are β -2CaO.SiO₂, calcite (CaCO₃), aragonite (CaCO₃), hematite (Fe₂O₃), gibbsite (Al(OH)₃) and perovskite (CaTiO₃).

Table 5. Major chemical composition of red mud generated in alumina plants in various countries

Country	Plant	Ref.	Major Composition (Wt %)		
No.	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂	Na ₂ O
	CaO				
Italy	Eurallumina	[27]	35.2	20	
	9.2	11.6	7.5	6.7	
Turkey	Seydisehir	[28]	36.94	20.39	
	4.98	15.74	10.10	2.23	
UK	ALCAN	[29]	46.0	20.0	
	6.0	5.0	8.0	1.0	
France	Aluminum	[12]	26.62	15.0	
	15.76	4.98	1.02	22.21	
Pechiney					
Canada	ALCAN	[30]	31.60	20.61	
	6.23	8.89	10.26	1.66	

Australia	AWAAK	[31]	28.5	
			24.0	3.11 18.8 3.4 5.26
Brazil	Alunorte	[31]	45.6 15.1	
			4.29	15.6 7.5 1.16
Germany	AOSG	[31]	44.8 16.2	
			12.33	5.4 4.0 5.22
Spain	Alcoa	[31]	37.5 21.2 11.45	
			4.4	3.6 5.51
USA	RMC	[31]	35.5 18.4 6.31	
			8.5	6.1 7.73

Red mud is a very fine grained material. Typical values for particle size distribution are 90 weight % below 75 microns. The specific surface area (BET) of red mud is between 10 and 30 m²/g, depending on the degree of grinding of bauxite.

6.STOCKPILING OF RED MUD

The stocking method of red mud can be divided into two types: wet stocking and dry stocking. As to wet stocking, red mud is transported into the yard as slurry and then is stocked after precipitation. Contrariwise, dry stocking involves the transport of desiccative red mud into the yard, where the red mud obtains accumulation capacity by the effect of solar and air drying. Wet stockpiling capacity can be increased in this way and it is suitable for the sintering process of red mud. But it has high requirements on the yard, especially on the initial dam, the construction and maintenance of which is costly. Because the red mud is slurry, the dam should be more firm and impermeable. Compared with the wet

stockpiling, dry stockpiling does not require such initial damming, causes little pollution and is suitable for stockpiling Bayer process of red mud.

Qiao [32] and Sun [33] proposed and developed a stockpiling technique known as “mixed stocking”, which is an intermediate method between the “dry” and “wet” methods. It is a novel method using sintering red mud and Bayer red mud in the initial dam and Bayer red mud in the sub-dams. The “mixed stocking” method combines the advantages of both, with small investment of the initial dam and sub-dam and uncomplicated operation management. So, the design of the yard depends upon specific conditions. The schematic diagram of the “mixed stocking” method is shown as Fig. 2.

Fig. 2. The schematic diagram of the “mixed stocking” method. Source [34]

As to the design of the stockpiling yard, it is necessary to recover and discharge the liquor, and improve the impermeability of the dam for the purpose of improving the safety factor of

the yard and reducing the risk of pollution or dam failure. Zhou [35] suggested that

increasing the quantity and quality overflow wells can improve the recovery rate of the liquor. He also indicated that well impermeability and ability to drain is conducive to keeping the dam stable. Furthermore, Wang [36] compared several drainage reinforcement methods commonly used in retention dams in particular horizontal well drainage, radiation well drainage, light

well point drainage and vertical and horizontal jointed drainage and verified vertical and horizontal jointed drainage with a specific case study.

Li et al. [37] successfully applied the finite element analysis in the risk evaluation of red mud. He also discussed how finite element analysis should be used in the calculation of the saturation line and dam slope in the red mud disposal field and proved the validity of the finite element numerical method with the safety assessment for a real yard capacity improvement case study. Rao [38] discussed the causes of cracks appearing in dry red mud, pointing out that factors such as settlement differences, dehydration shrinkage, dissolution of soluble salts and pressure differences led to the formation of cracks. Cracks bring potential danger to the integrity, impermeability and safe operation of yard. Research about crack formation mechanism, the crack growth mechanism and the regulation to prevent crack formation have very important significance and thus require more attention.

