



## Molybdenum recovery from molybdenite concentrates by low-temperature roasting with sodium chloride



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### ABSTRACT

The roasting of molybdenum concentrates using NaCl has been carried out. During the roasting process, Mo is present both as a gas (25–40%) and as solid residue (60–75%). Molybdenum chloride and oxychloride condensate both dissolve in the alkaline solution with molybdenum recovery up to 100%. The results of the study show that 30–32% of molybdenum (sodium molybdate) in the roasted residue is water-soluble. This paper proposes a methodology for leaching roasted residue in two stages: first by water, then by alkaline solutions. Using this methodology, molybdenum recovery from the roasted residue exceeds 99%. It was determined that up to 40% of the sulfur contained in the concentrate remains in the roasted residue after the roasting process in the form of sodium sulfate, which enables a significant reduction of SO<sub>2</sub> generation. The results were achieved under optimal roasting conditions: a roasting temperature of 420–430 °C, NaCl ratio of 100% (from concentrate weight), and 90 min roasting time.

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### 1. Introduction

Molybdenum concentrates are generally processed using technologies based on oxidizing roasting followed by hydrometallurgical processing of the roasted product (Zelikman, 1970). Although this method is the main way for the molybdenum production and has long been used in industry, studies on its application to different concentrates (Wang et al., 2015), as well as on the roasting kinetics (Marin et al., 2009; Kim et al., 2009) and roasting mechanism (Utigard, 2009) are still relevant. However as a result of the well known disadvantages of molybdenum pyrometallurgical extraction, hydrometallurgical processes are become more and more attractive. Among them nitric acid leaching (Medvedev and Aleksandrov, 2009; Khoshnevisan et al., 2012), oxygen pressure leaching (Wang et al., 2013; Smirnov et al., 2010) electric-oxidation extraction (Cao et al., 2010), sodium chlorate (Cao et al., 2009; Abdollahi et al., 2015) and hypochlorite leaching (Youcai et al., 2011) and bio-leaching (Olson and Clark, 2008; Abdollahi et al., 2013; Yu et al., 2015) are more popular.

As an alternative to the above processes, a combined method for processing sulfide raw materials can be used. It involves preliminary pyrometallurgical preparation; low-temperature roasting (below 500 °C) with alkali metal chlorides to completely transform MoS<sub>2</sub>, followed by subsequent hydrometallurgical processing of the product. One major

advantage of this process is the formation of Na<sub>2</sub>SO<sub>4</sub> during roasting, which enables elimination, or significant reduction, of SO<sub>2</sub> emissions. This technique was tested for sulfide concentrate processing of ores from Erdenet, Mongolia (Medvedev et al., 2010), Udokan, Russia (Medvedev and Tu, 2013) and other deposits (Charkavorty and Srikanth, 2000; Ngoc et al., 1989). Some promising results have been reported for the low-temperature chloridizing roasting of nickel (Imideev et al., 2014) and complex nickel-copper sulfide concentrates (Banerjee, 1988; Mukherjee et al., 1985). Processing of a gold-bearing pyrite concentrate by chloridizing roasting using sodium chloride is also well-known (Maslennitskiy, 1987).

Unfortunately, there are few studies regarding chloridizing roasting of molybdenum concentrate using sodium chloride as the agent. Rajic and Zlatanovic were the first to identify the solid products after reacting MoS<sub>2</sub> and NaCl (Rajic and Zlatanovic, 1988) and who studied the role of NaCl during the roasting process (Zlatanović et al., 1998). However, the chemistry of the process was not explained and no attention was paid to technological aspects. Recently the reaction products have been identified through XRD (Aleksandrov et al., 2012). In this work, product identification data has been supported by scanning electron microscopy. Additionally, the authors have demonstrated a possibility for treatment of molybdenite concentrates using the studied process and have identified the optimum operating conditions for leaching the roast residue (Aleksandrov et al., 2014).

Thus, the aim of this work was to define an optimal roasting process based on thermodynamic data, the products obtained at various

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roasting conditions during molybdenite transformation, and on the distribution of molybdenum between the gas and solid phase, which is suitable for either water or alkali leaching.

## 2. Chemical reactions during the roasting process

Thermodynamical analysis of possible reactions that can occur in the MoS<sub>2</sub>-NaCl-O<sub>2</sub> system was performed using the FactSage (<http://factsage.com/>) software. The roasting process was modelled as a mixture containing 8 g of MoS<sub>2</sub> and 12 g of NaCl. The oxygen availability was varied from 1 to 50 g. Results from the analysis (Table 1) indicate that, during the reaction between MoS<sub>2</sub> and NaCl in the presence of oxygen, the most likely products to form are: MoO<sub>2</sub>, MoO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> in the form of solid residue; SO<sub>2</sub>, Cl<sub>2</sub> and MoO<sub>2</sub>Cl<sub>2</sub> in the gaseous phase.

The roasting chemistry is quite complex. In general, the interaction between metal sulfides and sodium chloride in the presence of oxygen is described by the principal reaction:



However, from thermodynamics, a wide range of reactions take place and lead to the formation of chlorides, sulfates and metal oxides at temperatures from 300 to 500 °C (Table 2).

## 3. Experimental

### 3.1. Materials

The subject of this study is a molybdenum concentrate produced by flotation of copper-molybdenum ores from the Erdenet mineral deposit. The molybdenum concentrate composition (wt%) is 45.23% Mo, 2.30% Fe, and 1.41% Cu. The chemical composition of the concentrate was determined by ICP (inductively coupled plasma). NaCl was used as the chlorinator.

