Neutralization and utilization of red mud for its better waste management

Suchita Rai1,*, K.L. Wasewar2, J. Mukhopadhyay1, Chang Kyoo Yoo3, Hasan Uslu4
1Jawaharlal Nehru Aluminium Research Development and Design Centre, Wadi, Amravati Road, Nagpur-440 023, India
2Visvesaraya National Institute of Technology (VNIT), Nagpur- 440 010, India
3Department of Environmental Science and Engineering, College of Engineering, Kyung Hee University, Gyeonggi-Do, 446 701, South Korea
4Beykent University, Istanbul, Turkey
*To whom correspondences should be addressed
E-mail: suchitabr@yahoo.com

Received September 10, 2011, Revised manuscript received December 26, 2011, Accepted January 24, 2012

Abstract

In the Bayer process of extraction of alumina from bauxite, the insoluble product generated after bauxite digestion with sodium hydroxide at elevated temperature and pressure is known as ‘red mud’ or ‘bauxite residue’. 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 the field of building (geopolymers, clay material, cements, ceramics, fired and non-fired building materials, concrete industry), pollution control (in wastewater treatment, absorption and purification of acid waste gases), metal recovery (iron, titanium, aluminium, alkali, rare earths), coagulant, adsorbent, catalyst and in soil remediation. It also reviews the work carried out for rehabilitation of red mud ponds. This paper is an effort to analyze these developments and progress made which would be very useful in the context of environmental concerns for disposal and utilization of red mud.

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

1. Introduction

Aluminium is a light weight, high strength and recyclable structural metal. It plays an important role in social progress and has a pivotal contribution in transportation, food and beverage packaging, infrastructure, building and construction, electronics and electrification, aerospace and defense. It is the third abundant element in the earth’s crust and is not found in the free state but in combined form with other compounds. The commercially mined aluminium ore is bauxite, as it has the highest content of alumina with minerals like silica, iron oxide, and other impurities in minor or trace amount. The primary aluminium production process consists of three stages: Mining of bauxite, followed by refining of bauxite to alumina by the Bayer process (invented by Karl Bayer in 1887) and finally smelting of alumina to aluminium (Hall – Heroult process). Production of alumina is basically a chemical enrichment process. It is a process of separating alumina from undesired components like oxides of iron, titanium, silicium, calcium, vanadium, manganese etc. in bauxite. The Bayer process of extraction of alumina from bauxite remains the most economical process till date. In the Bayer process, the insoluble product generated after bauxite digestion with sodium hydroxide at elevated temperature and pressure to produce alumina is known as ‘red mud’ or ‘bauxite residue’. The waste product derives its colour and name from its iron oxide content. Red mud is a mixture of compounds originally present in the parent mineral, bauxite and of compounds formed during the Bayer process. As the bauxite has been subjected to sodium hydroxide treatment, the red mud is highly caustic with a pH in the range of 10.5-12.5. Bauxite ore mined globally amounts to be around 205 million tones per year for 2008 and 201 million tones per year for 2009 [1], posing a very serious and alarming environmental problem. Considerable research and development work for the storage, disposal and utilization of red mud is being carried out all over the world. 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, metal recovery and soil remediation. This paper reviews matters in the context of environmental concerns of disposal of red mud and its utilization.

2. 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 aluminium hydroxides.

Bauxite is a member of the family of lateritic rocks. It is characterized by a particular enrichment of aluminium-hydroxide minerals, such as gibbsite, boehmite and/or diaspor. 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 [2].

3. Production and Classification of Bauxite (World and Indian Context)

3.1. World Resources

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%) [1]. The worldwide metallurgical bauxite production for the year 2008 and 2009 is given in Table 1. Based on the production data from the International Aluminium 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 [1]. 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

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine production (x1000 tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2008</td>
</tr>
<tr>
<td>Australia</td>
<td>61,400</td>
</tr>
<tr>
<td>China</td>
<td>35,000</td>
</tr>
<tr>
<td>Brazil</td>
<td>22,000</td>
</tr>
<tr>
<td>India</td>
<td>21,200</td>
</tr>
<tr>
<td>Guinea</td>
<td>18,500</td>
</tr>
<tr>
<td>Jamaica</td>
<td>14,000</td>
</tr>
<tr>
<td>Russia</td>
<td>6,300</td>
</tr>
<tr>
<td>Venezuela</td>
<td>5,500</td>
</tr>
<tr>
<td>Suriname</td>
<td>5,200</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>4,900</td>
</tr>
<tr>
<td>Greece</td>
<td>2,200</td>
</tr>
<tr>
<td>Guyana</td>
<td>2,100</td>
</tr>
<tr>
<td>Vietnam</td>
<td>30</td>
</tr>
<tr>
<td>Other</td>
<td>6,550</td>
</tr>
<tr>
<td>World total</td>
<td>205,000 (rounded)</td>
</tr>
</tbody>
</table>

