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Molybdenite alkali fusion and leaching: reactions and mechanism

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Abstract: The production of MoO_3 from Sarcheshmeh molybdenite concentrate *via* a pyro-hydrometallurgical process was studied. The molybdenite concentrate and sodium carbonate were premixed and fused under air atmosphere. Then the fused products were leached in water and the dissolved molybdenum was recovered as ammonium molybdate. The ammonium molybdate was then calcined to produce molybdic oxide. At the fusion stage, the effect of the mass ratio of carbonate to sulfide on the reaction products and the solubility of the products was investigated. The results show that during the fusion, sodium molybdate and sodium sulfate are the final reaction products and sodium sulfide is detected as an intermediate reaction product. By melting at 850°C with 5wt% excess carbonate, the maximum solubility of the products is obtained. The molybdenum is recovered from the solutions as ammonium molybdate.

Keywords: molybdenite; alkali fusion; leaching; sodium molybdate; molybdic oxide

1. Introduction

The starting material for all pyro-processes of molybdenum is the molybdenite concentrate. Almost all molybdenite concentrates are subjected to roasting first to yield technical grade molybdic oxide, which forms the basic raw material for all commercially used products of molybdenum [1]. In the roasting process, the exhaust gas contains sulfur oxides, such as SO_2 and SO_3. However, it appears that some new problems concerning the exploitation of sulfur emission have arisen. In the past three decades, enhanced public awareness and governmental pressure have focused on the problem of sulfur oxide emission in the air. Many experiments have been carried out to develop leaching processes. Nevertheless, molybdenite has a refractory nature and its leaching rate is very low and requires strong oxidizing conditions [2]. It has been found that molybdenite leaches slowly in dilute (1-4 M) nitric acid at room temperature [3] and the leaching of MoS_2 by sulfuric acid is a very slow process [4]. Beyond these studies, other pyrometallurgical processes such as chlorination [5], salt roasting [6], lime roasting [7] and carbothermal reduction of molybdenite in the presence of lime [8] were investigated. Presently, increasing the dissolution rate of molybdenite is a key problem for this mineral. In this study, the alkali fusion of Sarcheshmeh molybdenite concentrate was investigated.

The alkali fusion of molybdenite as a pretreatment process makes it possible to increase the leaching reaction kinetics. There are a few studies about the molybdenite alkali fusion. Gupta [1] has given two flow sheets for molybdenite alkali fusion. In these flow sheets, iron oxide and sodium nitrate were used as oxidant. In this study, the alkali fusion process of molybdenite with sodium carbonate in the presence of air was investigated. The products of this process have high solubility in water. Thus, solutions with a high concentration of molybdenum can be obtained and by the addition of mineral acid and ammonia, and molybdenum could be recovered as ammonium molybdate. There is no SO_2 emission in this process and sulfur is released as sodium sulfate.

2. Experimental

This experiment was carried out with molybdenite concentrate samples from the Sarcheshmeh Copper Industries in Iran. The chemical composition of the studied molybdenite

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was 97.5wt% MoS_2 and 1.9wt% SiO_2 with the particle size of 60-80 μm. The sodium carbonate used was technical grade (98% in purity). The starting material and products were analyzed by using a Philips X-pert X-Ray diffractometer with PW 2273 tube and Cu K_α radiation at a scan rate of 0.04°/s. Fig. 1 shows the flow sheet of MoO_3 production from molybdenite by the alkali fusion process.

