

Chemistry and Mechanism of Interaction Between Molybdenite Concentrate and Sodium Chloride When Heated in the Presence of Oxygen



P.V. ALEKSANDROV, A.S. MEDVEDEV, V.A. IMIDEEV, and D.O. MOSKOVSKIKH

Roasting of molybdenum concentrates with sodium chloride has high potential and can be an alternative to oxidizing roasting and autoclave leaching; however, the chemistry and mechanism are poorly known. The chemical mechanism of the roasting process between molybdenite concentrate and sodium chloride in the presence of atmospheric oxygen is proposed. It is demonstrated that the process occurs through molybdenite oxidation, up to molybdenum trioxide, with subsequent formation of sodium polymolybdates and molybdenum dioxydichloride from molybdenum trioxide. It is found that the formation of water-soluble sodium polymolybdates from molybdenum trioxide stops over time due to passivation of sodium chloride surface by polymolybdates. It is proved experimentally that preliminary grinding of the mixture in a furnace charge leads to an increase in the polymolybdate fraction of the roasting products, which constitutes approximately 65 pct of molybdenum initially in the roasted mixture against 20 to 22 pct in a nonground mixture (or 75 to 77 pct against 30 to 33 pct of molybdenum in calcine). For the first time, the presence of the $\text{Na}_2\text{S}_2\text{O}_7$ phase in the calcine was confirmed experimentally. The suggested mechanism gives possible explanations for the sharp increase of MoO_2Cl_2 formation within the temperature range of 673 K to 723 K (400 °C to 450 °C) that is based on the catalytic reaction of molybdenum dioxydichloride from the $\text{Na}_2\text{S}_2\text{O}_7$ liquid phase as it runs in a melt.

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I. INTRODUCTION

MOLYBDENITE concentrate is the principal source from which molybdenum is extracted. The commercial route for the extraction of molybdenum involves roasting of its concentrate, purification of the resultant calcine by hydrometallurgical way to MoO_3 , and hydrogen reduction of the trioxide to the metal. Although this method is the main way for the production of molybdenum and has long been used in industry, studies on its application to different concentrates,^[1] as well as kinetics^[2,3] and mechanism^[4] of roasting, are still scarce. However, as a result of the well-known disadvantages of molybdenum pyrometallurgical extraction, hydrometallurgical processes have become more and more attractive. Among them, nitric acid leaching,^[5,6] oxygen pressure leaching,^[7,8] electric-oxidation extraction,^[9] sodium chlorate^[10,11] and hypochlorite leaching,^[12] and bio-leaching^[13–15] are more popular.

Another way to extract molybdenum from molybdenite concentrate is through the use of combined methods where the concentrate is roasted with various additives in order to convert Mo to a soluble form and to bind sulfur to form sulfates, thus enabling the elimination or significant reduction of SO_2 emissions. Lime^[16] or sodium chloride could be used as additives.^[17–19] In this paper, roasting of molybdenite concentrate with sodium chloride was studied.

Special aspects of the interaction between molybdenite concentrates and sodium chloride when heated in the presence of oxygen are not very well known, although their applied significance may be large. As it was shown,^[17] replacement of conventional oxidizing roasting of molybdenite concentrates with low-temperature roasting with sodium chloride makes it possible to significantly reduce the formation of SO_2 due to the capture of sulfur in sodium sulfate. When this occurs, about 30 to 50 pct of molybdenum is present in the roast residue in the form of water-soluble sodium molybdates, and the roasting temperature thus may be reduced from the conventional 853 K to 873 K (580 °C to 600 °C) to 698 K to 748 K (425 °C to 475 °C), thereby reducing the costs of the heating of the furnace charge and the hydrometallurgical processing of the roast residue.

The first paper on the interaction between molybdenite and sodium chloride in an oxygen flow was published in 1988, and is not very informative.^[18] Therefore, the authors concluded about the existence of chemical reactions in the $\text{MoS}_2\text{-NaCl-O}_2$ system when heated at

PAVEL V. ALEKSANDROV, ALEXANDER S. MEDVEDEV, and VITALIY A. IMIDEEV are with the Department of Non-Ferrous Metals and Gold, National University of Science and Technology MISiS, Moscow, Russia 119049. DMITRY O. MOSKOVSKIKH is with the Center of Functional Nano-Ceramics, National University of Science and Technology MISiS, Moscow, Russia 119049. Contact e-mail: mos@misis.ru

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temperatures 473 K to 903 K (200 °C to 630 °C); however, sodium sulfate, chlorides, or oxychlorides were not identified in the solid products of the reaction. The results of further research were published much later; the presence of the reaction products— $\text{Na}_2\text{Mo}_2\text{O}_7$, Na_2SO_4 , and MoO_3 —and “some gaseous compounds containing molybdenum and chlorine” was first established in the paper.^[19] The main conclusion drawn from the literature was that the solid products of molybdenite oxidation at temperatures above 673 K (400 °C) are more often chlorinate in a solid-liquid system rather than in a solid-gas system, *i.e.*, the primary chlorinator is mainly NaCl but the product of its decomposition in the presence of sulfur dioxide is not Cl_2 . While the authors failed to find any direct evidence of the presence of liquid $\text{Na}_2\text{S}_2\text{O}_7$ on the NaCl surface, they took into account the data of Fielder *et al.*'s study^[20] and assumed that as a fact, and then came to a conclusion that the melted sodium bisulfate increases the contact surface and creates proper conditions for transporting MoO_3 through the melted layer to NaCl. Thus, Zlatanović *et al.*'s study^[19] hypothesized the role of NaCl in roasting, but no description of the process chemistry and the mechanism of the reactions that had taken place was given there.

Earlier, the same authors determined the reaction products^[21] and suggested the principal chemical reactions accompanying the roasting process of molybdenite concentrates with sodium chlorides.^[17] The purpose of this research is not only to confirm experimentally the chemistry of roasting and specify its details, but also to suggest the reaction mechanism that is occurring.

II. EXPERIMENTAL

A. Materials

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

B. Procedures

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

Chlorine-containing molybdenum compounds were collected in a condenser and absorbers. Three types of molybdenum-bearing products were formed as a result of roasting process: the roasted concentrate, chlorides,

and oxychlorides which were recovered from condenser and absorber solutions.

