# A primary study of simultaneous leaching of silver containing manganese ore and a sphalerite concentrate

Li Zhizhang[1], Li Yanjun[2]
(1. Mineral Department, Kunming University of Science and Technology, Kunming 650093, China;
2. Medicine Department, Dali University, Dali, Yunnan 650071, China)

**Abstract**: It is demonstrated that a low grade, silver containing manganese deposit can be exploited by reaction with a ZnS concentrate. In the process, Mn(IV) is reduced to Mn(II) and the ZnS converted to $ZnSO_4$. In the process, Mn and Zn are solubilized. By studying the effects of quantity of reducing agent and sulfuric acid added and of time, temperature and liquid-to-solid ratio on the leaching process, the optimum technological conditions have been achieved under which the amount of manganese leached was 98 %. The silver can be removed from remaining solids by adding ammonia liquor. Then by adding hydrazine hydrate, sponge silver with purity up to 99 % can be obtained with a recovery of 87 %.

**Key words**: silver; manganese; sphalerite; reduction; leaching

## 1 Introduction

Low grade manganese deposits, sometimes containing silver, are present in various parts of the world. A large amount of this type deposits are present in Yunnan Province, China. Such deposits seldom can be economically exploited[1-3]. Furthermore, if they are to be exploited it will be necessary to recover both the manganese and the silver[3].

The conventional process used to extract zinc from sphalerite concentrate includes roasting, leaching and electrowinning[4,5]. The procedure is a well established and economically viable process. However, the process has the problem of $SO_2$ emission in the roasting process. Because environmental protection laws are becoming more restrictive, various processes for leaching sphalerite concentrate have been widely studied in recent years. Some of these new hydrometallurgical processes have been commercialized. According to the relevant, studies the dissolution of sphalerite is performed in two ways, i. e., oxidization and non-oxidization[6,7]. Oxidization dissolution is very important for it can convert sulfur into elemental sulfur without producing $SO_2$. Adding manganese dioxide ore to a sphalerite concentrate in sulfuric acid solution medium is conducive to dissolving sphalerite. The purpose of the present study is to make use of those characteristics to evaluate a new hydrometallurgical approach to recover zinc and at the same time recover silver and manganese from a silver containing low grade manganese material.

## 2 Experimental materials and methods

The silver-bearing manganese sample used in the experiments contained Mn 31.3 %, Ag 181.2 (g/t), Au 1.2 (g/t), Zn 0.41 %, Cu 0.13 %, Fe 13.1 %, Pb 0.72 %, MgO 1.3 %, CaO 1.51 %, $SiO_2$ 27.0 % and $Al_2O_3$ 7.1 %. The sample was crushed and ground to pass −75 μm (200 mesh). The sphalerite concentrate contained Zn 44.41 %, Cu 0.013 %, Fe 3.1 %, S 24.58 %, Cd 2.81 %, MgO 0.3 %, CaO 1.81 %, $SiO_2$ 20.08 %, $Al_2O_3$ 7.1 %, Pb 0.021 %. Particle size was 90 % −75 μm (200 mesh).

The grades of manganese, silver and gold are not sufficient for extraction of only one metal. Furthermore, no free silver minerals are found by electron probe analysis. Mineralogical analysis shows that silver is distributed in various minerals and associated with silicate minerals found in cracks. The maximum crystallization size is 0.6 mm, minimum size is 0.005 mm and general particle size is 0.3 to 0.03 mm. The experiment data obtained show that it is very difficult to separate minerals using mineral processing methods.

It was determined that the manganese in the material is in the form $MnO_x$ ($x > 1$) with the majority existing as $MnO_2$. The iron in the material exists mainly as

*Received* 16 *April* 2008

$Fe_2O_3$ and some iron becomes solubilized in leaching which is helpful in accelerating the reaction. $SiO_2$ exists in scattered quartz particles and has a little effect on the leaching of manganese and silver.

Various chemical reagents used were of reagent grade purity. The tests were carried out in 1000 ml flasks with mechanical stirring and leaching temperature was controlled using a water bath. For each experiment 100 g of ore sample was used and sampling analyses were conducted after a considerable reaction time.

## 3 Results and discussion

### 3.1 Stoichiometry

The reaction of reduction leaching silver-bearing low-grade manganese ore by use of a sphalerite concentrate is as follows:

$$MnO_2 + ZnS + 2H_2SO_4 = MnSO_4 + ZnSO_4 + 2H_2O + S^{\circ} \quad (1)$$

At 100 ℃, the reaction $\triangle G^{\circ}_{100} = -270.45$ kJ, and the reaction takes place spontaneously. The required theoretical quantity of reducing agent and sulfuric acid can be calculated from this equation.

