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Research Progress on Recovery of Valuable Elements from Electrolytic Manganese Slag and Treatment of Hazardous Substances

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Abstract: Electrolytic manganese slag refers to the filter residue produced in the process of manganese electrolysis. Generally, the filter residue is acidic hazardous substance. At present, the main method for the manganese slag is to carry out open-air treatment, which can seriously pollute the environment and occupy a large amount of land area for a long time. Therefore, stacking treatment of the electrolytic manganese slag has become a big problem in electrolytic manganese slag industry. The research shows that the electrolytic manganese slag contains a lot of available valuable substances and has great recovery value. In this paper, the background of electrolytic manganese slag, the recovery method of valuable elements, the recycling technology of electrolytic manganese slag and the removal of ammonia nitrogen, heavy metal ions and sulfur from electrolytic manganese slag are reviewed. The separation and recovery technology of electrolytic manganese slag mainly includes magnetic separation method, water washing method, ammonium salt roasting method, leaching method, bio-leaching method, and electrochemical methods. Through the analysis of some valuable elements of the existing manganese slag, the purpose is to realize the resource utilization of the electrolytic manganese waste slag, so as to “turn waste into treasure”, which is that the electrolytic manganese waste slag can be turned into valuable, thereby reducing the water pollution, soil pollution and air pollution caused by the electrolytic manganese slag. It is hoped to provide some references for the comprehensive resource recovery and utilization of electrolytic manganese slag. Therefore, the relevant research on the resource utilization of electrolytic manganese slag is of great significance.

1. Introduction

Manganese metal is a kind of incanus, with firm and brittle texture, ferrous luster metal. With the development of society, manganese is indispensable in non-ferrous metallurgy, iron and steel industry and chemical industry and it has become one of the important materials of the country. It is found that the leaching residue produced by electrolytic process of manganese metal contains gold, silver and other valuable elements. If these slags can be realized recovery, it will bring good economic benefits. But the manganese slag also contains arsenic, mercury, selenium and other hazardous atoms [1]. Therefore, we need to find ways to eliminate these harmful elements. In this way, we can not only reduce the waste of resources, but also avoid the damage to the ecological environment after these materials are discarded, thus reducing heavy metal pollution.

2. Composition of Valuable Elements in Electrolytic Manganese Slag

Electrolytic manganese slag contains a lot of heavy metal ions, soluble salts and other solid-phase mineral components, such as sulfates, ammonia nitrogen and water-soluble hazardous substances such as Cu, Zn, Cr, Pb, etc. Manganese slag will be produced in the production process of electrolytic manganese metal. According to statistics, every 1 ton of electrolytic manganese metal will produce 8~12 t of electrolytic manganese slag [2], which can be imagined that the output of electrolytic manganese slag is pretty high. Moreover, with the development of national industrialization, the production process using manganese will only increase day by day, thus the slag yield will only increase.

3. Separation and Recovery Technology of Electrolytic Manganese Slag

3.1. Magnetic Separation Method

Because there are some differences in the magnetism of minerals, magnetic separation is a mineral separation method based on the magnetic differences of minerals in the ore, in the non-uniform magnetic field to achieve mineral separation. Magnetic separation is a physical separation method to achieve the separation and enrichment of manganese in electrolytic manganese slag under the condition of magnetic field [3]. The technological process of manganese ore magnetic separation is roughly ore washing screening, high-intensity magnetic roughing, grading, medium-intensity magnetic concentration and enrichment.

3.1.1. Ore Washing Screening

With the aid of hydraulic washing or mechanical scrubbing, the manganese ore is separated from the surface mud, and the washed ore is sent to a screening machine for screening and grading, the ore with larger particles on the screen can be manually selected, and the other ores enter into a magnetic separation process.

3.1.2. High-Intensity Magnetic Roughing

Roughing is conducted by adopting a high-intensity magnetic separator, manganese ore is initially separated from other impurities, rough concentrate after roughing is sent to a spiral classifier for grading, and tailings are sent to a tailings densifier for concentration.

3.1.3. Grading

The rough concentrate grading underflow is sent to a magnetic separator for next step of magnetic separation, and overflow is sent to the densifier.

3.1.4. Medium-Intensity Magnetic Concentration

The tailings of medium-intensity magnetic concentration are discharged into the tailings densifier, and the concentrate is merged with the underflow after grading overflow concentration.

3.1.5. Enrichment

The concentrate overflow re-enters the system as return water, and the underflow merges with the concentrate to form the final concentrate.

