

REDUCTIVE LEACHING OF MANGANESE NODULE BY CHALCOPYRITE IN DILUTE HCL SOLUTION^①

Guo, Xueyi

*Department of Nonferrous Metallurgy,
Central South University of Technology, Changsha 410083*

ABSTRACT The leaching of manganese nodules together with chalcopryrite was done in dilute HCl solution. The factors which affect the leaching process include the ratio of amounts between chalcopryrite and manganese nodule (R), the initial HCl concentration, the temperature and time for leaching. It was found that the extraction of the metal values Mn, Co, Cu and Fe increased with the temperature, the time and the initial HCl concentration for leaching. More than 93% of Mn, Ni, Co could be easily leached in dilute HCl solution at 90 °C for 90 min as long as acid was sufficient and the chalcopryrite was charged equally with the nodule, and the extraction of Cu was also up to 80%. More than 90% of sulfur contained in the chalcopryrite remained in the residue in elemental form.

Key words: manganese nodule chalcopryrite leaching

1 INTRODUCTION

Many researches were done on leaching of deep sea manganese nodule in HCl solution^[1-3]. It was proved that the structure of δ -MnO₂ in nodule can be destroyed and the metal values Cu Ni Co and Mn can be released effectively only with the existence of reductant. Dr Cheng Xiaohong from CSUT has developed a new hydrometallurgical way of simultaneous leaching of manganese nodule together with nonferrous metal sulfide which can be used as the reductant for the leaching of manganese nodule^[4-5].

Chalcopryrite is the Cu containing mineral which exists widely in the nature. The leaching of CuFeS₂ being activated in dilute H₂SO₄ solution has been done with the manganese dioxide ore as oxidant^[6], but the research on reductive leaching of manganese nodule by chalcopryrite in dilute HCl solution has not ever been reported in references, so that in this paper such investigation has been done for the purpose of exploring a new effective way of simultaneous processing of deep sea manganese nodule together with chalcopryrite on land.

2 EXPERIMENTS

The sample of manganese nodule was dredged from the C-C area, pacific ocean (N-latitude 12°03', E-longitude 139°20') and the chalcopryrite was obtained by Hunan Provincial Museum of Geology. The analytical results of the two samples are shown in Table 1.

Table 1 The chemical analysis of samples composition

Materials	Mn	Fe	Cu	Ni	Co	S (%)
Nodule	21.36	11.08	0.51	0.91	0.29	-
Chalcopryrite	0.23	27.81	20.86	-	-	28.98

The X-Ray analysis shows that the metal sulfide is mainly composed of CuFeS₂.

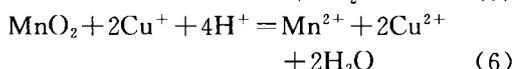
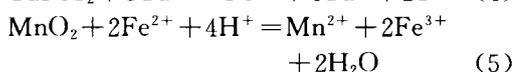
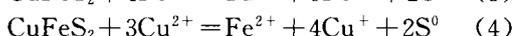
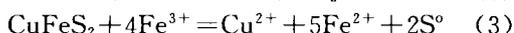
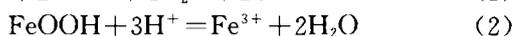
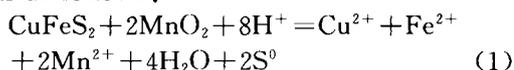
Before experiments, the sample of dry manganese nodule as well as chalcopryrite was ground below -100 mesh and -200 mesh respectively. The leaching experiments were conducted in three-neck flask of 500mL in volume. First, 200 mL HCl solution at certain concentration was added into the flask and

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heated by an electric heater and magnetics stirrer. When the leachant is heated to the pre-set temperature, 5g Mn-nodule and a certain quantity of chalcopyrite are put into the reactor, then keep stirring and temperature constant. When the leaching process ended, washed and the leaching solution was filtrated, and volumed in a 500 mL flask. The Mn, Cu, Fe, SO₄²⁻ were analyzed by chemical method and Ni, Co were detected by atom-absorbed spectrophotometry.

3 RESULTS AND DISSUSSION

In dilute HCl solution, main reactions between manganese nodule and chalcopyrite may occur as follows:



Because all the Mn²⁺, Cu²⁺, Cu⁺, Fe³⁺ and Fe²⁺ can form complex compounds with Cl⁻ the leaching process also follows the acid dissolution of Ni, Co, Cu oxides and small amount of elemental S⁰ deep oxidation to SO₄²⁻.

