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A review of the red mud utilization possibilities

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Abstract. Red mud, a voluminous industrial waste produced during the Bayer process in the alumina industry, has numerous application possibilities across various fields. Its potential uses are diverse, ranging from the construction industry and metallurgy to environmental protection and agriculture. There are three main aspects of red mud utilization. First, it can be analyzed from the point of view of resource utilization, where it could be applied as raw material mostly in the construction industry. Second, it could be a useful source of valuable components, such as rare earths and metals, especially iron. Third, red mud could have different environmental applications, in wastewater treatment, soil remediation, etc.The paper summarizes current data on red mud utilization methods and aims to emphasize the potential for red mud utilization in various fields.

Keywords: environmental protection; industrial waste utilization; metals recovery; red mud; secondary raw material.

1. Introduction

The primary and most widely used process for alumina production is the Bayer process. Over 95% of globally produced alumina comes from bauxite processed using the Bayer process [1].

The Bayer process can be summarized into three main stages [2, 3]:

1. extraction (leaching/dissolving bauxite, digestion),
2. precipitation (precipitating sodium aluminate from the solution after bauxite leaching), and
3. calcination (roasting the precipitated gibbsite to obtain anhydrous aluminium oxide).

A simplified diagram of the Bayer process is shown in Figure 1.

The digestion process is the most complex and crucial step in the Bayer technology. In this process, crushed bauxite ore is dissolved in a concentrated sodium hydroxide solution at elevated temperature and pressure in autoclaves. The temperature, pressure, and NaOH concentration in the digestion process depend on the mineralogical composition of the bauxite. During the digestion process, sodium aluminate $Na[Al(OH)_4](aq)$ is formed, as aluminate ions ($[Al(OH)_4]^-$) from the bauxite dissolve into the solution, while the insoluble minerals remain in the residue. This residue, in the form of sludge, is known as bauxite residue or red mud (due to its nature and brick-red color). The term "red mud" is much more commonly used (77%) [5], and will therefore be used. Red mud is a waste product in the form of a suspension, characterized by its fine-grained composition, high alkalinity, and thixotropic properties.

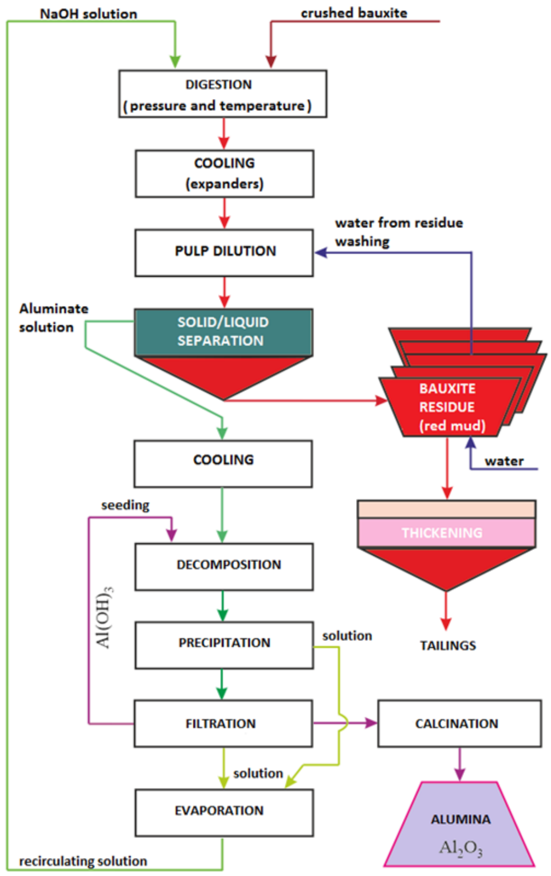

Figure 1. Simplified schematic of Bayer process and red mud generation[4]

It is estimated that around 4 billion tons of red mud have been generated, on a global scale, since 1974, with

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China having the biggest share, accounting for about 28.2% of the global red mud generation, followed by Oceania region (22.4%), South America (14.6%), Europe 12.9%), North America (8.8%), and Africa plus other parts of Asia (excluding China) (8%) [6], The rising demand for aluminium production has led to a rapid increase in the generation of red mud, necessitating effective management and disposal strategies due to its specific properties and potential environmental hazards.The disposal of red mud presents significant environmental risks and challenges for safe management, primarily due to its high alkalinity (pH 10–13), the presence of heavy metals and radionuclides, and the potential for groundwater contamination, dust generation and dispersal, accidents involving dams and storage facilities, and the large volume of red mud produced [7-10]. In general, disposal techniques can be divided into dry and wet disposal procedures, as well as traditional and modified techniques. Traditional disposal techniques involve land disposal (lagooning and ponding) and seawater disposal (which is now an abandoned practice) [11]. Modified techniques include wet and dry stacking, dry cake disposal, and other modified methods that are being developed to reduce moisture content, as well as red mud disposal and storage costs [11, 12].

