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Thermochemical decomposition of molybdenum concentrates with usage of magnesium-containing additives of natural origin

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Abstract. This article presents the results of research on the sintering of molybdenite concentrate with magnesium-containing natural additives — brucite ($\text{Mg}(\text{OH})_2$) and magnesite (MgCO_3). Physical and chemical properties of initial materials were studied. The thermodynamic assessment of the interaction of molybdenum with hydroxide and magnesium carbonate in an oxidizing medium is given. The process of thermochemical decomposition of molybdenum was optimized with usage of cheap magnesium-containing minerals to form molybdate and magnesium sulfate. The developed method makes it possible to reduce the cost of thermochemistry, to minimize the release of sulfur dioxide due to its rapid binding to magnesium sulfate.

1. Introduction

The raw material for the production of ferromolybdenum and chemical compounds based on molybdenum of different purity are molybdenum concentrates obtained by flotation. Regardless of the product type, the processing of molybdenum concentrate begins with oxidative roasting, as a result of which a calcine is obtained, which are consisted of molybdenum oxide (VI) contaminated with impurities. To obtain pure molybdenum oxide (VI), either the sublimation method or hydrometallurgical (chemical) processing of calcine is used [1]. The disadvantages of the oxidative roasting process are the release of sulfur dioxide, the formation of low-valent molybdenum oxide and difficulties with temperature control.

In addition to roasting, there are various methods for processing molybdenum concentrates: low-temperature chlorination; sintering with lime, with sulfate, sulfide and sodium chloride; with calcium-containing additives, followed by leaching [2-6]. Molybdenum concentrates can be decomposed by pure hydrometallurgical methods, excluding the preliminary oxidizing roasting. These include: decomposition of nitric acid, oxidation of molybdenum with oxygen under pressure in an alkaline solution, treatment of the concentrate with an alkaline solution of sodium hypochlorite, bacterial leaching, electro-oxidative leaching [7-10]. The extraction degree of molybdenum by these methods is high, but they all have a number of disadvantages, such as high power consumption, chemically pure reagents and complex equipment.



The purpose of this study is to improve the efficiency of thermochemical decomposition of molybdenum concentrates by using magnesite (MgCO_3) or brucite ($\text{Mg}(\text{OH})_2$) as a raw material additive. Their application will reduce the cost of the sintering process and will lead to effective interaction of decomposition products to form soluble compounds.

2. Models and Methods

The molybdenum concentrate used in the research (wt. %: 47.20 Mo; 35.18 S) was obtained by selective flotation of copper-molybdenum ores from the Erdenetein-Ovoo deposit (Mongolia). X-ray phase analysis of the concentrate showed that molybdenite is the main phase (Figure 1). Brucite of the Kuldurskoye deposit (Jewish Autonomous Region) and magnesite of the Savinskoye deposit (Irkutsk region) were used as additives.

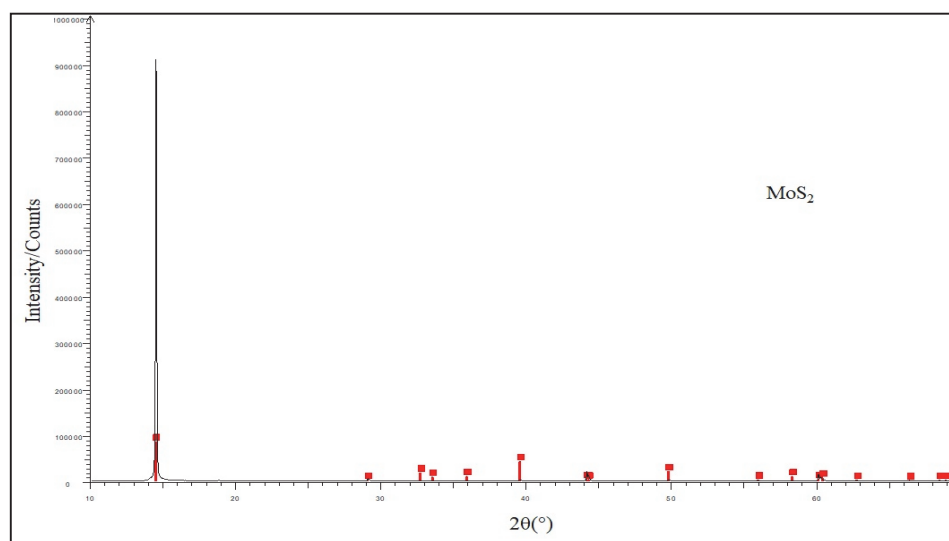


Figure 1. X-ray phase analysis of molybdenite concentrate.

