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Comprehensive Recycling Technology of Waste Residues in Zinc Hydrometallurgy

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Abstract: In order to improve the refining effect of zinc ore and promote the development of this industry, taking the hydrometallurgical zinc smelting process as an example, this paper first establishes a model for the recycling of waste residues in the hydrometallurgical process, proposes optimization measures based on proven comprehensive recycling technology for purifying residues to obtain higher valuable metal recovery rate, and provides reference for those in relevant fields.

Keywords: Zinc hydrometallurgy; Valuable metal; Comprehensive recycling technology; Waste residue

1. Introduction

Zinc is one of important mineral resources in China. Proved zinc reserves account for more than 18% of the world's total reserves. Due to the increasing demand for zinc in China, current production cannot meet the demand. Therefore, recycling from zinc-containing waste residues is of great significance, which can promote the recycling of this mineral resource and its sustainable development. Zinc-containing waste residue pollutes water, air, and soil, and it has high toxicity. It endangers the ecosystem and threatens human life and health [1]. In addition, zinc ore is usually associated with precious metals. such as copper, silver, and gold. Recycling its waste residue not only increases metal production, but also reduces environmental pollution. Therefore, it is necessary to develop a comprehensive recycling technology to improve the value in resource utilization. In China, the blast furnace and hydrometallurgical processes are used in zinc smelting. Zinc hydrometallurgy has several advantages, including low energy consumption and low pollution discharge; it is widely used in the production of metallic zinc [2-6]. Taking the zinc hydrometallurgical process as the research subject, a comprehensive recycling technology is proposed to promote scientific and standardized utilization of zinc-containing waste residues as well as provide a theoretical reference for the development of the zinc smelting industry.

2. Comprehensive recycling technology of waste residues in the zinc hydrometallurgical process

2.1. Establishing a thermodynamic model for the zinc leaching residue process

In order to realize the comprehensive recovery and utilization of zinc-containing waste residues, the thermodynamic model of the slag removal process is established. This model is mainly used to analyze the leaching process of the waste residue, the degree of dissolution, and the stability of various elements, so as to determine the equilibrium conditions of the reduction reaction. At a fixed temperature, the volatility of metal vapors increases with increasing pressure. According to the volatility of zinc [7], it is reduced from the leaching residue to steam and condensed to obtain solid metal, so as to realize the separation from other mineral elements and achieve the purpose of extracting zinc. Gibbs function is used to determine if a reaction can occur spontaneously; its formula is as follows:

$$G = G_0 + \alpha T \ln \left(\frac{p}{p_0} \right)^m \tag{1}$$

In formula (1), G and G_0 represent the reaction and standard Gibbs free energy, respectively; α is a constant; T represents the thermodynamic temperature; P and P_0 represent the reaction pressure and standard state pressure, respectively; M is the stoichiometric number. When $G < 0$, the reaction is considered to be able to proceed spontaneously; on the contrary, it cannot proceed spontaneously when the value of G is 0, in which the equilibrium state is reached. In the zinc leaching residue, zinc mainly exists in the form of sulfate and oxide, while valuable metals, such as copper, exist in the form of elemental substances. The residue is acid leached with a leaching agent, resulting in a reduction reaction [8]. Zinc enters the solution in a stable ionic state, so the leaching process is a heterogeneous reaction between solid and solution. At the junction of the solid phase and the liquid phase, there is an ion saturation layer through which the dissolved zinc ions diffuse outward, further aggravating the reduction. The degree of reaction can be measured by the leaching rate, and its formula is expressed as follows:

$$\frac{dw}{dt} = -z\lambda \tag{2}$$

In formula (2), w represents the leaching amount of the solid phase; T represents the time; Z represents the unit mass of the leaching material transferred from the solid phase to the liquid phase; λ represents the solid-liquid interaction area. The solid-liquid interaction develops from the surface to the center, which is closely related to the concentration of reactants, temperature, and other factors. When the reaction nucleus appears in the center, the interaction stops, indicating the completion of the leaching process.