This paper aims to explore the potential of red mud as a valuable resource for various applications. By highlighting opportunities for its utilization, the study seeks to add value to this industrial by-product, thereby reducing its environmental impact.

2. Properties of the red mud

Since the bauxite ore composition varies from each mine, and thus the process for refining needs to be modified according to that, the composition of the red mud also varies. However, the general composition of the red mud is the following: iron oxides (hematite, goethite, boehmite), other aluminium hydroxides, calcium oxide, titanium dioxide and aluminosilicate minerals such as sodalite [13]. Major constituents of red mud are: Fe_2O_3 Al_2O_3, TiO_2, SiO_2, Na_2O, CaO etc. Red mud particles are generally fine-grained with particle sizes smaller than 75 μm for up to 90 wt.% of particles. Surface areas ranging between 10–30 m^2/g [14, 15]. The pH of the red mud is about 10.5–13 [2, 16].

A wide range of other components may be present at lower levels e.g., arsenic, beryllium, cadmium, chromium, copper, gallium, lead, manganese, mercury, nickel, potassium, scandium, thorium, uranium, vanadium, zinc, zirconium, and rare earth elements (REEs). Non-metallic elements that may occur in the bauxite residue are phosphorus, carbon, and sulfur. Sodium could be found in the bauxite residue from the process, not from the ore itself. However, the current practice is that almost all bauxite refineries trying to maximize the recovery of the caustic soda [15, 17].

3. Utilization of the red mud

There are various opportunities for red mud utilization (Figure 2). The three main categories, according to the unique physical and chemical properties of the red mud are as follows [10, 11, 18]:

– Reuse of red mud as raw materials;
– Recovery of metals from the red mud;
– Application of red mud in the environmental protection field.

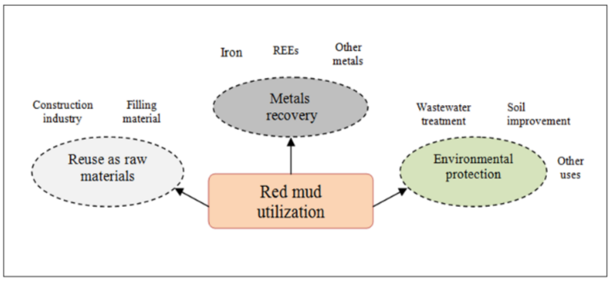

Figure 2. The most common red mud utilization possibilities

3.1. Reuse as raw materials

Red mud can be used as raw material inthe construction industry (especially the cement industry) and as a filling material [18, 19].

As a construction material, there are various possibilities. The red mud can be used in a raw or modified form as a supplementary cement material[20], in lightweight concrete, in pervious concrete, in ultra-high performance concrete, as the base course of roads, for asphalt mixtures, for autoclaved aerated concrete, as sustainable subgrade material [21]. Certain studies investigated use of red mud as raw material, as a clay substitute, to manufacture red bricks [22, 23], geopolymer composite [24-26], dyes and pigments [27, 28], ceramics production [29, 30] etc. Also, red mud can be used in bulk material applications or as a filling material [7, 19].

The most common and the most investigated uses are utilization for cement and concrete production, red brick and geopolymer composite production.

3.1.1. Use of red mud in the cement industry and concrete production

Red mud from the Bayer process can be used in three directions in cement industry: the preparation of cement clinkers, the production of composite cements, and the production of alkali-activated types of cement [20]. Different types of cement can be produced. Namely, authors Singh *et al.* investigated the properties of three types of cement made from different proportions of red mud, lime, fly ash, bauxite and gypsum. Some of the types show astrength comparable to ordinary Portland cement [31]. The Greek study investigated the use of the red mud as a raw material for the production of the Portland cement clinker. Study shows that the addition of the red my by 1% did not affect the properties of the final product, sintering or the hydration process during the Portland cement production. Thus, the bauxite residue (red mud) can be successfully used in cement production [32]. Besides cement production, red mud can be used as a cement substitute in concrete production, in raw form or with some pretreatment, like neutralization [16]. Non-calcined red mud can be a potential material for use in mortars and concretes for non-structural applications. According to the results, red mud can be replacement in significant percentage, for Portland cement in mortars used for non-structural application, which can be a good recycling option for this type of industrial waste, offering many environmental and economic benefits [33]. One of the newest studies conducted the LCA (*Life Cycle Assessment*) of red mud utilization in concrete production and its environmental impact assessment. The results show that the use of red mud in concrete production have positive effects to the environment overall, including freshwater ecotoxicity and human cancerogenic ecotoxicity, compared to traditional concrete production [34]. Table 1 shows the current status of red mud use in Portland cement production [7].

