ICHNM'2002

A NEW CENTURY INTERNATIONAL CONFERENCE ON

METALLURGICAL HIGH TECHNOLOGY AND NEW MATERIALS OF HEAVY NONFERROUS METALS

April 3~5, 2002
Kunming, China

Edited by: Peng Jinhui

Ma Keyi

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INNOVATIVE METALLURGICAL PROCESSES OF HEAVY NONFERROUS METALS

COLD ATMOSPHERIC ACTIVATING SULFURIC ACID LEACHING OF Co, Ni, Cu AND Mn FROM OCEAN COBALT-RICH CRUST

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Abstract

Ocean cobalt-rich crust, one of the important polymetallic mineral resources on ocean floor, contains Co, Ni, Cu, Mn, etc.On the basis of multi-scheme exploration and comparison test, a new process of cold atmospheric sulfuric acid leaching is proposed to treat the crust. Sulfur dioxide (or sulfurous acid) with double function of activating and leaching is adopted as activator. The activating leaching reaction is very fast and finishes in 15 minutes. The leaching rates are (%): Co 99.41, Ni 98.10, Cu 92.54 and Mn 97.89. The activator consumption is 0.177 t/t ore.
Keywords: Ocean cobalt-rich crust, Sulfuric acid leaching, Cobalt, Nickel

Introduction

Cobalt-rich crust is one of the important ocean polymetallic resources after the ocean polymetallic nodules was found. Comparing with polymetallic nodules, cobalt-rich crust mainly exists in the slope of the sea-mount and searidge upside which is about 800~3000 m under the sealevel, including cobalt, nickel, etc.It distributes abrosdly in the floor of international sea and the exclusive economic zone of some countries. The cobalt-rich crust in the oceans of the world contain 0.63%Co on average which is two or three times as much as that in the polymetallic nodules. Furthermore, there are more rare earth and Pt in the crust than in the nodules, but usually there are less Ni, Cu and Mn. According to the incomplete statistics, only in the volcano range of the west-pacific ocean, the cobalt-rich crust mineral deposit has potential resources about a billion tons, and contains cobalt about several million tons. Cobalt-rich crust has been the current hotspot of reconnoitring and researching about the ocean mineral resources, and it is considered that the exploitation of the cobalt-rich crust is probably earlier than the commercial production of the polymetallic nodules.

Cobalt and nickel in the crust mainly exist in manganese oxides by isomorphous substitution or adsorption. Cobalt-rich crust is complex oxide ore with low grades of the valuable metals and as high as 40% water content (the crystal water is up to 10~20%).

If the crust is treated pyrometallurgically, the energy consumption will be high because of the drying and reduction smelting at high temperature. Owing to the low Mn content and high P content in the crust, the smelting slag will contain low Mn but high P, and it will not be suitable for making Mn-Fe alloy. As to hydrometallurgy, its energy consumption is low, and it can obtain Mn material of high quality during recovery of cobalt and nickel. So, hydrometallurgy has prospect of treating the Co-rich crust.

This paper is focused on the research of extracting valuable metals from the cobalt-rich crusts by the way of SO_2 reduction leaching.

Experimental

1 Material of experiment

The material used in this research was collected by the explorating department of our country during the investigation of the cobalt-rich crust in the DY95-9 voyage. The crust is dried, dehydrated, crushed and ground to –0.074 mm (77.76%) at 110℃. The chemical composition of the material is given in Table 1.

Table 1 Chemical composition of the material

Component	Mn	Fe	Co	Ni	Cu	Zn	Mo	Al_2O_3	CaO
Content%	21.10	13.73	0.58	0.42	0.11	0.057	0.05	2.50	4.59
Component	MgO	TiO_2	SiO_2	Na_2O	K_2O	P	Cl	Pt	
Content%	1.30	1.58	4.97	0.74	0.38	0.86	0.23	0.41g/t	

2 Leaching Experiment

The leaching experiment is done in a multi-opening 250 ml flask. 20 g of the crust is put in the flask and leached at constant temperature by using of magnetic agitator. After leaching the residue is separated from the solution, washed and dried for chemical analysis and calculating the leaching rates of metals.