3.2. Water Washing Method

Electrolytic manganese slag contains a lot of manganese ions and ammonia nitrogen elements, so we can remove manganese ions by washing method. Through the changing of the removal rate of manganese ions and ammonia nitrogen in the leaching solution, it can be found that the optimal washing conditions are water-slag ratio of 2, washing times of 2 times and stirring time of 30 min, and the removal rates of manganese ions and ammonia nitrogen can respectively reach 78.31% and 81.56% [4].

3.3. Leaching Method

In the leaching method, Mn2+ is extracted from the electrolytic manganese slag with the help of some leaching agents. For example, LI et al. [5] adopted acid leaching method with the assistance of ultrasonic wave and sulfuric acid- hydrochloric acid mixture as solvent to extract manganese from electrolytic manganese slag. And the final leaching efficiency of manganese can reach 90%. In recent years, many scholars are also improving the extraction method. The results showed that the optimum conditions were as follows: time 9 d, 4.0 g/L sulfur and 4.0 g/L pyrite. Under these conditions, the leaching rate of manganese could reach 98.1%. LAN et al. [6] selected bacteria (Y1) isolated from electrolytic manganese slag, and cultured with waste preserved fruit as the only carbon source for 8 days, and then used bio-leaching method, the final leaching rate of manganese and ammonia nitrogen could reach 85%~98% and 95%~99%.

3.4. Ammonium Salt Roasting Method

Because the ammonium salt can convert the manganese carbonate salt from minerals into the soluble manganese salt at a certain temperature. The roasting conditions selected for the treatment of electrolytic manganese slag by ammonium salt roasting method are as follows: Ammonium-ore ratio is 1:1, roasting time is 1h, roasting temperature is 450 ℃, and highest leaching rate of manganese is 83% [7]. This method is simple in operation and a new way for extracting manganese slag, but the cost is high.

3.5. Bio-leaching

In order to evaluate the feasibility of bio-leaching of manganese from electrolytic manganese residue, two kinds of microorganisms with strong manganese-resistance, Serratia and Fusariumsp, were selected from manganese residue soil to study their leaching rates and the morphological changes of manganese before and after leaching. Meanwhile, the extraction efficiency of manganese by three extractants EDTA, HNO and CaC and the morphological change of manganese metal after extraction were investigated. The results showed that, both Serratia sp., and Fusarim sp. showed a certain leaching capacity for manganese, and the leaching capacity of Fu2 sarim sp was particularly significant. The results indicated that the acid-soluble manganese was relatively easy to be leached [8].

3.6. Electrochemical Method

There are many kinds of manganese slag ions in the leaching solution of manganese slag, and the problem that metal ions are easy to be oxidized should be considered in the electrochemical treatment of electrolytic manganese slag. The electrochemical principle is to observe the content of ammonia nitrogen in manganese slag leaching solution by changing the type of additives, the voltage intensity and solid-to-liquid ratio and other conditions, so as to observe the impact of these conditions on the removal rate of ammonia nitrogen.

The results show that the electrochemical oxidation of ammonia nitrogen in electrolytic manganese slag is realized by the effective action of active chlorine and ammonia nitrogen. Therefore, the method provides certain reference significance for the efficient removal of ammonia and hydrogen in the electrolytic manganese slag. From the analysis results, the following conclusions can be obtained:

1) Chloride ions can effectively remove ammonia nitrogen, and manganese ions in the solution affect the removal of ammonia nitrogen. Under the best experimental conditions after the removal of manganese ion, the removal rate of ammonia nitrogen can reach 98.57%.

2) The MnO_2 attachment formed by manganese ion on the anode prevents the production of active chlorine, and then affect the indirect oxidation of ammonia nitrogen.

3) In the electrochemical oxidation process, the oxidation products are mainly nitrogen and nitrate nitrogen, and the intermediate product which can oxidize ammonia nitrogen is active chlorine [9].

3.7. Comparison of Manganese Separation and Recovery Technologies

In conclusion, the separation technology of manganese from electrolytic manganese slag includes magnetic separation, water washing, leaching, and ammonium salt roasting, bio-leaching and electrochemical. Magnetic separation method and water washing method cannot be used to extract manganese slag, but can only be used for roughly screening. The leaching method and the ammonium salt roasting method are simple in operation and low in cost, but there is a problem of secondary pollution. Water washing precipitation method has the advantages of high extraction efficiency, but obvious disadvantages, which are complicated process, large water consumption, and may even cause secondary pollution. Relatively speaking, bio-leaching method is an environmental-friendly extraction technology, but the disadvantage is that the leaching efficiency is too low and the reaction time is too long. While the electrochemical method has high efficiency and short reaction time, but its operation is complicated.

