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Abstract

Environmental pollution and climate change continue to be a major cause for concern in the 21st century. Aluminium is the most abundant metal on the surface used in every walk of life. Red mud, a by-product produced during the extraction of Aluminium from Bauxite by Bayer's Process, causes serious hazards for the human and ecological systems. Red mud primarily has oxides of Fe, Ti, Al and Si. It is also extremely toxic due to its high alkalinity (pH 10-13). More than 90 million tons of red mud is produced globally in a year and its disposal without disturbing the ecosystem is extremely challenging. However, there are no efficient methods of disposal due to its tiny particle size (~10-15 µm) and incessant production rates. Many industries use pressurized pumping techniques followed by filtration to improve the red mud's consistency of around 72-75% solids and dumped into red mud ponds. These methods cause various detrimental effects on surface water bodies as well as groundwater affecting the flora and the fauna. Applications where Red mud can be used to reduce pollution effectively are also discussed. Current trends revolve around the effective utilization of the residue to produce composites, fabrication of tinted glasses, bricks, catalytic adsorbents, water purifiers, and Rare Earth Element extraction. This article provides a critical perspective on the harmful effects of red mud as a pollutant to the environment and emphasizes the need for its futuristic application in engineering innovations.

Keywords: Red mud; Water/Soil pollutant; Bayer's process; Disposal; Alkalinity; Engineering Applications

List of abbreviations: NALCO: National Aluminium Company

Introduction

Industrial waste management and environmental conservation have been an ever-growing concern in recent times. Metals are boon to mankind and their significance to industries is immoderate. Aluminium has become the most useful metal after steel because of its lightweight nature and its abundance. aluminium finds its applications in the manufacturing, aviation, automobile, and construction sectors. Aluminium is extracted from Bauxite ore through Bayer's process. Red mud is obtained as a solid residue from the Bayer process, which involves dissolving aluminium silicate by sodium hydroxide to produce alumina (Al₂O₃). Almost 40% of the bauxite ore which is being processed comes out as alkaline red mud slurry. For every ton of aluminium produced approximately 1-1.5 tonnes of red mud is generated [1]. However, on a global scale, almost 90 million tonnes of red mud are produced [2]. Major producers of red mud have been Australia and China which produce almost 30 million tons each with India averaging around 2 million tonnes annually. As emphasized earlier, although the significance of aluminium is immeasurable, the red mud that is produced as a by-product is extremely toxic and alkaline (pH 10-13) and can have detrimental effects on the environment if not disposed of properly. Significant research has been carried out globally to effectively dispose of the bi-product. However, no effective method or technique has been universally approved or adopted.

Conventionally red mud is dumped into mud lakes in the form of slurry impoundments or stacks. Production plants dump the red mud produced to the nearby water body or it is directly dumped into the sea by using pipelines. Due to which, various environmental problems such as soil contamination, ground and surface water pollution, fine particle suspension in the sea arise. Also, significantly large compositions of red mud are usually stockpiled in open fields which can be very hazardous and toxic [3].

Materials and Methods

Aluminium is extracted from bauxite ore. Bauxite is the common name given to the oxides of aluminium consisting of varying amounts of water and other impurities along with silica and ferric oxide. Alumina is acquired from bauxite by Bayer's process. In
This process, bauxite is leached with caustic soda (NaOH) to produce soluble (NaAlO\(_2\)) as shown in Figure 1. The aluminate is then decomposed to form Al(OH)\(_3\), which is calcinated to produce Al\(_2\)O\(_3\). During this process, a by-product called red mud is produced. The extraction process converts the aluminium oxide present in the ore to soluble sodium aluminate, 2NaAlO\(_2\), according to the chemical equation [4]:

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

This treatment also dissolves silica, but the other components of bauxite do not. The original alkaline solution was cooled and treated by bubbling carbon dioxide through it, a method by which aluminium hydroxide precipitates:

\[
2 \text{NaAlO}_2 + 3 \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2 \text{Al(OH)}_3 + \text{Na}_2\text{CO}_3
\]

But later, this gave way to seeding the supersaturated solution with high-purity aluminium hydroxide (Al(OH)$_3$) crystal, which eliminated the need for cooling the liquid and was more economically feasible:

\[
2 \text{H}_2\text{O} + \text{NaAlO}_2 \rightarrow \text{Al(OH)}_3 + \text{NaOH}
\]

Al\(_2\)O\(_3\) is generally subjected to heating procedures in rotary kilns or fluid flash calciners to a temperature in excess of 1000 °C to produce alumina

\[
2 \text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O} \quad [5]
\]

This alumina is further reduced to Aluminium by Hall-Heroult's process of two-phase electrolysis.

