

Separation chemistry in the refining of an off-grade molybdenite concentrate by leaching with an acid mix

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Abstract

Off-grade molybdenite concentrates, mainly derived from secondary sources as by-products of the processing of copper, uranium and tungsten ores, do not satisfy the purity requirements (percent MoS₂) for the production of molybdenum bearing products. This investigation is a continuation of a successful effort to refine a low-grade molybdenite concentrate to prepare a high-grade MoS₂ using a mixed acid (HF + HCl) leach procedure. Specifically, this investigation is concerned with an understanding of the separation chemistry underlying the removal of the oxide/silicate gangue and the base-metal sulfide associations present in the low-grade molybdenite by their selective dissolution in the two acids. Experiments were conducted on an off-grade concentrate containing 42.6% Mo. Results of the controlled dissolution tests indicate that both HCl and HF are suitable for the removal of the associated alumina and both work well for iron, nickel and copper. However, HF was found to be the most effective for dissolving silica/silicate and magnesia. An attempt was made to rank the leaching efficiencies of the acids used singly, sequentially or in a mixed mode. Scale-up (300 to 2,000 g) experiments were conducted to validate this approach. Excellent purification of the concentrate was possible by processing the off-grade concentrate with 10% HCl plus 15% HF at 363 K for 7.2 ks in open polypropylene reactors with internal stirring. These conditions leached practically all of the oxide and silicate gangue and 96% of the metallic impurities. Starting from the low-grade molybdenite concentrate (42.6% Mo; 71.1% MoS₂) it was found feasible to obtain a refined product containing 97.8% MoS₂, which is suitable for industrial use.

Key words: Molybdenite, Leaching, Refining

Introduction

High-grade molybdenite (MoS₂) is practically the only source for the production of molybdenum metal, its alloys and compounds. The bulk of the World's molybdenite production is confined to a few countries, with major producers being the United States, Chile, China, Peru, Canada, Armenia, Mexico and Russia (Magyor, 2005). Generally, molybdenite concentrates produced from the primary ores are high grade, and those containing about 95% MoS₂ are preferred for industrial use. On the other hand, molybdenite concentrates derived from secondary sources (e.g., by-products from the processing of copper or uranium mining) are low-grade and, hence, do not meet the purity requirement for use as raw material to produce molybdenum bearing products.

Two options may be considered for the utilization of off-grade concentrates. The first option is the dissolution of the MoS₂ present in the concentrate and conversion of the resulting salt or salts to MoO₃ or CaMoO₄. The sec-

ond option is the selective dissolution of the gangue and associated base metals, leaving behind an enriched MoS₂ concentrate that may be used like any high-grade MoS₂ concentrate. In this investigation, the second option was exercised. Many approaches have been reported on the refining (purification) of low-grade molybdenite concentrates. One approach involves repeated flotation of the low-grade concentrates by techniques such as column flotation (Rao and Sastry, 1998). In such attempts, upgrading is generally limited to 54% to 55% Mo (90% to 92% MoS₂). Besides inadequate refining, the recovery decreases with every successive flotation. A better approach seems to be the selective removal of the gangue by using lixivants such as HCl (Forward and Warren, 1960), mixed chlorides (e.g., FeCl₃ + NaCl + CaCl₂) (Jennings et al., 1973; Saha et al., 1985a), dichromate plus H₂SO₄ (Ruiz and Padilla, 1998), HF plus a chloridizing roast (Saha, 1998), HF followed by HNO₃ in the presence of chloride salts (Saha et al., 1985b), acid pug (Spedden et al., 1971) and HF plus HCl

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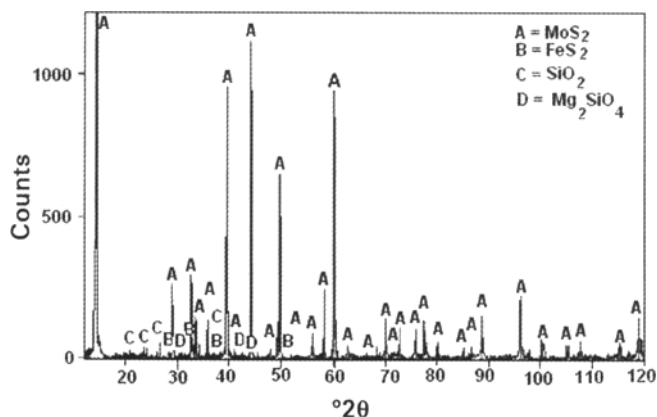


Figure 1 — XRD pattern of the low-grade molybdenite concentrate

(Mankhand and Prasad, 1982). Of these, the mixed (HF plus HCl) lixiviant appears to be most promising.

