

## Leaching Mo and Ni by Direct Oxygen Pressure from Black Shale with any other only water

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**Abstract.** The hydrometallurgical process of leaching molybdenum and nickel from black shale without reagent was investigated. The extraction of Mo and Ni from molybdenum-nickel ore by oxygen pressure leaching, which exploit the characteristic of molybdenum-nickel minerals contain high concentration amorphous sulfide which has highly active, and make the most of easily oxide to sulfuric acid and sulfate at low temperature and excess oxygen presence of the amorphous sulfide. Under oxygen pressure conditions, considerable molybdenum and almost all the nickel were extracted into solution in the leaching process. The results show that with the leaching time for 3~4h, temperature at 150°C, liquid-to-solid ratio of 2mL·g<sup>-1</sup>, mineral granularity of 0.074mm, oxygen partial pressure of 0.4~0.5MPa without other reagent, molybdenum leaching percentage can be over 80% and nickel leaching percentage can be more than 97%. Furthermore, about 80% sulfur in the Mo-Ni ore has been transformed into sulfuric acid.

### Introduction

The black shale is an important molybdenum and nickel source, which as a sediment-hosted ore layer of the lower Cambrian black shale has been known to local geologists for at least 50 years in China[1-2]. A partial evaluation of the Mo-Ni ore deposits and their genesis has been attempted in past decades [3].

The Mo-Ni ore contains more than 4wt% Mo, at least 2wt% Ni, up to 2wt% Zn, 2.5wt% As and 1~2g/t of precious metals, primarily Au, Pt, Pd, and Os. The classic process for molybdenum and nickel recovery is roasting, melting and concentration to produce a high impurity nickel-molybdenum alloy. In the process, sulfur dioxide (SO<sub>2</sub>) and arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) release may cause serious environmental pollution. Mineral processing routes have been proposed for the Mo-Ni ore[4], however, it is inefficient to enrich nickel and molybdenum through ore-dressing owing to the ore's complex mineralogical characteristics.

Several combined pyro-hydrometallurgical methods have been proposed to recover molybdenum from the Mo-Ni ore, such as roasting, NaOH/Na<sub>2</sub>CO<sub>3</sub> leaching under active oxygen conditions [5], direct leaching with NaOH+Na<sub>2</sub>CO<sub>3</sub>/NaClO<sub>3</sub> [6], direct NaOH leaching under active oxygen conditions [8] and direct leaching with H<sub>2</sub>SO<sub>4</sub> for nickel recovery only [8]. Moreover, direct bioleaching of molybdenum and nickel from the Mo-Ni ore has been investigated using a molybdenum-resistant thermophilic bacterium *Sulfolobus metallicus*, but the percentage leached is not very high and requires further research[9].

In this paper, a direct hydrometallurgical process of extraction molybdenum and nickel from molybdenum-nickel ore by pressure water leaching without reagent was studied. Various characteristics of the Mo-Ni ore are used beneficially and partial sulfur is transformed into sulfuric acid under oxygen pressure. The extraction of Mo and Ni from molybdenum-nickel ore by oxygen pressure leaching, which exploit the characteristic of molybdenum-nickel minerals contain high concentration amorphous sulfide which has highly active, and make the most of easily oxide to sulfuric acid and sulfate at low temperature and excess oxygen presence of the amorphous sulfide.

## Experimental

### Materials

The chemical compositions of Mo-Ni ore of black shale was listed in Table.1. The XRD pattern of the raw Mo-Ni ore was shown in Fig.1. It was confirmed that the Mo-Ni ore consists crystalline pyrite [FeS<sub>2</sub>], quartz [SiO<sub>2</sub>], calcite [CaCO<sub>3</sub>], millerite [NiS], elemental sulfur. Nickel occurs mainly as vaesite [NiS<sub>2</sub>], millerite [NiS] [10-11].

Table. 1 Chemical compositions of the Mo-Ni ore

components	wt.%	components	wt.%
Mo	6.89	CaO	8.52
Ni	4.73	MgO	0.82
V	0.17	P	0.82
Fe	15.85	F	0.085
S	25.86	Cu	0.24
C	9.7	Zn	0.38
SiO <sub>2</sub>	13.5	Ti	0.21
Al <sub>2</sub> O <sub>3</sub>	2.86	Pb	<0.05

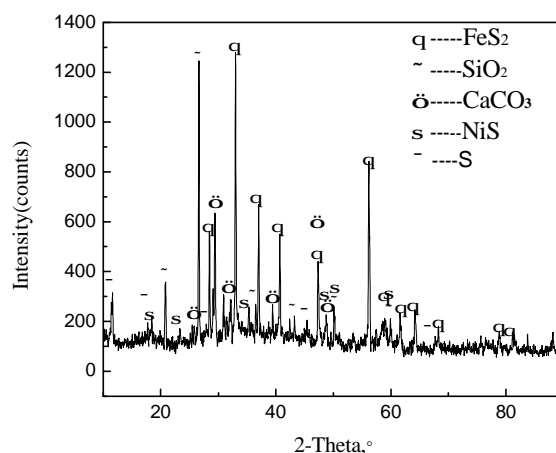


Fig. 1 XRD pattern of the Mo-Ni ore

The diffraction peak of the molybdenum (6.89%) was not detected in the XRD pattern, which occurs mainly due to in the form of amorphous sulfide, which was confirmed that molybdenum primarily exists in the form of jordisite[MoS<sub>2</sub>] in the Ni-Mo ore, and co-exists with clay, quartz .