In the Hall-Heroult's process the following simplified reactions take place at the carbon electrodes:

- Cathode: Al\(^{3+}\) + 3 e\(^-\) \rightarrow Al
- Anode: O\(_2\) + C \rightarrow CO + 2 e\(^-\)
- Overall: Al\(_2\)O\(_3\) + 3 C \rightarrow 2 Al + 3 CO

In reality, much more CO\(_2\) is formed at the anode than CO: 2 Al\(_2\)O\(_3\) + 3 C \rightarrow 4 Al + 3 CO\(_2\) [6]

The residue left after the digestion of bauxite forms red mud. The production process of aluminium differs for different types and varieties of bauxites. Red mud is mainly composed of coarse sand and fine particle. The properties and the phase depend mainly on the type of alumina produced by Bayer's process and the type of bauxite utilized for the same. The particle size distribution is roughly around (10-15µm). Red mud is formed after the refinement of aluminium is completed. The red mud residue from Hindalco Industries Limited, Belagavi was analyzed and based on their Environmental statement for the financial year ending 31st March 2018 [3]. The composition of red mud was ascertained and reflected in Table 1 and Figures 2 and 3.

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**Table 1:** Composition of red mud from HINDALCO Belagavi, India [3]

<table>
<thead>
<tr>
<th>Characterization of Bauxite residue (FY' 2017-18)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>8.46</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>41.49</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>14.28</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>17.42</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>6.54</td>
</tr>
</tbody>
</table>

---

Figure 1: Bayer’s Process [7]
Even in the present-day scenario, after investing millions of dollars in research and investigation to establish a safe and effective method to dispose of red mud, the answer remains to be a mystery. All countries around the world mining aluminium in large quantities continue to suffer. Industries and organizations processing aluminium must be very cautious while handling red mud, even a small glitch could lead to some serious damage and irreversible environmental degradation. There have been many accidents in the past, few of which were fatal. In the United States of America, the aggregate industry-wide generation of red mud waste by the facilities was approximately 2.8 million metric tons in 1988. The impoundments that receive the muds typically possess an estimated surface area of approximately around 44.6 to 105.3 hectares in all (110 and 260 acres).

In India, all the plants utilize close-cycle (wet slurry) disposal system except, HINDALCO in Belgaum. HINDALCO, Belgaum shifted to dry disposal mode from wet slurry disposal mode in 1985 [10]. An accident was reported very recently in HINDALCO, Muri. A red mud storage facility collapsed spreading the sludge for over 35 acres and flooding even the railway tracks. Few deaths were reported immediately and after the incident, many others were injured [11]. The 212 hectares pond of NALCO factory in Damandjodi (India), has a slurry composition comprising 55% solids and 45% liquids respectively. The output of Red mud is approximately 200 t/hour (solids). Roughly about 20 million tons of waste products are stacked up as shown in Figure 5. In China, things appear to be slightly different. It is proclaimed that most of the red mud residue is directly transferred into landfills, however, almost 10% of red mud is being recycled for further metal extraction process or as a raw material for brick production [12-14]. In Japan, the majority of the red mud residue is stashed into the ocean after effectively, exercising the process of neutralization. Half state-owned Norwegian aluminum company Hydro is accused of serious environmental damage in Brazil. In addition to a leak of toxic mining debris that has contaminated several communities in Barcarena, the Norwegian giant Hydro also faces accusations to have allegedly used a “clandestine pipeline to discharge untreated effluent”, according to the Brazilian media [15].