The roasted concentrate was removed from the crucible and then leached in either water or alkali solution. Water leaching was performed for 1 hour at 363 K (90 °C), with a liquid-to-solid ratio of 7:1 and stirring at 400 RPM. The alkaline leaching was conducted under the same conditions with sodium hydroxide solution ($[\text{NaOH}] = 50 \text{ g/L}$). The specified conditions were sufficient for the complete recovery of water-soluble molybdenum compounds during water leaching and all non-sulfide molybdenum during alkaline leaching.

C. Products' Identification

The solid products of roasting were analyzed by X-ray diffraction and scanning electron microscope (FEI Company SEM Quanta 650); microanalysis was carried out by means of Energy-Dispersive X-ray Spectrometry, EDAX.

III. THERMODYNAMIC CONSIDERATIONS

Thermodynamic analysis of possible reactions occurring in the MoS_2 -NaCl- O_2 system was performed using the software FactSage (<http://factsage.com/>). The roasting process was modeled for a mixture containing 8 g of MoS_2 and 12 g of NaCl. Oxygen availability was varied from 1 to 50 g. Results from the analysis (Table I) lead to a conclusion that the products most likely formed as a result of a reaction between MoS_2 and NaCl in the presence of oxygen: MoO_2 , MoO_3 , and Na_2SO_4 in form of solid residue; SO_2 , Cl_2 , and MoO_2Cl_2 in gaseous phase.

The chemistry of roasting process is quite complex. In general, the interaction between metal sulfides and sodium chloride in the presence of oxygen leads to the formation of metal chloride and sodium sulfate. However, from thermodynamics, a wide range of reactions can lead to the formation of chlorides, sulfates, and metal oxides at temperatures from 573 K to 773 K (300 °C to 500 °C) (Table II).

IV. RESULTS AND DISCUSSION

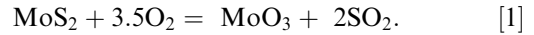
Figure 2 shows the molybdenum distribution in the products (depending on the roasting time); all products were measured at each time, including the gaseous phase during roasting, along with residue during water and alkali leaching. Earlier, it was determined, by XRD for solid products and by mass spectrometry for gas phase, that molybdenum is mainly present as molybdenum trioxide in products and as sodium polymolybdates in calcine, and as dioxydichloride in the gas phase.^[21] The molybdenum distribution between products and the initial molybdenite was then determined. Gas molybdenum compounds were collected from absorbers by alkali (Figure 1), and Mo quantity was determined by ICP analysis. Calcine was leached initially by water and then by alkali. Solutions after water and alkali leaching were

sent for ICP analysis as well as cake after alkali leaching. Mo quantity determined in water solution corresponds to Mo in sodium polymolybdates as polymolybdates are well soluble in water. Mo quantity determined in alkali solution corresponds to Mo in molybdenum trioxide as MoO₃ is well soluble in alkali and insoluble in water. Mo quantity determined in cake correspondings to Mo in initial molybdenite as MoS₂ is insoluble in water as well as in alkali.

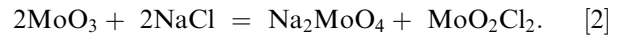
Each of the four areas (not lines) in Figure 2 corresponds to certain compound. For example, at the initial time, all Mo were found in system as part of MoS₂; 30 minutes after roasting, 25 pct of Mo was

found in system as part of gas MoO₂Cl₂, 20 pct as a part of sodium polymolybdates, and 55 pct as a part of initial non-reacted MoS₂. Formation of MoO₃ after 30 minutes of roasting did not occur.

The obtained data were in correspondence with the principle process chemistry proposed by Aleksandrov *et al.*^[17] During the first half-hour, intensive oxidation of molybdenite by atmospheric oxygen takes place, with the formation of trioxide, which is given in Reaction [1]:



Molybdenum trioxide reacts immediately with sodium chloride, with the formation of sodium molybdate and dioxydichloride, which is given in Reaction [2]:



Therefore, there is virtually no MoO₃ in the roast residue during the first 30 minutes of roasting. According to Reference 22, two variants of Reaction [2] are possible: in two stages with Reactions [3] and [4]:

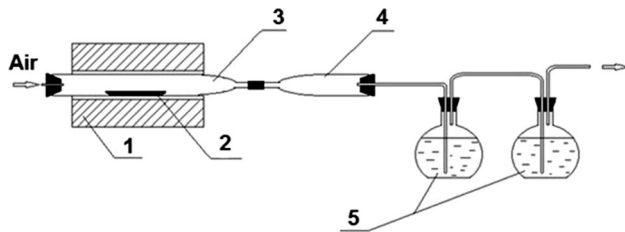
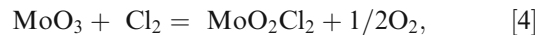
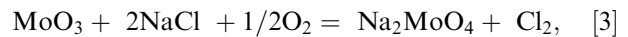


Fig. 1—Experimental setup of oxidizing-chlorination roasting: furnace (1), crucible (2), reactor (3), condensing apparatus, (4) and absorbers (5).

Table I. Thermodynamic Modeling Results (723 K (450 °C))

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

*Concentration of component given in brackets corresponds to weight percentage in gaseous phase.

Table II. Gibbs Free Energy of Reactions Occurring During Roasting Process at the Temperature Range of 573 K to 773 K (300 °C to 500 °C)

Chemical Equation	Temperature Range [K (°C)]				
	573 (300)	623 (350)	673 (400)	723 (450)	773 (500)
	Gibbs Free Energy (kJ/mol)				
MoS ₂ + 3.5O ₂ = MoO ₃ + 2SO ₂	-986	-976	-965	-955	-945
2NaCl + SO ₂ + O ₂ = Na ₂ SO ₄ (s) + Cl ₂	-144	-134	-123	-112	-101
MoO ₃ + 2NaCl(s) + 1/2O ₂ = Na ₂ MoO ₄ + Cl ₂	60	57	54	50	47
MoO ₃ + Cl ₂ = MoO ₂ Cl ₂ + 1/2O ₂	116	112	108	105	101
2MoO ₃ + 2NaCl(s) = Na ₂ MoO ₄ + MoO ₂ Cl ₂	176	169	162	155	148
MoS ₂ + 6MoO ₃ + 7Cl ₂ = 7MoO ₂ Cl ₂ + 2SO ₂	-177	-192	-206	-221	-235
CaO + MoO ₃ = CaMoO ₄	-165	-165	-166	-166	-166