Thermal analysis of magnesite and brucite was performed by thermogravimetry and differential scanning calorimetry using synchronous thermal analyzer STA 449 F1 Jupiter (NETZSCH, Germany). This thermal analysis allows to identify and investigate the phase transformations occurring in the samples during heating or cooling by thermal effects and mass loss [11].

Decomposition of initial materials and reaction products of oxidative roasting of molybdenum concentrate was carried out using the microwave decomposition system of MARS 6 samples (CEM, USA). Chemical analysis of initial materials and reaction products of oxidative roasting of molybdenum concentrate was determined by atomic absorption spectrometry on the Solaar M6 spectrometer (Thermo Electron, USA) and photocolometric method on the PE-5300B spectrophotometer (ECOCHM, Russia). Analysis of the sulfur volatilization was carried out by weighing the solid residue. Experimental studies of the process of roasting molybdenum concentrate with magnesite and brucite were carried out in the laboratory muffle furnace SNOL 16251/9-14.

3. Results and Discussions

In technological studies, during the sintering of molybdenum concentrate, magnesite (MgO 46.6 %) of the Savinsky Deposit and brucite (MgO 61.4 %) of the Kuldur Deposit (Figure 2) were used as raw materials additives.

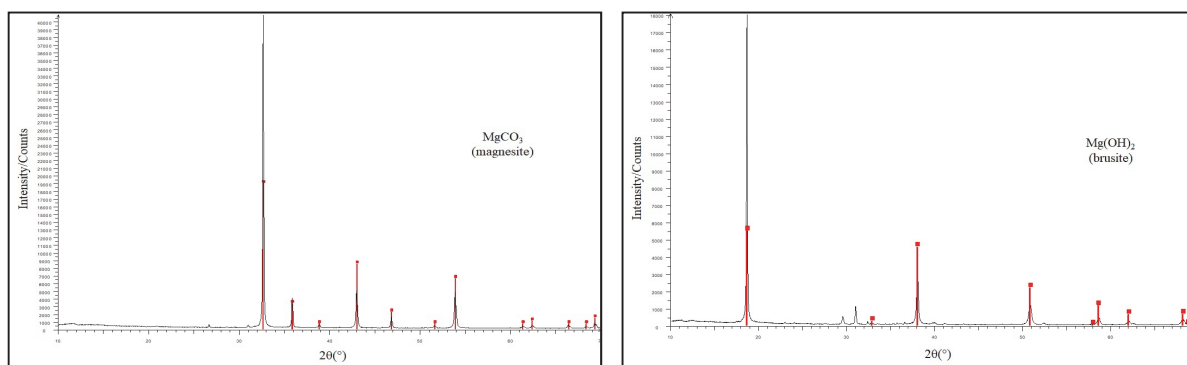


Figure 2. X-ray phase analysis magnesite and brucite.

According to the results of the thermal analysis of magnesite and brucite natural compounds, it was revealed that the decomposition of magnesite occurs in the temperature range of 540-640 °C. Endo-effect, which is shown on the thermogram, corresponds to the decomposition of magnesium carbonate with the formation of magnesium oxide (Figure 3). According to the thermogram, the process of decomposition of brucite with the formation of magnesium oxide occurs in the temperature range 325-450 °C, and the second endothermic maximum in the temperature range 550-750 °C corresponds to the decomposition of a small amount of impurity dolomite (Figure 4). The obtained thermograms of magnesite and brucite are consistent with the literature data [11].

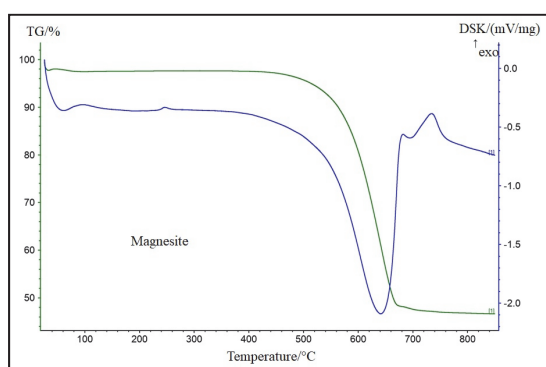


Figure 3. Thermogram of decomposition magnesite.

