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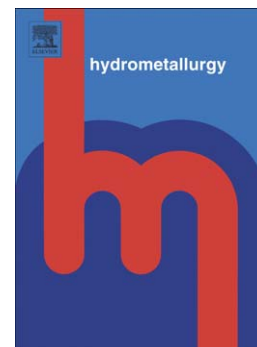
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Purification of molybdenum trioxide calcine by selective leaching of copper with HCl-NH₄Cl

By

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ABSTRACT

The leaching of Mo, Cu and Fe from MoO₃ calcines (59-61% Mo) containing 1-2% Cu, 1-2% Fe and other impurities produced from roasting molybdenite (MoS₂) concentrate was examined using water and a series of chloride lixiviants, including NH₄Cl (0.6M), HCl (0.115 – 1.40M) and a mixture of HCl (0.70M) + NH₄Cl (0.1 – 0.93M) at a solid/leachant (w/v) ratio of 1:1 and within the temperature range 25-70°C. Stabcal modeling showed there are many compounds formed from Cu, Fe and Mo co-exist in the solution. Optimisation studies show that HCl solutions of concentrations ≥ 0.35 M are capable of dissolving >80% of Cu within 1 hour. The addition of NH₄Cl (0.30 - 0.93M) to 0.7 M HCl reduces the dissolution of Mo to <0.5%, due to the formation of a precipitate containing mainly NH₃(MoO₃)₃, as confirmed by X-ray diffraction. A mixture of 0.7M HCl and 0.6M NH₄Cl at ambient temperatures removes Cu to <0.5% within 2 hours, as required for the production of Fe-Mo alloys at Kwangyang Ferro Alloys Co. (Korea). Although not required, Fe was removed to <0.6% whereas most other metal impurities were removed to <0.1%. Pilot plant trials over 7 campaigns, each treating 2.0-2.2 tonnes of MoO₃ calcine containing 2.1% Cu using 1.44M NH₄Cl and 0.97M HCl at an ambient temperature yielded final products containing 0.22% Cu as required. Mass balance calculations (closure to 96-99%) of the pilot plant trials confirm that the Mo loss during leaching is around 0.5%.

Research Highlight

- ✓ We determine the process chemistry of leaching Cu from MoO₃ calcine to reduce its content to <0.5%

- ✓ The optimum leaching conditions to treat calcines containing 1% Cu (0.6M NH_4Cl , 0.7M HCl at ambient temperature) were adopted to remove impurities to <0.5% Cu, <0.6% Fe and <0.1% for other impurities
- ✓ The dissolution of Mo by acid was minimized by the precipitation of ammonium molybdate
- ✓ Stabcal was used to model the speciation of the dissolution process.
- ✓ Pilot plant trials were conducted to treat 14 tonnes of calcines to confirm the results before plant operations were implemented.

Keywords: MoO_3 calcine, Cu dissolution, precipitation, ammonium molybdate, Stabcal modeling

1. Introduction

Molybdenum trioxide (MoO_3) has been traditionally produced by oxidative roasting of flotation concentrates produced from molybdenite (MoS_2) ores (Gupta, 1992). As the resources of high grade molybdenite are dwindling, most mineral processing plants have to treat lower grade or more complex and dirty ores. This scenario presents a great challenge to other end users as a low-grade MoO_3 cannot be used for the production of Fe-Mo alloys or hydrodesulphurization catalysts required in the petroleum refining process. An alternative secondary source of Mo is from hydrodesulphurization spent catalysts, which contain both Mo oxide and sulphide (Zeng, and Cheng, 2009a,b). These materials require oxidative roasting or leaching before MoO_3 can be recovered.

The direct roasting of molybdenite concentrates to produce MoO_3 calcines retains impurities such as Cu, Fe, Mg, Ca, K and many non-volatile oxides, except As and Re, which render themselves in the roaster's fume. A hydrometallurgical route which includes leaching of the roasted product (MoO_3) and other separation techniques such as solvent extraction, ion exchange and precipitation is therefore required to remove these impurities (Misra et al., 2010) before a high grade Mo product (>99.5% MoO_3) can be recovered. The process has been previously reviewed by Marafi and Stanislaus (2008) and Zeng and Cheng (2009b).

Junegar and co-workers (1996) roasted a low grade concentrate (20-45% Mo, 0.35% Cu, 0.17% Ni, 1.62% Fe) with slaked lime or soda ash at 550-650°C, followed by leaching in sulphuric acid or water to recover 99% of Mo from the feed. The dissolved Mo was recovered by

activated carbon (>98% recovery), which was then precipitated as oxide at pH2. The MoO_3 product contained less than 200 mg/kg totally of all 11 impurities measured.

Shariat and co-workers (2001) treated a MoO_3 calcine (60.9% Mo, 1.3% Cu, 2.9% Fe, 0.16% S and 1.2% SiO_2) by first dissolving it in ammonium hydroxide. The leach liquor was then treated with ammonium disulphide to remove Cu and other base metals before precipitating molybdic acid (H_2MoO_4) at pH2. The precipitate was then dissolved again in ammonium hydroxide from which ammonium paramolybdate ($3(\text{NH}_4)_2\text{O} \cdot 7\text{MoO}_3$) was re-crystallised at 60°C. The final roasted MoO_3 product contained less than 1 mg/kg each of Ca, Fe, Cu, As and 10 mg/kg of Sb.

The removal of impurities from calcines or partially roasted materials containing MoO_3 , MoO_2 and MoS_2 has also been dealt with in several patents. Brunelli and co-workers (1985) disclosed a process for removing K, Fe, Cu, Mg, Ca, etc. from an impure MoO_3 calcine, which involved leaching with a mineral acid (nitric, sulphuric or hydrochloric) mixed with an ammonium salt (nitrate, sulphate or chloride) within the temperature range 50-100°C. The use of a higher acid/ MoO_3 ratio (2.4-4.8% wt/wt) for leaching reduced K to < 50 mg/kg, but caused a higher dissolution of Mo in the leach (1-1.8%). The final stage involved re-dissolving the treated MoO_3 in ammonium hydroxide and recrystallisation to recover high purity ammonium molybdate compounds.

A similar approach based on the precipitation of magnesium complex salts (phosphate and arsenate) was patented by Cheresnowsky (1989) to deal with other impurities (As, P) which are difficult to be removed. The procedure involved an acid digestion to dissolve all metal impurities, followed by the addition of Mg salts and $\text{NH}_3\text{-H}_2\text{O}$. This process precipitated P (as MgNH_4PO_4) and As (as $\text{MgNH}_4\text{AsO}_4$) in addition to other metal hydroxides. The solubilised ammonium molybdate was re-crystallised. In another patent (Ronzio et al, 1976) different methods have been used to directly dissolve MoO_3 in $\text{NH}_3\text{-H}_2\text{O}$ and precipitate all metal impurities simultaneously.