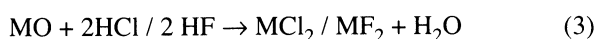
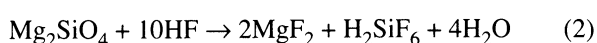
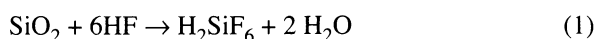
Earlier investigations (Prasad et al., 1999; Kumar, 2004) on an indigenous low-grade molybdenite concentrate (generated as a by-product at the Uranium Corporation of India Ltd., Jaduguda) established the feasibility of preparing a refined MoS_2 of high-grade suitable for industrial applications. Results of these studies on the refining of the off-grade molybdenite concentrate deploying dilute (HF plus HCl) lixiviant are summarized in Appendix A. However, being concerned with evolving a process for molybdenite refining, namely, the removal of the unwanted constituents and the potential applications for the product, the above work did not address the separation chemistry aspects. Hence, the present investigation is concerned with an understanding of the dissolution chemistry underlying the purification of an off-grade molybdenite concentrate similar to that used by Prasad et al. (1999) and Kumar (2004) and procured from the same source.

Chemical basis of upgrading molybdenites

The chemistry of refining of any off-grade molybdenite concentrates is essentially based on five assumptions:

- Being inert, molybdenite (MoS_2) is not attacked by non-oxidizing acids and pyrite (FeS_2) is refractory and does not dissolve in acidic media (Natarajan, 1990).
- Silicate gangue readily dissolves in hydrofluoric acid.
- A dilute mineral acid (e.g., HCl) can leach out the oxide gangue (nonsilicate) and base-metal sulfides.
- Any other minor oxide gangue (e.g., Al_2O_3 and CaO) and trace metal associations (e.g., ZnS, PbS and CdS) can also dissolve in one or both the acids.
- When the dissolved oxygen availability is high (as in open reactors), the elemental S^0 will get converted to sulfates.

The chemical reactions involved are as follows:



Materials and methods

Materials. A low-grade molybdenite, procured from the Uranium Corporation of India Ltd., (UCIL, Jaduguda), was analyzed and found to contain 42.6% Mo, 31.0% S, 1.0% C, 10.5% SiO_2 , 8.0% MgO, 1.4% Al_2O_3 , 4.3% Fe, 0.5% Ni and 0.3% Cu. The mineral phases, identified by XRD, include molybdenite (MoS_2), magnesium silicate (Mg_2SiO_4), pyrite (FeS_2) and free silica (SiO_2) (Fig. 1). The concentrate was found to be fine sized (75% -70+30 μm and 20% -30+20 μm), and it was not radioactive.

Techniques for characterization and chemical analyses. For identification of mineral phases in the feed and products X-ray diffraction (Xpert Pro, manufactured by Phillips) was used. Chemical analyses were carried out by a judicious combination of techniques such as Atomic Absorption Spectrometry (Varian, Model Spectra AA), UV Visible Double Beam Spectrophotometry (Elico India Ltd., Model SL 164), complexometry, gravimetry and titrimetry.

Procedures. The procedures used are as follows:

Separation/dissolution chemistry: Because considerable process information is available on the refining of a similar off-grade molybdenite concentrate, the conclusions from those studies (Prasad et al., 1999; Kumar, 2004) formed the basis of this investigation. Dissolution tests were conducted on 10 g samples of the off-grade molybdenite concentrate using glass or polypropylene beakers (depending on the lixiviant) using 100% excess quantity of 10% (by weight) of the acids (HCl, HF). The acids were added singly, sequentially or in a mixed mode at 363 K, 14.4 ks and 700 rpm using a magnetic stirrer. After each test, the product was filtered and washed. The leach liquors and purified molybdenites (residues after dissolution) were analyzed for Mg, Al, Fe, Ni, Cu, Si and SiO_2 .

Scale-up tests: Cylindrical reactors of varying capacities (2,000 to 10,000 cm^3) made of polypropylene with provision for external heating and fitted with appropriate mechanical stirrers were deployed for the refining tests (300 to 2,000 g level). All the experiments [controlled (10 g) as well as scale up (300 and 2,000 g)] were conducted at least twice, and the average values were reported. The effectiveness of separating the MoS_2 (the extent of purification) from the undesirable silicate, oxide and base metal associations was judged by analyzing the products for Mo and in typical cases complete analysis.

Results and discussion

It is relevant that a fully refined molybdenite (MoS_2) will contain a maximum of 59.94% Mo (theoretical limit) and to note that molybdenite mineral and carbon (known to be associated with molybdenite ores as graphite) as well as pyrite (FeS_2) do not dissolve in non-oxidizing lixivants.

