Research on recovering zinc from gossan of sulfide deposits

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Abstract: In this paper, the chemical formula of the main minerals in gossan were calculated, and the effects of the leaching agents such as NH3·H2O, NH3·(NH4)2CO3, NaOH, NH3·NH4Cl and NH3·(NH4)2SO4, mechanical activation leaching and leaching times were researched, respectively. It shown that the formula of siderite is (ZnCO3)0.1580·(ZnO)0.2156·FeCO3 and the formula of limonite bearing zinc is (ZnCO3)0.0623·(ZnO)0.1122·(FeO(OH)·0.7011H2O).

In the conventional leaching, the zinc leaching rate is less than 50%. The best zinc leaching rate is about 53% in the multi-leaching, and the highest zinc leaching rate is about 63% when mechanical activation and leaching at the same time. It is indicated that zinc in smithsonite could be dissolved in leaching solution, zinc on limonite could be partly desorbed under the action of external forces and zinc in siderite could not be recovered due to its solubility in leaching agent. Therefore, it could be concluded that the alkaline leaching is difficult to recover zinc from the gossan ore for the reasons above mentioned. The leaching results agree with the calculation of the formula of the main minerals.

1. Introduction

Gossan is the name given to a large mass formed by sulfide ore deposits after oxidation and weathering and distributed widely above or near sulfide ore deposits. Its composition is dominated by neoformed minerals bearing iron and manganese, mainly oxidate, secondary sulfate, vitriol and clay. Gossan is a special oxide ore with high contents of iron and other valuable metals and has greatly potential developing value.

The mechanisms of the supergene oxidation and the formation of gossan in the sulfide deposits are as follows. In the process of oxidation of sulfide deposits, metal sulfides are generally easy to be oxidized to various kinds of sulfates, while pyrite in the process of oxidation forms sulfates as well as sulfuric acid which reduces the pH value of groundwater and promotes the decomposition of other sulfide minerals. The solubility of various metal sulfides is very small, the solubility of sulfates formed by oxidation is high, and most of these sulfates are soluble in water. Therefore, the metal material in the oxidation zone will be transported and dispersed by surface water or groundwater. Under favourable conditions, these metals are transferred to the depths where redeposition takes place. Therefore, gossan is formed because of sulfide ore deposits after oxidation and weathering. The main compositions are oxide, neoformed minerals, secondary sulfate and vitriol and so on. Furthermore, there are gangue minerals[1-3]. The process of the sulfide weathering and leaching, many metals such as Pb, Zn, Cu, Ni and Co are dissolved in sulfuric acid which formed by sulfides oxidation and can either co-precipitate with the iron compounds[4]. During the weathering of sulfide minerals, Ag, Pb and Cu are strongly adsorbed by iron oxides under acidic conditions.

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addition, gold can form thiosulfate complexes which are oxidized to sulfates under higher oxidation conditions in sulfide-rich ore deposits. Therefore, gold is stable and retains as a primary residual mineral in gossan[5]. It is successful for recovering gold or silver from gossan. They include zinc-bearing minerals such as zincite, smithsonite, willemite, hydrozincite, hemimorphite, siderite and limonite[6,7]. To zinc oxide ores, many papers have been reported. It can be seen that there are two ways to deal with the ore. The first one is the conventional method such as flotation, gravity separation and magnetic separation, where the operating cost is high and the metal recovery is low[8,9]. The second one is hydrometallurgical and pyrometallurgical methods. The pyrometallurgical process is difficult to realize because of high capital investment, high consumption of energy and heavy pollution in practice[10]. Therefore, the hydrometallurgical process is developed quickly[11,12]. It showed that the alkaline leaching is an effective way. Due to the fact that the gossan ore is an oxidized ore, it is difficult to develop and utilize the resources comprehensively by using the traditional processing and metallurgy technology. Therefore, the gossan ore, except bearing gold and silver ore, it is directly discarded as waste rock in the process of sulfide mining. Gossan is often located on the upper part of the sulfide deposit, it is generally needed to be mined to create conditions for the mining of sulfide ore. Therefore, the gossan ore is not used after being mined which not only increases the mining production cost, but also caused a waste of metal resources. In view of the fact that the total amount of zinc and iron mineral resources in China is seriously insufficient and the high-quality mineral resources are rapidly decreasing, it is important to strengthen the research on the development and utilization of the complex zinc and iron mineral resources. It is of strategic significance to reduce the dependence of ore import, alleviate the shortage of zinc and iron ores and promote the healthy development of national economy. In addition, many reports of leaching zincite, smithsonite, willemite and hemimorphite are published, but there are no reports on recovering oxide ores with zinc such as siderite and limonite from gossan with alkaline solution, and calculating the chemical formula of the main minerals in gossan. Therefore, the objectives of this research were to research the zinc leaching law with alkaline solution from limonite and siderite bearing zinc, and to calculate the chemical formula of the main minerals in gossan.