These patents and earlier papers however did not deal with the high loss of Mo during acid leaching. The role of ammonium ions in precipitating ammonium molybdate compounds at a pH<2 and 80-90°C, yet solubilising MoO_3 at pH>9 has not been well understood. There is a

need therefore to study the different mechanisms governing the dissolution and precipitation processes taking place during the treatment of MoO_3 calcines to remove metal impurities.

The $\text{HCl-NH}_4\text{Cl}$ leaching system is the preferred process adopted at Kwangyang Ferro Alloys (KFA) to treat impure MoO_3 calcine to produce an intermediate product low in Cu ($<0.5\%$) as required by its Fe-Mo alloy plant. This paper therefore deals with the chemistry of the process employed for producing the intermediate MoO_3 product containing $<0.5\%$ Cu used as feedstock for Fe-Mo alloy making at KFA. The paper presents a brief review of chemical speciation, followed by simulation of leach conditions using the Stabcal program and results of leaching studies, using water and solutions of HCl , NH_4Cl and $\text{HCl}+\text{NH}_4\text{Cl}$ at different concentrations and temperatures. The removal of other minor impurities such as Mg, Zn, As, Mn, etc. is also reported.

2. Review of chemical speciation and Eh-pH diagrams of Mo solutions

The solubility of pure $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ varies with temperature, ranging from 2.12 g/L at 15°C to 5.185 g/L at 80°C (Gupta, 1992). Ryzhenko (2010) reported the dominance of MoO_2^{2+} in dilute (<1 mg/L Mo) acidic solutions ($\text{pH} < 1$) as found in groundwater systems (10^{-8} M Mo). Other cationic species such as $\text{H}_6\text{Mo}_2\text{O}_8^{2+}$, H_3MoO_4^+ could also exist in solutions of $\text{pH} < 2.5$ (Zeng and Cheng, 2009; Olazabal et al., 1992). It is generally believed that only MoO_4^{2-} exists at $\text{pH} > 6.5$, whereas there are neutral and anionic species such as H_2MoO_4^0 , $\text{Mo}_6\text{O}_{13}^{2-}$, $\text{Mo}_6\text{O}_{20}^{4-}$, $\text{Mo}_7\text{O}_{21}(\text{OH})_3^{3-}$ in the pH range 2.5-6.5 (Zeng and Cheng, 2009b; Gupta, 1992).

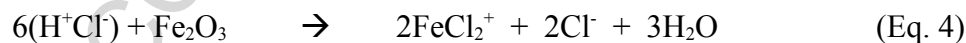
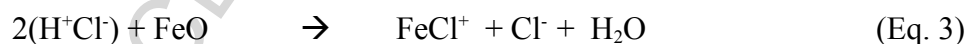
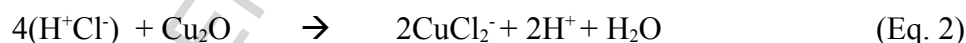
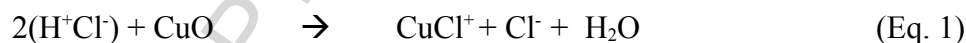
There is a possibility of re-precipitation of molybdate salts from Mo(VI), Fe(III) and Cu(II) ions formed during leaching (Gupta, 1992). Iron(II) molybdate FeMoO_4 cannot be formed from an aqueous solution containing Mo(VI) and Fe(II), as Fe(II) is oxidized to Fe(III) by Mo(VI) (Gupta, 1992). Iron(III) molybdate, $\text{Fe}_2(\text{MoO}_4)_3 \cdot \text{H}_2\text{O}$, is known to be sparingly soluble in the pH range 2.5-4.25 (~ 0.01 g/L Mo), but outside this range, the solubility of ferrimolybdate increases (Safarian and Furbish, 1965). Bright green copper molybdate can be precipitated as $\text{CuO} \cdot 3\text{CuMoO}_4 \cdot 5\text{H}_2\text{O}$ or $2\text{CuMoO}_4 \cdot \text{Cu}(\text{OH})_2$ (Gupta, 1992). Thus, it is important to examine the different species which may be formed or precipitated during the purification of MoO_3 containing Cu and Fe impurities on the basis of Eh-pH and species distribution diagrams.

Table 1 lists and compares standard Gibbs free energy data (ΔG°_f) (at 25°C) for molybdenum species reported by previous researchers and employed in various data bases. Significant differences in ΔG°_f of species such as $\text{MoO}_3(\text{s})$, H_2MoO_4 and CuMoO_4 shown in Table 1 are expected to be reflected in relevant species distribution diagrams. The speciation of Mo compounds (at 25°C) in the present study was modelled using the Stabcal program (Huang, 2008). Several solid species such as CuMoO_4 , $\text{Fe}_2(\text{MoO}_4)_3$, CuFeO_2 and CuFe_2O_4 at $\text{pH} > 1$ can be formed as shown in the Eh-pH diagram (Fig. 1) derived for 25°C. The software capability is limited to standard temperature and pressure conditions, therefore precluding the derivation of these diagrams at 70°C. Figs. 2a-d compare and contrast the species distribution diagrams for Mo(VI) solutions based on different data bases. Fig. 2d also shows dissolved Mo(VI) species in acidic solutions and the precipitation of CuMoO_4 at $\text{pH} > 2.7$ and Mo(VI) concentration greater than 0.28M. Fig. 2a shows that Mo(VI) can exist as H_2MoO_4 in highly acidic regions ($\text{pH} < 0.5$). Thus, the simulation proposes that CuMoO_4 could be precipitated alone or with H_2MoO_4 , MoO_3 or $\text{MoO}_3 \cdot \text{H}_2\text{O}$ from the leach solution at higher pH values. At higher concentrations of Mo (61 g/L or 0.63M) in the leach liquor, the H_2MoO_4 species seems to be predominant within the pH range 0-5.

The difference in the regions of stability for solid mixtures of ($\text{MoO}_3 + \text{CuMoO}_4$) or ($\text{H}_2\text{MoO}_4 + \text{CuMoO}_4$) in Fig. 2(a-d) are due to the different values of ΔG°_f from different databases (MinteqA2 or Russian or HSC) available in the Stabcal program (Table 1). Thus, the pH values at which the precipitation of CuMoO_4 takes place are at pH 0.6, 3.3 or 4.2 based on the three data bases MinteqA2, Russian or HSC, respectively. The standard Gibbs free energy of formation of ferri-molybdate, $\text{Fe}_2(\text{MoO}_4)_3$, of -2,719.968 kJ/mol (Table 1) as calculated from its formation constant of $K = 10^{35.29}$ (reported by Meima and Comans, 1998) was also included in the modelling. The simulation based on this value does not show the precipitation of $\text{Fe}_2(\text{MoO}_4)_3$ in the acidic zone in Figs. 2a-d, indicating the high solubility of $\text{Fe}_2(\text{MoO}_4)_3$ compared to H_2MoO_4 , MoO_3 or CuMoO_4 .