Separation/dissolution chemistry. Results of the tests carried out to understand the effectiveness of the two lixivants (HCl and HF), used singly, sequentially and in mixed mode, are presented in Table 1 and in Fig. 2. The extent of removal of each constituent was judged from its quantity reporting to the leach liquors.

Removal of oxide gangue: Results presented in Fig. 2 (a) indicate that in leaching with HCl, only 9% of the silica and 12% of the MgO present in the concentrate were removed and practically the whole of alumina was dissolved out. On the other hand, the bulk of all the oxides were found to dissolve in the hydrofluoric lixiviant — almost all of the alumina, 97% of the silica and 89% of the magnesia. These findings

Table 1 — Effectiveness of the different lixivants for dissolution — removal of gangue.

Quantity of the off-grade molybdenite concentrate: 10 g
 Lixiviant (HCl, HF or mixed): 10% (by weight)
 Quantity of lixiviant: 100% excess
 Temperature: 363 K
 Stirring speed: 700 rpm
 Duration: 14.4 ks

Constituents	Quantity (g) in 100 g of the molybdenite concentrate	Quantity (g) found in the leach liquor generated by using the lixiviant			
		HCl	HF	Sequential (HCl; HF)	Mixed (HCl + HF)
Oxides	Silica	0.94	10.23	10.3	10.25
	Magnesia	0.97	7.12	7.85	8.0
	Alumina	1.4	1.4	1.4	1.4
Metals	Iron	3.76	3.79	3.88	4.17
	Nickel	0.43	0.33	0.43	0.47
	Copper	0.25	0.22	0.22	0.24

are in conformity with the observations recorded by the XRD studies on the refined products. A comparison of Fig. 1 with Fig. 3 (a) clearly indicates the absence of Mg_2SiO_4 in the hydrofluoric-leached product. In addition, the peak height of magnesium silicate is seen to be significantly higher in the case of hydrochloric-refined product (compare Fig. 3 (b) with Fig. 1). As regards the removal of oxides as a whole (Fig. 2 (c)), HCl is seen to be a poor lixiviant and HF the most effective, which can be inferred from 17% and 94% removal, respectively, by the said lixivants. The superiority of hydrofluoric lixiviant for the effective removal of silica, magnesia, magnesium silicate and other related silicates is

understandable, as it is capable of attacking all of them. On the other hand, hydrochloric acid can remove only alumina, aluminosilicates and free MgO, if any.

Removal of metallic associations: Relevant results are presented in Table 1 and in Fig. 2 (b) and (c). It is obvious from these results that both the hydrochloric and hydrofluoric lixivants are of equal potency for the removal of metallic (total Fe + Ni + Cu) associations (85% to 87%). However, from Fig. 2 (b) it is clear that there seems to be subtle differences in respect to the dissolution efficiencies for Cu and Ni; hydrochloric acid appears to be a better lixiviant. Moreover, the authors note that the dissolution – removal of metallic associations is in