### 3.2. Procedures

The concentrate was mixed with sodium chloride in desired proportions and then roasted in a furnace at different temperatures and times. The experimental setup is shown in Fig. 1 and includes a tube furnace, a boat crucible, a quartz tube, a condenser for gaseous products, and absorbers. A sample of the mixture was placed into a combustion tray and then into the quartz reactor, which was heated by the tube furnace.

The chlorine-containing molybdenum compounds were collected in the condenser and absorbers. Three types of molybdenum-bearing products were formed as a result of the roasting process: the roasted concentrate, as well as the chlorides and oxychlorides, which were recovered from condenser and absorber solutions.

**Table 1**  
Thermodynamic modelling results (723 K).

No	Reagent (g)			Reagent residue (g)			Product (g)						
	MoS <sub>2</sub>	NaCl	O <sub>2</sub>	MoS <sub>2</sub>	NaCl	O <sub>2</sub>	MoO <sub>2</sub>	MoO <sub>3</sub>	MoO <sub>2</sub> Cl <sub>2</sub>	Cl <sub>2</sub>	SO <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	
1	8	12	1	6.34	12.00	–	1.32	–	–	–	1.34 (99.9%)	–	
2	8	12	2	4.66	12.00	–	2.66	–	–	–	2.67 (99.9%)	–	
3	8	12	4	1.33	12.00	–	5.33	–	–	–	5.34 (99.9%)	–	
4	8	12	5	–	11.26	–	5.58	–	0.46 (6.3%) <sup>a</sup>	–	6.79 (93.7%)	0.90	
5	8	12	6	–	9.05	–	–	3.56	2.47 (25.3%)	–	7.35 (74.7%)	3.58	
6	8	12	7	–	3.98	–	–	–	6.64 (50.0%)	2.48 (18.7%)	4.08 (30.9%)	9.75	
7	8	12	8	–	0.32	0.10 (0.15%)	–	–	6.72 (49.9%)	6.72 (49.9%)	–	14.19	
8	8	12	9	–	0.32	1.44 (14%)	–	4.13	1.86 (18.0%)	6.93 (67.0%)	–	14.19	
9	8	12	10	–	0.32	3.26 (31%)	–	4.95	1.05 (10.0%)	6.10 (58.0%)	–	14.19	
10	8	12	12	–	0.32	6.17 (51.5%)	–	5.38	0.73 (6.0%)	5.08 (42.0%)	–	14.19	
11	8	12	50	–	0.32	9.92 (66%)	–	5.58	0.55 (3.7%)	4.41 (29.6%)	–	14.19	

<sup>a</sup> Concentration of component given in brackets correspond to weight percentage in the gas phase.

**Table 2**  
Gibbs free energy of the reactions occurring during roasting from 300 to 500 °C.

Chemical equation	Temperature range (K)				
	573	623	673	723	773
	Gibbs free energy (kJ/mol)				
MoS <sub>2</sub> + 3.5O <sub>2</sub> = MoO <sub>3</sub> + 2SO <sub>2</sub>	–986	–976	–965	–955	–945
2NaCl + SO <sub>2</sub> + O <sub>2</sub> = Na <sub>2</sub> SO <sub>4</sub> (s) + Cl <sub>2</sub>	–144	–134	–123	–112	–101
MoO <sub>3</sub> + 2NaCl(s) + 1/2O <sub>2</sub> = Na <sub>2</sub> MoO <sub>4</sub> + Cl <sub>2</sub>	60	57	54	50	47
MoO <sub>3</sub> + Cl <sub>2</sub> = MoO <sub>2</sub> Cl <sub>2</sub> + 1/2O <sub>2</sub>	116	112	108	105	101
2MoO <sub>3</sub> + 2NaCl(s) = Na <sub>2</sub> MoO <sub>4</sub> + MoO <sub>2</sub> Cl <sub>2</sub>	176	169	162	155	148
MoS <sub>2</sub> + 6MoO <sub>3</sub> + 7Cl <sub>2</sub> = 7MoO <sub>2</sub> Cl <sub>2</sub> + 2SO <sub>2</sub>	–177	–192	–206	–221	–235
CaO + MoO <sub>3</sub> = CaMoO <sub>4</sub>	–165	–165	–166	–166	–166

The roasted concentrate was removed from the crucible and was then leached in either the water or the alkali solution. Water leaching was performed for one hour at 90 °C, with a liquid-to-solid ratio of 7:1 and continuous stirring at 400 RPM. The alkaline leaching was conducted under the same conditions with the sodium hydroxide solution ([NaOH] = 50 g/l). The specified conditions were sufficient for complete recovery of all water-soluble molybdenum compounds during water leaching and all non-sulfide molybdenum compounds during alkaline leaching.

### 3.3. Product identification

The solid roasting products were analysed by X-ray diffraction and scanning electron microscope (FEI Company SEM Quanta 650); micro-analysis was conducted using Energy Dispersive Spectrometry (EDAX). Gaseous products were analysed by mass-spectrometry (NETZSCH QMS 403C Aëolos®). The sample of concentrate and sodium chloride mixture (180 mg) was heated in an alundum crucible to 450 °C then kept under an oxidizing atmosphere for 1 h. The resulting solutions were analysed by photocolometry.

## 4. Results and discussion

### 4.1. Influence of roasting parameters on molybdenum distribution

During roasting, molybdenite oxidizes and partially chlorinates. As a result of chlorination, the molybdenite transforms into volatile chlorides and oxychlorides. The fraction of molybdenum that volatilizes can be up to 40% depending on the roasting process conditions. The transformation of molybdenite into the gas phase during low-temperature roasting as a function of NaCl to concentrate ratio is shown in Fig. 2. From the graph, if no sodium chloride is present at 450 °C, then molybdenum does not transfer to the gas phase. Formation of volatile

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