According to Fig. 2a, the dissolution of MoO_3 has to be conducted at $\text{pH} < 0.5$ in order to avoid the precipitation of Cu as copper molybdate species, which would remain in the refined MoO_3 calcine after treatment. There are other issues such as the formation of chloro-complexes

at increasing chloride content which affect the solubility of metal ions and kinetics of (Bryce and Berk, 1995; Kimura et al., 1984; Senanayake and Muir, 1988). Using Raman spectroscopy, Marston and Bush (1972) found that Fe^{3+} and FeCl^{2+} are more predominant at low ionic strengths whereas FeCl_2^+ and FeCl_3^0 are main species at higher concentrations of FeCl_3 . Above 4M FeCl_3 , the predominant species is FeCl_4^- . From the speciation modeling and distribution of these species reported in detail by Kimura et al. (1984), Awakura et al. (1987) and also recalculated by Bryce and Berk for FeCl_3 (0.5 - 3.5M) + HCl (0.85 - 2M), the predominant species for Fe(III) (74-90% distribution) is FeCl_2^+ . Chloro-complexes of Fe(II) and Cu(II) become more predominant at higher ionic strengths (Kimura et al, 1984), forming FeCl^+ , FeCl_2^0 , CuCl^+ and CuCl_2^0 . Copper(I) also exists in several complex forms, with the predominant species being CuCl_2^- and CuCl_3^{2-} as noted in published Eh-log[Cl⁻] diagrams (Senanayake and Muir, 1988, 2003). The following reactions are therefore possible for the dissolution of different Cu and Fe oxides from MoO_3 calcine in a chloride medium, highlighting the need for an investigation based on the leaching in HCl solutions of different concentrations to examine the maximum removal of Cu from the calcine.



2. Experimental

All chemical reagents used in the laboratory tests were of analytical grade. The MoO_3 calcine (61.6% Mo, 1-2% Cu, 1-2% Fe) used in the study was supplied from KFA. All experiments were performed by mixing 200g of MoO_3 calcine with 200mL of water or a leach liquor which contained known amounts of HCl (0-1.4M) and NH_4Cl (0.05-0.93M). The solid/leachant (w/v) ratio was fixed at 1:1 to minimize the wastewater generated from this washing process. The leaching was conducted at different temperatures (25, 50 and 70°C) for 2h using an overhead stirrer. Samples were taken at different time intervals, filtered using a 0.5 micron filter (Advantec 5C) and then analysed for Fe, Cu and Mo using ICP-AES. The

precipitate formed during the tests was collected and subjected to XRD analysis using a Rigaku D/MAS Ultima X-Ray diffractometer. The compositions of the untreated and treated calcines were also determined after full digestion and the resulting solutions and leach liquors analysed by ICP-AES. The solution potential (Eh) was measured using a platinum wire electrode relative to a standard calomel electrode (SCE) and pH of the solutions was also monitored throughout most tests.

3. Results and discussion

3.1 Characterisation of the untreated and treated MoO_3 calcines

Particle size analysis of the untreated MoO_3 calcine shows a size distribution in a wide range from $<1\ \mu\text{m}$ to $200\ \mu\text{m}$, with a mean particle size, d_{50} of $70\ \mu\text{m}$. Table 2 shows the elemental assay of a typical feed material, leach residue (recovered product) and the removal of each element (%) by the $\text{HCl-NH}_4\text{Cl}$ leaching process. At optimum conditions $>90\%$ of Cu can be removed. Similarly for other minor impurities such as Fe, Zn, Mn, Mg, etc., the removal is 60-80% (Table 2). The treated calcines in most cases reach the target of $<0.5\%$ Cu. Although not required most other impurities could be removed from the calcines to levels $<0.1\%$. The mapping of Mo, Fe and Cu, shown in Fig. 3, using Electron Probe Micro-Analyser (EPMA), indicated that there was no free Cu and Fe oxide left in the treated oxide. Most of the unleached Fe and Cu was distributed or trapped inside the microstructure of the MoO_3 particles.

3.2 Leaching in water

Figs. 4 and 5 show the changes in pH, solution potential (Eh) and concentration of Mo, Cu and Fe when 200 g of KFA MoO_3 calcine was mixed with 200 mL of distilled water at 25°C and 70°C . The initial rapid decrease in pH is followed by a slow decrease within 2 hours (Fig 4) indicating a continuous generation of acid throughout the test. The theoretical solubility for pure MoO_3 at 25°C and 70°C based on the equilibrium constant for Eq. 5 are 1.06 g/L and 20.5 g/L, respectively.

The initial dissolution of calcine in water therefore could be represented by the following

equation, showing the generation of hydrogen ions:



The dissolution of Mo from impure MoO_3 calcine after 2h, as shown in Figs. 5a-b, was much higher than that reported in the literature for pure Mo oxide (22 g/L and 60g/L Mo, at 25°C and 70 °C, respectively). The generation of H^+ ions from MoO_3 dissolution (Eq. 5) also causes the dissolution of Cu and Fe oxide. At 25°C Cu and Mo dissolution follow the same profile, resulting in ~3% Cu or Mo dissolution after 2 hours (Fig. 5a). These values increase to ~20% for Cu and ~8% for Mo at 70°C (Fig. 5b). The iron dissolution after 2 hours increases from 20% at 25°C to 50% at 70°C (Fig. 5). The measured potentials within 210-220 mV (vs SCE) (or 450-460 mV vs SHE) during the water leaching of MoO_3 shown in Figs. 4a-b are consistent with the Eh-pH diagrams in Fig. 1, indicating the involvement of Fe(III)/Fe(II) and Mo(V)/Mo(IV)/Mo(III) in these conditions. This suggests that other reactions such as the reduction of MoO_3 by the dissolved Fe(II) species might have taken place to enhance its dissolution.

3.3 Leaching in HCl solutions

Figs. 6a-c compare and contrast the effect of increasing HCl concentration on the dissolution of Mo, Cu and Fe at 25°C. An increase in HCl concentration from 0.115M to 1.40M causes faster initial dissolution of Cu reaching a plateau at ~90% dissolution in 1.40M HCl after 1 hour, as shown in Fig. 6b. In contrast Fe dissolves at a slower initial rate with a maximum dissolution at 80% after 2h (Fig. 6c). An increase in HCl concentration over 0.35M leads to the higher dissolution of Mo, after 40-60 min, unlike Cu and Fe (Figs. 6b&c). The Mo dissolution in 1.4M HCl reached 8% (yielding 50 g/L Mo liquor) after 1 hour, but the subsequent precipitation caused a decrease in Mo concentration to 30 g/L as shown in Fig. 6a. Possible precipitates formed that can lower the Mo concentration (as predicted from Fig.1) are H_2MoO_4 and CuMoO_4 in the oxidized zone.