### Experimental procedure

The samples were crushed and ball milled to 85% < 0.074 mm and dried at 75°C in an oven for 24 h. Leaching experiments were conducted at an oxygen partial pressure of 0.4~0.5MPa in an autoclave with 2L titanium alloy cylinder reactor.

### Analytical methods

The metal contents of the raw ore sample and leaching residues were analyzed by ICP-AES (SPECTROBLUE, Germany), and X-ray diffraction (D/max 3B, Japan) to determine the phase of molybdenum and nickel.

The solution was analyzed by atomic absorption spectrometry (WFX-110B, Beijing) to determine the content of the chemical compositions, and the pH of the leaching liquor was measured using a digital pH meter (PHSJ-5D, Shanghai).

## Results and discussion

### *Effect of leaching time on extraction*

The effect of leaching time on the extraction of molybdenum and nickel was studied under the conditions of the reaction time was varied between 3 and 9 hours, in 2 hours intervals. As shown in Fig. 2, the extraction of nickel increases strongly with the increase in leaching time from 3 to 5 hours at 150°C with a liquid to solid (L/S) ratio of 2 mL·g<sup>-1</sup>, and oxygen partial pressure of 0.4~0.5MPa, 97% nickel extraction was obtained in 5 hours without sulfuric acid. This is probably because the nickel sulfide oxidizes to NiSO<sub>4</sub>, which dissolves easily into the acid solution under such conditions. Therefore, 5 hours is sufficient for nickel extraction. While the extraction of molybdenum increases gradually with an increase in leaching time from 3 to 5 hours, a maximum extraction of 76% is reached at 5 hours. Therefore, to obtain high nickel and molybdenum recoveries, in subsequent experiments, the leaching time was chosen to be 5 hours.

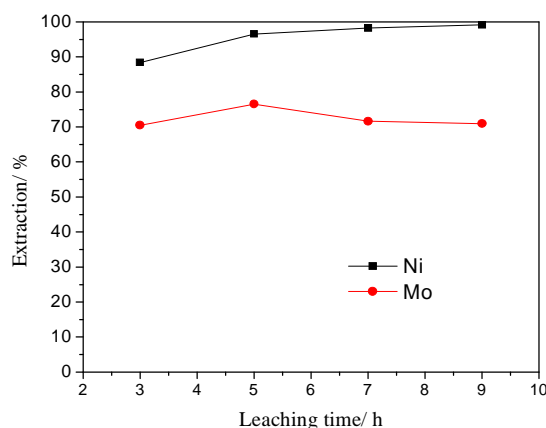


Fig. 2 Effect of leaching time on extraction

### *Effect of leaching temperature*

The effect of temperature on molybdenum and nickel extraction was investigated from 105 to 165°C with distilled water, under an oxygen partial pressure of 0.4~0.5MPa, and a liquid-to-solid(L/S) ratio of 2 mL·g<sup>-1</sup> for 5 hours without sulfuric acid. It can be seen from Fig. 3 that nickel extraction increases with increase in leaching temperature from 105 to 150°C. Beyond 150°C, the extraction of nickel increases slowly with an increase in temperature. Molybdenum extraction increased with increasing temperature and increased only slightly beyond 150°C.