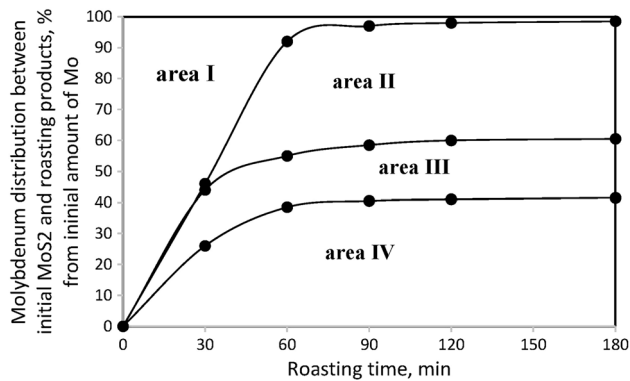
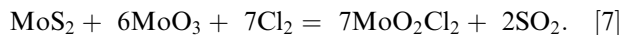


Fig. 2—Molybdenum distribution in the roasting products, depending on its duration (temperature 723 K (450 °C), NaCl ratio 150 pct of the concentrate weight).

or in an oxygen-lacking environment (for example, in case of agglomeration of the particles), in two stages with Reactions [5] and [6]:



Formation of molybdenum dioxidichloride is also possible as a result of chlorination of molybdenum disulfide and trioxide mixture,^[23] which is given in Reaction [7]:



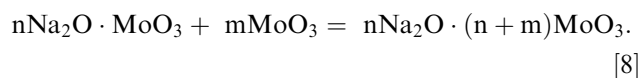
After 30 minutes of roasting, molybdenum trioxide appears in the roast residue, and simultaneously, the formation of sodium molybdate (polymolybdates) stops, which may be explained only by cessation of Reaction [3] due to passivation of sodium chloride particles by the reaction product, sodium molybdate (polymolybdates). Figure 3 shows a roast residue fragment after 15 minutes of roasting, where it can be seen that a sodium molybdate film begins to form on the sodium chloride particle.

After 90 minutes of roasting, the sodium chloride particle is completely covered. Figure 4 shows a crust of sodium polymolybdates and molybdenum trioxide that is formed during molybdenite oxidation, which does not start to react with NaCl due to passivation of the salt surface.

It is worth mentioning that most of the sodium chloride particles get fully passivated after 30 minutes of roasting (Figure 5), which corresponds to the data presented in Figure 2 and to the proposed mechanism.

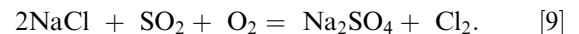
The identified phases (Figures 3 through 5) have been confirmed by XRD (Figure 6).

The fact that the film is composed of sodium polymolybdates justifies the proposed chemistry of reaction (8):



It is found in Reference 22 that at temperatures below 773 K (500 °C), Reaction [2] mainly runs through the

stages [5] and [6]. It is also known^[24] that at a low partial pressure of chlorine (below 35 kPa), Reaction [4] runs at noticeable rates only at temperatures above 773 K (500 °C), and active interaction begins at temperatures above 873 K (600 °C). Taking this into account, it would be logical to make a supposition that Reaction [2] runs according to the mechanism that includes Reactions [5] and [6]. However, sodium oxide was not discovered in the roasting products (including intermediate ones, obtained after 15-minute and 30-minute roasting). Obviously, the mechanism that includes Reactions [5] and [6] during sodium chloride passivation excludes the formation of molybdenum dioxidichloride as shown in Reaction [5]; however, it does not occur in practice, and the formation of MoO_2Cl_2 continues as long as the primary MoS_2 is present in the roasted mixture. All this warrants a conclusion about a more complicated mechanism: sodium molybdate forms according to Reaction [3], and formation of dioxidichloride takes place mainly with the participation of molybdenite according to Reaction [7]; in this case, we cannot completely rule out that Reactions [5] and [6] might also take place. The presence of chlorine in the system, after cessation of Reaction [3] as a result of NaCl surface passivation, is ensured due to sodium chloride decomposition according to Reaction [9]:^[25]



Diffusion of the gaseous compounds through the passivating film layer seems to be quite possible. Reaction [9] occurs at the very start of roasting and has a major role. First, NaCl allows the capturing and sulfur as sodium sulfate, thereby significantly decreasing the formation of SO_2 . Secondly, generated, according to Reaction [1], SO_2 is removed from the system with the help of sodium chloride, as shown in Reaction [9]. The generated MoO_3 , shown in Reaction [1], is also removed from the system with the help of sodium chloride, as shown in Reaction [2]. This leads to a shift in the equilibrium of Reaction [1] toward the products of reaction and explains the high oxidizing rate of molybdenite at 723 K (450 °C) (100 pct with NaCl ratio – 150 pct against 2 pct without any addition of NaCl).

As MoS_2 reacts with MoO_3 at temperatures above 673 K (400 °C), and MoO_2 is formed as a result,^[26] chlorination of a molybdenite and molybdenum trioxide mixture occurs in two stages which is presented in Reactions [10] and [11]:



Obviously, the chemistry of roasting is quite complicated, and all of the above reactions should be considered in total. Thus, for Reactions [1], [4], and [9], we can write an overall reaction either with chlorine emitting [12]:

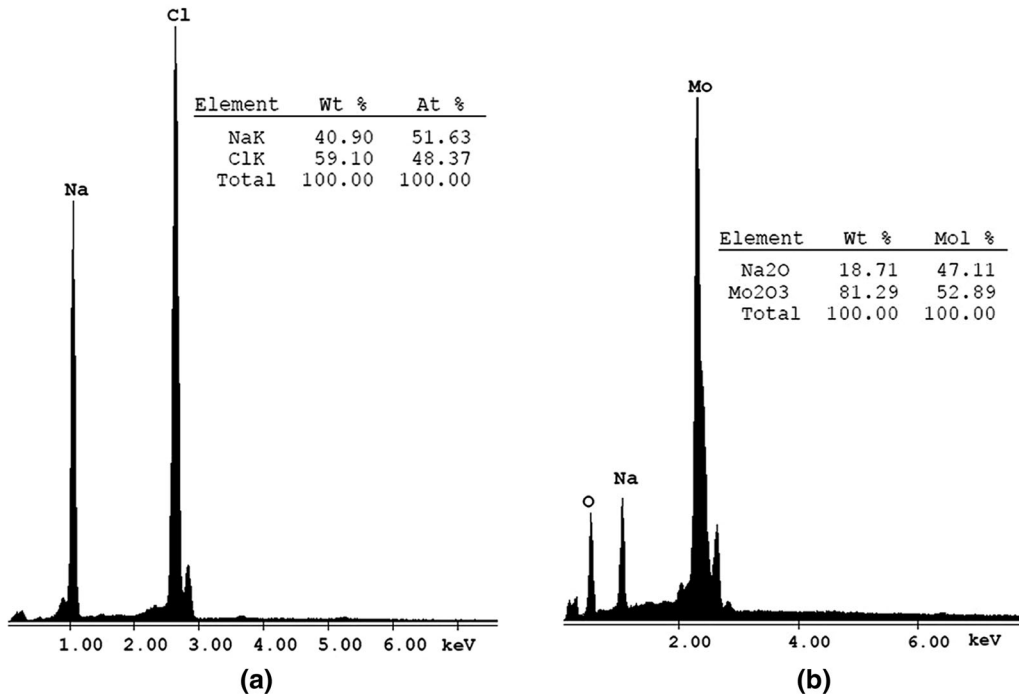
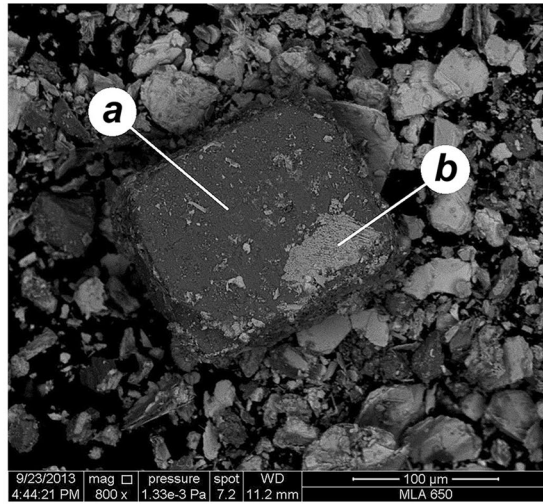
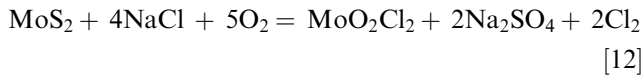
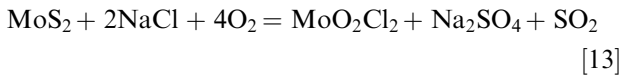


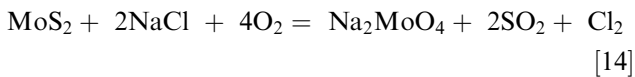
Fig. 3—SEM image and EDS spectrums of roast residue after 15 min of roasting at temperature of 723 K (450 °C) and NaCl ratio of 150 pct (a) NaCl and (b) Na₂MoO₄.



($\Delta G_{723}^0 = -1074$ kJ/mol);
or with sulfur dioxide emitting [13]:

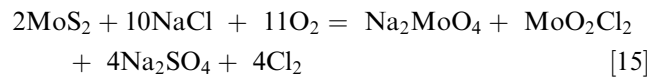


($\Delta G_{723}^0 = -962$ kJ/mol).
For Reactions [1] and [3], the overall reaction is [14]



($\Delta G_{723}^0 = -905$ kJ/mol).

Therefore, the overall reaction for Reactions [1], [3], [7], and [9] justifies the formation of sodium molybdate, molybdenum dioxidichloride, and sodium sulfate [15]:



($\Delta G_{723}^0 = -2203$ kJ/mol).

As shown above Reactions [12–15] are thermodynamically probable at roasting temperature 723 K (450 °C).

As it was found, the formation of water-soluble sodium polymolybdates stops due to passivation of sodium chloride surface; therefore, grinding of the initial mixture shall lead to an increase of the polymolybdate content in

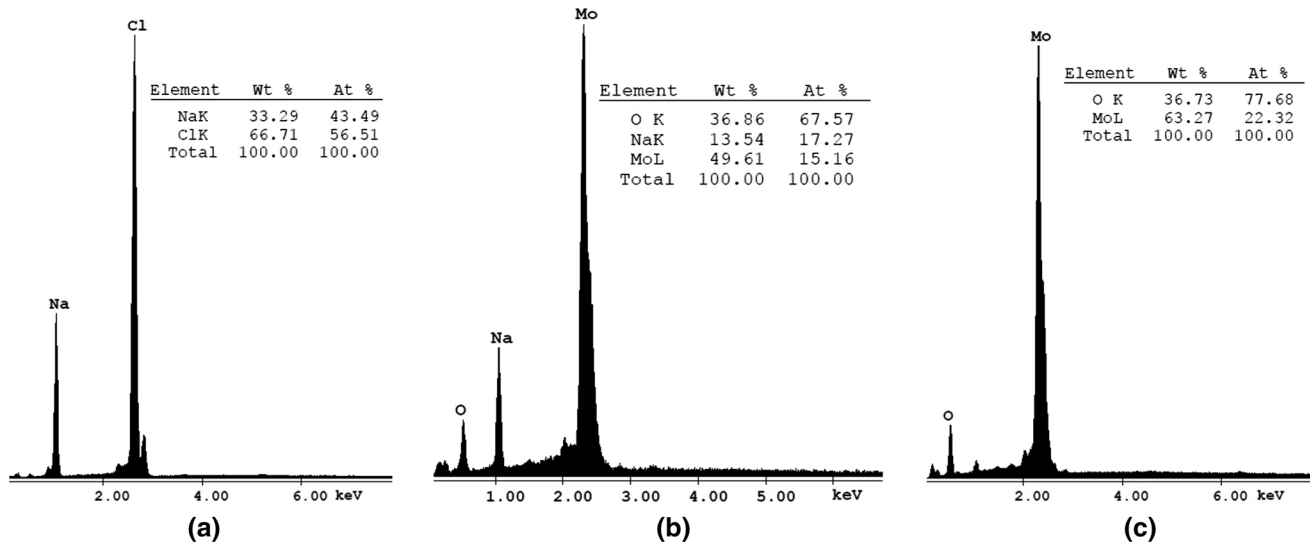
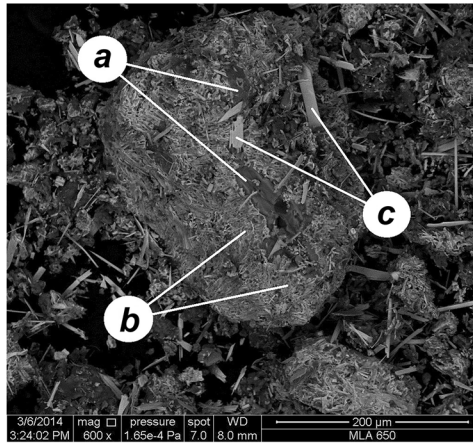


Fig. 4—SEM image and EDS spectrums of roast residue after 90 min of roasting at temperature of 723 K (450 °C) and NaCl ratio of 150 pct ((a) NaCl, (b) $n\text{Na}_2\text{O}\cdot m\text{MoO}_3$, and (c) MoO_3).

the roast residue due to an expansion of NaCl surface. Figure 7 shows the correlation between the molybdenum distribution in the roasting products in a ground and an unground mixture and the duration of the process: Grinding duration of 5 minutes; average NaCl particles size decreased from 100 to 200 μm to 20 to 40 μm .