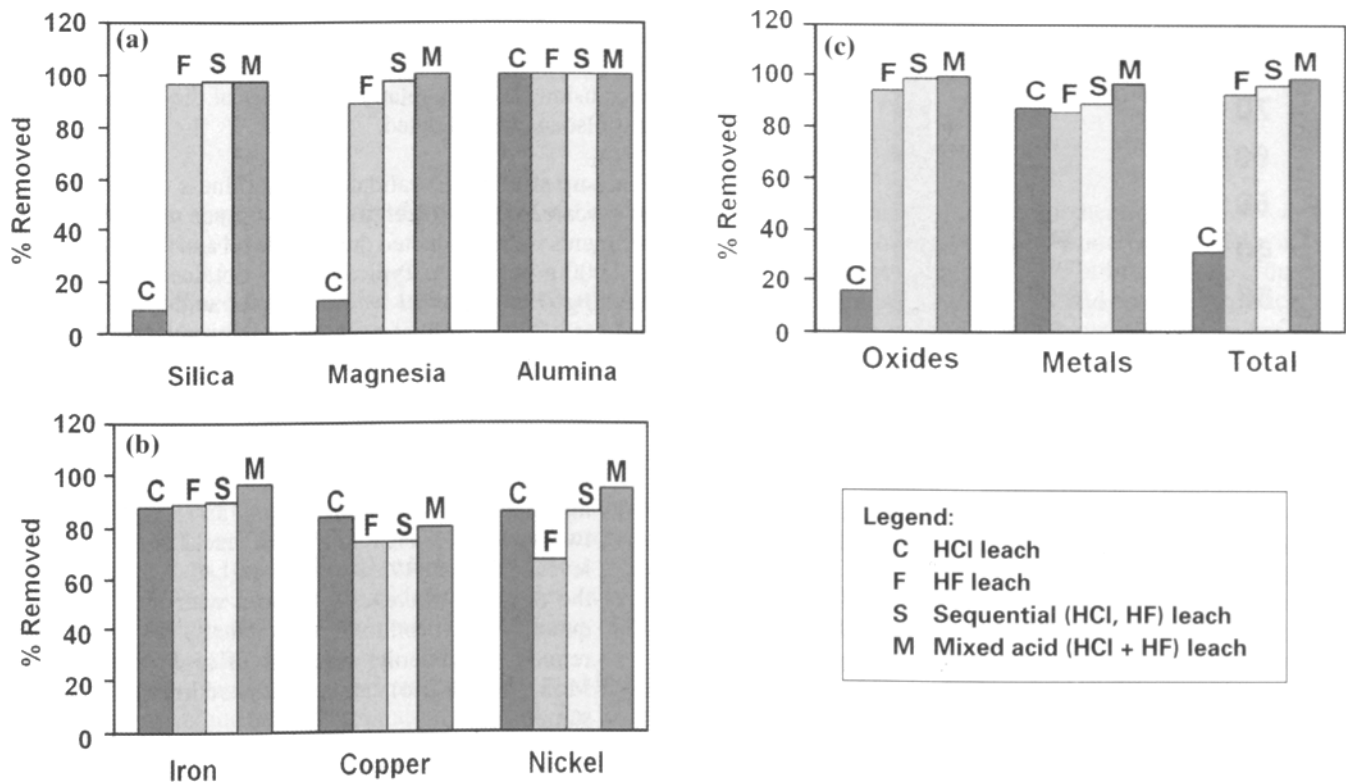


Figure 2 — Effectiveness of the lixivants for the refining of the low-grade molybdenite concentrate: (a) percent removal of individual oxides, (b) percent removal of individual metals and (c) percent removal of all gangue.

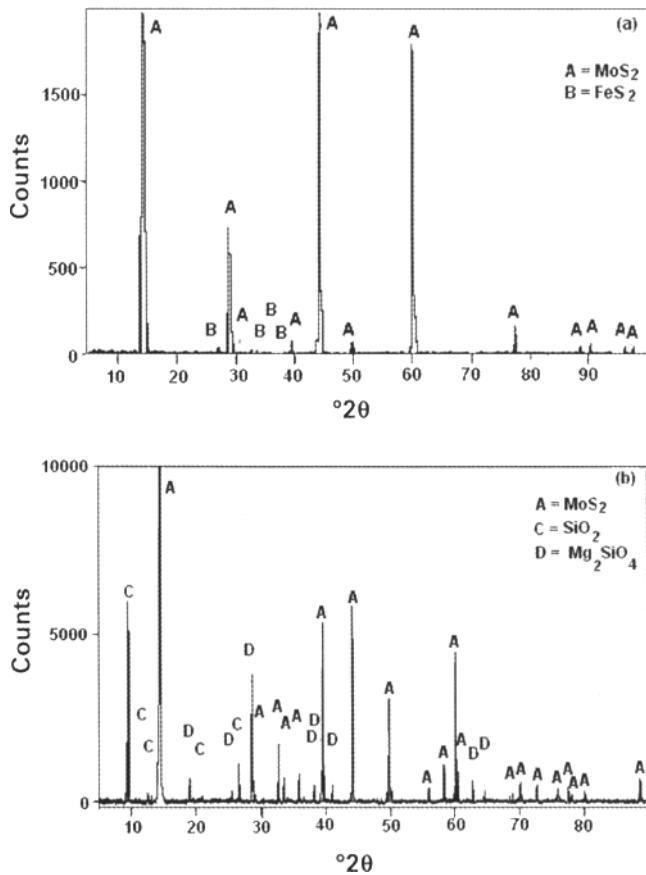


Figure 3 — XRD pattern of the refined molybdenite concentrate: (a) using hydrofluoric acid and (b) using hydrochloric acid.