(Source: [1]

Bauxites can be classified in function of the ore type. Alumina occurs in 3 phases defining ore type: gibbsitic (γ-Al(OH)₃), boehmitic (γ-AIO(OH)) and diasporic (α-AIO(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.

Table 2. Bauxite ore type of different countries

<table>
<thead>
<tr>
<th>Gibbsitic</th>
<th>Boehmitic</th>
<th>Diasporic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia, Brazil, Ghana, Guyana, India (eastern coast), Indonesia, Jamaica, Malaysia, Sierra Leone, Suriname, Venezuela</td>
<td>Australia, Guinea, Hungary, USSR, Yugoslavia, India (Central part)</td>
<td>China, Greece, Guinea, Romania, Turkey</td>
</tr>
</tbody>
</table>
3.2. Important Bauxite Deposits of India

Reserves and production of bauxite

India has confirmed 3 billion tonnes of bauxite reserves out of the global reserve of 65 billion tonnes [3]. 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 aluminium capacity rests at about 3%. India has large resources of high-grade bauxite deposits of the order of 3037 million tonnes (proved + probable + possible). The recoverable reserves are placed at 2525 million tonnes. The proved and probable reserves are 1218 million tonnes, placing the country 5th in rank in the world, next only to Australia, Guinea, Brazil and Jamaica [4]. 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 per cent), Maharashtra (13.3 per cent) and Madhya Pradesh/Chhattisgarh (11.4 per cent). Production from Gujarat, Andhra Pradesh and Tamil Nadu is also worth mentioning [2].

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.

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:
1. Gibbositic bauxite (Eastern ghats, Gujarat and coastal deposits of western India)
2. Mixed gibbositic-boehmitic bauxite (boehmite < 10%, diaspor < 2%; parts of Western Ghats and Gujarat deposits
3. Boehmitic bauxites (boehmite > 10 and diaspor < 2%; Central Indian bauxite
4. Diasporic bauxites (diaspor > 5%; J&K and some part of Central Indian and Gujarat deposits

Typical compositions of industrially used bauxite are Al₂O₃ (40-60%), combined H₂O (12-30%), Fe₂O₃ (7-30%), SiO₂ free and combined (1-15%), TiO₂ (3-4%), F, P₂O₅, V₂O₃ and others (0.0.5-0.2%) [5].

4. Production of Alumina in India

The worldwide alumina production is around 58 million tonnes in which India counts for 2.7 million tonnes [3]. The Indian aluminium sector is characterised by large integrated players like Hindalco and National Aluminium 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 Aluminium Company (Indal having two plants at Belgaum, Karnataka and Muri, Jharkhand), now merged with Hindustan Aluminium Company (Hindalco, Renukoot, Uttar Pradesh), Bharat Aluminium (Balco) and Madras Aluminium (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 Aluminium Company (Nalco) and Hindalco (Aditya Birla Group) [3].

5. Bayer Process of Alumina Production

Though alumina can be produced from bauxite under alkaline conditions using lime (Lime Sinter process) [6], sodium carbonate (Deville Pechiney process) [7], at high temperature in reducing environment with presence of coke and nitrogen (Serpeck process) [8], the alkalinisation by the use of sodium hydroxide (Bayer process) [9] is the most economical process which is employed for purification of bauxite if it contains considerable amount of Fe₂O₃.

In the Bayer process, bauxite is digested by leaching it with a hot solution of sodium hydroxide, NaOH, at 106-240°C and at 1-6 atm pressure. This converts the aluminium minerals into tetrahydroxidoaluminate Al(OH)₄⁻, while dissolving in the hydroxide solution. The other components of bauxite except silica (present in
kaolinite) do not dissolve. The insoluble compounds are separated by settling and the decant solution is further clarified by filtering off remaining solid impurities. 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 aluminium hydroxide precipitates as a white, fluffy solid. When heated to 1050°C (calcined), the aluminium 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 aluminium.