It is shown that, when roasting a pre-ground mixture, the molybdenite oxidation process is more intensive: ~60 pct of molybdenum is oxidized during the first 30 minutes, while for an unground mixture, molybdenum is present in 44 to 45 pct. Exactly as it was assumed, in the case of a ground mixture, there is a significant increase of polymolybdate in the roasting products; it constitutes about 65 pct of the initial quantity of molybdenum in the roasted mixture vs 20 to 22 pct for an unground mixture (or 75 to 77 pct vs 30 to 33 pct of molybdenum in the solid product of roasting). At the same time, due to some undetermined cause, there is a sharp decrease of molybdenum dioxydichloride—from ~40 pct to ~8 to 9 pct.

It is interesting to note that the chemistry of the process depends on its temperature but main reaction products containing molybdenum remain unchanged.

Figure 8 shows molybdenum distribution in products, in correlation to the roasting temperature.

Theoretically, the distribution of molybdenum between sodium molybdate and dioxydichloride must primarily depend on Reaction [2], because the ratio of molybdenum between the reaction products must be 1:1. Divergence from that ratio is determined by Reactions [4], [7], and [8], and may be used as an “indicator” of a shift in the roasting mechanism: if there is more molybdenum in water-soluble sodium molybdates than in dioxydichloride, it means that either a large contribution of Reaction [8] (and sodium polymolybdates formation accordingly) or that the rate of Reactions [4] and [7] is low. In the case that the molybdenum content in dioxydichloride is higher than in the sodium molybdates, the contribution of Reaction [7] is significant. A low rate of Reaction [6] might have been another cause, but the progress of Reaction [2] through the stages described by Reactions [5] and [6] was practically excluded before.

Depending on molybdenum distribution between the water-soluble sodium molybdates and dioxydichloride, three temperature ranges are singled out in Figure 8:

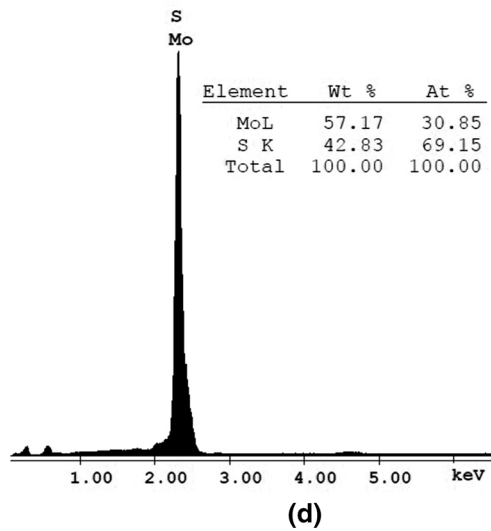
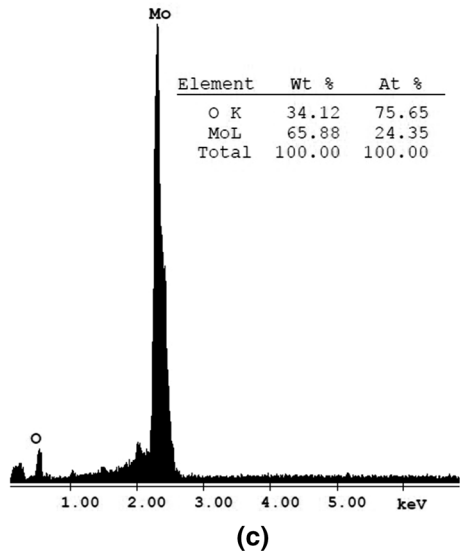
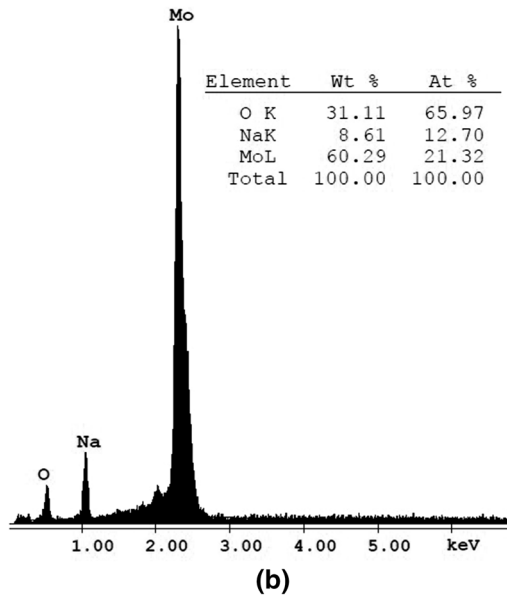
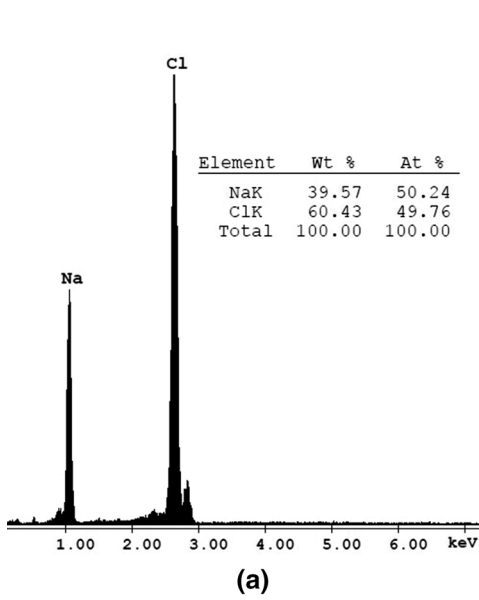
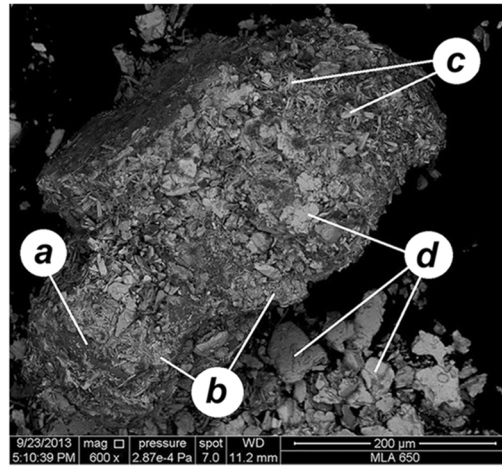