### 3.2 Effect of sulfuric acid addition

Under the conditions that liquid-to-solid ratio is 5:1, the leaching temperature is 95 ℃, the ZnS is theoretical quantity required and leaching time is 4 h, the effect of sulfuric acid concentration on leaching rate of manganese is shown in Fig. 1.

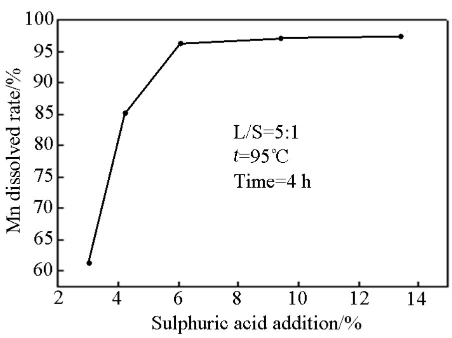


**Fig. 1 Effect of suphuric acid addition**

It can be seen from the figure that when sulfuric acid addition is increased up to a concentration equaling to that required by Eq. (1), leaching rate increases. However, at greater concentrations there is little influence of further increasing sulfuric acid concentration on the leaching rate. Thus, the quantity of sulfuric acid chosen for subsequent experimentation was 1.05 times the theoretical quantity indicated by Eq. (1).

### 3.3 Effect of temperature

The effect of leaching temperature on manganese leaching is shown in Fig. 2. It can be seen that under the experimental conditions, temperature has a large effect on manganese leaching. The leaching of manganese increases with reaction temperature and, thus, an appropriate temperature for experimentation is 95 ℃.

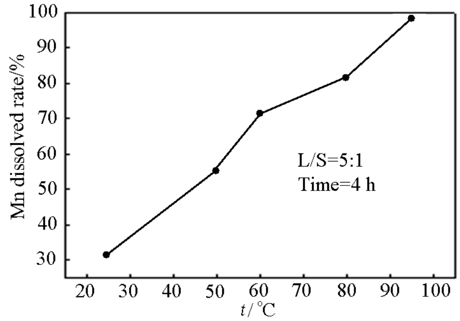


**Fig. 2 Effect of temperature**

### 3.4 Effect of leaching time and reducing agent quantity

When temperature is 95 ℃ and sulfuric acid addition is optimum and at 30 % optimum the effect of leaching time and ZnS concentration is depicted in Fig. 3. At the optimum experimental conditions (1 ~ 1.1 times stoichiometrically optimum) the dissolution can reach 98.0 % after 4 h. and further reaction time is unnecessary.

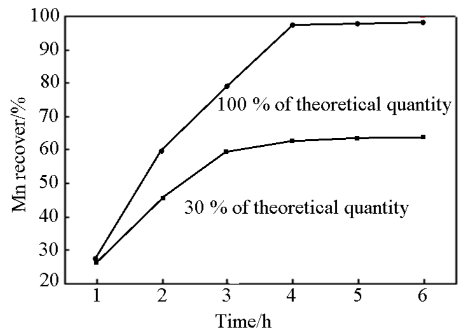


**Fig. 3 Effect of time and ZnS**

### 3.5 Effect of liquid-to-solid ratio

The effect of liquid-to-solid ratio on the dissolution of manganese is shown in Fig. 4. With increasing liquid-to-solid ratio the leaching rate of manganese increases accordingly. However, when the ratio is increased to 5∶1, a further increase in the ratio yields little additional dissolution.

Based on the above experiments the optimum parameters for leaching of silver bearing low grade manganese deposits can be determined. The leaching temperature should be 95 ℃, sulfuric acid quantity should be 1 ~ 1.05 times of the theoretical quantity, the re-

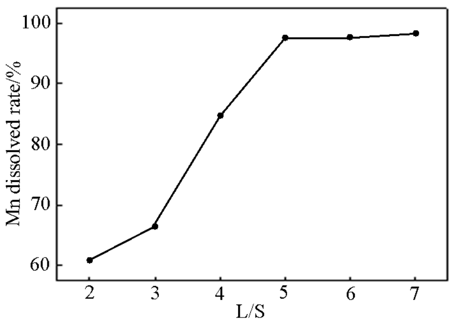


**Fig. 4 Effect of L/S ratios**

**ducing agent (ZnS) quantity should be** 1 ~ 1.1 of the theoretical quantity, the liquid-to-solid ratio should be 5∶1 and leaching time should be 4 h.

