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Extraction of manganese and zinc from their compound ore by reductive acid leaching

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Abstract: Comprehensive utilization of low grade manganese−zinc compound ore containing lead and silver with a method of reductive acid leaching was studied. According to the φ−pH diagram of Mn−Zn−H_2O system, Mn and Zn can be leached simultaneously in the pH range of −2 to 5.61. The results showed that both hydrogen peroxide and sucrose were effective reductants which could intensify the simultaneous leaching of Mn and Zn into leachate as well as enrich Pb and Ag in the residue. 95.88% of Mn and 99.23% of Zn were extracted when the compound ore was leached with hydrogen peroxide in sulfuric acid media, meanwhile the contents of Pb and Ag in the residue were enriched to 13.21% and 489.36 g/t, respectively. When sucrose was used as the reductant, the leaching efficiencies of Mn and Zn separately achieved 98.26% and 99.62%, and contents of Pb and Ag in the residue were as high as 13.92% and 517.87 g/t, respectively.

Key words: manganese−zinc compound ore; hydrogen peroxide; sucrose; comprehensive utilization; manganese; zinc; leaching

1 Introduction

With the continual exploitation of mineral resources, the grades of exploitable mineral resources take on degressive tendence, and the ore compositions of mineral resources become more and more complicated. Therefore, the researches on comprehensive utilization of low grade polymetallic ore have great significance [1].

Over the past few decades, the researches on comprehensive utilization of manganese−iron compound ore containing zinc and lead were mainly focused on pyrometallurgical processes. The most representative traditional pyrometallurgical processes were pellet roasting and blast furnace smelting, in which Zn and Pb were separated from Mn and Fe by volatilization [2]. Although the utilization efficiencies of Fe and Mn by pyrometallurgical processes are relatively high, the recovery rates of Zn and Pb are not satisfactory. On the other hand, the volatilization of Zn can cause the nodulation in blast furnace and block the gas pipeline. Furthermore, these processes have the common disadvantages of high energy consumption, heavy pollution and high investment.

In recent years, many researchers have paid more efforts to hydrometallurgical leaching. However, manganese usually occurs as pyrolusite in low grade ores. Pyrolusite, which is a kind of high valence manganese oxide, needs to be converted to low valence state Mn (II) before leaching because Mn (IV) is insoluble in dilute acid and alkaline media [3,4]. The pyro-reduction processes of pyrolusite mainly used coals as reductant in industries [5−7]. Later on, sulfur and cornstalk instead of coal as reductant also have been explored in laboratory [8,9]. However, all these pyro-reduction processes require more energy consumption and lead to serious environmental pollution and large amount of greenhouse gas emissions [10]. Compared with the pyro-reduction processes, the directly reductive leaching processes, using pyrite, oxalic acid, hydrogen peroxide, glucose and CaS as reductants, have drawn more attention recently because of their low reagent consumption, high efficiency and environmental friendliness [11−14].

All these methods mentioned above were mainly focused on the recovery of Mn. However, hydrometallurgical research on the comprehensive utilization of manganese−zinc compound ore was

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seldom reported. In this study, the material was a kind of manganese−zinc compound ore containing Pb and Ag. Combining with its characteristics, a method of reductive acid leaching was proposed to utilize the main valuable elements comprehensively. The reduction of pyrolusite as well as the extractions of Mn and Zn can be accomplished in one step leaching by this method. Mn and Zn were dissolved in solution, and Pb and Ag were enriched in the residue because the dissolutions of Pb and Ag were both negligible. The obtained residue containing high Pb and Ag can be mixed with lead concentrate appropriately and then used in lead smelting process [15,16].

2 Experimental

2.1 Material and reagents

The material used in this work was a kind of low grade manganese−zinc compound ore. In order to identify the main chemical composition and valuable elements in this ore, chemical multi-element analysis and chemical phase analysis have been done.

As shown in Table 1, the contents of Mn (27.38%), Zn (11.46%), Pb (4.06%) and Ag (150.53 g/t) in this compound ore are all relatively high, and these metallic elements need to be recovered effectively.

Table 1 Main chemical composition of manganese−zinc compound ore (mass fraction, %)

Mn	Zn	Pb	Ag*	Al_2O_3
27.38	11.46	4.06	150.53	2.81
Fe	Cu	Cd	Co	Ni
4.41	0.05	0.33	0.01	0.02

* g/t

As seen in Table 2, the main phases of Mn are manganese dioxide (MnO_2) and manganese carbonate ($MnCO_3$). As shown in Table 3, 68.5% of Zn occurs as zinc oxide, and 29.84% of Zn combined with manganese.

Table 2 Results of chemical phase analysis of Mn in manganese−zinc compound ore

Phase	Mass fraction/%	Distribution/%
Manganese dioxide	13.23	48.32
Manganese carbonate	12.21	44.60
Ferromanganese oxide	1.72	6.28
Manganese silicate	0.22	0.80
Total	27.38	100

The reagents, such as sulfuric acid, sucrose, hydrogen peroxide and oxalate, used in this study, were all analytically pure. The grade of pyrite was 99%, and the type of the coal was anthracite. Proximate analysis of anthracite coal and chemical composition of ash was shown in Table 4. Deionized water was used throughout all experiments.

Table 3 Results of chemical phase analysis of Zn in manganese−zinc compound ore

Phase	Mass fraction/%	Distribution/%
Zinc oxide	7.85	68.50
Combined with manganese	3.42	29.84
Zinc sulfide	0.085	0.74
Zinc ferrous	0.055	0.48
Zinc sulphate	0.05	0.44
Total	11.46	100

Table 4 Proximate analysis of anthracite coal and chemical composition of ash (mass fraction, %)

Proximate analysis of coal			Chemical composition of ash				
Fixed carbon	Ash	Volatile constituent	TFe	CaO	SiO_2	Al_2O_3	MgO
77.21	16.81	5.98	2.12	4.57	6.28	2.28	0.51

2.2 Methods

The raw material was crushed and finely ground to more than 70% finer than 0.074 mm. In each leaching experiment, 20.00 g of ground material and desired quantities of reductant were added to sulfuric acid solution, and the liquid-to-solid ratio was fixed as 5:1. Sulfuric acid was chosen as the lixiviant due to the characters of high boiling point and good stability. Because the hydrogen peroxide is instable and easily decomposed, reductive acid leaching experiments with this reductant were performed under the low leaching temperature of (25±0.5) °C and the slow agitation speed of 120 r/min in order to reduce its loss caused by decomposition of hydrogen peroxide. There were two methods of adding the hydrogen peroxide into the leaching system: one was that hydrogen peroxide was dropwise added at the beginning of the leaching, the other was that hydrogen peroxide was dropwise added after 30 min of leaching. Both of the two adding methods lasted for 15 min. A faster agitation speed of 400 r/min was applied and different temperatures of 50, 60, 70, 80 and 90 °C were tested in reductive acid leaching with other reductants, such as pyrite, pulverized coal, oxalate and sucrose. The fluctuation ranges of the leaching temperatures in this work are all within ±0.5 °C.

The analyses of Mn, Zn, Pb and Ag in solid and leachate were all implemented with an atomic absorption spectrometer (AA−6800, Shimadzu). Phase constitution analysis was employed to determine the distribution percentage of an element for its every phase in research