7. RED MUD NEUTRALIZATION

Neutralization of red mud will help to reduce the environmental impact caused due to its storage and also lessen significantly 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. The cost of neutralization will, to some degree at least, be offset by a reduction in the need for long-term management of the residue deposits. Instead of accruing funds to deal with a future liability, the funds can be invested in process improvements, which reduce or remove the

liability. 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 [39]. 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 [40]. 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, seawater neutralization, bioleaching and sintering.

Acid Neutralization

Various aqueous acidic solutions have been considered for neutralization of alkalinity, including acidic industrial wastewater. The use of carbonic acid has also been considered. A number of studies have been done to assess the feasibility of treating bauxite residue with acid as for instance on Kwinana red mud slurry. Large volumes of reagent are required to fully neutralize the residue at a relatively high cost, even if spent (waste) acid could be used. The use of acid also introduces large volumes of impurities to the process water stream (sulphate in the case of sulfuric acid, chloride in the case of hydrochloric acid). It is therefore likely that the return of any water from the residue deposits to the production process will be unacceptable without further

treatment to remove these added impurities. Treating red mud with acidic spent pickling solutions (SPSs), derived from the steelmaking process, provides a coagulant a mixture of aluminum and iron salts- for waste water treatment [41].

CO₂ Treatment

Gas phase CO₂ or CO₂-containing flue gas has been bubbled through aqueous slurries to form carbonic acid in the aqueous phase [42]. Mechanisms of neutralization of red mud by carbon dioxide gas have been studied [43]. The carbonic acid reacts with basic components of the red mud, lowering its pH. At the short contact times which industrial process rates demand, only a fraction of the alkaline material in red mud is neutralized using gaseous CO₂. Hence although the pH of the aqueous phase drops rapidly upon exposure to CO₂ gas, it soon rises again to unacceptable levels as additional alkaline material leaches from the mud. The pH of water exposed to gaseous CO₂ is not likely to drop below 5.5 (approximately), and hence the rate of neutralization of the solids in the aqueous slurry is typically not fast enough to satisfy industrial needs. Hence researchers [44] have investigated the use of high-pressure liquid carbon dioxide rather than vapor phase carbon dioxide for the pH reduction of red mud. A laboratory study on neutralization of red mud using CO₂ in multiple cycles has been investigated [45].

Seawater Neutralization

When seawater is added to caustic red mud, the pH of the mixture is reduced causing hydroxide, carbonate or hydroxycarbonate minerals to be precipitated [46]. 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 (SO₄⁻²), 3.65% magnesium (Mg²⁺), 1.17% calcium (Ca²⁺), 1.13% potassium (K⁺) and 0.7% others [47]. Seawater neutralization does not eliminate hydroxide from the system but converts the readily soluble, strongly caustic wastes into less soluble, weakly alkaline solids. The carbonate and bicarbonate alkalinity of the waste is removed primarily by reaction with calcium to form aragonite and calcite [48].

Bioleaching

Bioremediation of bauxite residue in Western Australia by Alcoa of Australia [50] has been carried out by adding some organic substrate to the red mud for growth of microorganisms which generate different organic acids and CO₂ (in some cases) which in turn neutralize the red mud. Similar work has also been carried out by [51] using microbes. There are different types of organic substrates used for producing each type of organic acid. Commercial substrates 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.

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 used for making bricks and blocks from red mud. A comparison of all the neutralization processes has been made by [52].

8.UTILIZATION OF RED MUD

The key to solving red mud stockpiling is to develop a comprehensive utilization technology that consumes red mud or converts it into a secondary resource. Since the 1950s, scientists have carried out research projects that explore disposal and utilization of red mud, according to the unique physical and chemical properties of red mud.

Recovery of Components in Red Mud

Red mud primarily contains elemental components such as, Fe_2O_3 , Al_2O_3 , SiO_2 , CaO , Na_2O and K_2O . Besides, it also contains other components, such as Li_2O , V_2O_5 , TiO_2 and ZrO_2 . For instance, the content of TiO in red mud produced in India can be as much as 24%. Because of the huge amount of red mud, value elements like Ga, Sc, Nb, Li, V, Rb, Ti and Zr are valuable and abundant secondary resources. Therefore, it is of great significance to recover metals, especially rare earth elements from red mud.