3.4 Leaching in HCl+ NH_4Cl solutions

Figs. 7(a-c) plot the concentration and dissolution(%) of Mo, Cu and Fe during the 2h long leach tests and compare the effect of NH_4Cl concentration (0-0.93 M) in solutions of 0.7M HCl. Table 3 lists the extraction of Mo, Cu and Fe at 25°C after 2 hours. The results show more Cu could be leached with 0.6M NH_4Cl (Fig. 7b), compared to water alone (Fig.5) indicating that the Cu(I)/(II) ammonia and/or chloride complexation assists the leaching. However, NH_4Cl does not seem to affect the leaching of Cu in 0.7 M HCl as it could reach 80-90% dissolution within 20 minutes (Fig. 7b). The effect of increasing chloride, added as NH_4Cl , is more pronounced for the Fe leaching as shown in Fig. 7c, where the Fe extraction increases as the lixiviant changed from 0.6M NH_4Cl to 0.7M HCl and to a mixture of 0.7M HCl + 0.6M NH_4Cl (Table 3). This indicates the chloride assisted leaching of Fe(II) or Fe(III), as experienced with most chloride leaching systems (Bryce and Berk, 1995; Kimura et al, 1984, Senanayake and Muir, 2003).

The loss of Mo to HCl leach liquor could be minimized by adding NH_4Cl . Less Mo was dissolved in 0.6M NH_4Cl alone (compared to water), but the purification of MoO_3 calcine using this leachant alone was unsuccessful due to the incomplete dissolution of Cu. Acid promotes the dissolution of Fe and Cu as well as Mo, but NH_4Cl in excess of 0.2M re-precipitates the dissolved Mo as shown in Figs. 7a-c. A larger addition (>0.6 M) of NH_4Cl is better for the re-precipitation of Mo species to reduce its dissolution to a lower level of $<0.5\%$ (Table 3). To identify the solid formed, the precipitate formed by adding NH_4Cl to a clear solution obtained from the leaching of MoO_3 by 0.28 M HCl was collected for XRD analysis. The XRD pattern for this precipitate confirms $\text{NH}_3(\text{MoO}_3)_3$ as the main species formed at 70°C as shown in Fig. 8.

Fig. 6b shows no benefit when the HCl acid of $>0.7\text{M}$ was used to dissolve copper from calcines containing 1.04% Cu. From Fig. 7a, the passivation of Mo seems to be highest at ammonium chloride concentration of 0.6M when Mo dissolution was limited to less than 1%. No benefit was gained at 0.93M NH_4Cl . Mixtures of 0.7M HCl + 0.6M NH_4Cl were therefore used for the removal of copper from Mo calcines containing 1.04% Cu.

3.5. Effect of elevated temperature

The effect of increasing temperature on the two processes involved, namely (i) dissolution of Mo, Fe and Cu and (ii) precipitation of ammonium molybdate is depicted in Figs 10(a-c). An increase in temperature to 70°C has a marked beneficial effect on Fe dissolution

(~100%), while Cu dissolution is decreased from 90% at 50°C to 80% at 70°C. The precipitation of ammonium molybdate at 70°C causes a reduction in extraction to <0.5% within ~0.5 hour. However, the increasing dissolution of Mo after 10 min at 50°C has been observed (Fig. 9a) indicating the two opposite processes taking place which have to be optimized for the treatment of MoO₃ calcine. At the optimum conditions, copper from MoO₃ calcines containing 1.04% Cu could be removed to <0.5% within 1 hour, while the dissolution of Mo is limited to <0.5% (Table 3). The full analysis by ICP-AES of the product produced from this process shows that other impurities such as Zn, K, Al, etc. could also be removed from the calcine products to <0.1% (Table 2).

3. 6 Pilot Plant Study

The first series of experiments were conducted with MoO₃ calcines containing 1.04% Cu, conditions and results of which are summarized in Table 3 for better comparison with subsequent studies. Subsequent tests and pilot plant trials were conducted using materials containing 2.1% Cu, and the results are summarized in Tables 4a&b.

The efficiency of the HCl-NH₄Cl leachants used for dissolving Cu from MoO₃ calcines was confirmed in a series of tests (Tables 4a&b), conducted within 1 hour at 25°C or 70°C. A higher acid concentration (0.82, 1.16 or 1.4M) was used for HCl as the level of Cu in the material used for this series of tests was higher (at 2.1% Cu), compared to laboratory optimisation studies based on 0.7M HCl for a lower Cu material (1.04% Cu, as shown in Table 3). The reproducibility of Cu grades in the calcine product in duplicate tests was within +/- 0.04% in most cases. Tables 4(a)&(b), list the conditions for the tests and the results obtained (dissolution of Cu, Mo and the grades of Mo and Cu of the leached calcines, as analysed by complete digestion techniques) for calcines containing 2.1% Cu. A minimum of 1.16M HCl is required to keep Cu to within the range 0.48-0.53% at room temperature although a higher acid would ensure the Cu level to below 0.39%. The loss of Mo is higher than 0.5% at 1.4M HCl compared to <0.3% at a lower acid level (1.16M HCl) as expected. At 70°C, the effect of ammonium molybdate precipitation in reducing the Mo dissolution is more pronounced, limiting the loss of Mo to less than 0.1%. The increasing concentration of ammonium chloride seems also to have

little or no effect on limiting the loss of Mo. On the other hand, temperature has a more drastic effect as shown in Table 4(b), reducing Cu grade to <0.13% at 1.4M HCl, while the loss of Mo is limited to <0.08%. The effect of hydrochloric acid, ammonium chloride concentrations and temperature was therefore confirmed before larger pilot studies were conducted.

The pilot plant trials conducted subsequently confirmed the effectiveness of the Cu removal process on a larger scale, according to the flowsheet presented in Fig. 10. A total of 7 campaigns, each treating about 2.0-2.2 tonnes MoO₃ calcine containing 56.4% Mo and 2.1% Cu, has been conducted successfully at KFA. For each pilot plant trial 200 kg of NH₄Cl and 216 L of concentrated HCl were dissolved in water forming a leach liquor of 2.6m³. The concentrations of NH₄Cl and HCl were 1.44M and 0.97M, respectively. All pilot trials were conducted at ambient temperature (24-26°C).

The overall mass balance and the results of the trials are summarized in Table 5, showing the amounts of feed, materials collected after treatment (leachant, wash solutions and solids recovered) and the final product and its grade.

