Research Progress on Comprehensive Utilization of Red Mud

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Abstract. Red Mud(RM), a kind of hazardous solid wastes produced during the process of alumina production, is disadvantageous for our environments owning to its characters of strong alkali and rich salt. It is essential to conduct innocent treatment. Summarizing the hazards of RM and methods of its comprehensive utilization, A reference for the deeper comprehensive utilization of RM in the future in this review was provided.

1. Introduction
As one of the largest industrial wastes in China, Red Mud(RM) is a strong alkaline waste produced in the process of alumina production. It is named because it contains abundant iron oxide and is reddish brown, and its appearance is slurry. The production of RM is related to raw ore, production technology and technical level. According to these conditions, RM can be divided into Bayer RM, sintered RM and combined RM. Only about 2.5% of alumina is produced by sintering, and more than 90% is produced by Bayer. As of 2016, the global RM accumulation has reached 4.2 billion tons and continues to grow. Most of these excess RM is stored in the open air. On the one hand, it wastes useful components of RM and occupies a large amount of land. On the other hand, strong alkali and high salt solid waste cause incalculable pollution and damage soil and water resources. In summary, the harmless and resource utilization of RM is imminent.

2. Properties and Composition of RM

2.1. Physical Properties of RM
RM is mostly red slurry waste residue, because of the different iron content will also show dark reddish brown, brown and gray white and so on. The RM is granular with a particle size of 0.005 mm to 0.075 mm, surface area of 64.09 m²/g to 186.9 m²/g, density of 2.7 g/cm³ to 2.89 g/cm³, and a melting point of 1200°C to 1250°C.

2.2. Composition of RM
Bauxite is the main raw material for producing Alumina, which is mainly composed of aluminum trihydrate, bohmite and bauxite, and also contains goethite, hematite and a small amount of other mineral. The composition of bauxite in different producing areas is different and different...
production processes lead to different composition of RM. Table 1 summarizes the chemical composition of Bayer method, sintering method and combined method. The analysis shows that there are six main components of RM, such as Al₂O₃, Fe₂O₃, SiO₂, CaO, Na₂O and TiO₂.

| Composition | Al₂O₃ (%) | Fe₂O₃ (%) | SiO₂ (%) | CaO (%) | Na₂O (%) | K₂O (%) | MgO (%) | TiO₂ (%) |
|-------------|-----------|-----------|----------|---------|----------|---------|---------|---------|
| Bayer       | 10-20     | 30-30     | 3-20     | 2-8     | 2-10     | ---     | ---     | 10-15   |
| Sintering   | 5-7       | 7-10      | 20-23    | 46-49   | 2.0-2.5  | 0.2-0.4 | 1.2-1.6 | 6-10    |

3. Hazards of RM
RM is solid waste with strong alkali and high salt, and its main pollutants are alkali, fluoride, sodium salt and aluminum salt, etc. According to national emission standards (Nonferrous Metals Industrial Solid Waste Pollution Control Standards GB5058-85), we can launch RM as general solid waste because the pH value of RM was 10.3 to 11.3, fluoride content was 4.89 to 8.6 mg/L, and RM effluent exceeding standard. Since its pH > 12.5, fluoride < 50. As a result, RM (and its attached liquid) is waste residue.

3.1. Occupying a lot of land resources
At present, the output of RM in China accounts for about half of the world output, and the cumulative stacking capacity is as high as hundreds of millions of tons. However, due to the influence of strong alkali, high salt and radioactivity, there is no of energy efficiency utilization in RM. Excessive RM mostly open-air stacking, resulting in a large amount of waste of land resources. With the development of aluminum industry, RM stacking is bound to cause more waste of land, which will become a serious obstacle to the development of aluminum industry.

3.2. Causing environmental pollution
Long-term open-air piles of RM will leak a lot of harmful substances, soil, water resources and air will cause serious pollution. RM with strong alkali and high salt will change the chemical composition and structure of the corresponding soil layer, aggravate the salinization of the soil, make the plant difficult to grow, and the damaged land difficult to repair. Because of its process, RM has very fine particles, these particles float or carefully into groundwater with Rain Water, resulting in the increase of water salinity, fluoride content and other metal elements, which pollutes the quality of Water. Fine particles of RM float easily in the air after air drying to form haze, resulting in air pollution.

4. Comprehensive utilization of RM

4.1. Recycling of valuable metals

4.1.1. Recovery of iron in RM. The content of iron in RM is about 20% to 50%, which has great recycling value. The iron in RM was reduced to 95.76% by roasting reduction-magnetic separation of Zhu and others under the condition of grinding fineness 0.074 mm, magnetic field strength 0.08 T and adding 8% sodium carbonate. Fan Yanqing and others under the condition of reduction calcination, the coke ratio is 20%, the melting time is 90 minutes, the calcium-aluminum ratio is 2.0 and 100°C the red mud is reduced and melted, and the iron recovery rate is over 99.4% at high temperature. Liu Peikun and others adopted the method of gravity separation, and obtained 48.83% iron concentrate when the swirl machine concentrated desliming concentrator selected and enriched double conditions, the swirl machine bottom flow-5um, the separator rotation speed 6 r/min, vibration frequency 35 Hz.