Undoubtly once the Cu, Fe in raw mineral dissolved, they can act as catalyst and accelerate the decomposition of the minerals.

First, the experiments were done to investigate the effect of leaching at different addition of chalcopyrite.

It can be seen from Table 2 that the leaching of Mn, Ni, Co keeps rising with the increasing of R, especially when R changed from 0 to 0.25 which proves that the nodule is easily to be reduced and leached by CuFeS₂. But the Cu and Fe decrease with the addition of chalcopyrite. This is due to the fact that the amount of CuFeS₂ is much more than the needs for dissolution of nodule and the excess

amount of CuFeS₂ remains undissolved.

Moreover, the results in Table 2 show that the leaching percentage of Mn, Co, Cu reaches 40.86%, 72.53%, 53.10%, 89.69% respectively even if in the case of R = 0, i.e. no chalcopyrite charged. This is due to the following reaction resulting in the damage of MnO₂ structure in nodule and relative quantity of Ni, Co, Cu being leached^[7], the leaching of Ni and Cu much higher just because of their difference existing in manganese nodule^[8].

Table 2 The leaching percentage of each metal at different R

R	leaching percentage(%)				
	Mn	Ni	Co	Cu	Fe
0.00	40.86	72.53	53.10	89.69	86.28
0.25	80.66	89.21	89.33	85.66	83.94
0.50	85.18	92.8	94.45	82.65	83.24
0.75	86.92	94.2	95.33	81.42	77.32
1.00	92.69	97.4	96.62	80.63	74.77
1.25	93.31	97.0	97.53	72.22	70.21
1.50	94.25	95.2	96.29	65.86	62.85

T -90 C ; t -90 min; 1.5 mol/L HCl 200 ml; different R



The results of Table 3 reveal that the metal values Mn, Ni, Co in nodule keep high leaching percentage and are little affected by the initial HCl concentration when the acidity is over 1.0 mol/L, but the leaching of Cu and Fe keeps rising with the increasing of initial HCl concentration. High HCl concentration can cause high Cu leaching, but simultaneously more quantity of Fe will dissolve and raise relative difficulties for Fe removal in successive step. Comprehensively, the 1.5 mol/L initial HCl concentration is suitable. The results in Table 4 show that the leaching percentages of all the metal values increase with the temperature. Mn, Ni, Co containing in the nodule are above 90% when temperature reaches 80C. From the results of Cu leaching, it is proved that higher leaching temperature is also in favor of CuFeS₂ dissolution.

It can be seen from Table 5 that the lea-

Table 3 The effect of initial HCl concentration on the leaching process

Initial [HCl]mol/l	leaching percentage(%)				
	Mn	Ni	Co	Cu	Fe
1.0	82.34	89.56	83.80	54.49	59.14
1.5	92.69	97.4	96.62	80.63	74.77
2.0	93.34	98.21	97.59	83.80	78.84
2.5	94.23	98.0	97.93	86.94	84.28
3.0	93.40	98.57	98.14	88.85	86.04

$T = 90\text{ }^\circ\text{C}$; $t = 90\text{ min}$; $R = 1$; different initial [HCl] 200ml

Table 4 The effect of temperature on the leaching process

Temp.	Leaching percentage(%)				
	Mn	Ni	Co	Cu	Fe
40	75.84	76.81	72.07	25.54	38.31
60	86.91	86.70	85.19	41.86	54.74
80	90.23	92.89	91.28	72.31	72.46
90	92.69	97.40	96.62	80.63	74.77

$t = 90\text{ min}$; $R = 1$; 1.5 mol/L HCl 200ml

leaching percentage of Mn, Ni, Co are all more than 70% after 10 min. The longer the test time is, the more the amount of the metal values dissolves. 120 min later, only or less 5% of Mn, Ni, Co remain undissolved, and

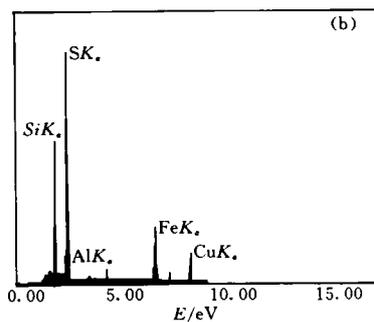
the extraction of Cu reaches 83.49%. The analytical results reveal that just a little amount of sulfur will further oxide to form SO_4^{2-} , most of it remains in the residue in elemental form. See Fig. 1, 2 in the following.