Discussion

Toxic Effects and Global Accidents

Even in the present-day scenario, after investing millions of dollars in research and investigation to establish a safe and effective method to dispose of red mud, the answer remains to be a mystery. All countries around the world mining aluminium in large quantities continue to suffer. Industries and organizations processing aluminium must be very cautious while handling red mud, even a small glitch could lead to some serious damage and irreversible environmental degradation. There have been many accidents in the past, few of which were fatal. In the United States of America, the aggregate industry-wide generation of red mud waste by the facilities was approximately 2.8 million metric tons in 1988. The impoundments that receive the muds typically possess an estimated surface area of approximately around 44.6 to 105.3 hectares in all (110 and 260 acres).

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A major challenge alumina plants across the world face is the disposal of red mud. The most common method of disposal is by stockpiling. Dry stacking and wet stacking are the two different techniques used for stockpiling. In wet stacking, the red mud slurry is pumped into a yard and then stacked once the precipitation is done. Whereas in dry stacking, the slurry is first dehydrated and then transported into the yard. Dry stacking unlocks the opportunity to store more residue by employing solar and air-drying techniques respectively [16]. Wet stacking has a very high land requirement and it is more expensive due to the initial construction and maintenance of the dam. The dam has to be rigid and impermeable due to the slurry form of the red mud residue. Comparatively, dry stacking has fewer land requirements, provides a safer mode of disposal with less pollution, and doesn’t require the construction of dam facilities initially, resulting in a more effective method of disposal. There is also another technique of stockpiling, which is an intermediate technique between dry and wet stockpiling referred to as mixed stacking [17,18]. Few alumina plants due to deficiency of appropriate land space, directly dump the red mud residue into the sea. This procedure of disposal has critical impacts on marine life as the residue is toxic [19]. Air pollution is also caused by drying red mud in the open fields [20]. The Presence of soluble compounds such as carbonates and hydroxides of sodium present in the red mud residue can sometimes easily dissolve in rainwater and subsequently pollute nearby water bodies [21]. The fine particle size and high alkalinity of red mud is a major cause for its extensive effects on the environment including vegetation [22]. Dried and dusty red mud present in the air can get into the respiratory system of various life forms, which is extremely dangerous. The construction of dams for stockpiling should be carried out with extreme care.

Cracks can cause serious issues when subjected to prolonged usage. One such incident occurred in Ajka alumina plant when the dam of reservoir number 10 collapsed freeing almost One million cubic meters of liquid waste from the red mud lakes as shown in Figure 4. The mud residues were released in the form of waves, which were almost 1-2m high, flooding all nearby localities including few villages of Kolantar and the towns of Devecser. The whole incident reported 10 casualties and 150 serious injuries. It was estimated that almost, 40 square kilometers of land was initially affected and the spill even reached the Danube River [23]. Another incident occurred in Jharkhand at Hindalco, Muri plant where many workers were trapped and swept away in the debris as the caustic pond suddenly broke up following a land cave-in. The head of the mud caved in due to which the mud started spreading away rapidly. Several other such incidents are reported across the globe. All these accidents which occurred and the environmental pollution caused by them, prove that the current disposal methods being followed are not very effective [24].

Figure 4: Ajka Alumina Plant Accident, Hungary [25]

Red mud when dumped into the sea, gets dissolved in the water due to its fine particle size and high solubility. This pollutes the water and has deleterious effects on the marine life of aquatic species. Generally, when the red mud residue is dumped into the sea, a substantial decrease in the fauna was noted. When there is significant concern about the likely effects of the disposal of red mud, it is necessary to proceed with caution. Red mud may be safely dumped in certain areas, but not in others. A decision to dump or
not can be made only after consideration of the circumstances relating to each proposal [27]. If the red mud slurry is left in the open yard while wet stacking, it will penetrate the ground polluting both the soil and the groundwater. This polluted groundwater cannot be used for any other purpose since it is highly toxic, mainly due to high alkalinity and the presence of heavy metal oxides. These pose a serious hazard if consumed if the red mud is mixed with soil, then the soil becomes infertile.