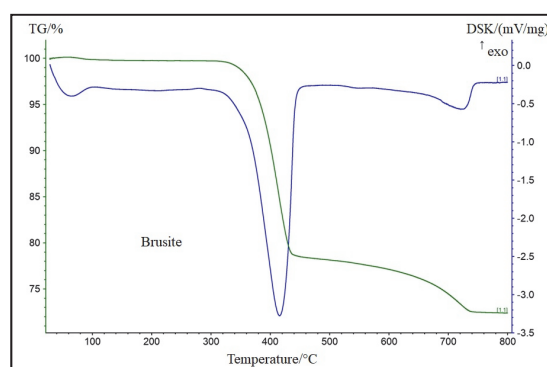


Figure 4. Thermogram of decomposition brucite.

The possibility of the molybdates formation by heating a number of oxides and carbonates with molybdenum oxide (VI) was established by Tamman and others, according to the heating thermograms of their mixtures. Magnesium oxides and carbonates actively react with molybdenum (VI) oxide, forming magnesium molybdates. The high chemical activity of molybdenum oxide (VI) in the reactions under consideration is explained by two circumstances:

- the low temperature of the beginning of sintering of MoO_3 (550-600 °C), in which the atoms acquire sufficient mobility to exchange places;
- relatively high vapor elasticity at temperatures above 500 °C, causing the possibility of reactions involving the gas phase [1].

It is known that in the temperature range of 400-600 °C, molybdenite interacts with atmospheric oxygen to form MoO_3 and to release sulfur dioxide SO_2 . Hydroxide and magnesium carbonate react with molybdenum oxide (VI) takes place at temperatures of 500-700 °C to form magnesium molybdate. Both reactions are endothermic, due to the endothermic effect of the dissociation of carbonate and

magnesium hydroxide. Thus, magnesite and brucite can be used as additives during thermochemical decomposition of molybdenum concentrate.

3.1. Thermodynamic analysis of the reactions of the interaction of molybdenite with magnesite and brucite in an oxidative medium

The probability of any chemical reaction is determined by the change of Isobaric-isothermal potential (Gibbs energy). Thermodynamic assessment of the reaction probability was carried out according to the method of Temkin and Schwartzman, according to which the isobaric-isothermal potential is determined by the formula (1).

$$\Delta G_T^0 / T = \Delta H_{298}^0 / T - \Delta S_{298}^0 - (M_0 \Delta a + M_1 \Delta b + M_2 \Delta c) \quad (1)$$

Values of M_0 , M_1 , M_2 for different temperatures are calculated by Temkin and Schwarzman. Values ΔS_{298}^0 , ΔH_{298}^0 , Δa , Δb , Δc are given in the literature [12].

Table 1. The results of calculating the values of the Gibbs free energy for reactions depending on the temperature.

Possible reactions	ΔG_{298}^0 , kJ / mol					
	673	773	873	973	1073	1173
1 $\text{MoS}_2 + 3\text{MgCO}_3 + 4.5\text{O}_2 \rightarrow \text{MgMoO}_4 + 2\text{MgSO}_4 + 3\text{CO}_2$	-1403.6	-1379.80	-1355.9	-1332.1	-1308.2	-1259.8
2 $\text{MoS}_2 + 3 \text{Mg}(\text{OH})_2 + 4.5\text{O}_2 \rightarrow \text{MgMoO}_4 + 2\text{MgSO}_4 + 3\text{H}_2\text{O}$	-1395.7	-1365.40	-1334.5	-1302.8	-1270.2	-1236.5
3 $\text{MoS}_2 + 3.5\text{O}_2 \rightarrow \text{MoO}_3 + 2\text{SO}_2$	-884.9	-864.80	-844.8	-824.8	-804.9	-785.1
4 $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$	1.13	-16.01	-32.9	-49.7	-66.1	-82.3
5 $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$	-20.6	-35.10	-49.2	-62.8	-75.8	-88.3
6 $\text{MgO} + \text{MoO}_3 \rightarrow \text{MgMoO}_4$	-62.7	-64.60	-66.9	-69.4	-72.2	-75.4
7 $2\text{MgO} + 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{MgSO}_4$	-460.8	-404.80	-349.3	-294.4	-240.1	-186.1

The negative values of the Gibbs free energy change, which were obtained in the calculations in the investigated temperature range, confirm the possibility of reactions with the formation of molybdenum and magnesium sulfate in the studied systems.