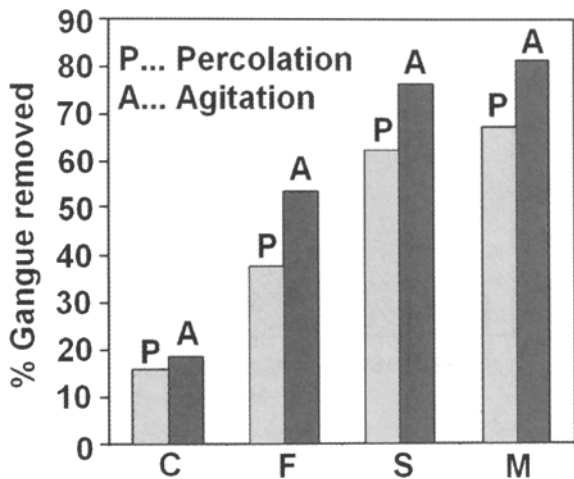


Figure 4 — Comparison of the effectiveness of percolation with stirred leach at 300 K for 7.2 ks: lixiviant 10% (by weight) and 100% excess.

accordance with the galvanic series for sulfides in acidic media reported by Natarajan (1990). To clarify further the detection of pyrite (FeS₂) in the refined molybdenite and finding no molybdenum in the leach liquor are noteworthy.

Sequential versus mixed acid leaching: To realize the potential of both lixivants (HCl and HF), in practice their

deployment was tested sequentially (HCl followed by HF) and in a mixed mode. Careful examination of the results presented in Table 1 and Fig. 2 (c) indicates that, though the overall removal of the oxides (individual and total) is nearly the same in sequential and mixed modes, the latter (i.e., mixed acid lixiviant) is slightly better (Table 1). Regarding the removal of the Fe, Ni and Cu and their total, the mixed lixiviant offers a greater promise. To be specific, whereas sequential leaching enabled up to 89% removal, mixed acid leach resulted in a 96% removal of these metals.

Overall removal of all gangue (oxides and metals): If one considers the overall removal all the gangue constituents (see Table 1 and Fig. 2c) present in the low-grade molybdenite concentrate feed, the leaching efficiency of hydrochloric acid is only 31%, as compared to 85% removal by the hydrofluoric lixiviant. Interestingly, though both the sequential and mixed acid leaches are quite effective for achieving excellent overall refining, purification by the latter seems to be distinctly superior. This may be attributed to the synergistic effects that may prevail when using the acid mix, enabling simultaneous attack by fluoride and chloride ions on the oxide gangue as well as the associated base metal sulfides. Thus, the following ranking can be assigned to the different lixivants for delineating their effectiveness for molybdenite refining:

- | | |
|------------------------------------|-------------|
| • Hydrochloric acid: | Poor |
| • Hydrofluoric acid: | Very potent |
| • Sequential — HCl followed by HF: | Excellent |
| • Mixed acid — HCl + HF: | Outstanding |

For a better understanding of the leaching process, dissolution tests were conducted in the percolation and stirred modes at room temperature. From the results presented in Fig. 4 it is obvious that percolation leach is not as efficient as the leaching under stirred conditions with any of the lixivants. Further, the earlier observation that for achieving a higher level of refining of the molybdenite, treatment with mixed acids (HCl + HF) is superior to the sequential mode (see Table 1 and Fig. 2) is confirmed there by indicating the synergism in leaching. The conclusion about the relative potencies of the different lixivants also stands validated.

Scale-up studies. To validate the usefulness of the results of 10-g-scale tests on the refining of low-grade molybdenite, experiments were conducted on 300-g level and further upscaled to 2,000 g per batch. Typical results obtained by sequential leaching (HCl followed by HF), mixed acid leach on 300-g scale as well as the final scale up are presented in Table 2. A scrutiny of the results reveals the following:

- excellent leaching efficiencies of hydrofluoric acid, which is eight times more effective than the hydrochloric lixiviant;
- mixed acid lixiviant consisting of any proportion of the two acids (10% HCl or 15% HF each) enable a similar level of refining (95% to 96%);
- the refining efficiency enhances with increase in the quantity of hydrofluoric acid; and
- refined molybdenite products of high grade (97.8% MoS₂; 58.6% Mo) can be produced irrespective of the sample size.

An additional observation from the results presented in Table 2 concerns the good potential for recycling the mother liquor to prepare an intermediate product containing 55% Mo.

Table 2 — Scale-up tests on the refining of an off-grade molybdenite.

Sample size:	300 g	Duration:	7.2 ks
Temperature:	363 K	Reactor:	Polypropylene, cylindrical
Stirring speed:	300 rpm		

Method	Lixiviant				Product grade		Refining, %
	HCl		HF		Mo, %	MoS ₂ , %	
	Wt%	Excess, %	Wt%	Excess, %			
Sequential (HCl followed by HF)	10	200	–	–	44.6	74.4	12
	–	–	15	200	58.7	97.9	98
Mixed	10	200	15	200	58.2	97.1	95
	15	200	15	200	58.6	97.8	98
Effect of quantity of HF (HCl constant) (given as percent excess)	10	50	15	10	52.3	87.3	59
	10	50	15	30	53.3	88.9	65
	10	50	15	50	54.9	90.3	75
Scale-up test (2,000 g)	10	200	15	200	58.6	97.8	98
					Recycle liquor ¹ :		78
					55.4	92.4	

¹Mother liquors from all the scale-up tests deploying mixed (HCl + HF) acid lixiviant.