5.1. Reactions in Bayer Process

Desilication

In the Bayer process, scaling problems are caused by silica dissolving in the caustic liquor affecting the quality of the product. This silica arises from the presence of kaolinite (Al₂O₃·2SiO₂·H₂O) in the bauxite. A process for removing this kaolin comprises contacting the bauxite with sodium hydroxide solution to form a mixture, and subjecting the mixture to 95-100°C for 10-12 hrs. This enhances both the dissolution of kaolin and precipitation of sodium aluminium silicate or DSP (desilication product) also called sodalite causing loss of alumina as well as caustic soda.

\[
2\text{NaOH} + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Na}_2\text{SiO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \quad (2)
\]

Digestion of bauxite with NaOH

After desilication, the bauxite undergoes a digestion process at elevated temperatures. The alumina phases get dissolved in caustic solution to form sodium aluminate.

Gibbsite

\[
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 106-150°C \rightarrow (3)
\]

\[
2\text{NaAlO}_2 + 4\text{H}_2\text{O}
\]

Boehmite

\[
\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 240°C \rightarrow (4)
\]

\[
2\text{NaAlO}_2 + 2\text{H}_2\text{O}
\]

Diaspore

\[
\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 280°C \rightarrow (5)
\]

\[
2\text{NaAlO}_2 + 2\text{H}_2\text{O}
\]

The sodium aluminate liquor is separated from the undigested bauxite which is called as ‘Red mud’ or ‘Bauxite Residue’ and is disposed off in red mud ponds. Sodium is present mainly in two forms in red mud, free sodium as ionized sodium aluminate and sodium hydroxide and bound sodium in desilication product (sodium aluminosilicates) which are least soluble sodalites.

Precipitation

Crystalline alumina hydrate is extracted from the digestion liquor by hydrolysis.

\[
2\text{NaAlO}_2 + 4\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 2\text{NaOH}
\]

6. Production and Main Characteristics of Red Mud/Bauxite Residues

6.1. Output of Bauxite Residues

About 1 tonne of alumina is produced from 3 tonnes of bauxite and about 1 tonne Aluminium is produced from 2 tonne of alumina [4]. Depending on the raw material processed, 1-2.5 tonnes of red mud is generated per ton of alumina produced [10].


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. Typical chemical composition of red muds generated by Indian alumina plants is as given in Table 4 [12].

**Table 3. Typical composition of red mud**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>30-60%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10-20%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3-50%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2-10%</td>
</tr>
<tr>
<td>CaO</td>
<td>2-8%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>trace-25%</td>
</tr>
</tbody>
</table>


Mineralogically, red mud has a very high number of compounds present. These are:
Hematite (Fe₂O₃), goethite Fe_(1-x)AlₓO₃(OH)ₓ (x = 0.33), gibbsite Al(OH)₃, boehmite AlO(OH), diaspare AlO(OH), calcite(CaCO₃), calcium aluminium hydrate (xCaO·Al₂O₃·H₂O), quartz (SiO₂), rutile (TiO₂), anatase (TiO₂), CaTiO₃, Na₂TiO₃, kaolinite Al₂O₃·2SiO₂·2H₂O, sodalites, aluminium silicates, cancrinite (NaAl₃SiO₆CaCO₃), hydroxycancrinite (NaAl₃SiO₆NaOH·H₂O), chalantite CaO·Al₂O₃·SiO₂·2H₂O, hydrogarnet Ca₂Al₂(SiO₄)₄(OH)₁₂·₄n.