Table 1. Bauxite residue use in Portland cement production [7]

Bauxite residue (BR) use in Portland cement production			
Status	**BR source**	**User(s)**	**Quantity used (kt/y)**
		Actual usage	
Now	Mykolayiv, Ukraine	Formerly 10 plants (now 6)	~250
Now	Distomon, Greece	3 cement plants in Greece, 1 cement plant in Cyprus	~80
Now	Shangdong, China	Integrated cement plant	?
Now	China - several plants	Local cement plants	?
Now	India - Several plants	Approx. 40 cement plants	>2100
		Potential	
Potential	Distomon, Greece	Trial Lafarge, 3500 tonnes	300
Potential	India	Various	2500
		Abandoned	
2011	Ewarton, Jamaica	St Catherine cement plant	100
2003/2004	Showa Denko, Japan	Trial 700 tonnes	-
1986/1987	Ewarton, Jamaica	Caribbean Cement Limited, Kingston	40-50

3.1.2. Red bricks production

There are two directions in red mud brick production: fired and non-fired brick production [35]. Authors Arrojo *et al.* used red mud as a clay substitute to manufacture fired bricks, with a replacement ratio of up to 80%wt. The results regarding mechanical strength showed higher strength with the higher producing temperatures. Leaching tests showed the possibility that some heavy metals pass the regulations limit values (e.g. Cr), but it depends on the country's regulations, which should be homogenized globally. According to radiological regulations, all the bricks met the limit values [22]. The best mechanical properties at higher sintering temperatures are obtained earlier in the experiments as well [36, 37]. He *et al.* also showed that the best condition for brick manufacturing was the red mud content of 40% and sintering at 1050ºC for 2h. From an environmental point of view, sintering can decrease a leaching concentration of toxic metals [37]. Red mud in combination with fly ash was used for the production of burnt bricks, and the properties of the final product were compared with regularly produced bricks. Results show that industrial waste-based bricks have the lowest water absorption and highest comprehensive strength among the curing conditions. Also, there is the possibility of saving up to 50% of clay used for regular brick production, which is one of the benefits of red mud recycling [23].

When it comes to the preparation of unburned bricks, it is important to determine the ratio of components which bricks are made from, because different ratios and preparation processes influence the product's performance. It is possible to obtain good mechanical properties and satisfy other important parameters and meet national regulation standards regarding heavy metal content [38, 39]. One of the studies shows the results of the unfired brick preparation from the red mud and calcium sulfoaluminate (CSA). It is concluded that the soluble Na could promote the hydration of CSA cement, as well as the soluble Na, soluble F and heavy metals are well immobilized. The strength of unfired bricks satisfies the requirements [40]. There are several benefits of using red mud in the preparation of non-fired bricks, both economic and environmental. It lowers the costs of using the waste material, as well as the environmental impact by recycling this industrial waste.

3.1.3. Geopolymer composite production

Geopolymers are aluminosilicate materials in a network structure, formed by activators containing calcium and alkali in addition to the main aluminosilicate component. Those materials are getting more attention in the construction industry, as binders [41]. Geopolymers have a high potential to be replacement for ordinary Portland cement [42]. Various waste materials are investigated for geopolymer production, among them fly ash, red mud, rice husk etc. Detailed investigation of red mud utilization as a geopolymer precursor is pointed out by authors Kumar *et al.* The use of red mud in geopolymerization addresses the need for an alternative disposal method, reducing its harmful environmental impact. Additionally, red mud helps to lower the high costs associated with alkali activator solutions, as its high concentration of NaOH contributes to the process [43]. He *et al.* synthesized a new type of geopolymer composite from two industrial wastes, red mud, and rice husk (RHA). They investigated the impact of various ratios of these two components, and other process parameters (curing duration, particle size, etc.), on an obtained final product. The mechanical properties of the RM-RHA geopolymer are very complex and dependent on varied parameters. So further improvement in the optimization of these parameters is necessary [24]. Authors Silveira *et al.* proposed red mud use in geopolymer production, which can be used in civil construction to replace Portland cement in some applications. A limitation of developing such an idea is red mud drying, as it contains precursor and activator components. They suggested drying only at ambient temperatures because higher temperatures can initiate a geopolymer reaction. Another suggestion is to use sodium silicate as an activator, for better strength results [41]. Better mechanical properties of waste-material-based geopolymers can be achieved by combining waste materials in geopolymer production, such as red mud and fly ash [44]. According to the abovementioned and numerous other studies, red mud can be a potential replacement for ordinary Portland cement in a certain percentage, and in a combination with other geopolymer source materials.