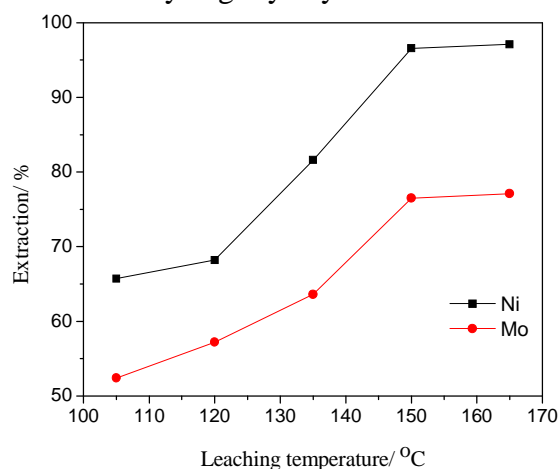


Fig. 3 Effect of leaching temperature on extraction

### Effect of liquid-to-solid ratio on extraction

The effect of liquid-to-solid ratio on molybdenum and nickel extraction was examined at an oxygen partial pressure of 0.4~0.5 MPa, and temperature of 150°C for 5 hours without sulfuric acid. A series of experiments were carried out by varying the liquid-to-solid ratio in the range of 1.5 to 6 mL·g<sup>-1</sup>. It can be seen from Fig. 4 that nickel extraction decreases slightly from 98 to 96% with increasing in liquid-to-solid ratio from 1.5 to 3.0 mL/g and decreases sharply with increase in liquid-to-solid ratio from 3.0 to 6.0 mL·g<sup>-1</sup>. Molybdenum extraction decreases slowly from 76 to 75% with increase in liquid-to-solid ratio from 1.5 to 2.5 mL·g<sup>-1</sup> and also decreases sharply with increase in liquid-to-solid ratio from 3.0 to 6.0 mL/g. The extraction of molybdenum and nickel decreases sharply with increase in liquid-to-solid ratio from 3.0 to 6.0 mL·g<sup>-1</sup>. Considering various other factors such as agitation and pipe-line delivery in industrial plants, in subsequent experiments, the leaching liquid to solid(L/S) ratio was chosen to be 2 mL·g<sup>-1</sup>.

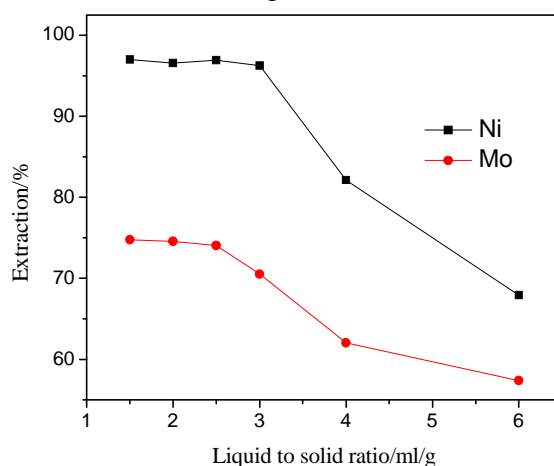


Fig. 4 Effect of liquid-to-solid ratio on extraction

### Characterization of the leaching residue

The acid leach residue used in this study (composition in Table 2) was obtained after oxygen pressure leaching. Almost all nickel and a substantial part of the molybdenum were leached. The leaching rate of nickel and molybdenum achieve respectively 97% and 80%.

Table.2 Chemical compositions of the acid leach residue

components	wt.%	components	wt.%
Mo	3.16	CaO	12.46
Ni	0.45	MgO	0.13
V	0.024	P	1.14
Fe	5.21	F	0.076
S	10.5	Cu	0.044
C	13.2	Zn	0.055
SiO <sub>2</sub>	20.91	Ti	0.23
Al <sub>2</sub> O <sub>3</sub>	1.83	Pb	0.24

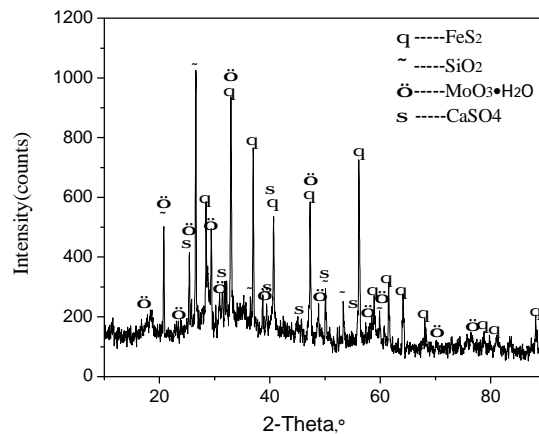


Fig. 5 XRD pattern of the acid leach residue

And in the process, 80% sulfide was oxidized to sulfate. The X-ray diffraction spectrum of the acid leach residue shown in Fig. 5 indicates that the amorphous phase molybdenum disulfide ( $\text{MoS}_2$ ) in the Mo-Ni ore had changed crystalline phase to  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  in the pressure leaching process.

## Conclusions

Oxygen pressure conditions, considerable molybdenum and almost all the nickel were extracted into solution in the leaching process. With leaching time for 3~4h, temperature at  $150^\circ\text{C}$ , liquid-to-solid ratio of  $2\text{mL} \cdot \text{g}^{-1}$ , mineral granularity of 0.074mm, oxygen partial pressure of 0.4~0.5MPa without other reagent, molybdenum leaching percentage can be over 80% and nickel leaching percentage can be more than 97%. Furthermore, about 80% sulfur in the Mo-Ni ore has been transformed into sulfuric acid, which provided sufficient acid for the leaching of nickel and molybdenum. Then yielding the leach liquor of 10~15g/L  $\text{H}_2\text{SO}_4$ .

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