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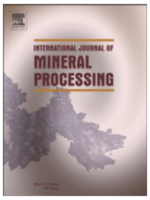

The role of CaO in the extraction of Ni and Mo from carbonaceous shale by calcification roasting, sulphation roasting and water leaching

Xue-Wen Wang *, Jun Peng, Ming-Yu Wang, Pu-Hong Ye, Yuan Xiao

School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China

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ABSTRACT

The role of CaO in the extraction of Ni and Mo from carbonaceous shale by calcification roasting, sulphation roasting and water leaching was studied. Experimental results showed that 97.23% Mo and 93.16% Ni were extracted from the Ni–Mo ore by mixing 100 g the raw Ni–Mo ore with 36 g CaO and grinding to less than 106 μm, then oxidation roasting at 700 °C for 2 h, sulphation roasting with 70 ml 98% sulphuric acid at 240 °C for 2 h and, water leaching at 98 °C for 2 h with a liquid/solid ratio of 2:1. But only 60.67% Ni was extracted for the oxidation roasting without adding CaO. The addition of CaO in the ore is both propitious to environment protection and nickel extraction. XRD analysis showed that the nickel in the calcification roasted ore was in the form of NiO, while the nickel in the oxidation roasted ore was in the form of $NiFeO_4$. It was found that the $NiFeO_4$ formed in the oxidation roasted Ni–Mo ore was included by chemically inert iron silicates, which results in the $NiFeO_4$ irresolvable in sulphuric acid. Experiments confirmed that CaO can decompose not only the $NiFe_2O_4$ but also the iron silicates at the roasting temperature.

1. Introduction

The carbonaceous shale containing nickel, molybdenum and vanadium is an important source of molybdenum and nickel ores in China (Wang and Wang, 2010), which sometime is called Ni–Mo ore. In the ore, the content of nickel and molybdenum varies between 0.17%–7.03% Ni and 0.35%–8.17% Mo, respectively.

Although molybdenum mainly occurs in the form of MoS_2 and nickel mainly occurs as NiS_2, Ni_3S_4, NiS and NiAsS in the ore (Bao et al., 2001), it is difficult to separate and extract molybdenum and nickel from the Ni–Mo ore by mineral processing treatment (Chen et al., 2006; He, 1996). The classic process for recovering molybdenum and nickel from the Ni–Mo ore containing molybdenum less than 1.5% is roasting–melting reduction–Ni–Mo–Fe alloy production. The Ni–Mo–Fe alloy is used to produce ammonium molybdate (Wang et al., 2006). The high grade Ni–Mo ore is directly used to produce ammonium molybdate. Several processes have been proposed to recover molybdenum from the Ni–Mo ore, such as direct leaching with NaOH/NaClO (Wu, 2008; Li et al., 2007) or roasting followed by mixed alkali leaching with NaOH/Na_2CO_3 (Wang et al., 2009). The two processes have been successfully applied to commercial operations in China with high recovery of molybdenum. However, nickel still remained in the leach residue cake, which needs to be recovered. Therefore, a process of oxidation roasting–sulphation roasting–water leaching to extract both molybdenum and nickel from the Ni–Mo ore was carried out (Wang and Wang, 2010). But the poisonous gas was released during the oxidation roasting and the recovery of nickel is not satisfied.

The purpose of this study is to increase nickel extraction from the Ni–Mo ore and to protect the environment against SO_2 pollution in the treatment of Ni–Mo ore.

2. Experimental

2.1. Materials and analysis

The raw Ni–Mo ore used in this study was obtained from Guizhou province in China. Sulphuric acid, burnt lime and distilled water were used in the experiments. The composition of the Ni–Mo ore was listed in Table 1. The XRD pattern of the raw ore was shown in Fig. 1. As seen, there were only the crystalline phases quartz, pyrite, muscovite, calcite and hydroxylapatite in the Ni–Mo ore. The diffraction line of molybdenum and nickel was not detected, which means both metals in an amorphous phase form in the Ni–Mo ore or too low in quantity for XRD.