Foundamental Principle

In the crust, manganese exists in the form of tetravalent oxide. With the action of reductant, the tetravalent manganese can be changed into the soluble bivalent manganese, and then the structure of manganese mineral in the crust will be destroyed. So, the oxide of Ni, Cu and other metals in the matrix of manganese mineral will be naked or free,which can decrease the activation energy of the leaching reaction of Co, Ni, Cu, Mn and realize the quick sulfuric acid leaching of Co, Ni, Cu, Mn in the cobalt-rich crusts in the condition of normal temperature and pressure. The routine reduction activators are: metallic sulfide (for example: pyrite, hydrogen sulphide and matte), sulphurous acid and sulphite (such as H_2SO_3, SO_2, Na_2SO_3 and $(NH_4)_2SO_3$), H_2O_2, ferrous salt and organic reagent, etc. In view of economy and technology, SO_2 or H_2SO_3 is more advantageous. Their virtues are fast leaching velocity and high leaching rate of valuable metals. The two activators are very clean ,and will not take new cation impurity into the leaching liquor .The main reactions of the active leaching process are :

$$MnO_2+SO_2 \rightarrow MnSO_4$$
$$CoO+H_2SO_4 \rightarrow CoSO_4+H_2O$$
$$NiO+H_2SO_4 \rightarrow NiSO_4+H_2O$$
$$CuO+H_2SO_4 \rightarrow CuSO_4+H_2O$$

Additionally, part of the iron minerals in the cobalt-rich crust will also be dissolved. The iron minerals are mainly FeOOH, and part of FeOOH is reduced of SO_2 into ferrous iron, forming ferrous sulfate and going into solution. The reaction is:

$$2FeOOH+SO_2+H_2SO_4 \rightarrow 2FeSO_4+2H_2O$$

But in the system, there exists manganese dioxide, so under proper condition the following reaction will happen, which make part of the dissolved iron go back into the leaching residue again:

$$2FeSO_4+2H_2O+MnO_2 \rightarrow MnSO_4+Fe_2O_3 \cdot H_2O+ H_2SO_4$$

Results and Discussions

Dosage of sulphur dioxide has a evident effect on the leaching rate of the metal (Table.2). When the dosage of sulphur dioxide is 0.177 t/t ore, the leaching rate is 99.45%Co, 98.71%Ni, 95.85%Cu and 99.16%Mn.

Table.2 Effect of sulfur dioxide dosage on the leaching rate

SO_2 (g/g)ore	Composition of the leach residue (%)				Leaching rate(%)			
	Co	Ni	Cu	Mn	Co	Ni	Cu	Mn
0.151	0.26	0.15	0.021	12.47	82.85	86.34	92.70	77.39
0.177	0.011	0.019	0.016	0.62	99.46	98.71	95.85	99.16
0.204	0.012	0.020	0.018	0.56	99.44	98.71	95.54	99.28
0.225	0.007	0.010	0.015	0.14	99.69	98.38	96.45	99.83
0.252	0.006	0.009	0.014	0.13	99.74	99.45	96.72	99.84

The temperature has a little effect on the leaching rate of the valuable metals. At the normal temperature, all kind of valuable metals can be leaching, all the leaching rates of Co, Ni, Mn are more than 99% and the leaching rate of Cu also reaches 96%. But the leaching rate of Fe depresses when the temperature rises(Table.3).