Table 4. Chemical composition of Indian red muds

<table>
<thead>
<tr>
<th>Company</th>
<th>Al₂O₃ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>SiO₂ (%)</th>
<th>TiO₂ (%)</th>
<th>Na₂O (%)</th>
<th>CaO (%)</th>
<th>LOI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BALCO, Korba</td>
<td>18.10-21.0</td>
<td>35.0-37.0</td>
<td>6.0-6.5</td>
<td>17.0-19.0</td>
<td>5.2-5.5</td>
<td>1.7-2.2</td>
<td>11.8-14.0</td>
</tr>
<tr>
<td>HINDALCO, Renukoot</td>
<td>17.5-19.0</td>
<td>35.5-36.2</td>
<td>7.0-8.5</td>
<td>16.3-14.5</td>
<td>5.0-6.0</td>
<td>3.2-4.5</td>
<td>10.7-12.0</td>
</tr>
<tr>
<td>HINDALCO, Muri</td>
<td>19.0-20.5</td>
<td>44.0-46.0</td>
<td>5.5-6.5</td>
<td>17.0-18.9</td>
<td>3.3-3.8</td>
<td>1.5-2.0</td>
<td>12.0-14.0</td>
</tr>
<tr>
<td>HINDALCO, Belgaum</td>
<td>17.8-20.1</td>
<td>44.0-47.0</td>
<td>7.5-8.5</td>
<td>8.2-10.4</td>
<td>3.5-4.6</td>
<td>1.0-3.0</td>
<td>10.8-14.0</td>
</tr>
<tr>
<td>MALCO, Metturdam</td>
<td>18.0-22.0</td>
<td>40.0-26.0</td>
<td>12.0-16.0</td>
<td>2.5-3.5</td>
<td>4.0-4.5</td>
<td>1.5-2.5</td>
<td>11.0-15.0</td>
</tr>
<tr>
<td>NALCO, Damanjodi</td>
<td>17.7-19.8</td>
<td>48.2-53.8</td>
<td>4.8-5.7</td>
<td>3.6-4.1</td>
<td>3.8-4.6</td>
<td>0.8-1.2</td>
<td>10.8-13.5</td>
</tr>
</tbody>
</table>

Source: Chaddha et al. [12]

A wide variety of organic compounds are also present. The following compounds have been reported [14]: the organic compounds such as polybasic and polyhydroxy acids, alcohols and phenols, humic and fulvic acids, carbohydrates, sodium salts of succinic, acetic and oxalic acids that give red mud a distinctive odour and are derived from decomposed remains of vegetation. Under the alkaline oxidative conditions existing in the Bayer process, they break down to more simple compounds such as the sodium salts of succinic, acetic and oxalic acids. Predominant among these salts is sodium oxalate.

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.

7. Environmental Concerns

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% and with a high ionic strength. The environmental concerns relate to two aspects: very large quantity of the red mud generated and its causticity.

Problems associated with the disposal of red mud waste include:
- its high pH (10.5-12.5)
- alkaline seepage into underground water
- Instability of storage
- alkaline air borne dust impact on plant life
- Vast areas of land consumed

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

8. Storage and 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.

8.1. Red Mud Disposal

Safe treatment and storage of high volume industrial waste streams pose unique waste management challenges. Seawater discharge, lagooning, dry stacking and dry disposal are the methods currently in use for the disposal of bauxite residue.

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. Nevertheless, French and Japanese practices have favoured disposal at sea as the best option on economic and environmental grounds. In Japan, the alumina plants are restricted to available land area for disposal of residues, and so have discharged the residue into the deep sea. The plants of Gardanne Alumina in France and Aluminium De Greece in Viotia, Greece still use marine dumping but are now pursuing other alternatives.

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 [14]. This minimizes the liquor leakage to the underlying water. The red mud ponds are lined with soil and bentonite. 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. Most of the alumina refineries till 1975 were using lagooning method for red mud disposal but some of them such as Pinjarra, Kwinana and Wagerup refineries in Australia have shifted to Dry stacking method. Queensland Alumina Ltd (Australia) after treatment of its red mud with seawater [15] and CVG Bauxilium (Venezuela) still use wet disposal method by disposing their red mud in lagoons [16]. 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 have been successfully applied at the MOTIM plant in Hungary [17]. The original wet disposal method at NALCO, India has been replaced by Thickened Tailings Disposal (TTD) system [18]. 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. Solids contents of greater than 75% have been achieved with Bokela hyperbaric filtration technology at the Stade plant in Germany [19]. Even with the excellent washing performance offered by hyperbaric steam filtration, significant alkalinity remains associated with the solids because of the complex nature of red mud. Hence these hazards associated with alkalinity may be further reduced by employing suitable methods of neutralizing the red mud slurry.

8.2. 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 [20]. 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 [21].

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 aluminium and iron salts- for waste water treatment [22].

CO₂ treatment

Gas phase CO₂ or CO₂-containing flue gas has been bubbled through aqueous slurries to form carbonic acid in the aqueous phase [23]. Mechanisms of neutralization of red mud by carbon dioxide gas have been studied [24]. 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 [25] 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 [26].