3.1.4. Red mud as a filling material

To reduce the negative impact on the environment, and reuse more waste materials, such as red mud, its potential use as filling materials was investigated. Zhang *et al.*conducted experimental tests to investigate the substitution of the mineral filler in the asphalt mixtures. They concluded that the addition of red mud can improve the stiffness and elasticity of asphalt mastic, especially the sintering red mud. It can be considered as a replacement for the natural mineral filler for asphalt pavements [45]. Other studies also confirmed use of the red mud in road construction as filler in bituminous mixtures or in pavement base layers [7, 19, 46]. In such uses, there is a need for a high volume of red mud to achieve the desired quality and be competitive in terms of properties and risks [19]. Wang and the authors investigated how additives (cement, lime, and phosphogypsum) affect the strength of amended red mud as road base material, and optimized proportions of each additive to achieve the best properties of the final product [47]. A similar study was conducted, with the use of gangue, flue gas desulfurization gypsum, and silicate cement used to assist red mud in the preparation of red mud-based composite filler material, aiming at the large-scale resource utilization of RM [48].

3.2. Metals recovery

Red mud presents significant potential for metal recovery and it can be considered as a secondary raw material for the recovery of valuable metals, particularly iron, due to its high iron content.

3.2.1. Iron recovery

Red mud could serve as a promising feedstock for iron production, especially in iron plants located near alumina processing facilities. Utilizing red mud in this way could reduce iron ore transportation costs and decrease the reliance on natural resources [49]. In red mud, iron is predominantly present in the forms of hematite and goethite, with hematite accounting for more than 90% of the iron content [14]. The iron content in red mud depends on bauxite ore composition, and it can be in a wide range (up to more than 50%). For iron recovery from the red mud, it is desirable to have an iron content in the red mud more than 51%, to be competetive with iron ore, since the red mud could be promising replacement for the utilization of this natural resource [50]. Many techniques have been investigated for iron extraction from the red mud. In general, those techniques can be classified as:

1. Direct magnetic separation;
2. Pyrometallurgical recovery;
3. Hydro-metallurgical recovery;
4. Other techniques (biotechnologies and bioleaching).

A detailed explanation is offered by authors Liu and Naidu [8]. The newest experiments on iron extraction from the red mud using fossil fuel-free technology hydrogenplasma-based reduction, making it available for the production of several hundred million tonnes of green steel [51].

3.2.2. Other metals and REEs recovery

Except for the iron recovery, many studies explained the possibility of extraction of other major elements such as Al, Ti, Na, Si etc. [8, 14, 49, 52-55]. From the metallurgical aspect, titanium has very good potential to be recovered from the red mud [55, 56]. Red mud potential for titanium recovery is also approved by SEM and EDS analysis, which could be a reason for additional research from the aspect of the recovery of this valuable metal [57]. Iron, titanium and aluminium can be recovered from the red mud calcining it, preferably between 800 °C and 1350 °C, and smelting the material with a carbonaceous reducing agent in an electric furnace, thus obtaining molten iron, and a slag containing substantially all the titania, alumina and silica [55, 58].

One of the directions of metals recovery from red mud is rare earths (REEs) recovery, since their consumption and production are increasing rapidly, and REEs are classified under the most critical raw materials group, with the highest supply risk [59]. The rare earths are the fifteen metallic elements of the lanthanide series, together with yttrium and scandium [60]. They have many applications, especially in the electronic industry, where they are used in many devices such as mobile phones, screens, high-capacity batteries, permanent magnets for wind power stations, ceramics, etc. [61]. The concentration of these elements in bauxite residues varies, but (for example) atypical Jamaican residue (which can be 5-10 times higher in REEs than bauxites from other regions) contains (in ppm): scandium 135, lanthanum 500, cerium 650, neodymium 250, samarium 65, europium 15, terbium 10, ytterbium 30, lutetium 5, tantalum 10 [7]. Scandium is the most extensively researched REE, and it has a great value to be recovered from the red mud [14]. The recovery of REEs from red mud mainly focuses on hydrometallurgical methods [8], with acid-leaching technology as the predominant method [14]. The choice of extraction method depends on the forms of existence of the REEs in the solution [61].