Fig. 5—SEM image and EDS spectrums of roast residue after 30 min of roasting at temperature of 723 K (450 °C) and NaCl ratio of 150 pct ((a) NaCl, (b) $n\text{Na}_2\text{O}\cdot m\text{MoO}_3$, (c) MoO_3 , and (d) MoS_2).

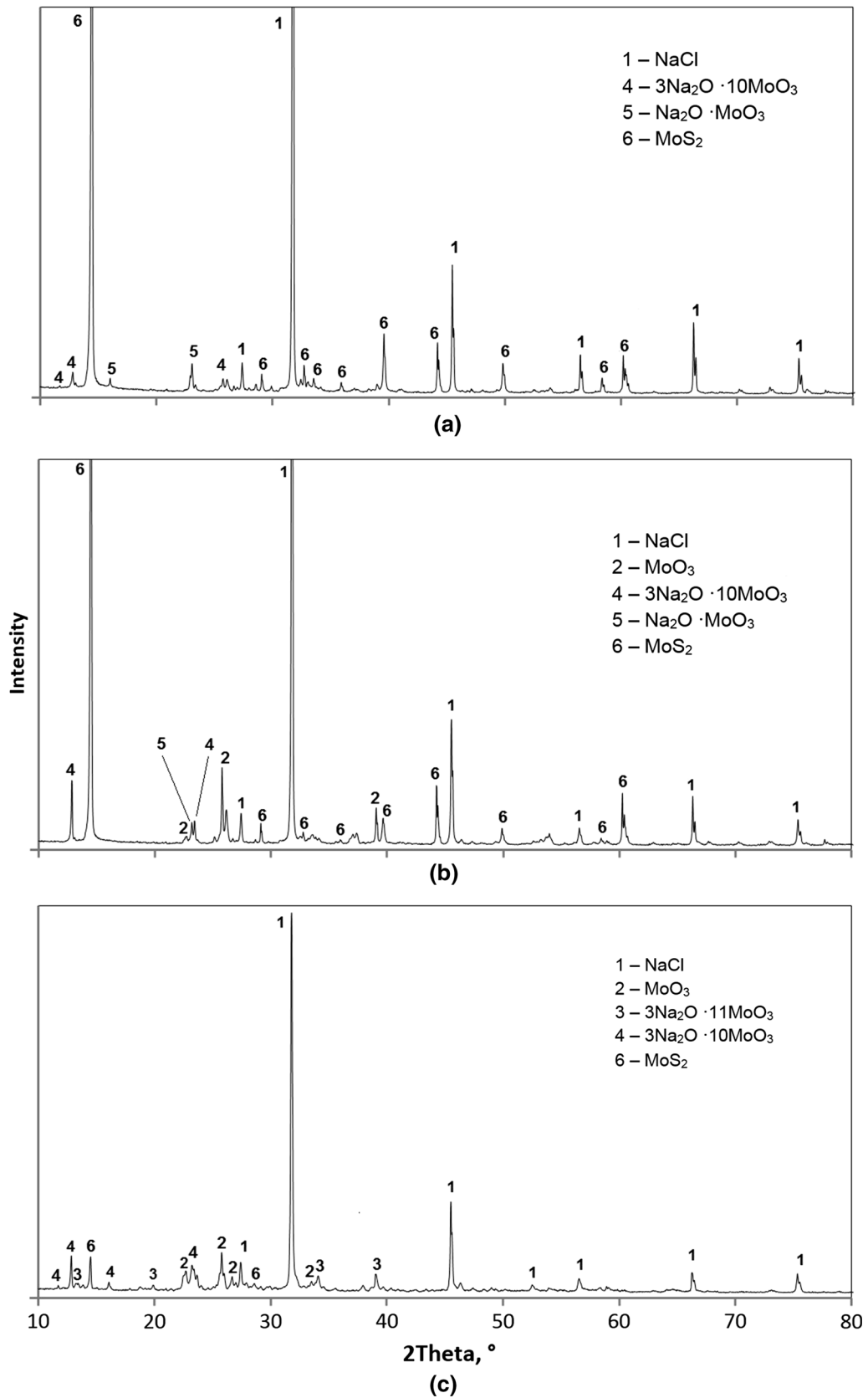
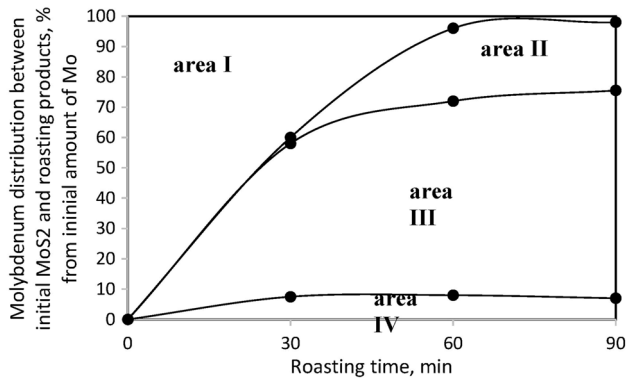
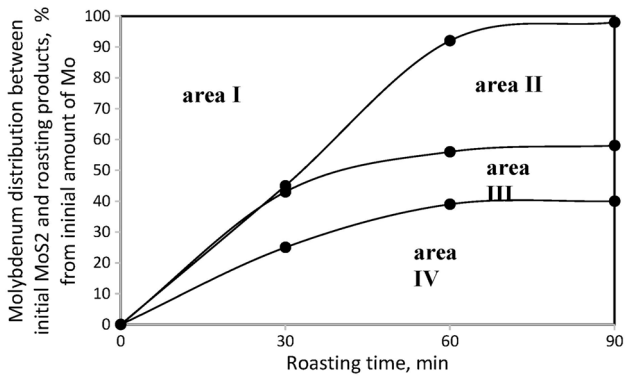


Fig. 6—XRD patterns of roast residues after 15 min (a), 30 min (b), and 90 min (c) of roasting at temperature of 723 K (450 °C) and NaCl ratio of 150 pct.