Table 3 — Comparison of the grades of different molybdenites.

Type of molybdenite	Constituent, wt%					
	MoS ₂	Acid insol.	Fe	Cu	Ni	C
Low-grade molybdenite concentrate (input)	71.1	1.4	4.3	0.3	0.5	1.0
Refined molybdenite (product)	97.8	N.D.	0.18	0.07	0.04	1.4
Climax technical-grade molybdenite (imported)	98.1	0.27	0.17	–	–	1.0
Lubricant grade: Technical ¹	96.85-97.13	0.5	0.3	–	–	1.8-1.9

¹Source: M/s Electro-Ferroalloys Ltd., Ahmedabad, India.

Obviously a two-stage countercurrent leaching would enable optimal utilization of the lixiviant.

Grade of the refined molybdenite and effluent treatment.

The grade of the refined molybdenite prepared in this study is found to compare well with that of a technical- (high-) grade molybdenite of the Climax Molybdenum Company and also satisfy the grade for direct industrial usage (e.g., Lubricant-grade MoS₂) (Table 3). Further, the effectiveness of refining of the low-grade molybdenite concentrate achieved in this study can be gauged by an examination of the XRF patterns. Comparisons of the concerned XRF peaks taken on our refined molybdenite product vis-à-vis the reference technical grade molybdenite (Climax) give a good idea of the relative presence of the constituents (it may be noted that the scales of the Y-axis (KCPS) are different).

From Figs. 5A and 5B, it is obvious that the Si (and hence silica; (a)) and Al (and hence alumina; (b)) contents are lower and Mg (and hence magnesia; (c)) content is similar. As for the contained metals (Fe, Ni and Cu; (d)), their percent is low and within acceptable limits in the refined product but slightly higher than in the reference molybdenite. Before concluding,

it should be mentioned that the mother liquor generated in the refining of the low-grade molybdenite was treated with soda ash to ensure environmental compatibility of the effluent. In the process, sodium silicofluoride and cryolite were recovered by selective precipitation, respectively, at pH values of 1.5 and 2.2.

Conclusions

From the controlled dissolution tests conducted on the off-grade molybdenite (a by-product of uranium ore processing and, hence, a secondary source) and the subsequent scale-up tests, the following conclusions were made:

- Though practically complete removal of alumina is feasible with either hydrochloric or hydrofluoric acid lixiviants, the latter is the most potent for the removal of the other oxide gangue, namely, magnesia and silica (silicates).
- Very good removal (87% to 88%) of the associated iron can be achieved with equal effectiveness by using any of the two lixiviants.