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 [27]. 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 (SO₄²⁻), 3.65% magnesium (Mg²⁺), 1.17% calcium (Ca²⁺), 1.13% potassium (K⁺) and 0.7% others [28]. 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 [29]. The neutralizing effect of the calcium and the magnesium ions is initially large but decreases rapidly as pH 8.5 is approached and calcium and magnesium carbonates precipitate. Neutralization is considered to be complete when the liquid that can be separated from the treated red mud has a pH less than 9.0 and a total alkalinity less than 200 mg/l (as calcium carbonate equivalent alkalinity) and decant of seawater neutralized red mud can be safely discharged to the marine environment [30].

Bioleaching

Bioremediation of bauxite residue in Western Australia by Alcoa of Australia [31] 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 [32] using microbes.

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.

A comparison of all the neutralization processes has been made by [33].

9. Red Mud Utilization

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

9.1. Building Materials

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. Red mud is considered as a raw material for production of these materials.

Preparation of construction materials from bauxite residues

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 [34]. 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. 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 [35]. 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 [36].

Giannopoulou et al. [37] 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 material

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 [38]. Ekrem [39] 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 [40] was carried out at National Institute of Technology, Rourkela, Orissa, India. A study carried out by Pontikes. et al. [41,42] 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).

**Cements**

Red mud from HINDALCO, Renukoot, India was investigated for its application in cements and they found that cements made from lime + red mud + bauxite + gypsum exhibit strengths comparable or superior to ordinary Portland cement (OPC) [43]. It was stated that as red mud is very rich in iron, red mud can be used as cheap pigment for coloured concrete [44]. Also a uniform and durable coloured concrete could be obtained using white cement interground with 11% of burnt red mud. The red coloration could be enhanced by calcination in the range of 600 to 800°C. They found that such operation transforms the aluminium hydroxides (goethite and boehmite) and clays minerals into pozzolanic admixtures that are able to consume the calcium hydroxide produced by cement hydration. Thus, it is possible to develop a new admixture for concrete: a pozzolanic pigment. Tsakiridis et al. [45] in Greece studied the addition of red mud residue by 1% in the raw mix for the production of Portland cement and found that it did not affect either the sintering or the hydration process and concluded that the red mud can be utilized as a raw material in cement production, at no cost to the producer, contributing in reduction of the process cost.

Preparation of building materials from bauxite residues

Vast usage of red mud can be made in preparation of building materials such as ceramics, glass ceramic products, fired and non-fired bricks and concretes.

**Ceramics**

Red mud is made into useful ceramics articles by mixing 51-90% by weight of red mud with 49-10% by weight of at least one mineral and/or silicate containing material, shaping the mixture and firing it at a temperature of 950°-1250°C [46]. The investigators [47] have successfully converted red mud into glass ceramic products which involves addition of a small quantity of glass former along with traces of nucleating agents to a specific mixture of red mud, fly ash, followed by melting at around 1200°C and vitrification by cooling. The feasibility of recycling red mud and fly ash by producing glasses and glass-ceramics has also been investigated by Yanga et al. [48]. Glass has been obtained by melting red mud from Shandong Province in China with different additives. Suitable thermal treatments were employed to convert the obtained glass into nano-crystal glass-ceramics. X-ray diffraction (XRD) patterns showed that the main crystalline phase in both the glass-ceramics is wollastomite (CaSiO₃). These crystals are homogeneously dispersed within the parent glass, with an average crystal size of less than 100 nm. The size of nano-crystals varies when different thermal processes were used. These glass-ceramics have potential for a wide range of construction application [49].

**Fired building materials**

United States Patent 3886244 [50] claims a process for manufacturing fired bricks wherein 50-90 wt % of red mud can be used along clay and a water fixing agent. The raw bricks are dried with heated gases at a temperature below 70°C, and subsequently fired at a temperature between 900°-1,100°C. Efforts have been made at Central building Research Institute, CBRI, India [51] to produce burnt clay bricks by partially replacing the clay with red mud (from the Indian Aluminium Company), lime and flyash.