3.3. Environmental protection

Red mud has found a possibility for utilization in the environmental protection field. Its most common uses include wastewater treatment, soil amendment, and various other applications.

3.3.1. Wastewater treatment

Many studies investigated the possibilities of red mud application in water treatment [62-68]. Due to suitable adsorption properties, small particle size and specific surface area, red mud can be used to treat wastewater from various sources [69]. The use of raw or treated red mud in wastewater treatment primarily focuses on its sorption properties for the removal of metals, metalloids, radionuclides, phosphates, nitrates, fluorides, dyes, and phenols from wastewater. Additionally, its potential for the removal of microorganisms and the neutralization of acidic water is being investigated [70]. As heavy metal ions sorbent, red mud is experimentally applied for the removal of cadmium, copper, lead, zinc, nickel etc. [69-71]. Depending on the type of wastewater, sorbent dosage, temperature, and other sorption conditions, red mud can achieve high pollutant removal efficiency. For instance, red mud has been shown to effectively remove Pb, Cd, and Cu, with the adsorption/desorption theory and detailed process explanations provided by Bai *et al.* [69]. Experiments have also been conducted to enhance red mud's adsorption capacity, including modifications through physical and chemical treatments to improve nickel adsorption from water solutions [70]. Other studies found that the adsorption capacity of modified red mud for Pb(II) ions was significantly increased, nearly tenfold compared to untreated red mud [72]. Inorganic anions (phosphate, nitrate, fluoride,sulfate, etc.) are among the most common aquatic pollutants, and its removal using modified and non-modified red mud was examined. Favorable results are obtained from different research studies, using red mud for phosphorus removal from different aquatic solutions [73-78], nitrate removal [63, 79, 80], sulfate removal [81, 82] etc. Red mud can be also effectively applied for the removal of dyes [83-86], phenolic components [87-89], pharmaceuticals [77, 90, 91],and other toxic and polluting components.

3.3.2. Soil improvement and other uses

Another potential use of red mud is in acidic soil neutralization and soil remediation, particularly when combined with additives like biochar and paper ash [92, 93], as well as for treating metal- and metalloid-contaminated soils [94]. Additionally, red mud can serve as a neutralizing agent and assist in metal immobilization in acidic mine tailings, where generating sufficient alkalinity to neutralize excess acidity is crucial. Favorable results have been achieved, supporting the use of red mud in larger quantities for such applications [95]. Authors Klauber and others, in their detailed study, also describe red mud application in waste gas treatment, and other agronomic and environmental applications [5].

4. Conclusions

One of the sustainable development and circular economy ideas is to reuse as much as possible waste materials, to avoid unnecessary disposal into the environment. Industrial wastes have special attention, because they are in most cases more harmful and toxic to the environment and living beings, due to their specific properties and composition.

Bauxite residue, commonly known as red mud, is one of the industrial byproduct with high potential for recycling. Due to its generation in large quantities and potentially toxic properties, promoting its utilization is crucial, with disposal into the environment being the least favorable option.

Many research studies investigated red mud utilization, and probably the most common and the most investigated applications are utilization for cement and concrete production, red brick, and geopolymer composite production. Regarding the metal recovery from the red mud, iron recovery is most extensively investigated, because the iron content in the red mud could be competitive with iron ore, so the replacement of the natural ore with waste material could have many economic and ecological benefits. Besides iron, researchers studied possibilities to recover aluminium, titanium, silicon, etc. Rare earth metals are also of special interest in this field. In environmental protection, red mud has primarily been used in wastewater treatment, especially as a sorbent for pollutants like heavy metals, phosphates, and nitrates. As a soil amendment, it can be used as a neutralizing agent and for metal immobilization, particularly in acidic mine tailings. New perspectives on red mud utilization are seeking to find a better option for its utilization, to reduce carbon-dioxide footprint (example of „green“ steel production, using new technologies of plasma reduction of red mud).

However, the industrial-scale use of red mud remains limited. Several factors contribute to this, but it is clear that raising public awareness, especially in regions with alumina production plants, is crucial. The benefits of red mud utilization are many, ranging from economic savings to environmental protection, and they should be the starting point of red mud utilization.

Conflict of interest

The authors declare that there is no conflict of interest concerning the publication of this research article.

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