(a)



(b)

Fig. 7—Molybdenum distribution in the roasting products depending on its time in a ground (a) and an unground (b) mixture (temperature 723 K (450 °C), NaCl ratio—150 pct).

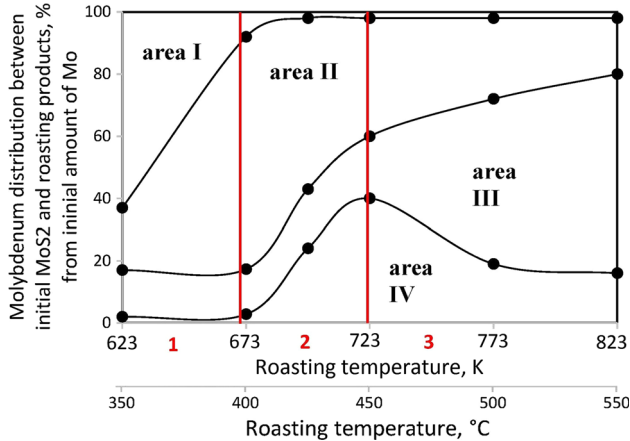


Fig. 8—Molybdenum distribution in the roasting products, depending on the roasting temperature (time—90 min, NaCl ratio—150 pct).

- (1) Only sodium molybdates, but no molybdenum dioxidichloride, form with temperatures ranging from 623 K to 673 K (350 °C to 400 °C).
- (2) In addition to the formation of sodium molybdates, molybdenum sublimation occurs at temperatures in the range of 673 K to 723 K (400 °C to 450 °C); moreover, increasing the temperature leads to a corresponding increase in the molybdenum fraction in the gaseous phase, and the molybdenum content

in MoO_2Cl_2 is actually twice as large as in the molybdates at 723 K (450 °C).

- 3) As the temperature rises, molybdenum redistributes between dioxidichloride and the molybdates in favor of the latter within the range of 723 K to 823 K (450 °C to 550 °C), and, moreover, their total quantity increases.

As only sodium molybdates form in the first temperature range, it is obvious that only Reaction [3] occurs in this case and, possibly, Reaction [8]. The temperature is insufficient for Reactions [4] and [7] to occur at a noticeable rate.

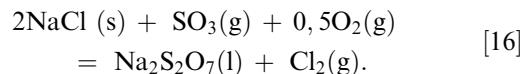
In addition to Reactions [3] and [8], Reaction [7] begins in the second temperature range, which causes the formation of MoO_2Cl_2 . Reaction [7] dominates as the temperature increases. The temperature is still insufficient for Reaction [4] to occur at a noticeable rate.

The contribution of Reaction [7] decreases sharply in the third temperature range. At the same time Reaction [8] rate seems to be growing significantly and the importance of that reaction becoming determinant even in spite of the possibility that:

- Reaction [4] might also occur within that temperature range;
- the chlorine partial pressure might increase due to a growing degree of sodium chloride decomposition according to Reaction [9].^[25]

The following questions now arise: why does Reaction [7] only run at a noticeable rate within the temperature range of 673 K to 723 K (400 °C to 450 °C), and why does the formation of molybdenum dioxidichloride decrease at temperatures above 723 K (450 °C)? Additionally, as seen in Reaction [7], an interaction between one MoS_2 particle and six MoO_3 particles in a chlorine atmosphere is unlikely to occur, much less at 723 K (450 °C). Evidently, there is a certain factor that catalyzes Reaction [7] within the temperature range of 673 K to 723 K (400 °C to 450 °C).

The cause of that effect may be connected with the form of sulfur presence in the roast residue. Reference 20 shows that within the temperature range of 673 K to 723 K (400 °C to 450 °C), the melted compound $\text{Na}_2\text{S}_2\text{O}_7$ is the main product of the interaction between sodium chloride and a mixture of sulfur trioxide and oxygen (besides Na_2SO_4), as shown in Reaction [16]:



With further heating in an oxygen flow up to 773 K (500 °C), $\text{Na}_2\text{S}_2\text{O}_7$ transforms into porous solid Na_2SO_4 . At temperatures above 723 K (450 °C), the main product of the interaction is directly solid Na_2SO_4 . The presence of both a $\text{Na}_2\text{S}_2\text{O}_7$ compound and porous Na_2SO_4 was determined by SEM and EDS analyses in the roast residue obtained at the temperature of 723 K (450 °C) (Figure 9).

Figure 10 shows the data on sulfur distribution in the roasting products, depending on the temperature. Within the temperature ranges of 673 K to 723 K