Table 5 The effect of time on leaching process

Time /min	leaching percentage(%)					
	Mn	Ni	Co	Cu	Fe	SO_4^{2-}
10	43.03	71.87	74.21	21.59	53.51	-
30	71.76	82.75	78.76	41.08	58.63	4.35
60	86.14	95.21	84.14	66.33	71.70	5.26
90	92.69	97.40	96.62	80.63	74.77	8.10
120	94.73	98.12	98.58	83.49	75.30	8.12

$T = 90\text{ }^\circ\text{C}$; $R = 1$; 1.5 mol/L HCl 200ml

Fig. 1, Fig. 2 are the second electronic photographs of SEM and their spectrum of XPS of single chalcopyrite and the leaching residue. By comparing the two Figures, it is clear that the sulfur in leaching residue exists mainly in the form of S^0 (little amount of unreacted CuFeS_2 still remains in residue) which attaches on the unreacted particle surface loosely. Thus the H^+ and Cl^- can still pass through the crack of s^0 , diffuse to the unreacted particle surface to dissolve the solid. This is in accordance with the results obtained from

**Fig. 1 The SEM of CuFeS_2 and its XPS**

(a) The secondary electron micrography; (b) X-Ray energy spectrum

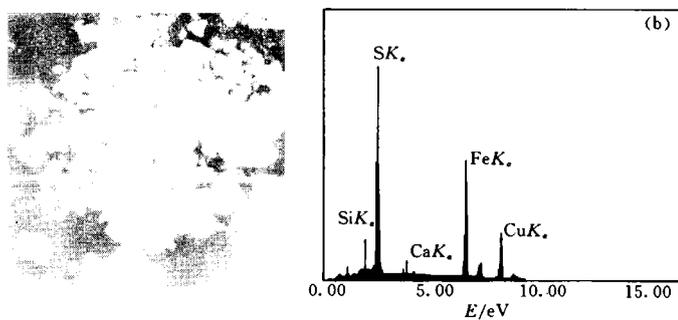


Fig. 2 The SEM of leaching residue and its XPS

(a) The secondary electron micrography; (b) X-Ray energy spectrum

the experiments.

There are clear particular peaks of Si, Al in spectrum of Fig 2. It is no doubt that those are leaching residues of manganese nodule.

4 CONCLUSIONS

(1) In dilute HCl solution, chalcopyrite can be used as reductant to leaching deep sea manganese nodule effectively and the metal values contained in the two minerals such as Mn, Ni, Co, Cu are easy to be leached. When $R = 1$, i. e. the manganese nodule are equally charged with the CuFeS_2 in amount. The extractions of Mn, Ni, Co are close to or over 93%, and Cu also more than 80%.

(2) The manganese nodule has high leaching percentage in 1.5–3.0 mol/L initial HCl solution. But the higher acidity will not only result in more acid consuming but also cause much amount of Fe into the solution which made it much difficult for Fe-removal in the next step. By comparison, the initial HCl concentration 1.5 mol/L is the optimum condition.

(3) Higher temperature, and longer time are beneficial for the dissolution of manganese nodule together with chalcopyrite. It is proved

that the leaching temperature over 90 C, or more are necessary for the leaching process.

(4) The sulfur contained in the mineral, except that little amount are oxidized deeply into SO_4^{2-} , more than 90% remained in the residue in elemental form.

REFERENCES

- 1 Cheng, Hiaohong; Fu, Chongyue. In: Fu, Chongyue ed. Proceedings of the International Conference on Mining and Metallurgy of Complex Nickel Ores. Jin Chang, P. R. China. International Academic Publishers, 1993: 334-338.
- 2 Kanungo, S B; Jena, P. K. Hydrometallurgy, 1988, 21: 41-48.
- 3 Kanungo, S B; Das, R P. Hydrometallurgy 1988, 20:135-146.
- 4 Cheng, Hiaohong; Fu, Chongyue; Zheng, Dji. Hydrometallurgy, 1992, 28(2): 269-276.
- 5 Cheng, Hiaohong; Fu, Chongyue. Journal of Central-South Institute of Mining & Metallurgy 1994, 25: 39-43.
- 6 Ma, Rongjun. New Technique on Copper Hydrometallurgy. Changsha: Hunan Press of Science & Technology, 1985, 187.
- 7 Ranungo, S; B; Das, P K. Hydrometallurgy 1983, 21:23-29.
- 8 Bao, Gengde. Science of China, 1991, B(9), 970-978.