**Non-fired building materials**

Efforts have also been made at CBRI to incorporate a small percentage of lime in red
mud and compress the mix at optimum moisture content in the form of bricks with the purpose of examining their strength and stability to the erosive action of water. A maximum wet compressive strength of 3.75 MPa with 5% lime and 4.22 MPa with 8% lime has been obtained after 28 days of casting and humid curing of these bricks in the month of August. Studies were carried out at Jamaica Bauxite Institute and the University of Toronto [52] using red mud to make bricks for inexpensive housing. The red mud was pressed into bricks using a standard brick press, immersed in sodium silicate followed by drying in the sun. Non-fired bricks by mixing red mud, Portland cement and river sand were also made by the researchers at the institute. Liu et al. [53] studied the recovery of iron from Bayer red mud with direct reduction roasting process followed by magnetic separation, and then building materials were prepared from aluminosilicate residues. Then brick specimens were prepared with aluminosilicate residues and hydrated lime and the mean compressive strength of specimens was 24.10 MPa. It was indicated that main mineral phase nepheline (NaAlSiO₄) in aluminosilicate residues transformed into gehlenite (Ca₂Al₂SiO₇) in brick specimens as demonstrated by X-ray diffraction (XRD) technology. Combining the recovery of iron with the reuse of aluminosilicate residues, it can realize zero-discharge of red mud from Bayer process. Unsintered bricks have been developed from red mud disposed from Chinese sintering alumina process cured at ambient conditions. The optimal proportions of red mud brick are suggested as the following: 25–40% red mud, 18–28% fly ash, 30–35% sand, 8–10% lime, 1–3% gypsum and about 1% Portland cement [54].

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) [55]. 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 [56] after hot water leaching filtration, drying and sieving.

9.2. 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 [57]. 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 [58]. Neutralized red mud in batch adsorption technique was used for the removal of phenol from aqueous phase [59]. Tor et al. [60] 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 [61]. Red mud has been converted into an inexpensive and efficient adsorbent to remove cadmium, zinc, lead and chromium from aqueous solutions [62,63]. Brunori et al. [64] 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 Eurallumina SpA 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 [65,27]. 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 aluminium with a ratio between 3.5:1 and 4:1 [27]. Removal of arsenate from aqueous solutions has also been studied by other researchers [66]. Fuhrman et al. [67] 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 > 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 favoured by slightly alkaline pH values with maximum adsorption recorded at pH 8.5.

Hofstede et al. [68] have made use of bauxite refining residue to reduce the mobility of heavy metals in municipal waste compost. A US Patent Application 20090234174 [69] 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 [70] of Kaiser Aluminium & 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 [71]. 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 [72,73]. 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 [74] investigated that the sea water-neutralised red mud can strip all trace metals in cyanide spills and neutralise the pH.

Absorption and purification of acid waste gases with bauxite residues

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) [75]. 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.

9.3. 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 [76].

Use of red mud as a catalyst can be a good alternative to the existing commercial catalysts [77]. Its properties such as iron content in form of ferric oxide (Fe₂O₃), high surface area, sintering resistance, resistance to poisoning and low cost makes it an attractive potential catalyst for many reactions. US patent 4017425 [78] 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. [79] 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. [80] 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. [81].

9.4. Recovery of Metals

The analysis of red mud shows that iron is the major constituent of red mud and hence much work has been carried out till now for its recovery. Some red mud also contains titania in substantial amount which if successfully recovered has the most potential value. Iron can be obtained as value-added product and alumina and soda can be recycled in the process.