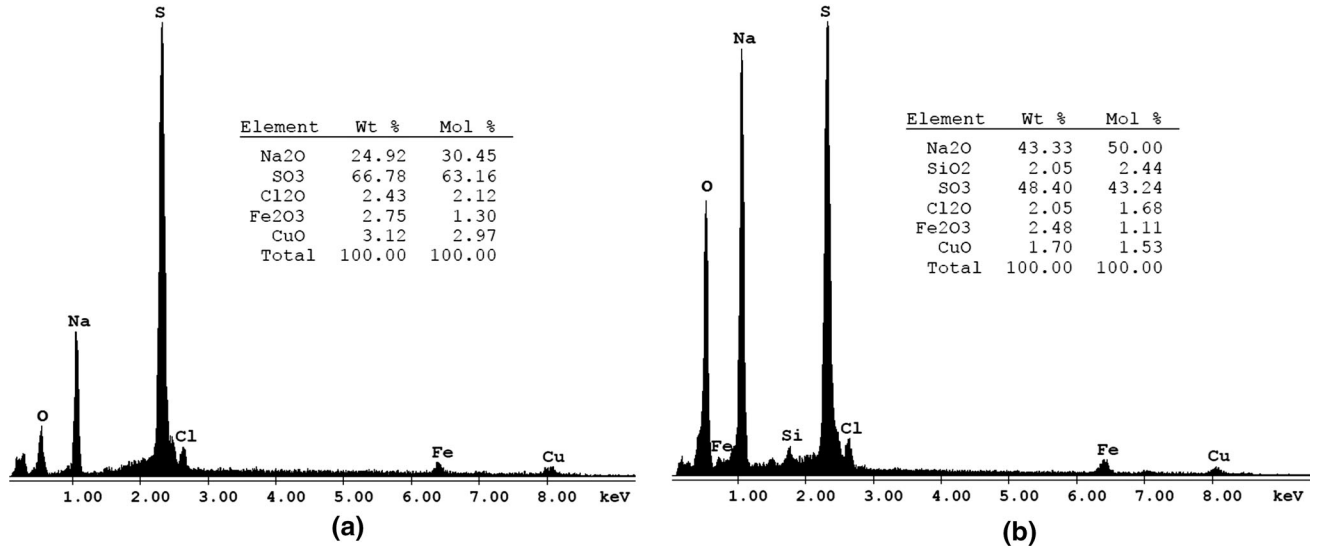
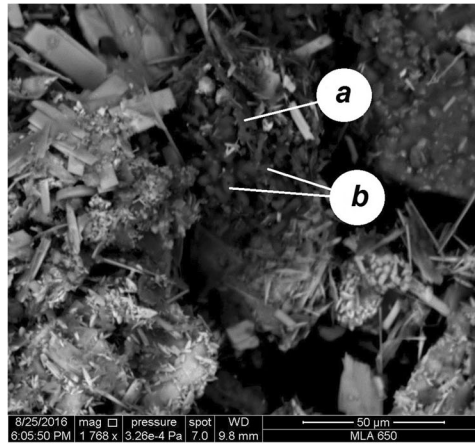


Fig. 9—SEM image and EDS spectrums of roasting residue obtained at a temperature of 723 K (450 °C), NaCl ratio of 150 pct, time of 90 min ((a) $\text{Na}_2\text{S}_2\text{O}_7$, (b) Na_2SO_4).

(400 °C to 450 °C) and 723 K to 823 K (450 °C to 550 °C), the degree of desulfurization is close to 100 pct; however, within 673 K to 723 K (400 °C to 450 °C), sulfur binds with sodium twice as frequently as in the range of 723 K to 823 K (450 °C to 550 °C), which corresponds to the formation of $\text{Na}_2\text{S}_2\text{O}_7$ and Na_2SO_4 compounds within those ranges, respectively.

Therefore, the possibility of Reaction [7] running within the range of 673 K to 723 K (400 °C to 450 °C) is determined by the formation of the $\text{Na}_2\text{S}_2\text{O}_7$ liquid phase [it is confirmed by the correlation of the MoO_2Cl_2 formation in Figure 7 and $\text{Na}_2\text{S}_2\text{O}_7$ formation in Figure 10 at temperatures between 673 K (400 °C) and 723 K (450 °C)] during roasting within that temperature range, *i.e.*, Reaction [7] de facto runs in the melt. The authors of the paper^[19] conclude that the presence of the $\text{Na}_2\text{S}_2\text{O}_7$ liquid phase increases the contact surface area between NaCl and MoO_3 , facilitating the MoO_3 transfer through the melted layer to a sodium chloride particle, which results in the formation of $\text{Na}_2\text{Mo}_2\text{O}_7$ and “sublimated compounds containing molybdenum and chlorine” (Reaction [2] is probably meant). The obtained data develop this theory and show that

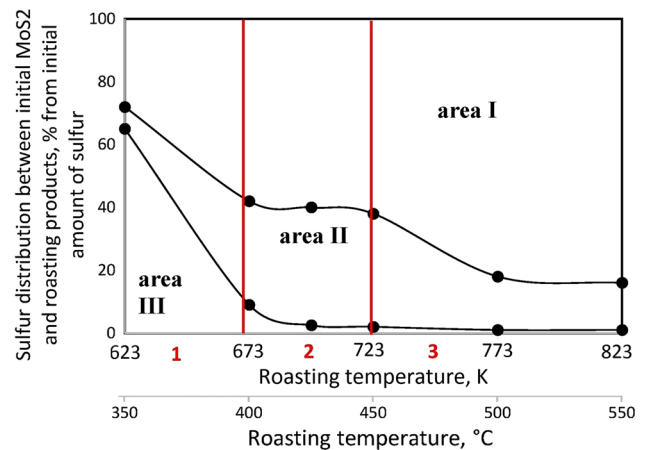


Fig. 10—The sulfur distribution in the roasting products, depending on the temperature (NaCl ratio—150 pct, time—90 min).

$\text{Na}_2\text{S}_2\text{O}_7$ primarily influences the formation of MoO_2Cl_2 but not of sodium molybdates, *i.e.*, it mainly catalyzes the chlorination of MoO_3 according to Reaction [7].

In the absence of a liquid phase, the probability of Reaction [7] to occur significantly decreases from 723 K to 823 K (450 °C to 550 °C), which leads to a sharp decrease in the quantity of dioxydichloride formed. However, the formation of $\text{Mo}_2\text{O}_2\text{Cl}_2$ does not cease completely due to the increase in the rate of Reaction [4] at temperatures between 773 K and 823 K (500 °C and 550 °C).

V. CONCLUSION

1. This study describes the possible chemical mechanism of the roasting process between molybdenite concentrate and sodium chloride in the presence of atmospheric oxygen. It is demonstrated that the process runs through the stage of molybdenite oxidation into molybdenum trioxide, with subsequent formation of sodium polymolybdates and molybdenum dioxydichloride from molybdenum trioxide.
2. It has been discovered that the formation of water-soluble sodium polymolybdates from molybdenum trioxide ceases over time due to passivation of sodium chloride surface by polymolybdates. It has been proven in experiments that pre-grinding of the roasted mixture in a furnace charge leads to an increase of the polymolybdate fraction in the roasting products, and that the latter constitutes approx. 65 pct of molybdenum initially in the roasted mixture vs 20 to 22 pct for an unground mixture (or 75 to 77 pct vs 30 to 33 pct of molybdenum in a solid product of roasting).
3. The reduction of the $\text{Na}_2\text{S}_2\text{O}_7$ phase in the roast has been confirmed experimentally for the first time. This study suggests a mechanism that helps explain a sharp increase of the MoO_2Cl_2 quantity within the temperature range of 673 K to 723 K (400 °C to 450 °C); the mechanism is based on the fact that the formation of molybdenum dioxydichloride is catalyzed by the $\text{Na}_2\text{S}_2\text{O}_7$ liquid phase as it runs in the melt.

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