4. Utilization and Recovery of Silicon in Electrolytic Manganese Slag

Silicon is a semiconductor material that can be used to make integrated circuits, transistors, solar cells, etc. We use sodium hydroxide direct soaked in liquid reduction, the filtrate after filtration is sodium silicate solution. The optimum conditions were confirmed as follows: leaching time 5h, leaching temperature 130 ℃, alkali concentration close to 12.5 mol/La, solid-liquid ratio 5 ml/g, stirring rate 300 r/min.

5. Removal of Ammonia Nitrogen, Heavy Metal Ions and Sulfur in Electrolytic Manganese Slag

5.1. Removal of Ammonia Nitrogen

With the rapid development of electrolytic manganese enterprises, a large amount of untreated ammonia nitrogen wastewater is wantonly discharged into the environment, and its discharge amount is gradually increased, so that the aquatic ecological balance is damaged, etc. [10]. Through research, there are several methods to remove ammonia nitrogen from electrolytic manganese slag, which are biological method, air stripping method, ion exchange method, folding point chlorination method, chemical precipitation method and electrochemical oxidation method.

5.1.1. Biological Method

Biological treatment of ammonia nitrogen has the advantages of good economy, high working efficiency and simple operation process. It finally converts the ammonia nitrogen in the waste water into harmless N2 through a series of biological reactions such as assimilation, ammonification, nitrification, denitrification and the like by using microorganisms [11].

5.1.2. Air Stripping Method

The basic principle of air stripping method is to utilize the difference between the actual concentration of volatile components such as ammonia nitrogen contained in waste water and the equilibrium concentration under certain conditions, and use air to strip under alkaline condition, so as to realize the purpose of reducing the concentration of ammonia nitrogen in waste water.

5.1.3. Ion Exchange Method

The effect of ion exchange method for treating ammonia nitrogen wastewater is very good, the process flow is simple, but the disadvantage of this method is that the adsorption capacity of zeolite is very limited, thus it cannot treat high concentration ammonia nitrogen wastewater.

5.1.4. Folding Point Chlorination Method

The characteristic of the folding point chlorination method is that the reaction rate is fast, the denitrification effect is stable, the operation is simple, but the action of chlorine and ammonia nitrogen will cause the secondary pollution.

5.1.5. Chemical Precipitation Method

Chemical precipitation method has the advantages of simple process, rapid reaction and high purification rate, and is especially suitable for the treatment of high-concentration ammonia nitrogen wastewater [12].

5.1.6. Electrochemical Oxidation Method

The electrochemical oxidation method adopts the chemical precipitation method to treat the ammonia nitrogen in the wastewater, which has the advantages of simple operation, high reaction rate and good solid-liquid separation performance. But the excessive phosphorus introduced by the precipitant is easy to cause secondary pollution and the cost of the precipitant is high.

5.2. Removal of Heavy Metal Ions

Electrolytic manganese slag contains many heavy metal ions, such as Mn, Fe, Cu, Ti and other element ions [13]. The long-lasting toxicity of these heavy metals can continuously amplify the harm to humans through bio-concentration. At present, there are engineering treatment, biological treatment and agricultural treatment for heavy metal ion pollution recovery.

5.3. Removal of Sulfur

The cement industry has a strong ability to consume waste residues. At present, most of the industrial waste residues are digested by the cement industry. Using electrolytic manganese slag to prepare cement or as cement admixture not only save a large amount of cement clinker, but also improve the utilization rate of manganese slag, which has good environmental and economic benefits. High temperature reduction roasting method was used to reduce the content of S (calculated by SO_3). The optimum experimental conditions were found by analyzing the influence of roasting temperature and coal content on the content of S in the slag. The results show that the high-temperature reduction roasting method is favorable for reducing the S content [14].

6. Conclusion

In this paper, the separation and recovery technology of electrolytic manganese slag, i.e. magnetic separation method, water washing method, leaching method, ammonium salt roasting method, bio-leaching method and electrochemical method are acknowledged. Methods that can be used to extract silicon are activated roasting and alkaline leaching method. Heavy metal atoms in manganese slag can be removed by engineering treatment, biological treatment and agricultural treatment. While the manganese slag can be used as a cement additive.

As the volume of cargo in storage of electrolytic manganese slag reaches new heights, the pollution caused by it also arises. However, there are many unavoidable problems to realize harmless and resource utilization, such as being affected by many factors such as immature technology, difficult cost control, market disapproval and lack of guidance in politics. There are few technologies that can achieve large-scale industrial applications. The pollution problem of electrolytic manganese slag has seriously affected the development of electrolytic manganese industry in China. Therefore, the research on the resource utilization of electrolytic manganese slag is of great significance.

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