3.2. Experimental part

The study of the sintering process of molybdenite concentrate using magnesite and brucite as additives were performed under laboratory conditions. The molybdenum concentrate was mixed with magnesite or brucite, then the charge of the batch was placed in an electric muffle furnace.

The optimal conditions for the thermochemical decomposition of molybdenite concentrate with each of the mineral additives, in which molybdenum transforms into soluble forms, are established. If molybdenum is sintered with magnesite, the temperature should be 600 °C and the roasting time - 60 minutes, consumption of magnesite 110 % of the stoichiometrically required quantity for binding to molybdenum oxide (VI) and sulfur (IV). If molybdenum concentrate is sintered with brucite, the temperature should be 600 °C, duration 60 minutes, consumption of brucite 105% of the stoichiometric amount required. The resulting calcines were subjected to x-ray phase and chemical analyses.

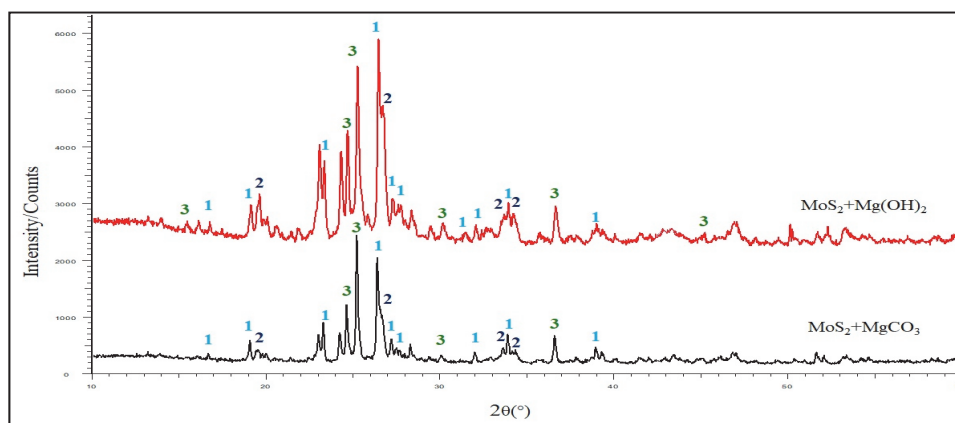


Figure 5. XRD patterns of molybdenum concentrate after roasting with magnesite 1 – MgMoO_4 , 2 – MoO_3 , 3 – MgSO_4 .

As can be seen from X-ray patterns (Figure 5) as a result of sintering with magnesite and brucite, the final products are molybdate, magnesium sulfate and molybdenum oxide (VI). According to chemical analysis during roasting with brucite, sulfur losses in the form of sulfur dioxide about 0.8% and molybdenum losses with exhaust gases less than 0.5%, that is less in comparison with sulfur losses - 1.4%, molybdenum is less than 1% using magnesite. Thus, the lower temperature range of decomposition of brucite (325–450 °C) and the high content of pure MgO in comparison with magnesite provided the most effective interaction of decomposition products with minimal loss of molybdenum and sulfur oxides in the gas phase. In addition, carbon dioxide is not released into the atmosphere during application of brucite.

4. Conclusion

Thermodynamic analysis of the interaction of molybdenite with carbonate and magnesium hydroxide in an oxidizing medium showed the possibility of using brucite and magnesite as raw material additives in the thermochemical decomposition of molybdenite with the formation of magnesium molybdate (MgMoO_4). Experiments have shown that the use of natural magnesium-containing additives significantly reduces the emission of sulfur dioxide into the atmosphere. Based on the results of the work, it was found that the use of brucite as an additive for the decomposition of resistant mineral molybdenite is more preferable due to the lower consumption of the additive and lower losses of sulfur (1.4 %) and molybdenum (less than 1%) with the gas phase.

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