The mass balance of all solids recovered (as product and solids precipitated/remained in the wash liquors) is within 93.4% of the 14,160 kg feed with minimal loss of material throughout the 7 campaigns. The mass balance for Mo is 95.7% and for Cu is 94.8%. The average dissolution of Cu is 85%, resulting in the average grade of the treated MoO₃ calcine product as 0.22%. The amount of Mo dissolved into the leachant and wash liquor (40 kg) represents a loss of just above 0.5% of the total 7.982 kg Mo available from the 14,160 kg feed. The total Mo and Cu dissolved in the leach liquor and wash solution (293 kg) represents 2.1% of the total mass of the feed. The Fe dissolved in the leached liquor was not measured during the pilot plant studies although it is expected that 7-10 g/L of Fe would be found in the leach liquor (Fig. 3c). This would be equivalent to 240-250 kg (similarly to Cu mass balance) in the leach liquor and wash solution which would account for 2-3% weight loss from the feed. The overall mass balance therefore is close to 99%.

The resulting wash liquors containing Fe and Cu could be further treated in a solvent extraction circuit. The process describing this treatment was reported in earlier papers (An et al, 2009a&b)

4. Conclusions

Mixtures of HCl and NH_4Cl were used to remove Cu, Fe and other impurities from a MoO_3 calcines produced from roasting molybdenite concentrate. An increase in HCl concentration enhances the dissolution of Cu and Fe, but incur higher losses of Mo, unless ammonium chloride is also added to precipitate Mo as $\text{NH}_3(\text{MoO}_3)_3$. At room temperature the leachant of 0.7 M HCl and 0.6 M NH_4Cl would remove >80% Cu and 50% Fe from a MoO_3 calcine containing 1.04% Cu and 1.42% Fe within 2 hours. The loss of Mo is limited to <0.5% under these conditions. An increase in temperature to 70°C seems to promote faster precipitation of ammonium molybdate and dissolution of Fe, while no effect was observed on Cu removal. Pilot plant trials over 7 campaigns, each treated 2.0-2.2 tonnes of MoO_3 calcine containing 56.4% Mo and 2.1% Cu, using 1.44M NH_4Cl + 0.97M HCl yielded final products containing 57.4% Mo and 0.22% Cu as required. During the pilot plant trials, a total mass of 93.4% of the feed was recovered as solids, with 40 kg Mo and 253 kg Cu (and similar amount for Fe) dissolved in the liquor and wash solution, representing 4-5% of the initial feed. The process developed is now being used effectively at KFA to treat MoO_3 calcines having high Cu to produce a feed material containing less than 0.5% Cu for Fe-Mo alloy production.

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Table 1. Standard Gibbs free energy data (at 25°C) of Mo(VI) species for Stabcal simulation

Species	Standard Gibbs Free Energy, kJ/mol			
	MINTEQ	Russia	NBS	HSC
MoO_4^{2-} (a)	-836.2979	-838.0552	-836.2979	-836.1849
HMoO_4^- (a)	-860.8362	-866.632	-863.5776	-868.6193
MoO_3 (s)	-644.8351	-667.9714	-667.9714	-667.4777
MoO_2^{2+} (a)	-411.2872	-411.2872	-	-411.237
H_2MoO_4^0 (a)	-882.8972	-877.1337	-	-882.7194
$\text{MoO}_2(\text{OH})^+$ (a)	-645.8840	-645.884	-	
MoO_3^0 (s) Molybdate	-667.7664	-667.7664	-	
$\text{Mo}_7\text{O}_{24}^{6-}$ (a)	-5208.051	-	-	-5250.25
$\text{HMo}_7\text{O}_{24}^{5-}$ (a)	-5244.506	-	-	
$\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$ (a)	-5271.802	-	-	
$\text{H}_3\text{Mo}_7\text{O}_{24}^{3-}$ (a)	-5290.333	-	-	
H_2MoO_4^0 (s)	-909.7991	-	-	-912.2668
CuMoO_4^0 (s)	-845.4471	-809.604	-	-810.2609
$\text{Fe}_2(\text{MoO}_4)_3^0$ (s)	-2719.968	-2719.968	-2719.968	-2719.968
$\text{MoO}_3 \cdot \text{H}_2\text{O}^0$ (s)				-916.9152

Table 2. Composition of a MoO₃ calcine (containing 1.04% Cu) from KFA before and after acid treatment (At room temperature using the leachant of 0.7 M HCl and 0.6 M NH₄Cl)

Metal	Before treatment %	After treatment %	Removed %
Cu	1.04	0.08	92.3
Re	0.027	0.018	33.3
Fe	1.94	0.590	69.6
Al	0.255	0.034	86.7
Ca	0.390	0.359	7.95
Mg	0.089	0.021	76.4
Ti	0.012	0.010	16.7
V	0.001	0.001	0
Cr	0.002	0.001	50.0
Mn	0.011	0.002	81.8
Co	0.002	0.001	50.0
Ni	0.007	0.001	85.7
Zn	0.056	0.009	83.9
As	0.033	0.022	33.3
Pb	0.050	0.046	8.00
P	0.014	0.009	35.7
S	ND	ND	

^a ND: non-detectable by ICP-AES

Table 3: Dissolution of Mo, Cu and Fe in different lixivants (Data from Figs. 5, 6, 7 and 9)

using MoO_3 calcines containing 1.04% Cu.

Lixiviant	T, °C	DIssolution % (after 2h)		
		Mo	Cu	Fe
H ₂ O	25	3	3	20
0.6 M NH ₄ Cl	25	0.2	40	10
0.7 M HCl	25	4.5	90	30
0.6 M NH ₄ Cl + 0.7 M HCl	25	0.5	80	50
	50	~2	90	90
	70	<0.5	80	98

Table 4(a): Effect of HCl concentration at 22°C and 70°C on the Cu and Mo dissolution and grade of the final products after 1 hour leaching. Feed contained 2.1% Cu.

Exp. No.	Concentration mole/L		Temp. (°C)	Grade (%)		Dissolution (%)	
	NH ₄ Cl	HCl		Mo	Cu	Mo	Cu
A1a	0.93	1.16	22	57.4	0.53	0.31	73.9
A1b	0.93	1.16	22	57.8	0.48	0.25	75.4
A2a	0.93	1.40	22	58.6	0.32	0.75	71.7
A2b	0.93	1.40	22	58.6	0.39	0.80	73.2
A3a	0.93	1.16	70	59.0	0.39	0.02	81.5
A3b	0.93	1.16	70	58.4	0.44	0.08	79.8
A4a	0.93	1.40	70	60.5	0.13	0.05	74.8
A4b	0.93	1.40	70	60.3	0.13	0.06	75.4

Table 4(b): Effect of NH₄Cl concentration at 22°C and 70°C on the Cu and Mo dissolution and grade of the final products after 1 hour leaching. Feed contained 2.1% Cu.