Due to the characteristics of a high iron content, extensive research into the recovery of iron from Bayer process red mud have been carried out by scientists all over the world. The recycling process of iron from red mud can be divided into roasting magnetic recovery, the reducing smelting method, the direct magnetic separation method and the leaching- extraction method, according to the

different ways of iron separation. 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 [53]. 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. [54] 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.

In consideration of high content of aluminum and sodium in the red mud, only by recovering them can we make full use of these resources. Zhong et al. [55] recovered Al_2O_3 and Na_2O in red mud by the Sub-Molten Salt Method, with a one-way Al_2O_3 recovery rate of 88%. After dealuminization, the red mud undergoes a deep sodium removal treatment by NaOH solution, recycling Na_2O from red mud. Zheng et al. [56] discussed an aluminum and sodium recovery process of a soda lime method after adding silicon slag into red mud. Under the optimum conditions, the dissolution rates of aluminum and sodium is up to 95%, with red mud after the dissolution a Na_2O content of less than 1%, meeting the requirements for cement materials.

Production of Construction Materials from Red Mud

Among the uses standing out are those reported on the utilization of red mud for building materials production such as cement, bricks, roofing tiles and glass-ceramics. The

bulk production of building materials could eliminate the disposal problem.

A successful pilot project of a road embankment construction using Greek bauxite residue has been carried out by laboratory of Road Engineering of the Aristotle University of Thessaloniki, Greece [57]. The performance of the embankment with regards to its deformability was studied by means of the elastic behavior theory. This is an attractive option with a high potential for large volume reuse of red mud use. Bauxite residues have other options for its reuse in preparation of construction materials as stated below:

Geopolymers

Geopolymer is a term covering a class of synthetic aluminosilicate materials with potential use in a number of areas, essentially as a replacement for Portland cement and for advanced high-tech composites and ceramic applications. Advanced high tech composite materials are products for space, aerospace, defence, marine, petro chemicals and effluent treatment etc. Carbon epoxy/phenolic and silica phenolic components for space applications. All composite like fibre glass boats. Composite Aircraft components. Railway FRP Sleeper. The geopolymerization process involves a chemical reaction between red mud and alkali metal silicate solution under highly alkaline conditions. The product of this reaction is an amorphous to semi-crystalline polymeric structure, which binds the individual particles of red mud transforming the initial granular material to a compact and strong one. The potential use of red mud for synthesis of inorganic polymeric materials through a geopolymerization

process was studied to use it in the construction sector as artificial structural elements such as massive bricks [58]. Red mud was reacted with fly ash, sodium silicate via geopolymerization reaction to get red mud geopolymers which are a viable cementitious material that can be used in roadway constructions [59].

Giannopoulou et al. [60] studied the geopolymerization of the red mud and the slag generated in the ferronickel production, in order to develop inorganic polymeric materials with advanced mechanical and physical properties. The inorganic polymeric materials produced by the geopolymerization of the red mud developed compressive strength up to 21 MPa and presented water absorption lower than 3%. They stated that red mud may be viewed as alternatives in the industrial sectors of construction and building materials.

Clay based products:

Investigations of the use of red mud and fly ash for the production of heavy clay products have been extensively undertaken at the Central Building Research Institute, Roorkee, India [61]. Ekrem [62] studied the potential use of red mud for the preparation of stabilization material. The test results show that compacted clay samples containing red mud and cement–red mud additives have a high compressive strength, decreased hydraulic conductivity and swelling percentage as compared to natural clay samples. Consequently, it was concluded that red mud and cement–red mud materials can be successfully used for the stabilization of clay liners in geotechnical applications. Study on the exploitation of red mud as a clay additive

for the ceramic industry or as a compound for self-binding mortars in the fabrication of stoneware [63] was carried out at National Institute of Technology, Rourkela, Orissa, India. A study carried out by Pontikes et al. [64,65] was aimed at using bauxite residue in heavy clay industry in which the plasticity of clay mixtures with bauxite residue and polymer addition was evaluated. They found that addition of 30 wt% bauxite residue substituting the clay mixture increases the max. cohesion of the mixture. To make its use as a traditional ceramic, behavior of bauxite residue was studied in different firing atmospheres (Air, N₂, Ar/4% H₂) for different maximum temperature (950-1050°C) and different soaking time (30-300 min).

Cement

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 SiO₂ and Al₂O₃, 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 [66].