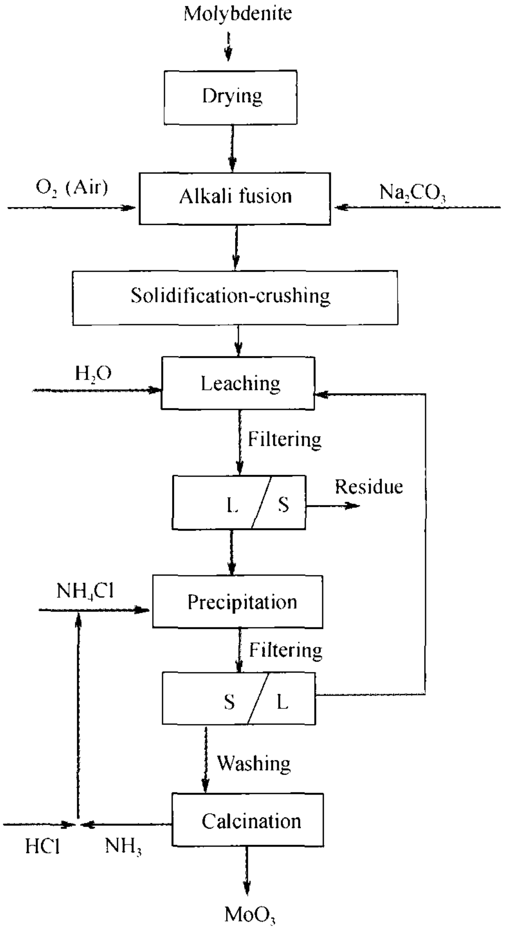

Fig. 1. Flow sheet of the MoO_3 production from molybdenite by the alkali fusion process (L: liquid, S: solid).

The concentrate was first dried at 180°C for 2 h. Then molybdenite concentrate and sodium carbonate were premixed with the stoichiometric ratio, 5wt% excess carbonate (EC) and 10wt% excess sulfide (ES). The total content for all the samples was 10 g. The samples were melted at 750, 850, and 950°C under airflow with a flow rate of 0.2 $L\cdot min^{-1}$ in a tube furnace. The SO_2 content in the exhaust gas was measured with a gas chromatograph (Shimadzu). The melting time was examined up to 160 min. Then the molten materials were discharged from the furnace, solidified and crushed. 5 g of the fused sample was leached with 200 cm^3 distilled water at 60°C for 20 min. After leaching, the solution was filtered and the PH of the solution measured with a Schott Gerate (GG818) PH meter. Then, 1 cm^3 of the filtered solution was diluted with 100 cm^3 distilled water and analyzed with an ICP-AES (JY-124, French) spectrophotometer for molybdenum concentration. The pH of the filtered solutions was adjusted to 2.5-3 by the addition of H_2SO_4 and dissolved molybdenum precipitated by NH_4Cl.

3. Results and discussion

Fig. 2 shows the XRD pattern of the studied molybdenite concentrate with characteristic peaks of MoS_2. It is clear that all the peaks of Sarcheshmeh molybdenite concentrate are MoS_2 diffraction lines.

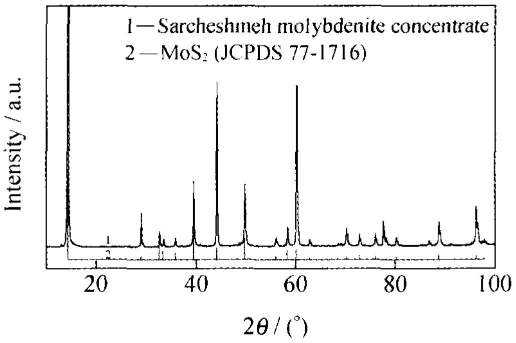

Fig. 2. XRD pattern of molybdenite concentrate with MoS_2 characteristic lines.

Fig. 3 shows the dissolution percent of EC samples fused at 750, 850, and 950°C. It shows that the maximum solubility of the sample, which was fused at 750°C, is 75% after 160 min. At 850°C, the solubility of the sample fused for 120 min reaches 95%. For the samples fused at 950°C, the solubility of the products at melting times less than 60 min is greater than the samples fused at 850°C. However, in the samples whose melting time is greater than 60 min the solubility reduces. This is due to the evaporation of Na_2O under these conditions. Therefore, there is not enough Na_2O to react with MoS_2. Thus, the best condition is obtained at 850°C.

Figs. 4 and 5 show the XRD patterns of the samples fused with 5wt% excess carbonate for 25 and 120 min, respectively.