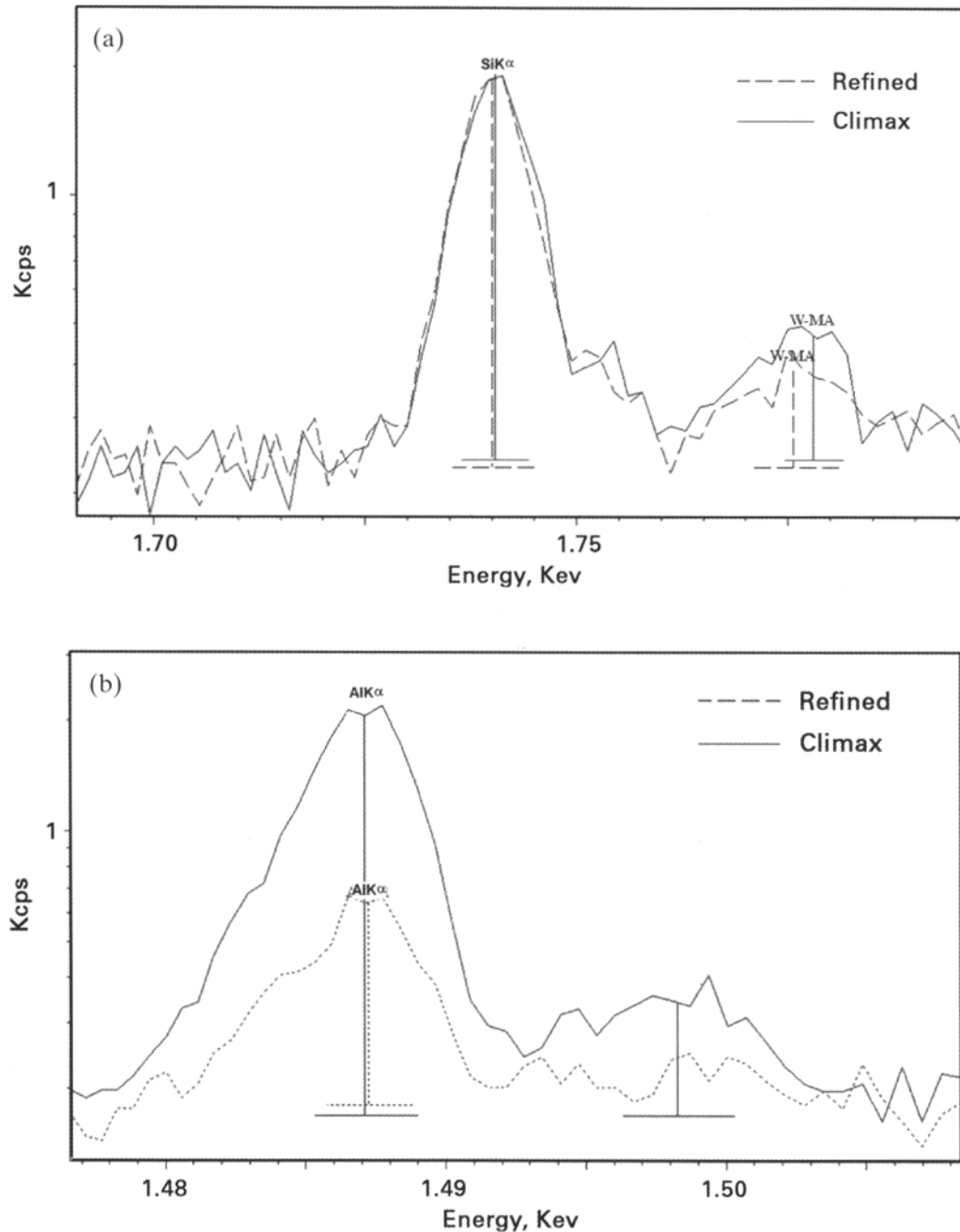


Figure 5A — XRF patterns comparing the impurity levels in the refined molybdenite of this study with a technical- (high-) grade molybdenite of the Climax Molybdenum Company: (a) Si and (b) Al.

- Compared to hydrofluoric acid, hydrochloric acid exhibits a better ability to dissolve out the associated copper (83% and 73%, respectively) and nickel (86% and 66%, respectively).
- The highest level of refining (99% removal of all gangue plus metals) can be realized by deploying the lixiviants in the combined mode — leaching with mixed acids (dilute HCl plus dilute HF) may be preferred over their sequential deployment, viz., HCl followed by HF.
- Results of the controlled refining tests have been reproduced in the scale-up studies.
- The grade of the refined molybdenite product prepared in this study (97.8% MoS₂) compares well with that of technical/high-grade molybdenite produced by the Climax Molybdenum Company.