Red Mud generated from Guangxi Province (China) was treated with Chinese coal and coal-sort for direct reduction of iron. Bauxite of this province was treated by Bayer process on alumina first – iron second basis due to its composition (~27 wt % Al₂O₃ and ~43 wt% Fe₂O₃) and factors related to reduction performance were reported including quality/property of coal [82]. An extensive study on the possibility of magnetic separation of red mud from Fria Deposit (Guinea) reported that ~ 85 % of the iron present in red mud was recovered at 0.06 Tesla magnetic intensity. Best result was obtained by treating -125 μm + 90 μm size fraction [83]. Red mud was mixed with dolomite and coke to make pellets and sintered (1100°C) followed by smelting (1500°C) to produce pig iron [84]. The slag was further treated with sulphuric acid followed by solvent extraction of iron, then silica and alumina. Pigment grade titania was also recovered from the slag. Laboratory-scale research has been focused by on the recovery of titanium from red mud in which the leaching process is based on the extraction of this element with diluted sulfuric acid from red mud under atmospheric conditions and without using any preliminary treatment [85]. Leaching followed by solvent extraction was tried in Japan using sulphuric acid and some solvents like diisopropyl ether, DP-10R or PC-88A (Daihachi Chemical Industry Co., Ltd.) to recover iron and titania respectively. At the end, iron, titania and alumina were separated [86]. Red mud of Alcoa Alumina, Kaiser Alumina and Reynolds Metals (all in USA) were reacted with different reductants (sawdust, bagasse etc) at a temperature of about 350°C to reduce different forms of iron to magnetite followed by magnetic separation to produce high iron containing and soda free product/material for further usage [87]. Studies were done on Jamaican red mud to recover all possible metal values: at first alumina was recovered by soda-ash sintering process followed by reduction (partial or complete) of iron to magnetic/metal phase followed by magnetic separation to separate iron and titania from the non-magnetic portion [88,89]. Different parametric conditions are also highlighted in the paper. A patent [90] was also filed in the same field claiming all possible metal values recovery by reacting red mud with acid followed by selective precipitation of salts at different pH. Iron mineral transformation during thermal treatment of red mud has been studied [91]. Liquid-liquid extraction (LLE) of iron and titanium by bis-(2-ethyl-hexyl) phosphoric acid (D2EHPA) has been studied [92]. Studies have been carried out to investigate the optimum condition for sulfuric acid leaching of iron from red mud and a diffusion model has also been developed to support the study [93]. Dissolution kinetics of iron and aluminium from red mud in sulfuric acid solution for different parameters such as calcination temperature, acid concentration, agitation rate, particle size and time have been studied by researchers [94]. Red mud of Shandong province of China has also been tried for reduction roasting in presence of proper additives (reduction enhancer such as CaCO₃,
MgCO₃ etc.) and an encouraging metallization ratio of 96.97% has been reported with scope for better usage for non-magnetic fraction in building material industry because of removal of iron and increase in percentage of aluminosilicate compounds which helps to set the building material more strongly in presence of lime [95]. Krause and Rohm [96] have patented a process wherein iron oxide in red mud has been reduced to magnetite by suitable hydrocarbon and was then recovered. A process Mud to Money [97] claims to recover virtually all of the residual alumina from bauxite residue at attractive economics. The inventors claim the environmental benefits of this technology include a reduction in residue generation per ton alumina by some 8% and a reduction of bauxite consumption per ton of alumina by some 4%.

Work on microbiological leaching of aluminium from red mud with selective fungi has been carried out [98]. United States Patent 3876749 [99] claims a process wherein the red mud is mixed with a reducing agent, separating it into molten steel and molten slag, reacting the slag with CaO, leaching out the useful aluminates for recirculation to the Bayer process, and utilizing the remaining calcium silicates in cement manufacture.

For soda recovery, a patent [100] relates to a process for the treatment of red mud, and in particular relates to a process capable of both ameliorating the pH of red mud and allowing soda recovery from red mud by passing carbon dioxide through a stream of red mud. United States Patent 4045537 [101] discloses a process for recovering the caustic and alumina values from red mud utilizing the so-called lime-soda-sinter process wherein a carbonaceous material such as coke is included in the sintering operation and leaching is carried out without any intermediate iron separation step. WO/1997/029992 [102] relates to a method for recovering soda and/or alumina values from red mud from DSP (desilicated product) formed in a Bayer process, the method comprising mechanically activating the DSP to induce a mechano-chemical reaction. Any reagent which is thermodynamically capable of reacting with DSP to solubilise soda and/or alumina values may be used. Suitable reagents include oxides and hydroxides such as CaO, NaOH and Ca(OH)₂.

In addition to compounds of main elements, red mud also comprises of small quantities of rare earth elements such as Yttrium (Y), Scandium (Sc) and Lanthanides (Ln). SO₂ dissolved in water can be introduced in red mud slurry to selectively dissolve the rare earth elements while leaving iron substantially undissolved in the red mud [103]. An innovative method for the recovery of rare earth elements from the red mud and separation of Sc was developed on a laboratory and pilot scale by Aluminium of Greece (Pechiney group) in Greece. The annual production of red mud in Greece was about 0.6 million tonne and the Sc concentration was high and uniform, about 130 gm of Sc/ton of dry red mud corresponding to 0.02% Sc₂O₃ [104].

9.5. Soil Remediation with Bauxite Residues

Soil amendment is a technique used to create fertile topsoil by increasing the soil’s ability to retain moisture and nutrients, and filter some contaminants, such as heavy metals, before they infiltrate the groundwater. Soil amendment involves adding an agent to the soil to improve its structure, porosity, water holding capacity and nutrient recycling capacity. Potential amendment agents in an urban environment include compost, organic rich soils, loam soils, natural clay, crushed limestone and gypsum. ‘Soil amendment agents’ are generally distinguished from ‘fertilisers’ by having a lower nutrient content, and a greater ability to retain and recycle both moisture and nutrients.