Fig. 4 indicates that there is no MoS_2 left in the sample fused at 850°C for 25 min and sodium sulfide and sodium molybdate lines are seen brightly. Therefore, it can be suggested that at the first stage, sodium carbonate is calcined to Na_2O and CO_2, and Na_2O reacts with MoS_2 to produce Na_2S and MoO_2. At the next stage, MoO_2 reacts with oxygen and MoO_3 is formed. Then, MoO_3 rapidly reacts with Na_2O and sodium molybdate is produced. In Fig. 4, the strong peaks of unreacted Na_2CO_3 and Na_2O are seen. Fig. 5 indicates that after 120 min there is no Na_2S in the sample. Instead, the strong lines of sodium sulfate appear. Thus, after the formation of Na_2S, it reacts with oxygen and changes to sodium sulfate. In this pattern, there are very weak peaks of Na_2O where Na_2MoO_4 peaks are very strong.

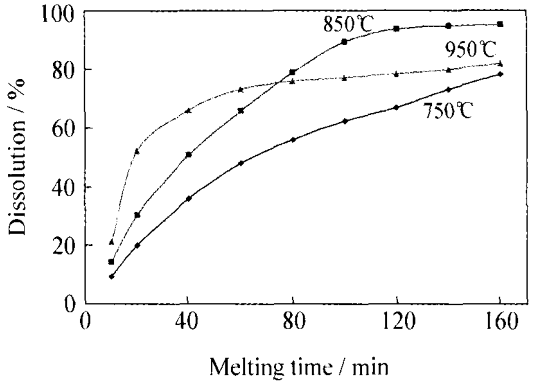

Fig. 3. Dissolution percent of the samples fused at 750, 850, and 950°C with 5wt% excess carbonate.

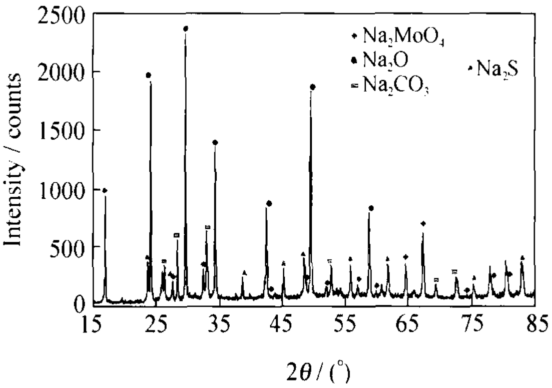

Fig. 4. XRD pattern of the samples melted at 850°C for 25 min with 5wt% excess carbonate.

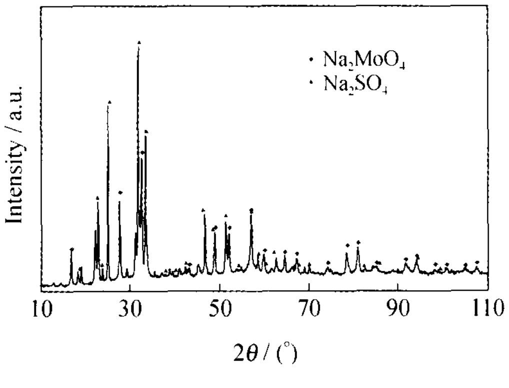

Fig. 5. XRD pattern of the samples melted at 850°C for 120 min with 5wt% excess carbonate.

According to the results, the reaction mechanism can be written as:

$$Na_2CO_3 = Na_2O + CO_{2(g)} \quad (1)$$

$$MoS_2 + 2Na_2O = MoO_2 + 2Na_2S \quad (2)$$

$$MoO_2 + 0.5O_2(Air) = MoO_3 \quad (3)$$

$$Na_2O + MoO_3 = Na_2MoO_4 \quad (4)$$

$$Na_2S + 2O_2 = Na_2SO_4 \quad (5)$$

The overall reaction is:

$$3Na_2CO_3 + MoS_2 + 4.5O_2 = Na_2MoO_4 + 2Na_2SO_4 + 3CO_2 \quad (6)$$

The MoO_2 and MoO_3 lines were not detected in the XRD patterns for different simples. Thus, it can be concluded that reactions (3) and (4) are fast.

To show the possibility of molybdenum oxide formation from the reaction of MoS_2 with oxygen, the SO_2 content in the exhaust gas was measured with a gas chromatograph.

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

$$MoS_2 + 3O_2 = MoO_2 + 2SO_2 \quad (8)$$

No SO_2 was detected. This indicates that reactions (7) and (8) cannot occur. The formation of Na_2S and Na_2SO_4 is another reason.