2.2. Selecting a waste residue leaching agent

The thermodynamic model shows that the zinc leaching residue process is a multi-intersection and interactive segmental process. In order to improve the leaching speed of the reaction, the major influencing factors need to be controlled. Among them, the waste residue leaching agent has a huge influence on the recovery and utilization of zinc. In this paper, sulfuric acid is selected as the leaching agent in the pickling process. When the acid concentration is low, the dissolution probability of zinc is higher and the degree of enrichment in the solution is higher, while the dissolution probability of other valuable metals is relatively low. In that way, the separation of zinc can be achieved. Generally speaking, the higher the acidity of the leachate, the better the effect, but excessively high acidity will prolong the reaction time. Therefore, it is necessary to control the acidity during the leaching process to ensure a weak acid environment at the end of the reaction, so as to facilitate the leaching of zinc metal [2]. During the leaching process, emulsification inevitably occurs to form an organic phase, which affects the mutual leaching of solid and liquid phases. The organic phase usually appears at the solid-liquid interface and is equivalent to a surfactant. It not only reduces the solubility of the solid phase, but also contaminates the solution. Therefore, it is necessary to prevent emulsification in the leaching process. The organic phase materials can be removed by adding a suitable extractant. In this paper, phosphoric acid extractant is used to purify the leaching solution to realize the separation and cleaning of the organic phase [9-16]. In this paper, the process acidity of the residue leachate is set to pH 3.5, and the termination acidity is set to pH 4 to ensure the effective dissolution and enrichment of metallic zinc.

2.3. Setting the replacement process for comprehensive recovery

After pickling and water washing, there are still some valuable metal elements that have not completely dissolved in the leaching solution. In order to increase the zinc content in the waste residue, it is necessary to comprehensively recycle the waste residue [11]. In this paper, the recovery process of zinc ore is controlled in accordance with the replacement process to ensure a higher leaching rate, so as to complete the comprehensive recovery and utilization of waste residues. The technical flow chart is shown in **Figure 1**.

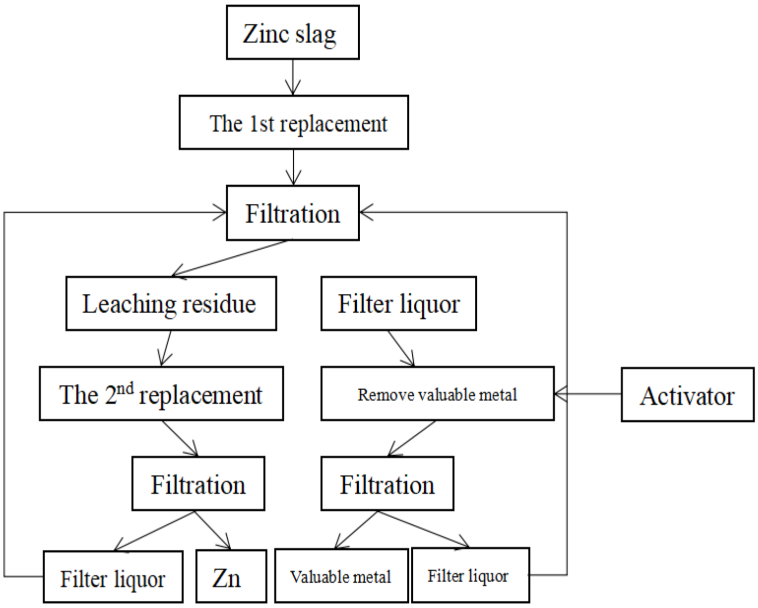

Figure 1. Comprehensive recycling process of waste residues in zinc hydrometallurgy

As shown in **Figure 1**, the comprehensive recycling process mainly includes primary and secondary replacement processes. The aim of the first replacement is to produce crude zinc, in which zinc is directly replaced in the leaching solution of waste residue, and crude zinc is produced after molding. According to the thermodynamic model, the negative migration range of zinc in metal replacement solution is smaller than that of valuable metals, and the difference in terms of their electrical property is about 0.25 V. Therefore, a large amount of zinc ions in the solution are required to achieve complete replacement. In practical engineering, it is impossible to achieve effective recovery by one-time replacement of waste residue, and only the result of coarse zinc condensation can be obtained [3]. The zinc ore filter residue is grounded, pulped, and put into a stirring tank, leached with sulfuric acid, and the changes of temperature and acidity are detected. The temperature of the first replacement process is controlled at 50°C, the time is 1 hour, and the initial acidity and end acidity are 5.3 h, respectively. Under this condition, not only the residual zinc in the acidic solution can be ensured, but also the improvement of the molding success rate. After the first replacement is generated, the acid dissolution process is further carried out. The operation procedure is the same as that of the first leaching, and the second replacement can then be completed. Compared with the primary leaching filtrate, the zinc enrichment rate of the secondary leaching filtrate can reach more than three times, and the success rate of zinc clustering is greatly improved. The temperature of the secondary process is controlled at 85°C, and the time and acidity conditions are consistent with the primary replacement. The filter residue after the reaction comprises of zinc residue. The activator is added several times to the primary leaching solution, and the acidity is controlled at pH 4.5. After the completion of the reaction, the valuable metal is obtained by filtration. On the premise of ensuring the quality of zinc ore, the associated valuable metal resources can be obtained, and the comprehensive recycling of waste residues can be realized.