Exp. No.	Concentration mole/L		Temp. (°C)	Grade (%)		Dissolution (%)	
	NH ₄ Cl	HCl		Mo	Cu	Mo	Cu
B1	0.93	1.40	22	58.6	0.32	0.75	71.7
B2	1.31	1.40	22	59.3	0.30	0.82	74.1
B3	1.87	1.40	22	58.5	0.30	0.58	73.3
B4	0.93	1.40	70	60.5	0.13	0.05	74.8
B5	1.31	1.40	70	59.8	0.16	0.05	73.4
B6	1.87	1.40	70	58.7	0.17	0.01	74.3

Table 5: Grade of MoO₃ calcine product and mass balance of feed and recovered solids in product, treating liquors and wash solutions. Labels A-F are shown in the treatment flowsheet (Fig. 10).

	kg or m3	Grade, (% or g/L)		Metal content, kg	
		Mo	Cu	Mo	Cu
Feed (Impure Calcine) (A)	14,160	56.4	2.1	7,982	297
Total Liquid				40	253
Leachant (B)	18,500	1.86	12.91	34	239
Wash Solution (C)	1,935	2.81	7.23	5	14
Total Solids recovered				7,597	29
Solid in Leachant (D)	2,028	57.37	0.22	1,163	4
Solid in Washing (E)	15	57.45	0.22	9	0
Residue (Product) (F)	11,181	57.46	0.22	6,425	25
Solid Mo recovery				95.2%	
Cu Dissolution					85.0%
Balance (Total solids recovered)/Feed					
	Total Mass			Mo	Cu
	93.4%			95.7%	94.8%

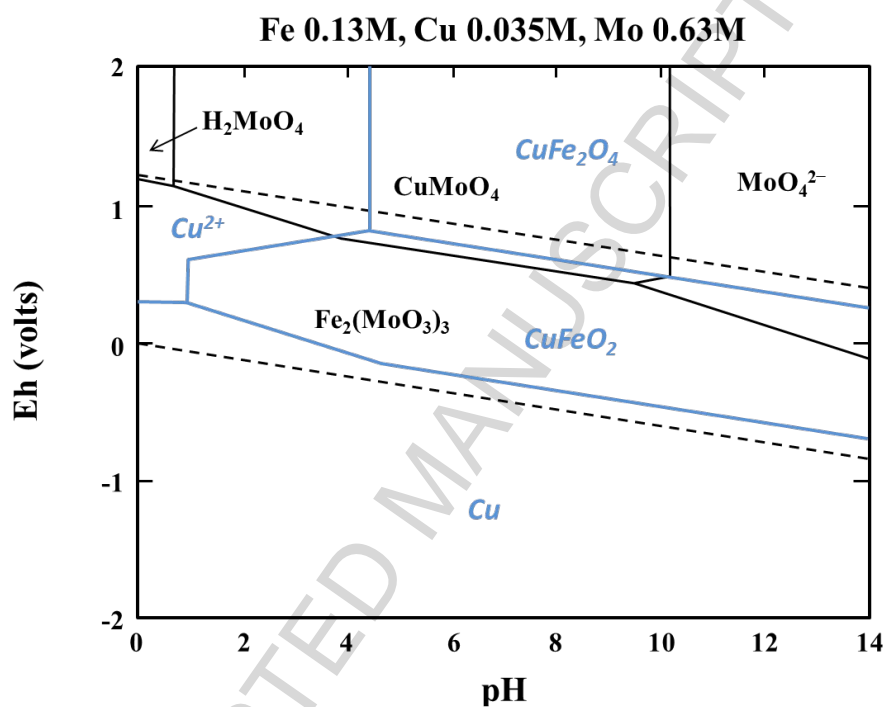


Fig. 1: Eh-pH diagram based on Stabcal simulation for a solution containing 0.63 M Mo, 0.035 M Cu and 0.13 M Fe (at 25°C)..