2 Experimental

2.1 Material and analysis
The material was obtained from a mine of Guangxi. The X-ray powder diffraction analysis is shown in Fig.1. From Fig.1, the main minerals are siderite, smithsonite, limonite bearing zinc and quartz. The XRF results showed that it contained ZnO16.2%, Fe₂O₃57.4%, SiO₂5.9%, Al₂O₃4.5%, SO₃0.9%, CaO0.8%, PbO0.18%, MgO0.3%. Table 1 and Table 2 show the mineral composition and the zinc and iron distributions in the main minerals of the ore, respectively. It can be seen from Table 1 and Table 2, the zinc content in siderite bearing-zinc is about 33.93% of the total zinc content, the zinc content in the limonite bearing-zinc is about 55.35%, the zinc content in siderite is about 10.33%, and the zinc content in gangue minerals accounts for about 0.39% of the total zinc content. Similarly, the iron content in siderite bearing-zinc accounts for about 40.25%, the iron content in the limonite bearing-zinc for about 58.92%, and the iron content in gangue minerals is about 0.83% of the total iron content.
2.2 Leaching experiments
The leaching reagents were NaOH, NH₃·H₂O, NH₃·(NH₄)₂CO₃, NH₃·NH₂Cl and NH₃·(NH₄)₂SO₄. The effects of leaching agents, leaching times and mechanical activation on the leaching of zinc were investigated.

3 Results and discussion

3.1 The chemical formula calculation of the main minerals
Table 1 and Table 2 show that zinc and iron content is 15.85% and 36.55% in the siderite bearing zinc, respectively. It can be calculated that mole ratio of zinc and iron is 0.3736 in the siderite bearing zinc. It is assumed that the formula of the siderite bearing zinc is (ZnCO₃)ₓ·(ZnO)ᵧ·FeCO₃. Combined with zinc content, iron content and the mole ratio of zinc and iron, it may be calculated that x and y is 0.1580 and 0.2156, respectively. Therefore, the chemical formula of the siderite bearing zinc is (ZnCO₃)₀.₁₅₈₀·(ZnO)₀.₂₁₅₆·FeCO₃. It can be seen from Table 1 that zinc distribution in the siderite
bearing zinc is 51.03%. Therefore, it can be counted that zinc of ZnCO$_3$ and zinc of ZnO in total zinc is 21.58% and 29.45% in the siderite bearing zinc, respectively. Based on the same principle, the chemical formula of the limonite bearing zinc is (ZnCO$_3$)$_{0.0623}$·(ZnO)$_{0.1122}$·(FeO(OH)·0.7011H$_2$O). Zinc of ZnCO$_3$ and zinc of ZnO in total zinc is 13.64% and 24.57% in the limonite bearing zinc. The results are shown in Table 3.

| Minerals                | Mineral content/% | Zinc of ZnCO$_3$/% | Zinc of ZnO/% |
|-------------------------|-------------------|-------------------|--------------|
| Siderite bearing Zn     | 41.87             | 21.58             | 29.45        |
| Smithsonite             | 2.58              | 10.33             |              |
| Limonite bearing Zn     | 51.93             | 13.64             | 24.57        |