The presence of highly soluble Fe and Al with a high pH concentration level in the soil makes it a potential threat for vegetation. Red mud residues also have high hydraulic conductivity and the coarse fraction which further makes it a greater threat due to which, leaching increases and there is a significant decrease in the alkalinity and salinity of the soil [22]. Apart from all these direct effects, another significant concern is the dust which is formed by drying the red mud [23]. Since red mud particles are extremely small in size (~10-15 µm) they can be easily carried away even by a gentle breeze [23,28].

**Engineering applications**

Since disposing of red mud effectively without disturbing the hydrological or ecological balance is not easy, red mud is being utilized alternatively on other significant prospects mainly being for construction purposes involving cement, bricks, roofing tiles, and glass-ceramics. The alternative engineering applications are listed as follows:

Geopolymer: Geopolymers are inorganic, typically ceramic, materials that form long-range, covalent bonded, non-crystalline networks. It fundamentally serves as an alternative for Portland cement and hi-tech composites used for other ceramic applications. Geopolymerization process involves a chemical reaction that takes place between the alkali metal solution and red mud in highly alkaline conditions. As a result of this reaction, the product obtained is amorphous to semi-crystalline nature, which binds the fine particles of red mud transforming it from a granular material to a compact and strong material. The red mud subjected to polymerization process can find its application in construction sectors and also in artificial structural elements including massive bricks [29] (Figures 6 and 7).

Cement: Dicalcium silicate which is present in red mud is also a major phase present in clinker cement, so red mud can be used for crystallization in the manufacturing process of clinker cement. The constituents of fly ash are SiO$_2$ and Al$_2$O$_3$, thus it can be used to absorb the water content present in the red mud and enhance the reactive silica content of the cement. By employing cement made of red mud the energy consumption of cement production is reduced and also there is a significant increase in the early strength and the resistance of the cement to sulphate attack [30].
Brick: The convectional raw materials used in manufacturing bricks are not only environmentally friendly but they are also not economical. Using red mud addresses these issues in manufacturing bricks. Xing and Jiao (1993), Yang (1996), Zhang (2000), Yalçın and Sevinç (2000) worked and disclosed the production of non-fired brick and non-steam cured fly ash brick, black pellet decorative ceramic glazed tiles, and bricks [31-34].

Glass: Yang et al. (2004) conducted innovative extensive experiments on fly ash and red mud glass [35]. The maximum content of red mud and fly ash was more than 90% was obtained. A suitable heat treatment process was used and a detailed study on crystallization and the factors influencing the crystal growth and nucleation were studied. Using red mud and chromium slag as unprocessed materials along with toner, fluorite, manganese slag, quartz sand, and other materials were used as auxiliary components. Liang (1998) [36] was successful in producing black glass and decorative materials, which were having phenomenal mechanical strength, optical properties, and chemical stability.

Aerated concrete blocks: Aerated concrete is a lightweight and porous material that inhibits great thermal insulation, fire resistance, and seismic resistance properties. It is usually composed of siliceous materials and calcareous materials. However, Red mud aerated concrete, developed using silica (33% - 35%), lime (12% - 15%), cement (15%) and red mud (33-35%) has exceptional compressive strength and bulk density, satisfying the lowest intensity level (MU7.5) of Chinese standards about the strength of concrete blocks [37]. Apart from this, it is also important to note that, the production process is similar to the production of other aerated concrete blocks. As a result of which, the production cost is reduced by using red mud, and also it is believed that this process will become a new alternative method of utilizing red mud effectively.

Road Base Material: Road material utilizing red mud as base material obtained from the sintering process has shown very promising results. Qi (2005) recommended utilizing red mud as alternative road material [38]. Concerning the work of Qi, a 15m wide and 4 km long highway was constructed using red mud as a base material was constructed in Zibo, Shandong Province. A related department examined the strength and the subgrade stability of this product and concluded that the red mud base road meets the strength criteria of the highway [39].