Ekrem Kalkan [67] studied using red mud as a cement stabilizer. In 1980, Barsherike [68] studied the possibility and rationality of producing cement with red mud as the raw material component of Portland cement, and successfully prepared cement complying with

the relevant standards. Vangelatos [69] studied the preparation of ordinary Portland cement from red mud, lime and freestone, and the 28-day compressive strength of the cement strength can reach 63MPa. In China, research has been completed on the production of sulfo-aluminate cement from red mud in 1955 [70]. This kind of production process is simple and inexpensive. However, the performance of the cement, with the exceptions, which may be considerable, of some individual indicators such as soundness, is close to or greater than ordinary Portland cement. Pan et al. [71] studied slag and red mud activated by a composite solid alkaline activator and developed alkali slag red mud cement which has the properties of greater early strength (the initial and final setting is separately 62 min and 95 min), high compressive strength (the 28-day compressive strength can be up to 125 MPa) and excellent resistance to corrosion, utilizing 30% of the red mud. Liang [72] and Zhong [73] prepared cement—red mud concrete using red mud. The compressive and flexural strength of this kind of concrete is close to or even higher than that of ordinary concrete, meeting the requirement of cement concrete used for pavement materials (the 28-day compressive strength is about 30–40 MPa; the 28-day flexural strength is about 4.5–5.5 MPa).

Brick

As an alternative to traditional raw materials used in brick production, red mud utilization can not only reduce the cost of raw materials, but also have great environmental significance. Xing [74], Yang [75], Zhang [76], Nevin et al.[77] separately reported the

production of non- steam-cured and non-fired brick, fly ash brick, black pellet decorative brick and ceramic glazed tile. For instance, non-steam-cured and non-fired brick is developed by using industrial residues as raw materials, by adding cement and lime as binder and by pressing and natural curing technology. The Institute of Shandong Aluminum Company and the Institute of Chinese Great Wall Aluminum Company separately achieved the production process of non-steam-cured and non-fired brick using red mud and fly ash as raw materials.

Glass

Yang et al. [78] conducted an experiment for red mud-fly ash glass, in which the maximum content of red mud and fly ash is collectively more than 90%. They acquired the optimum heat treatment process through investigation of crystallization and the factors influencing the crystal nucleation and growth. With red mud and chromium slag as the main materials, and quartz sand, fluorite, toner, manganese slag and other substances as the auxiliary materials, Liang et al. [79] successfully produced black glass decorative materials, which have good mechanical strength, chemical stability and optical properties.

Aerated concrete block

Aerated concrete is a new light porous building material that has great performances such as thermal insulation, fire resistance and seismic resistance and is made from calcareous and siliceous materials. Red mud aerated concrete, developed by using cement (15%), lime (12%–15%), red mud (35%–40%) and silica sand (33%–35%) has the compressive strength and bulk density,

complying with the lowest intensity level (MU7.5) of Chinese standards about the strength of concrete block [80]. But its production process is basically the same as that used to produce other aerated concrete. So, this process can reduce the costs of the production of aerated concrete by taking advantage of red mud. It is said that this process will become one of the new methods of red mud utilization.

9.UTILIZATION OF RED MUD AS FILLING MATERIAL

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 [81] 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 [82].

Mining

Yang et al. [83], 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 [84].

Plastic

For PVC (polyvinyl chloride), red mud is not only a filler that has a reinforcing effect, but is also an efficient and cheap thermal stabilizer, providing the filled PVC products with an excellent anti-aging property. Its lifetime is 2 to 3 times that of ordinary PVC products. At the same time, the fluidity of red mud is better than other fillers, which makes it plastic with good processing properties. And the red mud+PVC composite plastics have fire retardant property and can be made into red mud plastic; solar water heaters and plastic construction profiles [85].

10.APPLICATION IN POLLUTION CONTROL

The interesting applications of red mud are however in the environmental field, after adequate neutralization for the remediation of contaminated sites and treatment of contaminated liquid waste.