Acknowledgment

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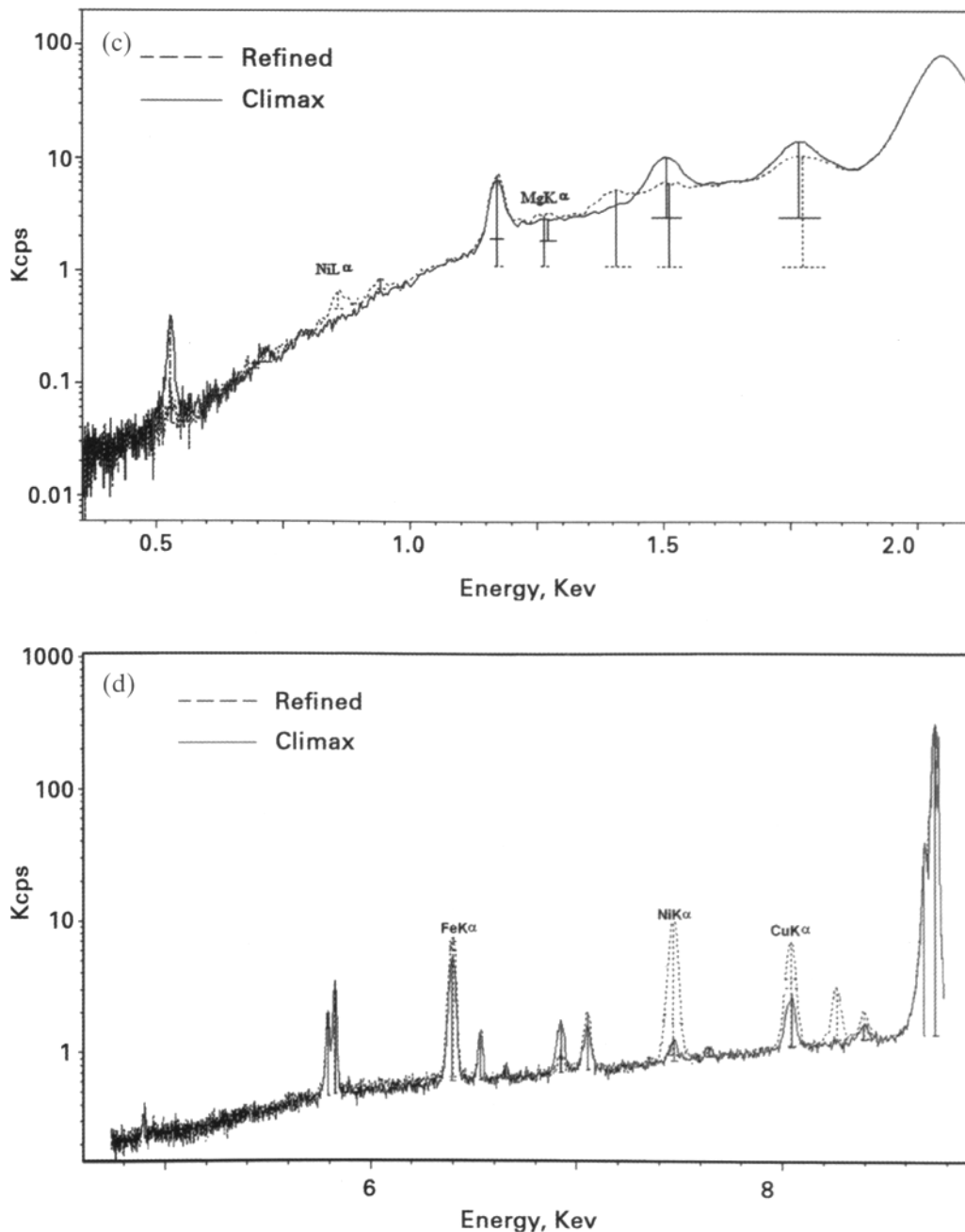


Figure 5B — XRF patterns comparing the impurity levels in the refined molybdenite of this study with a technical- (high-) grade molybdenite of the Climax Molybdenum Company: (c) Mg and (d) Fe, Ni and Cu.

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Appendix A — Summary of findings on the refining of a low-grade molybdenite concentrate.¹

Acid	Conc. Wt%	Percent excess	Temp., K	Time, Hours	Grade of product		Refining, %
					Mo, %	MoS ₂ , %	
HCl	5	200	368	2	42.7	71.2	7
				4	42.9	71.5	8
HCl	7.5	120	378	2	43.9	73.2	14
			388	2	44.1	73.5	15
			398	2	44.3	73.8	16
HCl	7.5	120	388	4	44.5	74.2	17
	10	100	388	2	46.8	73.0	13
	15	100	388	2	43.9	73.2	14
HF	5	25	293	2	46.8	78.0	30
	5	25	293	4	47.7	79.5	36
	5	25	293	8	49.1	81.8	44
Sequential: HCl, HF	7.5	120	388	2	44.1	73.5	15
	5	None	358	2	51.9	86.5	60
	10	None	358	2	54.9	91.5	77
Mixed: HCl + HF	5	200	363	2	55.6	92.7	81
	5	25	383	2	56.3	93.8	85
	5	25	403	2	56.9	94.8	88
	5	25	403 ²	2	58.6	97.8	99

¹ Compiled from the work of Prasad et al. (1998) and Kumar (2004) on low-grade molybdenite from UCIL concentrate containing 41.5% Mo (69.2% MoS₂).

Note : Percent refining was calculated by the above authors based on the assumption that on complete removal of the gangue, the fully refined molybdenite will contain 98.2% MoS₂ and ~1.7% C. Thus, the percent refining = $\frac{((\text{Percent MoS}_2 \text{ in the product} - 69.2)/29.0) * 100}{1}$, where 29% represents the difference between the fully refined and input molybdenites.

² Well stirred at 1,540 rpm; 100 g tests. In all the other tests there was no mechanical stirring.

Note: For sequential leaching with HF, the pre-refined product (HCl leached) was used.