Fig. 6 shows the XRD pattern of the leaching residue of the sample melted at 850°C for 120 min with 5wt% excess carbonate.

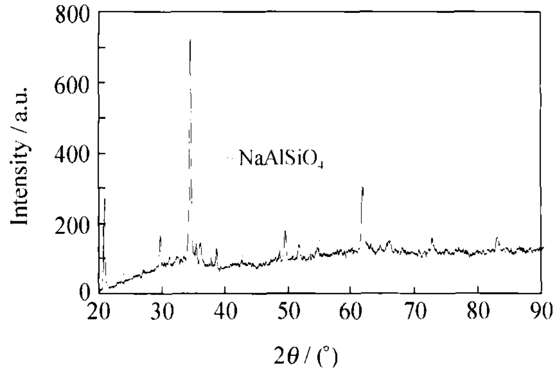

Fig. 6. XRD pattern of the leaching residue of the sample melted at 850°C for 120 min with 5wt% excess carbonate.

It illustrates that the main compound in the leaching residue is $NaAlSiO_4$ that is formed during alkali fusion, from the molybdenite gangue and Na_2O according to the following reaction.

$$Al_2O_3 + Na_2O + 2SiO_2 = 2NaAlSiO_4 \quad (9)$$

There are no molybdenum compound peaks in the XRD pattern of the leaching residue and this indicates that all MoS_2 has been changed to soluble products.

Fig. 7 shows the solubility of the samples with 10wt% excess sulfide fused at 750 and 850°C for different times. It indicates that, the samples fused at 850°C for 80 min, have the maximum solubility. Beyond this time, the solubility of the products starts to decrease.

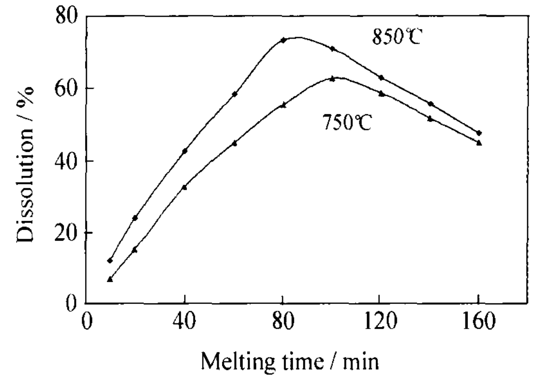

Fig. 7. Solubility of the samples fused at 750 and 850°C with 10wt% excess sulfide *vs.* melting time.

A similar trend has been reported by Kar *et al.* [6]. In this sample, there is not enough Na_2O to react with MoO_3. Thus, excess MoO_3 reacts with Na_2MoO_4 and produces $Na_2Mo_2O_7$ according to the following equation:

$$MoO_3 + Na_2MoO_4 = Na_2Mo_2O_7 \qquad (10)$$

$Na_2Mo_2O_7$ is insoluble in water [9] and the formation of this compound causes molybdenum loss. Fig. 8 shows the XRD pattern of the samples with 10wt% excess sulfide fused at 850°C for 2 h with characteristic lines of $Na_2Mo_2O_7$.

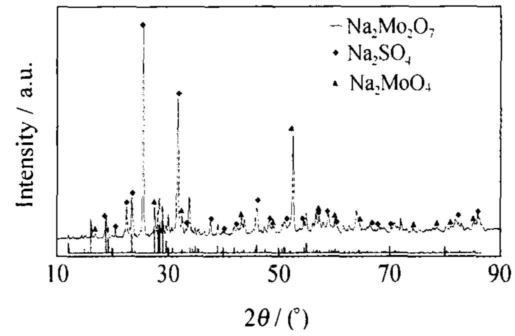

Fig. 8. XRD pattern of the sample fused at 850°C for 2 h with 10wt% excess sulfide and characteristic lines of $Na_2Mo_2O_7$.

Fig. 8 represents that $Na_2Mo_2O_7$ is the major component in the samples with 10wt% excess sulfide after fusion. It also shows strong peaks of Na_2MoO_4 and Na_2SO_4.

To determine the melting time, when a significant decrease in Na_2O content of the samples occur, the pH of the solutions was measured after leaching the fused samples.