Wastewater 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 [86]. The researchers have used acid and acid-thermal treated raw red mud to develop effective adsorbents to remove phosphate from aqueous solution. Study on the use of red mud for removal of dyes from textile effluents has also been conducted. Efforts have been made to use red mud for the removal of chlorophenols from wastewater [87]. Neutralized red mud in batch adsorption technique was used for the removal of phenol from aqueous phase [88]. Tor et al. [89] have also used granular red mud for removal of fluoride from water. Removal of boron from aqueous solution has also been studied by using neutralized red mud [90]. Red mud has been converted into an inexpensive and efficient adsorbent to remove cadmium, zinc, lead and chromium from aqueous solutions [91,92]. Brunori et al. [93] studied the possibility of reusing treated red mud (through the technology patented by Virotec International, consisting of a seawater treatment for pH neutralization) in the EuralluminaSpA bauxite refinery, located in Sardinia (Italy) for treating contaminated waters and soils. Researchers have investigated the effectiveness of using thermally activated seawater neutralised red mud for the removal of arsenate, vanadate and molybdate in individual and mixed solutions [94, 46]. They found that thermally activated seawater neutralised red mud removes at least twice the concentration of anionic species than thermally activated red mud alone, due to the formation of 40–60% hydrotalcite during

the neutralisation process in seawater neutralised red mud. Hydrotalcite structure in the seawater neutralized red mud has been determined to consist of magnesium and aluminum with a ratio between 3.5:1 and 4:1 [46]. Removal of arsenate from aqueous solutions has also been studied by other researchers [95]. Fuhrman et al. [96] studied arsenic removal from water using 4 sorbents namely seawater-neutralised red mud (Bauxsol), acid treated Bauxsol (ATB), activated Bauxsol (AB), Bauxsol coated sand (BCS) and activated Bauxsol coated sand (ABCS). The affinity of the developed sorbents towards arsenic in a decreasing order is $AB > ATB > ABCS > BCS > \text{Bauxsol}$, and sorptive capacity of all tested sorbents compares well with conventional sorbents such as activated alumina and ferric oxides. The removal of arsenate using seawater neutralized red mud is sensitive to several parameters such as pH, ionic strength, adsorbent dosage, initial arsenate concentration and the source water composition. Arsenate adsorption is favored by slightly alkaline pH values with maximum adsorption recorded at pH 8.5.

Hofstede et al. [97] have made use of bauxite refining residue to reduce the mobility of heavy metals in municipal waste compost. A US Patent Application 20090234174 [98] shows that a neutralized and activated red mud is suitable for heavy metals remediation in soil and water. Entrapped metals are not easily exchangeable and removable. However, more investigation would be needed to further understand the metal trapping mechanisms of red mud. Seymer and Kirkpatrick [99] of Kaiser Aluminum and Chemical Corporation and Tulane University

have successfully developed and tested bauxite residue as liquid waste absorbent. They have researched soil synthesis as well as the use of red mud to reduce or eliminate sewage pathogens. They have shown that 0.5 mg/l red mud was sufficient for near complete removal of metals such as silver, arsenic, barium, cadmium, mercury and lead but not selenium at an initial water pH of 8.0 and at contact/reaction times as low as one minute. Cadmium and selenium were present at a concentration of 0.5 mg/l while other metals at 2.0 mg/l in the wastewater. Selenium removal is very pH dependant with an optimum pH around 6.0.

A laboratory investigation to evaluate the capacity of red mud to inhibit acid mine drainage has been carried out [100]. The investigators have studied the effectiveness of covers and liners made of red mud and/or cement kiln dust for limiting acid mine drainage. It has been proposed to use red mud that is very alkaline to neutralise acidic tailings [101,102]. Previous experiments showed that red mud has a good neutralizing capacity for a short time, but the long-term neutralization potential is uncertain. So brine was added to red mud to verify if it can improve long-term alkalinity retention of red mud. McConchie [103] investigated that the sea water-neutralised red mud can strip all trace metals in cyanide spills and neutralise the pH. Red mud can be used to neutralize acid forming gases produced during coal combustion. Studies have been carried out on absorption of SO₂ on red mud (Sumitomo scrubbing process) [104]. Also studies on CO₂ sequestration by red mud are being carried out to neutralize red mud as explained earlier which would help in absorption of CO₂

and purification of flue gases from thermal power plant.