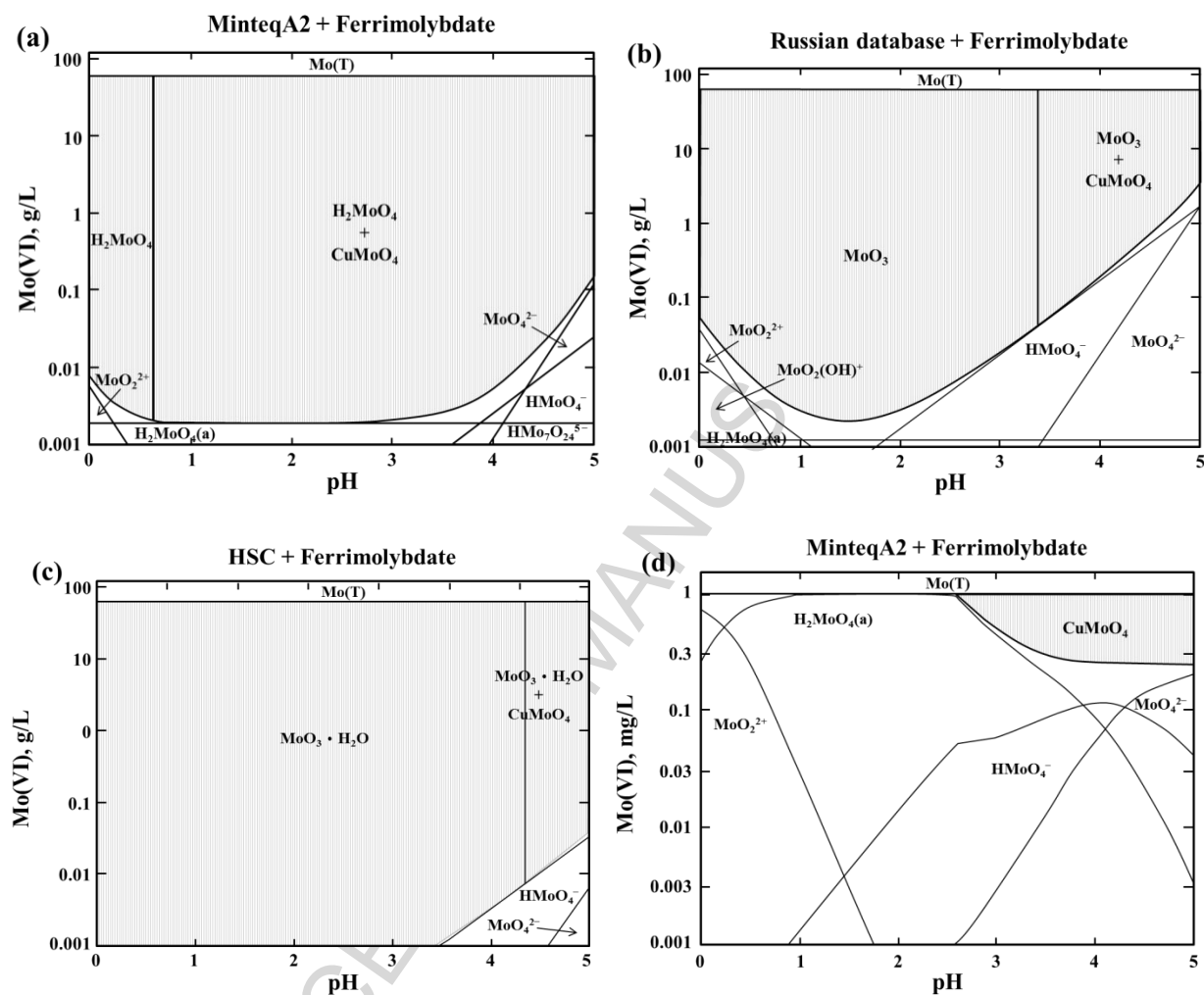


Fig. 2: Stabcal simulation (for 25°C) for a solution containing 0.63 M Mo, 0.035 M Cu and 0.13 M Fe using (a) MinteqA2 or (b) Russian database available within the Stabcal program, (c) HSC database (d) Same as (a) at mg/L range. Solid area is shaded in (a) – (d).

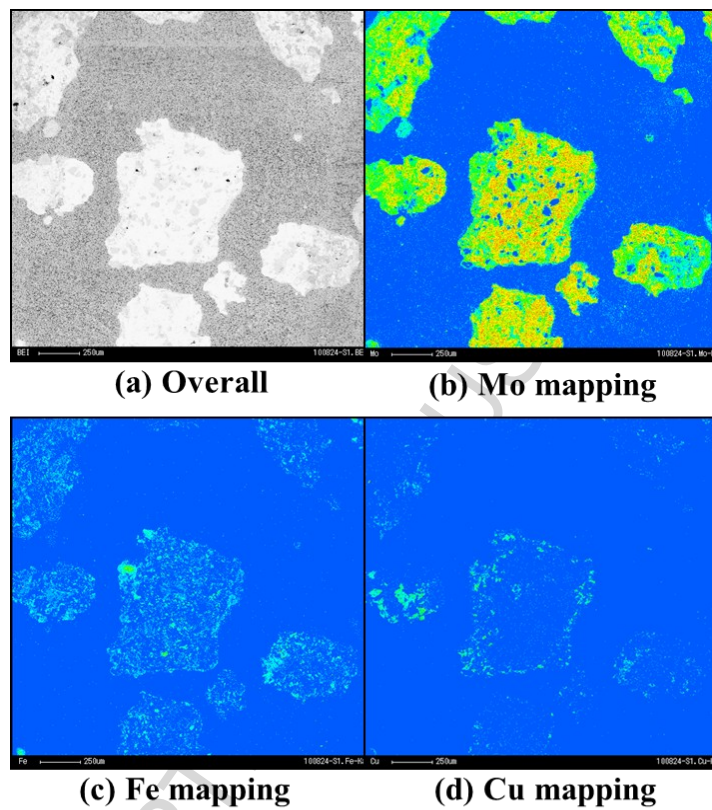


Fig. 3: EPMA mapping showing the fine distribution of Fe and Cu impurities within the Mo particles of the treated calcine.

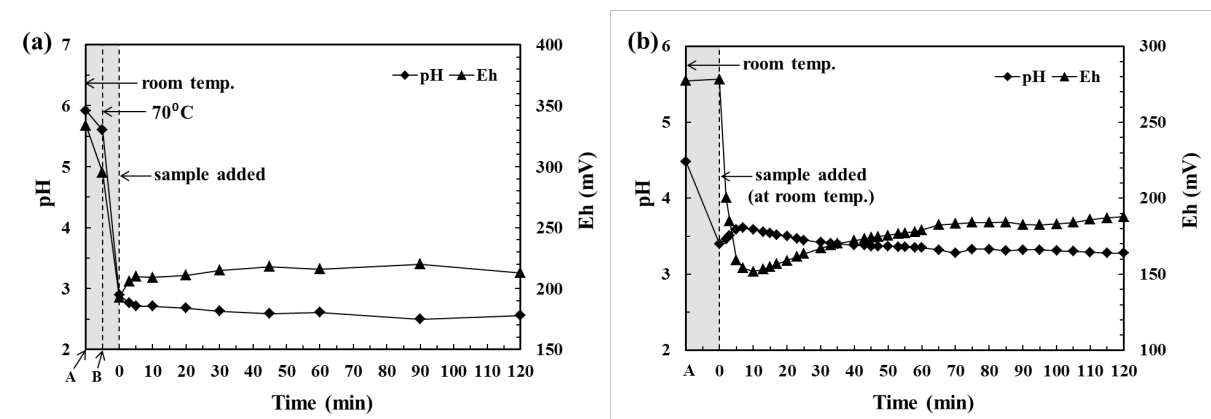


Fig. 4: Variation of Eh and pH with time for the dissolution of MoO_3 calcine in water at (a) 70°C and (b) 25°C. Measurements at A: room temperature, B: at 70°C and time 0 starts when the sample was added.

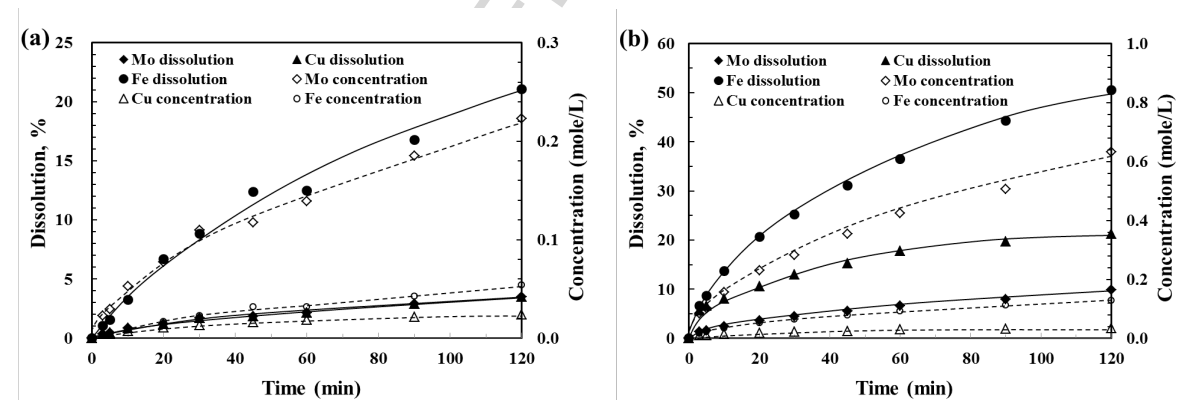


Fig.5: Concentration profile for Mo, Cu and Fe during the leaching of MoO_3 calcine by water at (a) 25°C and (b) 70°C.