Table3: Effect of temperature on the leaching rate

Temperature °C	Composition of the leached mud(%)				Leaching rate(%)			
	Co	Ni	Cu	Mn	Co	Ni	Cu	Mn
30	0.010	0.012	0.021	0.62	99.69	99.48	96.52	99.74
40	0.009	0.015	0.020	0.76	99.69	99.29	96.36	99.28
50	0.013	0.020	0.018	0.58	99.42	98.79	95.83	99.30
60	0.008	0.013	0.016	0.50	99.64	99.19	96.18	99.38
70	0.008	0.016	0.019	1.10	99.66	99.05	95.68	98.70

The effect of the terminal pH on the main objective metals such as Co, Ni, and Mn in the cobalt-rich crust is minor, but its effect on the leaching rate of Cu and Fe is remarkable (Table 4). With the depressing of terminal pH, the leaching rate of the valuable Cu will increase, but leaching rate of Fe will also increase evidently. Because the Cu grade is very low in the crust, if we make the terminal pH higher to control the leaching of Fe, the following load of solution purifying and the consumption of the neutralizing agent can be decreased.

Liquid-solid ratio has a very little effect on the leaching rate of the valuable metal, but the leaching rate of Fe goes up with a decrease in liquid-solid ratio. The leaching reaction is fast and can finish basically within 15 minutes. After 30 minutes, the leaching reaction of the valuable metals trends to equilibrium, and the leaching rates of Co, Ni, Mn can reach more than 99% and the rate of Cu can reach more than 95%. The longer the leach time of Fe is ,the less the leaching rate of Fe is.

Table 4 Effect of terminal pH on the leaching rate

pH	Leaching rate(%)				
	Co	Ni	Cu	Mn	Fe
3.73	95.17	94.29	45.45	95.14	13.87
2.88	99.31	96.89	83.79	97.26	28.75
2.33	99.18	97.51	92.60	97.36	44.12
2.02	99.45	98.58	94.85	98.93	61.18
1.08	99.73	99.54	96.50	99.79	92.47

There is no clear effect of particle size on the leaching rate of Co, Ni and Mn, but the leaching rates of Fe and Cu decrease while the particle size become smaller (Table5).

Table 5: Effect of particle size on the leaching rate

Percentage of -0.074 mm	Leaching rate(%)				
	Co	Ni	Cu	Mn	Fe
77.76	99.19	97.51	92.60	97.36	44.12
82.50	99.48	97.93	88.53	97.65	29.38
89.50	98.92	97.24	85.09	95.75	19.74

According to the results of above research, the optimum conditions of the leaching process are: consumption of SO_2 0.177 t/t ore, temperature 30℃, particle size (-0.074 mm) 77.76%, the ratio of liquid-solid (L/S) 3 ml/g, the leaching time 30min, terminal pH2.12, and rate of agitation 400 rpm.The leaching rates in these conditions are: Co99.41%, Ni 98.10%, Cu92.54%, Mn97.89%. The leaching liquor contains Co1.93g/L, Ni 1.41 g/L, Cu0.34 g/L, and Mn72.17 g/L. Cu can be recovered Cu by solvent extraction, Fe can be removed by oxidizing neutralization, Co can be separated from Ni by solvent extraction, and Mn can be precipitated in use of ammonium carbonate.

The mineral research of the leaching residue indicates that after activating sulfuric acid leaching only chemically stable silicate mineral in the crust is left while there is almost no original Mn-rich mineral left in the residue. The main components of the residue are Fe, Si, Ca, Al, etc. (see Table 6).

Table.6 Main composition of the leaching residue

Component	Co	Ni	Cu	Mn	Zn	Fe	Mo
Content（%）	0.009	0.021	0.021	1.17	0.016	21.20	0.12
Component	CaO	MgO	Al_2O_3	SiO_2	P	Cl	TiO_2
Content（%）	14.90	0.18	3.47	7.21	1.68	0.009	3.77

Conclusion

Using the method of activating sulfuric acid leach at the normal temperature and normal pressure we can directly deal with the wet crust without any pyrometallurgical pretreatment. The process is simple and its energy consumption is low. Because sulfur dioxide or sulfurous acid has double functions of reduction activator and leaching agent, the reagent consumption is low, the speed of the leaching reaction is fast and the leaching rates of the valuable metals are high.

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