3. Technology improvement

In modern hydrometallurgical zinc smelting process, the comprehensive recovery and utilization of purification slag uses the full wet method as well. On the basis of the mature process, this paper further improves the process of slag purification and improves the leaching rate of valuable metals. The main reason for the lower index of lead slag is the low leaching rate of zinc and cadmium in high cobalt slag. Zinc in lead slag mainly exists in the form of metal zinc and a small amount of zinc sulfate, while cadmium mainly exists in the form of metal cadmium. In the process of purifying and removing copper and cadmium, there are two reaction tanks, and zinc powder is only added in one of the reaction tanks. The distribution ratio of zinc powder is unreasonable, and its reaction and filtration require time. The reaction period is usually 1.5 hours, and it takes approximately an hour to filter the liquid entirely and separate the slag. The longer the contact time of the cadmium slag obtained after the zinc powder replaces cadmium with the solution, the easier it is to reverse-dissolve; that is, the metal cadmium becomes Cd^{2+} and enters the solution again. As a result, the cadmium content in the liquid fluctuates greatly after removing copper and cadmium.

3.1. Improvement of iron removal process

For iron removal, the original method is to add hydrogen peroxide for oxidation and then limestone slurry for neutralization to remove the colloidal precipitate produced by iron. However, the iron hydroxide colloid produced by this method is difficult to filter by pressure, which seriously restricts the production progress. With improvement, limestone slurry is first added to adjust the pH to 5.0, and hydrogen peroxide is then slowly added for oxidation. If the pH is not enough, lime slurry is added to adjust the pH to 5.0. Qualitative methods are used to quickly judge whether the iron content in the liquid after iron removal is qualified. The effect of the improvement is as follows: the slag properties of iron precipitation change, and the formation of $Fe(OH)_3$ colloid becomes goethite-like. With the improvement, the filtration performance of the pulp is significantly improved, the slag is dried, the thickness of the slag cake is significantly increased, and the filtration speed of the iron-removing pulp has doubled, thus meeting the production needs.

3.2. Improvement of one permutation

Before improvement, the hybrid motor is a non-variable frequency motor, and the speed cannot be adjusted. From adding zinc powder to the end of the reaction, its operating frequency is high. Before adding zinc powder, the pH value is not adjusted, and zinc powder is added directly to replace at a pH of 5.0. In that case, the activity of zinc powder is not high. When grooving, compressed air is supplied from the bottom, and after one-time replacement, the cadmium content in the solution is controlled at about 500 mg/L. Due to the above factors, the prepared cadmium sponge is finely crushed, and it is not easy to be pressed into a group. The quality of extruded cadmium cake is poor, with cadmium less than 80%, and the recovery rate of sponge cadmium is as high as 50%. With improvement, the motor is replaced with a variable frequency motor; the speed is reduced when adding zinc powder and increased slightly after adding zinc powder. Before adding zinc powder, the pH value is adjusted to 3.0 to improve the activity of zinc powder. The bottom compression air inlet is stopped, and the cadmium content in the liquid is increased after one replacement and controlled to 1 g/L to 2 g/L. The effect of the improvement is as follows: the cadmium sponge produced is significantly larger, the cadmium sponge is easier to suppress, the quality of the cadmium cake is better, including cadmium more than 85%, the recovery rate of the cadmium sponge is reduced to less than 10%, and only a small amount of material extruded by the molding machine needs to be returned.

3.3. Improvement of secondary replacement

In the original method, after the first replacement, the liquid is pumped into the second replacement tank, stirred continuously, and a sample is taken to detect the cadmium content before the second replacement. After the results are in, zinc powder is added to remove cadmium. The excess coefficient of zinc powder is as high as 1.8 times the theoretical value, but when it is lower than 50 mg/L, cadmium cannot be removed, which seriously increases the production cost. During the second replacement process, steam is always used for heat preservation, and the temperature is controlled at about 65°C. With improvement, stirring should be started five minutes before sampling and stopped after sampling. After obtaining the liquid cadmium detection results, zinc powder should be added before secondary replacement. The reaction temperature is then lowered and controlled at 55°C to 60°C. The effect of the improvement is as follows: the excess coefficient of the secondary replacement zinc powder is reduced from 1.8 times of the theoretical amount to 1.2 times, and the cadmium content in the post-liquid is stably reduced to below 50 mg/L, which significantly reduces the cost.