Soil Improvement by Red Mud

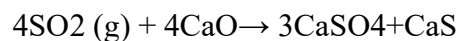
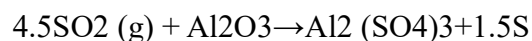
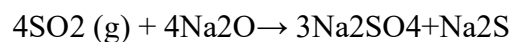
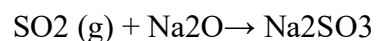
Red mud has a favorable environmental repair effect on the soil that has been contaminated by heavy metal elements [105]. One of the explanations for the mechanism is that red mud can absorb heavy metal ions such as Cu^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Cr^{6+} , Mn^{4+} , Co^{3+} and Hg^{2+} in the soil; the form of heavy metal ions changes from exchangeable ions into bonding oxides. Another mechanism is the precipitation reaction of carbonate in red mud with the heavy metal ions, and that causes these ions to deposit. In turn, the activity and reactivity of heavy metal ions in the soil are reduced, microbial activity and plant growth are promoted. Gao et al. [106] conducted some studies and showed that red mud can significantly decrease Cd and Zn at the exchangeable state or effective state in the soil. Ciccu R. [105]

used red mud to modify soil polluted by heavy metal. The result showed that red mud can reduce the heavy metal content in seriously polluted soil and reduce the absorbed dose of heavy metal. Lombi [107] found that adding 2% of red mud to the soil restrained the absorption of crops for Cu^{2+} , Ni^{2+} , Zn^{2+} and Cd^{2+} . After the modification, the mass concentrations of Zn in the soil pore water and lettuce body decreased respectively by 95% and 97%.

Treatment of Waste Gas Containing Sulfur by Red Mud

Bekir et al. [108] activated red mud by drying and roasting, and studied the absorption of

this activated red mud for SO_2 gas. The desulfurization rate is initially 100%, and is still as high as 94% after 10 cycles. Chen et al. [109] carried out research on the absorption and purification of waste gas containing SO_2 by red mud. They pointed out that the adsorption by Bayer red mud is a process of chemical reaction and physical adsorption, and that it requires small particle sizes (more than 50% of the particles are smaller than 45 μm) and a large specific surface area (10~20 m^2/g) to improve the speed and depth of the chemical reaction, determining that the Bayer process red mud is an excellent absorbent for SO_2 . The main chemical reactions are as following:



Reserves of high grade and high-sulfur bauxite are rich in China. The roasting pretreatment process for desulfurization will generate a lot of SO_2 gas. Lv et al. [110], when studying high-sulfur bauxite, put forward a new roasting pretreatment technology that absorbs the acidic SO_2 exhaust generated by the roasting process directly by alkaline red mud generated in the alumina production process. This technology can simultaneously solve the problems of the absorption of SO_2 exhaust and the neutralization reaction of alkali red mud. What is more, the modified neutral or

alkalescent red mud can also be used as construction material.

11. RED MUD AS A COAGULANT, ADSORBENT AND CATALYST Red mud can also be employed as catalysts for hydrogenation, hydrodechlorination and hydrocarbon oxidation. It has also been studied as a support in catalytic wet oxidation of organic substances present in industrial wastewaters [111]. Use of red mud as a catalyst can be a good alternative to the existing commercial catalysts [112]. Its properties such as iron content in form of ferric oxide (Fe_2O_3), high surface area, sintering resistance, resistance to poisoning and low cost makes it an attractive potential catalyst for many reactions. US patent 4017425 [113] describes a method developed for the red mud to be used as adsorbent, catalyst, ion-exchanging substance and clarifying substance particularly with respect to the catalytic cracking, decolorization of hydrocarbon, clarification of waste gas and adsorption processes.

The method comprises digesting red mud with acid, before adjusting the pH of the acid digested mixture comprising the sludge product to above 4, removing the residue acid employed from the gelating product with washing and heat treating the product to provide an active red mud. Cakici et al. [114] studied the utilization of red mud as catalyst in conversion of waste oil and waste plastics to fuel in comparison with a commercial hydrocracking.

catalyst (silica–alumina) and a commercial hydrotreating catalyst (Ni–Mo/alumina). Garg et al. [115] have made a comparison of the catalytic activity of pyrite, red mud & flue

dust and based on selective analysis showed that red mud was the most desirable disposable catalyst in the conversion of coal and oil production. Novel applications of red mud as a coagulant and adsorbent for water and gas treatment as well as catalyst for some industrial processes have been reviewed by Shaobin et al. [116].