Mining: Yang et al. (1996) [40], from the Institute of Changsha Mining Research, performed many experiments to determine the properties, preparation, and pump pressure transmission process of red mud paste binder black fill material. Based on this innovation a new technology called ‘pumped red mud paste cemented filling mining’ was developed and tested by the Institute of Changsha Mining Research, in collaboration with the Shandong Aluminium Company. Red mud was mixed with fly ash, lime, and water in the ratio 2:1:0.5:2.43, and the mixture was pumped into the mine to counter the effects of ground subsidence which occurs during bauxite mining. They tested 28th-day strength can reach up to 3.24 MPa. This technology utilizes red mud which can be used for non-cement cemented filling. This effectively solves the problem faced using mining methods of Huitan bauxite stop (Figures 8 and 9).

Figure 8: Application of red mud as road substrate [29]

Figure 9: Application of red mud in mine restoration [29]
Waste Water Treatment: Red mud shows a promising application in the field of water treatment employed mainly to eliminate toxic heavy metal and metalliod ions, inorganic anions, bacteria, phenolics compounds and dyes [42]. Scientists have utilized acid and acid thermal treated raw red mud to produce effective and efficient absorbents to address the phosphates present in aqueous solutions. Significant research is going on to relate the utilization of red mud for eliminating dyes from textile effluents. Significant strides have been made to use red mud for eliminating chlorophenols from wastewater [43]. Neutralized red mud in the batch adsorption technique has been effectively used for eliminating phenol from aqueous phase [44]. Tor et al. (2009) [45] also used granular red mud for eliminating fluoride from water. The process of eliminating boron from aqueous solution has also been researched and studied by employing neutralized red mud [46]. Red mud has also been converted into an economical and efficient adsorbent to remove chromium, lead, zinc, and cadmium from aqueous solutions [47,48].

Soil Improvement by red mud: Red mud has a promising environmental replenishing effect on the soil which has been polluted by heavy metal elements [49]. The mechanism on which it operates goes as follows, red mud can absorb heavy metal ions mainly Cu²⁺, Ni²⁺, Zn²⁺, Pb²⁺, Cd²⁺, Cr⁶⁺, Mn⁴⁺, Co³⁺ and Hg²⁺, which is present in the soil. The structure of the heavy metal ions changes from exchangeable ions into bonding oxides. An alternate mechanism explains the precipitation reaction taking place between carbonate in red mud and the heavy metal ions, which in turn causes these ions to deposit. The activity and reactivity of heavy metal ions present in the soil are significantly reduced to a major extent promoting microbial activity and plant growth significantly. Gao et al. (2008) [50] conducted some studies and concluded that red mud can drastically decrease Cd and Zn at the exchangeable state or affective state present in the soil. Zhang et al. (2018) [51] used red mud in a bid to modify the soil polluted by heavy metal. The result showed that red mud can drastically reduce the heavy metal content present in seriously polluted soil and also lessen the absorbed dose of heavy metal. Lombi et al. (2002) [52] discovered that adding about 2% of red mud to soil restrained the absorption of crops for Cu²⁺, Ni²⁺, Zn²⁺, and Cd²⁺. After several modifications, the mass concentration percentage of Zn in the soil pore water and lettuce body decreased respectively by 95% and 97%.

Conclusion

Overall, the utilization and disposal of the red mud produced in the process of industrial production of alumina is still a worldwide problem. It's very difficult to achieve a uniquely cost-effective and environmentally sustainable technique for managing this by-product. Numerous studies and experiments have been conducted and are still being conducted even today for extracting the minerals from red mud but all these studies provide information and data only for laboratory scale applications. However, this has never been applied in a more practical oriented scheme. In the present-day scenario, the capacity of utilization and secondary consumption of red mud is inadequate. The current methods of disposal involving red mud are ineffective and hazardous to the environment. The stockpiling technique used currently worldwide is not safe, which has been proven by many accidents in the past. This study provides insight regarding the role played by red mud in polluting soil, air, and water. The study also explains the suitable methods and techniques that can be implemented to effectively and efficiently utilize the red mud residues in everyday general applications and also in numerous engineering applications. Not all the methods promoted in this study are 100% safe and completely applicable at all the places but by following these methods, the pollution that is being caused by currently due to conventional methods can be lowered to an extent and this is worth the effort.

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