3.4. Improvement of cobalt removal

Before improvement, the cobalt removal agent is directly added to the cobalt removal tank in powder form, resulting in uneven addition, yellow smoke, and a large amount of cobalt removal. In addition, the pH value is not adjusted before adding the cobalt removal agent. The pass rate of the slot is about 50%, and frequent secondary slotting is required, which reduces the production efficiency. With improvement, the pH value is adjusted to about 4.0 before adding the cobalt removal agent. After mixing mud and water, the cobalt removal agent is added. The effect of the improvement is as follows: the yellow smoke problem before the improvement is solved, and the amount of cobalt removal agent is reduced. The dose is reduced from 14Co + 6Ni + 3Cd to 12Co + 6Ni + 3Cd. The cobalt removal effect is stable, and the success rate of one-time slotting is increased to more than 85%.

4. Conclusion

In conclusion, after optimizing the valuable metal extraction process during residue purification in zinc hydrometallurgy, the filtration performance of the iron removal slurry has significantly improved, increasing to 85%, and the return rate of cadmium has decreased from 50% to 10%, greatly improving the leaching rate of cadmium; the amount of zinc powder added has reduced from 1.8 times to 1.2 times theoretically, while the content of cobalt has also reduced from 14 times to 12 times; the efficiency of removing cobalt from the filtrate has improved significantly, which is a noteworthy accomplishment.

Disclosure statement

The author declares no conflict of interest.

References

[1] Wang Z, 2021, Industrialization Practice of Comprehensive Recovery and Harmless Treatment of Jarosite Slag in Hydrometallurgy. World Nonferrous Metals, 2021(24): 4-6.

[2] Yang C, Ju J, Guo S, et al., 2021, Research Status of Zinc Impurity Removal Technology in Hydrometallurgy. Yunnan Metallurgy, 50(05): 56-58, 69.

[3] Wu F, 2021, Production Practice of Several Cobalt Removal Purification Processes in Hydrometallurgical Zinc Smelting. China Nonferrous Metals, 50(04): 53-59.

[4] Qiu W, 2021, Research on the Recovery Process of Zinc Metal from Zinc Hydrometallurgy Purification Slag. World Nonferrous Metals, 2021(16): 175-176, 181.

[5] Jian J, Deng Z, Wei C, et al., 2021, Combined Wet and Fire Processing Technology for Zinc Leaching Residue from Hydrometallurgy. Nonferrous Metals Engineering, 11(06): 59-65.

[6] Wang J, Tan D, Ding J, et al., 2021, Recovery of Cobalt, Zinc and Nickel by Citric Acid Leaching from Zinc Slag in Hydrometallurgy. Mineral Protection and Utilization, 41(02): 137-143.

[7] Zhang J, Zhang W, Wu C, et al., 2021, Methods and Measures to Remove Organic Matter from Zinc Hydrometallurgy Solution. Metal World, 2021(03): 36-40.

[8] Peng Z, Shen Q, He G, et al., 2020, Recovery of Silver from Hydrometallurgical Slag. Nonferrous Metal Science and Engineering, 11(05): 118-126.

[9] Wang Y, Ren J, Cui H, et al., 2020, Analysis on the Production of Nickel Removal by Reuse of Cobalt Slag, A New Chemical for Zinc Hydrometallurgy. China Nonferrous Metals, 49(04): 32-35.

[10] Zhu J, Li W, Liu M, et al., 2020, Pollutant Analysis and Comprehensive Utilization Technology of Zinc Hydrometallurgy Slag. Comprehensive Utilization of Minerals, 2020(04): 59-65.

[11] Chen W, 2020, Research on Comprehensive Recycle Technology of Valuable Metals from Zinc-Lead-Silver Slag in Hydrometallurgy. China Metal Bulletin, 2020(07): 88-89.

[12] Gong Y, Wang X, Zhang Y, et al., 2020, Exploration on the Comprehensive Recovery and Utilization of Zinc Hydrometallurgy Leaching Residue and the Applicability of the Main Process Process. World Nonferrous Metals, 2020(12): 9-10.

[13] Geng Y, 2020, Basic Research on Efficient Separation of Zinc and Cobalt from Cobalt Slag Purified by Hydro-Zinc Smelting, Zhengzhou University.

[14] Luo Z, Wang H, Xie W, et al., 2020, Experimental Study on Dechlorination of Copper Slag During Zinc Hydrometallurgy. China Nonferrous Metals, 49(02): 17-20.

[15] Liu Z, Yang J, Yan H, et al., 2020, Research on Iron Removal Technology of Hydrometallurgical Zinc Smelting. Copper Engineering, 2020(02): 51-54.

[16] Wu W, 2020, Experimental Research on Comprehensive Utilization Technology of Hydrometallurgical Jarosite Slag. Guangdong Chemical Industry, 47(06): 75-76.