**Table1 Chemical composition of final solution / ($g \cdot l^{-1}$)**

| Test No. | Mn | Zn | Fe | Pb | Cu | As | Sb | $H_2SO_4$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 51.67 | 61.48 | 3.04 | 0.11 | 0.18 | 0.01 | 0.001 | 13.53 |
| 2 | 51.33 | 62.11 | 3.12 | 0.09 | 0.17 | 0.01 | 0.001 | 14.15 |
| 3 | 52.15 | 61.04 | 2.87 | 0.12 | 0.18 | 0.01 | 0.001 | 14.33 |
| 4 | 52.35 | 61.68 | 3.13 | 0.10 | 0.19 | 0.01 | 0.001 | 13.87 |

### 3.6 Experiments on recovering silver from slag

The leached solution contains about 23 mg/L silver after dissolution with ammonia. Cementation with zinc powder can remove the Ag(I) from solution and accompanies the slag. The composition of the liquid obtained can be seen in Table 1. The final solution contains 3.0 g/L iron and $H_2SO_4$. The concentration of zinc is relatively low and can be put into an electrolytic zinc purifying system.

The slag produced from the experiment contains a significant amount of sulfur which can be removed by volatilization at 300 ℃. Using 4 mol/L of ammonia liquor, 4∶1 liquid-to-solid ratio, 2 h stir-leaching at room temperature, filtering and washing with mixture solution of ammonia liquor and ammonia carbonate, the amount of silver leached is about 97 %. Using hydrazine hydrate to reduce silver, a sponge silver can be obtained with the purity of silver up to 99 % and a silver recovery up to 87 %.

## 4 Conclusions

The experiments show that silver-bearing low-grade manganese ore can be reduced by reaction with a sphalerite concentrate followed by leaching. Recovery of silver and manganese is then feasible and technological conditions for recovery can be easily achieved. The optimum parameters for reaction with a sphalerite concentrate followed by are: leaching temperature 95 ℃, sulfuric acid quantity 1 ~ 1.05 times of the theoretical stiochiometric quantity, reducing agent (ZnS) 1 ~ 1.1 of theoretical quantity, liquid-to-solid ratio 5:1 and leaching time 4 h. Any silver in the liquor can be precipitated by zinc precipitation and can be leached out with ammonia liquor and reduced with hydrazine hydrate. Sponge silver can be obtained of 99 % purity with a of silver recovery of 87 %

## References


[1] Ehrlich H L. Microbes in Biohydrometallurgy [A]. Bioprocessing [C]. Pennsylvania: TMS, 1991.

[2] Noble E G, Baglin E G, Lampshire D L, et al. Bioleaching of manganese from ores using heterotrophic microorganisms [A]. Mineral Bioprocessing[C]. Pennsylvania: TMS, 1991. 233-245.

[3] Rusin P A, Sharp J E. Enhanced recovery of manganese and silver from refractory ores through biotreatmant[A]. Mineral Bioprocessing[C]. Pennsylvania: TMS, 1991. 207-218.

[4] Ozberk E, Jankola W A, Vecchiarelli M, et al. Commercial operation of the Sherritt zinc pressure leach process[J]. Hydrometall, 1995, 39: 49-52.

[5] Zhao Tianchong. Extractive Metallurgy of Non-metals[M]. Beijing: Metallurgical Industry Press, 1988.

[6] Rath P C, Paramguru P K. Kinetics of dissolution of sulphide minerals in ferric chloride solution, 1: dissolution of galena, sphalerite and chalcopyrite[J]. Trans. Instn. Min. Metall. (Sec C), 1988, 97, 150C-158C.

[7] Madhuchhanda M, Devi N B, Srinivasa Rao, et al. Oxidation of sphalerite in hydrochloric acid medium in presence of manganese dioxide[J]. Trans. Instn. Min. Metall. (SecC), 2000, 109, 150C-155C.


## Author


Li Zhizhang, male, born in 1964, obtained Master's degree from the Kunming University of Science and Technology, China, in 1990. He is now a professor in the Kunming Metallurgy College and a doctorial student in the Kunming University of Science and Technology, China. His research fields include extractive metallurgy, mineral processing and natural resources comprehensive utilization. He can be reached by E-mail: lzzblake@163.com