3.2 Effect of leaching agent
The effects of leaching time on leaching rate of zinc in different leaching agents are shown in Fig.2. It indicates that the leaching rate of zinc increased greatly when the leaching time was increased from 10 min to 120 min. After 120 min, the leaching speed is slow. The zinc leaching rate is less than 50%. The XRD patterns of the leaching product by different agents are shown in Fig.3. Compared with the XRD pattern of the raw ore, the different diffraction peaks of smithsonite are off in the leaching products by different agents. They simply indicated that smithsonite was leached by the alkaline solutions.

3.3 Effect of multi-leaching
The effects of leaching time on leaching rate of zinc in different leaching times are shown in Fig.4. According to Fig.4, the leaching times is conducive to the extraction of zinc, and the zinc leaching rate increases with increasing the leaching times, but it does not change too much. The zinc leaching rate is about 53% after the fourth leaching. Fig.5 shows the XRD patterns of the leaching products by ammonia-ammonium sulfate. According to Fig.5, the different diffraction peaks of smithsonite are off. It was indicated that smithsonite was extracted by ammonia-ammonium sulfate. The reason for the low leaching rate is that the leaching process is mainly the desorption of adsorbed zinc from limonite. Compared with the single leaching, the more the leaching times, the lower the concentration of zinc ion in the leaching solution. It is obvious that beneficial to the adsorption and desorption of zinc in limonite.
3.4 Effect of mechanical activation

Mechanical activation refers to the crystal lattice distortion and local destruction of minerals under the action of mechanical force, and the formation of various defects, resulting in the increase of their internal energy and the enhancement of their reaction activity. Thus, the leaching of mineral can be realized under the conditions of lower concentration and lower temperature. The leaching tests were carried out with the leaching time varying from 10 min to 420 min using three leaching modes such as mechanical activation and leaching at the same time, leaching after mechanical activation and leaching without mechanical activation. Fig. 6 shows the variation in the leaching rate of zinc as a function of the leaching time under three leaching modes. It is obvious that mechanical activation contributes to the extraction of zinc, the zinc leaching rate is about 63%, and the trend of zinc leaching rate ascend with the leaching time. The results show that the zinc leaching rate increased greatly at three leaching modes when the leaching time is less than 120 min. After 120 min, the leaching speed is slow. The maximum leaching rate of mechanical activation and leaching at the same time is close to the sum of the partition rate of zinc in siderite and limonite (65.68%). It is indicated that mechanical activation is beneficial to the desorption of adsorbed zinc in limonite. The reason may be that the local high temperature and impact effect of mechanical activation reduce the desorption activation energy of zinc.
4 Conclusions

(1) In alkaline leaching, the zinc leaching rate of single leaching was less than 50%, and that of multi-leaching and mechanical activation leaching could be improved to a certain extent, up to 63% maximally. The results show that zinc in smithsonite could be dissolved in leaching solution, zinc on limonite could be partly desorbed under the action of external forces and zinc in siderite could not be recovered due to its solubility in leaching agent. Therefore, it could be concluded that the alkaline leaching is difficult to recover zinc from the gossan ore for the reasons above mentioned.

(2) Based on leaching experiments, the ore displayed a complex nature. The chemical formula calculation of the main minerals were researched in this paper. The results show that the formula of siderite bearing zinc is (ZnCO$_3$)$_{0.1580}$·(ZnO)$_{0.2156}$·FeCO$_3$, and it can be counted that zinc of ZnCO$_3$ and zinc of ZnO in total zinc is 21.58% and 29.45% in siderite bearing zinc, respectively. The formula of limonite bearing zinc is (ZnCO$_3$)$_{0.0623}$·(ZnO)$_{0.1122}$·(FeO(OH)·0.7011H$_2$O). Zinc of ZnCO$_3$ and zinc of ZnO in total zinc is 13.64% and 24.57% in limonite bearing zinc.

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