Fig. 9 shows pH of leaching solutions for the samples fused at 850°C with different mass ratios of carbonate to sulfide. It can be seen that after melting 60 min, the solution pH starts to decrease. In samples fused with 5wt% excess carbonate the decrease in pH is very low and it changes from 13.2 to 12.2. The remaining Na_2O in these samples is responsible for high pH. For the ES samples fused with excess sulfide, there is a significant decrease in the pH of solutions. This reveals that there is no Na_2O remaining in the fused ES samples.

The results of this study indicate that for the higher recovery of molybdenum, the mass ratio of carbonate to sulfide must be greater than the stoichiometric ratio. However, the increase in the carbonate to sulfide ratio increases the acid consumption at the stage of molybdenum precipitation by ammonium chloride. Therefore, the mass ratio of carbonate to sulfide must be near the stoichiometric ratio.

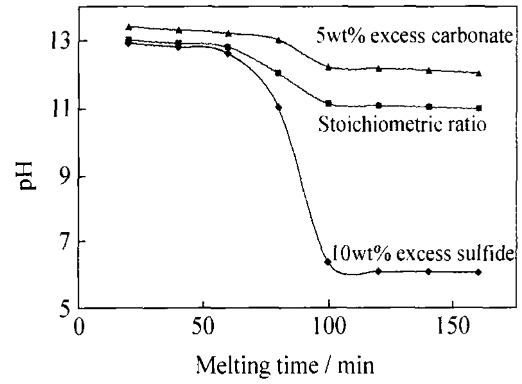

Fig. 9. pH of leaching solutions *vs.* melting time for the samples fused at 850°C with different mass ratios of carbonate to sulfide.

The solution containing sodium molybdate is then treated with H_2SO_4 to adjust the pH at 2-3. At this stage, by decreasing the pH, MoO_4^{2-} anions change to $Mo_7O_{24}^{6-}$ according to the following reaction.

$$7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O \qquad (11)$$

$Mo_7O_{24}^{6-}$ is less soluble in aqueous solutions compared to other molybdates [10]. So the precipitation process of molybdenum at pH 2-3 will have a high efficiency.

The solution is then treated with ammonium chloride for precipitating the molybdenum as ammonium molybdates according to the following reactions.

$$Mo_7O_{24}^{6-} + 6NH_4^+ = (NH_4)_6Mo_7O_{24} \quad (12)$$

$$(NH_4)_6Mo_7O_{24} + 4H_2O = (NH_4)_6Mo_7O_{24} \cdot 4H_2O \quad (13)$$

Then, the precipitates were filtered and washed with warm water. Fig. 10 shows the XRD pattern of the precipitated product. It indicates that the products are mainly ammonium molybdates.

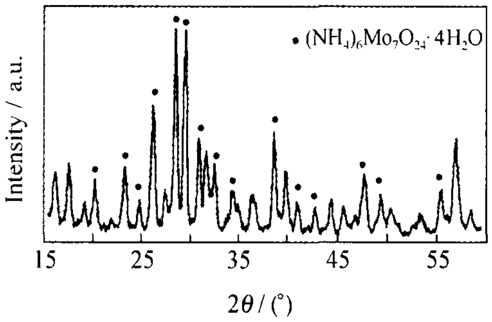

Fig. 10. XRD pattern of the precipitated product with ammonium chloride.

Finally, the product was calcined at 490°C, where the ammonia escaped out, leaving molybdenum trioxide as the final product.

4. Conclusion

The alkali fusion was found to be suitable for molybdenum extraction, where a water-soluble molybdate product is obtained in a one-step operation. The molybdenite alkali fusion was carried out in the presence of oxygen. The study shows that at the first stage, sodium carbonate is calcined to Na_2O and CO_2, and then Na_2O reacts with MoS_2 to produce Na_2S and MoO_2. At the next stage, MoO_2 reacts with oxygen and MoO_3 is formed. Then, MoO_3 reacts with Na_2O to produce soluble sodium molybdate. The solubility of the products decreases with the formation of sodium dimolybdate if the mass ratio of carbonate to sulfide is less than the stoichiometric ratio. After leaching of the fused products, molybdenum is recovered from the solutions as ammonium molybdate.

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