Molybdenum was determined with ammonium thiocyanate colorimetry by spectrophotometer (Chemistry Department, 1982). Iron, nickel, arsenic, phosphorus, silicon and so on were determined by chemical methods and inductively coupled plasma emission spectroscopy (ICP) with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu Kα X-ray radiation at 35 kV and 20 mA.

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* Corresponding author. Tel.: +86 731 88830247; fax: +86 731 88830143.
E-mail address: wxwcsu@163.com (X.-W. Wang).

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Table 1
Experiment results of molybdenum and nickel recovery from carbonaceous Ni–Mo ore by oxidation roasting or calcification roasting, sulphation roasting and water leaching, wt.%.

Elements	Mo	Ni	Fe	Mg	Al	SiO_2	S	Ca	P	V_2O_5	As
Raw ore	5.42	3.01	7.66	1.48	3.67	23.6	10.2	7.91	2.19	0.19	0.53
OR ore	6.05	3.38	8.61	1.66	4.12	26.5	1.59	8.88	2.45	0.20	0.26
CR ore	3.63	1.95	4.97	0.97	2.38	15.3	6.36	22.1	1.42	0.12	0.34
ORSRL cake	0.26	1.71	8.59	0.26	1.67	31.1	9.15	11.2	0.16	0.14	0.08
CRSRL cake	0.09	0.12	1.44	0.02	0.15	10.6	20.1	25.4	0.02	0.01	0.04

2.2. Experimental procedure

The raw Ni–Mo ore was first crushed and ground to less than 106 μm. A pre-determined weight of the burnt lime was mixed with 100 g grinded ore by grinding and then was roasted at 700 °C for 2 h in air. The roasted Ni–Mo ore were ground and sieved and particles below 120 μm were used in this study. A portion of the ground roasted ore and a pre-determined volume of 98% sulphuric acid was mixed equably in a crucible and then heated in an electric muffle furnace. According to our previous study (Wang et al., 2007; Liu et al., 2009; Wang and Wang, 2010), the sulphation roasting was kept at 240 °C for 2 h.

After roasting, the sulphation roasted ore was leached by water in an agitated flask, which was heated by an electric jacket. After the required contact time, the supernatant was vacuum filtered and the leach residue cake was submitted to successive rinsing with water; lasting up to 10 min., before it was dried and analyzed for molybdenum and nickel contents.

3. Results and discussion

3.1. Oxidation roasting

To avoid the release of SO_2 to environment, the CaO was mixed with the raw Ni–Mo ore before the oxidation roasting. Fig. 2 is the relationship between CaO addition and SO_2 adsorbed ratio during the roasting. Fig. 2 shows that the adsorption of SO_2 increased with the increase of CaO addition. When the addition of CaO was increased to 35 g per 100 g raw Ni–Mo ore, the adsorption of SO_2 was raised to 96.01%, and then the adsorption was maintained stable. Therefore, the addition of CaO was kept to 36 g per 100 g raw Ni–Mo ore for flowing experiment. It was also found that the adsorption of SO_2 depends on not only the addition of CaO but also the thickness of the roasted ore layer. The thicker the Ni–Mo ore layer was, the more the SO_2 was adsorbed by the CaO during roasting. But the oxidation of the Ni–Mo ore became difficult with the thickness increase. The thickness of the Ni–Mo ore layer was kept about 2.0 cm in the roasting, and the maximum concentration of SO_2 was 1073 mg/m^3 in the calcification roasting flue gas. The addition of CaO can markedly save the cost of environment protection for the roasting. The main chemical reactions in the roasting can be expressed as follows:

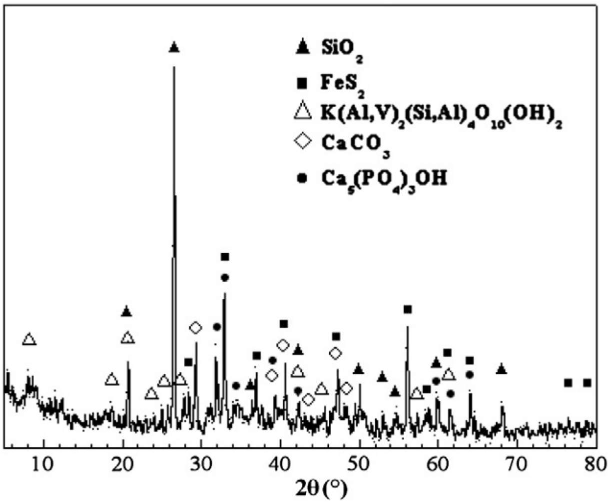

Fig. 1. XRD pattern of raw carbonaceous Ni–Mo ore.

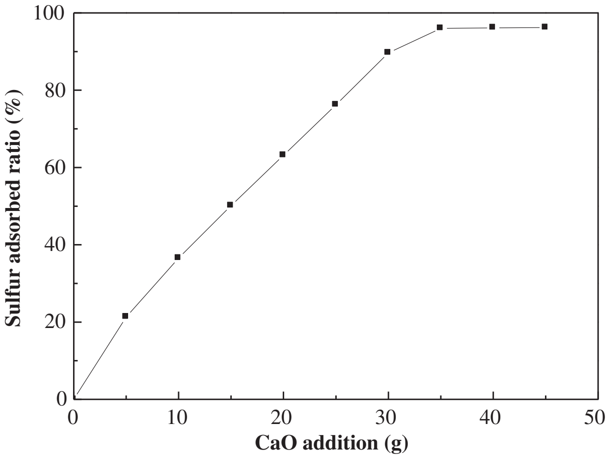

Fig. 2. Relationship between CaO addition and sulfur fixed ratio during the Ni–Mo ore oxidation roasting.

$$2MoS_2 + 7O_2 = 2MoO_3 + 4SO_2 \quad (1)$$

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 \quad (2)$$

$$2NiS + 3O_2 = 2NiO + 2SO_2 \quad (3)$$

$$C + O_2 = CO_2 \quad (4)$$

$$CaO + MoO_3 = CaMoO_4 \quad (5)$$

$$CaO + SO_2 = CaSO_3 \quad (6)$$

$$2CaSO_3 + O_2 = 2CaSO_4 \quad (7)$$

$$CaO + SiO_2 = CaSiO_3 \quad (8)$$

$$2SO_2 + O_2 + 2CaCO_3 = 2CaSO_4 + 2CO_2 \quad (9)$$

It was interesting that the addition of CaO cannot only contribute to environment protection but also alter the form of nickel existing in the roasted Ni–Mo ore. Fig. 3 shows the phase changes in the Ni–Mo ore. Comparing Fig. 3 with Fig. 1, it can be seen that three crystal mineral phases, namely, pyrite (FeS_2), muscovite ($K(Al,V)_2(Si,Al)_4O_{10}(OH)_2$) and calcite ($CaCO_3$) disappeared during oxidation roasting. For the pattern of the oxidation roasted Ni–Mo ore (OR ore) without adding CaO in Fig. 3A-1, there were five crystal mineral phases, namely, quartz (SiO_2), hematite (Fe_2O_3), trevorite ($NiFe_2O_4$), powellite ($CaMoO_4$) and hydroxy-apatite ($Ca_5(PO_4)_3(OH)$). But for the pattern of the calcification roasted Ni–Mo ore (CR ore) in Fig. 3B-1, there are six crystal mineral phases, namely, anhydrite ($CaSO_4$), quartz (SiO_2), powellite ($CaMoO_4$), bunsinite (NiO), hematite (Fe_2O_3) and hydroxy-apatite ($Ca_5(PO_4)_3(OH)$). This indicates that the addition of CaO can prevent $NiFe_2O_4$ crystalline phase generation during the oxidation roasting.