4.1.2. Recovery of titanium from RM. There are abundant titanium resources in RM. We know that more than 20% of the RM discharged by Indian alumina enterprises has TiO₂. So titanium in RM has
high utilization value. Jiang Pingguo and others\textsuperscript{[18]} used the secondary acid leaching process, the primary acid leaching at the pH of 3 to remove 80% calcim salt, the secondary acid leaching at the concentration of 6 mol/L hydro chloric acid, at the temperature of 80 to 95°C can recover more than 80% titanium. Zhang Jiangjuan and others\textsuperscript{[19]} carried out acid leaching of RM with HCl and H\textsubscript{2}SO\textsubscript{4} respectively, The recovery of titanium dioxide is 91%, purity up to 95%. Wang Qi and other\textsuperscript{[20]} roasted RM particles (particle size is 0.15 to 0.18 mm) at 600°C for 5 hours and soaked in 12 mol/L of H\textsubscript{2}SO\textsubscript{4} acid, 46.7% of titanium can be recovered by leaching.

4.1.3. Recovery of aluminum from RM. The aluminum content in RM is usually high, and the aluminum mainly exists in the form of Al\textsubscript{2}O\textsubscript{3}. If it is not recovered, it will cause a large amount of waste of aluminum resources\textsuperscript{[21]}. Therefore, a large number of scholars have studied and explored the aluminum recovery process in RM. Ma Shuhua and others\textsuperscript{[22]} analyzed the principle and characteristics of alumina recovery in RM by acid dissolution method, melting acid dissolution and extraction coupling method. It is pointed out that each process has its own advantages and disadvantages, but it can recover most of alumina. Wang Keqin and other\textsuperscript{[23]} carried out industrial tests on RM recovery alumina. The results showed that thealumina recovery rate could reach 80.26% after two stage leaching-evaporation-decalcification, titanium-neutralization pH treatment of RM under 80°C. Liu Guihua and other\textsuperscript{[24]} used sodium carbonate decomposition method, When 180°C, carbon-alkali concentration greater than 180 g/L is recovered in water fossils, The dissolution rate can be more than 50%.Jiang Wenchen\textsuperscript{[25]} used microwave oven sintering technology to heat 3% iron powder and 4% KF Bayer RM to 1100 to 1150°C and heat preservation for 10 minutes, which can recover 73.68% aluminum.

4.2. Application of Red Mud in Building Materials

4.2.1. Material of cement. RM contains a lot of iron, aluminum and its oxides and other salts, which is a good raw material for the production of cement and other building materials. At present, RM is mainly used in cement production in the following three aspects: 1. Preparation of cement clinker; 2. Production of composite cement; 3. Preparation of alkali activated cement\textsuperscript{[20]}. Zhao Hongwei and others\textsuperscript{[27]} used red mud as the main raw material and sintered cement clinker at 130°C afterformula design. Wu Feng and other\textsuperscript{[28]} used the RM of Datang High Aluminum Coal Research and Development Center of Mongolia to produce cement clinker with alkali content below 1%. The results show that this method can make the cement clinker with lower firing temperature and more uniform. Yang Jiujun\textsuperscript{[29]} and others explored the effect of different RM content on the preparation of composite cement. The results showed that RM composite cement decreased with the increase of RM content, and the radioactivity of hydrated composite cement could be effectively regulated. That is, the addition of RM is beneficial to the hydration process of cement.

4.2.2. Material of briks. RM has the properties of curing, low cost and superior performance, and can be used as raw material for the production of many kinds of bricks. Yang Jiakuan and others\textsuperscript{[30]} expounded the pilot production and industrialization of RM-free bricks. The results of the pilot test were as follows: both natural maintenance and autoclaved maintenance reached the industry standard and the economic cost was low, which had the feasibility of industrial production. Ren Mengjie and other\textsuperscript{[31]} put forward the method of sintering brick by acid calcium fluoride and Bayer RM. The results showed that under the condition of 61.1% ratio of calcium fluoride sludge to RM, 21.4% clay and 15% aluminum ash were added and sintered at 1000°C, non-bearing bricks with good performance can be obtained.

4.3. Environmental remediation

Because RM is a porous material with small particles, it has large specific surface area and good chemical stability in water, so it can be used as adsorption material water treatment field\textsuperscript{[32]}.
and other\textsuperscript{[33]} studied the adsorption properties of RM by seven processes. After roasting acid leaching, the specific surface area of RM was increased from 144.7 m$^2$/g to 532.8 m$^2$/g. Fu Jinli\textsuperscript{[34]} points out that RM can be used to adsorb metal, non-metallic ions and other pollutants in water, and can also be used as flocculant to participate in other aspects of water treatment.

RM can also be used in soil remediation. On the one hand, it can solidify heavy metals and reduce heavy metal pollution in soil; on the other hand, RM contains elements such as Ga, Mg needed for plant growth, which can improve soil quality. Zhang Xue \textsuperscript{[35]} pointed out in research progress of RM solid waste soil remediation that soil conversion is a feasible method to realize the effective utilization of RM, which can reduce the utilization rate of RM and improve the utilization rate of resources at the same time.

The alkaline substance in RM can react violently with acid gas to deal with gas pollution. The SO$_2$ test of removing industrial flue gas from RM by combined method by Jia Shuaidong and others\textsuperscript{[36]} shows that the desulfurization efficiency can reach 93\%. Zuo Xiaolin and other\textsuperscript{[37]} pointed out in the study of RM desulfurization by Bayer method that the RM slurry was introduced into the desulfurization reactor at 25$^\circ$C, and the RM with sulfur capacity of 362.7 mg/g could be obtained after the reaction.

5. Conclusion
As one of the largest wastes in aluminum industry, RM has not been treated with large-scale industrialization at home and abroad, and its excessive stacking has brought great threat and waste to the environment and resources. It is hoped that the researchers will take the performance of RM as the focus, deeply study the recycling and harmless utilization of RM in building materials and environmental restoration without secondary pollution, and put forward a reasonable process of environmental friendly and efficient utilization of resources.

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