12. OTHER USES

Along with successfully developing and testing bauxite residue as liquid waste absorbent, Seymer and Kirkpatrick, 1999 [99] of Kaiser Aluminium and Chemical Corporation at their Gramercy Louisiana Plant along with red mud as liquid waste absorbent have also studied red mud as landfill cover material and as levee construction material. A novel process for making radiation- shielding materials utilizing red mud has been developed by adopting ceramic- chemical processing route using phosphate bonding [117]. Efforts were made to utilize red mud for developing plasma spray coatings (ceramic and cermets) on metal substrates, stainless steel, mild steel, Cu and Al [118,119]. Sutar et al. [120] studied that red mud the waste generated from alumina plants is eminently coat able on metal substrates employing thermal plasma spraying technique. Sliding wear behavior under different operating condition was investigated by Prasad et al. [121] to identify suitable application areas. As red mud consists of metal oxides of iron, titanium, silicon, aluminum it was felt that red mud can possibly be spray coated. Building Material and Technology Promotion Council of India (BMPTC) has produced composite from red mud, polymer and natural fibres, called Red

Mud Jute Fibre Polymer composite (RFPC), to replace wood in the wood based panel products in the building industry [122].

13.DISCUSSION

As it is apparent red mud is a highly complex material that differs due to the different bauxites used and the different process parameters [14]. 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 impacts of the alumina industry is environmentally sustainable discharge and storage of digestion residue [14]. In the recent years it has been seen that there has been a 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. Neutralization with seawater operates differently than acid neutralization as Ca^{+} and Mg^{+} remove alkaline anions from solution as precipitates and are less soluble in place of simple reactions of hydroxide and other alkaline anions that occur with acid [14].

Therefore Ca^{+} and Mg^{+} rich solutions may be used for the neutralization of red mud which would render pH of red mud to the optimal value. The use of carbon dioxide from the atmosphere or from industrial emissions can be a potentially significant source of acid for neutralizing red mud. The initial cost of processing CO_2 in the red mud would be quite significant; the long term benefits of carbonation cannot be ignored including entrapment of CO_2 from the environment to neutralize an alkaline waste. In addition to the soil and water pollution caused due to disposal of red mud, its neutralization with CO_2 would also be able to lock up large amount of greenhouse gas that otherwise would be released into the atmosphere. Suitable amenders such as gypsum and other organic wastes can also be added to red mud to ameliorate its caustic properties.

Until now several applications of red mud have been studied. In general all these applications concern the use of red mud in relatively small amounts while the current need is safe disposal of red mud and its bulk utilization. The sustainable use of bauxite residue for road construction as an embankment landfill is an attractive option with a high potential for large volume reuse. Metal extraction processes are found to be uneconomic as iron (hematite) in the red mud has first to be converted into magnetite using reductants at relatively high temperature of $400\text{-}1000^{\circ}\text{C}$ before magnetic separation. The recovery of iron metal from the magnetic fraction needs a still higher temperature. Nearly for all of the above-mentioned applications of red mud in building materials, pollution control and metal recovery, a fairly high temperature is required and bulk

utilization of red mud remains a distant dream. However, application of red mud in geopolymers requires minimum heat treatment. Nevertheless, bulk utilization of red mud can be realized by refilling the abandoned bauxite mining open pits and by rehabilitating bauxite residue disposal area with red mud through development of a suitable vegetation cover on it.

14.CONCLUSION

Overall, the comprehensive utilization of red mud generated in the process of industrial production of alumina is still a worldwide problem. At current levels technology and practice, the capacity of consumption and secondary utilization is seriously insufficient. The secure stockpiling of red mud has to see a reduction of stockpiling costs and improvement of efficiency. So stockpiling is not a fundamental way to resolve the problems of red mud. Only through economical and viable comprehensive utilization can people resolve them effectively in the long term. As to the recovery of components from red mud, there are a lot of problems making for significant increases in recycling process costs and energy consumption, becoming serious impediments to industrial development. Therefore, we need to promote the industrialization of precious metal recovery processes, optimize complex processes and develop new ones. Although the added value is relatively low, the resources utilization of red mud is the most widely used way and the most effective way to resolve the red mud stockpiling problem. Red mud can also be used to produce other construction materials. A mature, relevant technology would greatly promote the consumption of red

mud. Applying red mud as an environmental remediation material is a new hot point in terms of utilization. Due to the simple process, low cost, it is worth promoting its application in the field of environmental protection. However, there is a risk of introducing new contamination, and a difficulty of recycling it after the application. Therefore, more in-depth studies are needed and a comprehensive assessment of chemical and biological effects.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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