The Department of Agriculture, Western Australia has been working with Alcoa World Alumina Australia Ltd for more than ten years investigating the potential to use bauxite refining residues as soil amendments for the poor, acidic, sandy soils of the Swan Coastal Plain in south west Australia. Extensive laboratory, field and catchment-scale trials have shown the ability of soil amendment with fine bauxite refining residue (now trademarked in this context as Alkaloam™) to reduce the leaching of nutrients to sensitive regional waterways by up to 75%, whilst increasing pasture productivity by up to 25% (up to 200% in well-controlled experimental situations). The potential applications of bauxite residue in soil/sediment remediation and soil/sediment stabilization have been investigated [105].
Bauxite residue was mixed with a variety of soil types such as acid soils, saline soils, organic rich material and silicate soil. Appropriate pH conditions were achieved to promote vegetation growth. Preliminary studies have also been carried out [106] at Louisiana State University, to investigate the use of red mud to enhance coastal wetlands.

9.6. Other Uses

Along with successfully developing and testing bauxite residue as liquid waste absorbent, Seymour and Kirkpatrick, 1999 [70] of Kaiser Alumium & 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 [107]. Efforts were made to utilize red mud for developing plasma spray coatings (ceramic and cermet) on metal substrates, stainless steel, mild steel, Cu & Al [108]. As red mud consists of metal oxides of iron, titanium, silicon, aluminium 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 [109].

9.8. Rehabilitation of Red Mud Pond

Red mud ponds and abandoned bauxite mine pits can be rehabilitated through vegetation. The ecological rehabilitation of red mud residue deposits is complicated by many factors, including its hazardous nature, extremely high pH and salinity, poor water-holding capacity, and extremely low microbial activity [110]. Hence, caustic properties of red mud are to be modified using suitable modifiers for the growth of proper flora and fauna on it. Vegetation cover will not only prevent deterioration of soil erosion but also act as method of suppressing dust generation due to the dried red mud. In this process, bulk utilization of red mud would be possible.

Work carried out for rehabilitation of red mud pond for an alumina refinery situated at Belgaum (Karnataka, India) show that a combination of 55% red mud, 25% FYM (farmyard manure), 15% gypsum, and 5% vegetative dry dust, inoculated with both bacteria and mycorrhizae, resulted in good responses from three tree species—kikar (Acacia nilotica), karanj (Pongamia pinnata ), and vilayati babul (Prosopis juliflora)—while other two species—drek (Melia azedarach) and Israeli babul (Acacia tortilis)—did not survive in any of the treatment combinations. Among the grass species, para grass (Brachiaria mutica), signal grass (B. decumbens), and shrubby stylo grass (Stylosanthes scabra) performed well in the same treatment combination as the trees, along with sesban (Sesbania sesban), a legume species [111]. The effectiveness of various industrial wastes and low cost chemicals such as gypsum, sewage sludge, ferrous sulfate, ammonium sulphate, ammonium nitrate and calcium phosphate as ameliorants for red mud to develop and maintain a low cost, self sustaining vegetation cover has been studied by many researchers [112]. It was found that the addition of 5% or more gypsum reduced the pH, electrical conductivity and sodium and aluminum content of the soil, as well as providing a continuous supply of calcium ions, thus reducing the exchangeable sodium percentage, and was effective in treating the soil to permit revegetation by Agropyron elongatum (tall wheat grass) and Cynodon dactylon (Bermuda grass) [113]. The survival of the plant species C. dactylon (bermudagrass), Atriplex nummalaria (oldman saltbush), and Atriplex canescens (fourwing saltbush) in red mud indicated that it was more vigorous with gypsum amendments [114]. Recently researchers after reviewing neutralization and utilization methods [115,116,117] have modified dried red mud with different amenders and utilized it for growth of ornamental plants [118].

10. 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. 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. 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. 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 400-1000°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.

11. Conclusion

A wide variety of potential uses of red mud have been reviewed, yet there is no economically viable and environmentally acceptable solution for the utilization of large volumes of red mud. Though methods have been developed for maximum recovery of soda and alumina from red mud, recovery of other metals should be made economical by further investigations to reduce high reaction temperatures required. 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. Continuous research is required by studying residue neutralization technologies to reduce the alkalinity of red mud which is the most important barrier for its reuse and disposal management. Use of proper amendments can be made to ameliorate red mud and red mud ponds can be rehabilitated by growing suitable flora and fauna on it. 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.

References