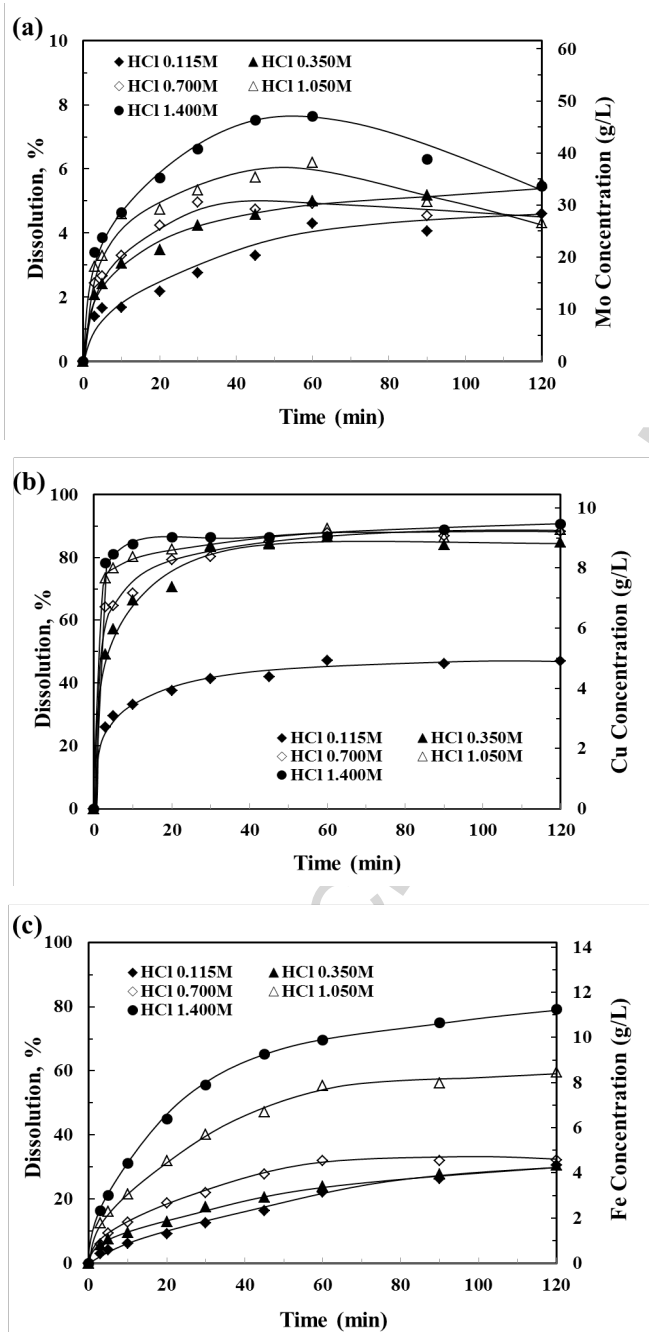
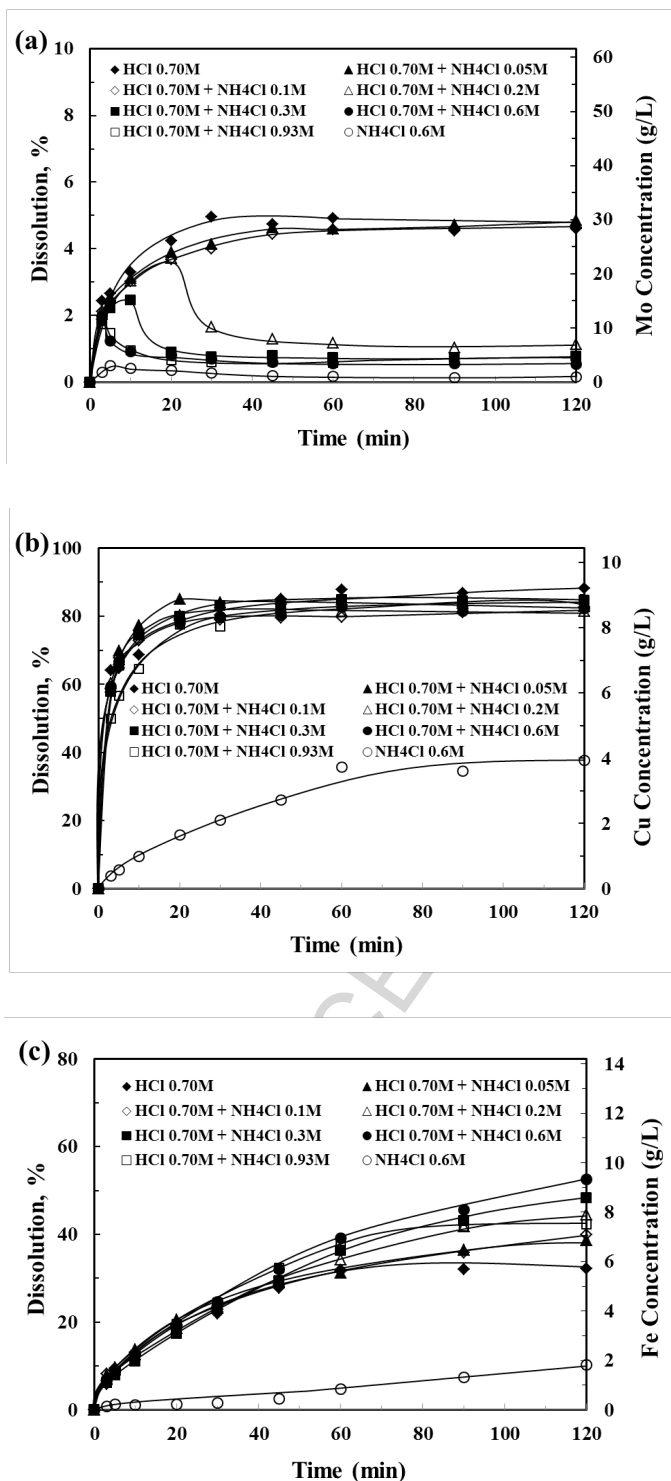


Fig.6: Leaching profiles showing the dissolution of (a) Mo, (b) Cu and (c) Fe at different HCl concentrations (0.115 M -1.4 M) at 25°C.



Figs. 7: Concentration profiles of (a) Mo, (b) Cu and (c) Fe during the leaching of impure calcine using HCl (0.70M) + NH₄Cl (0-0.93M).

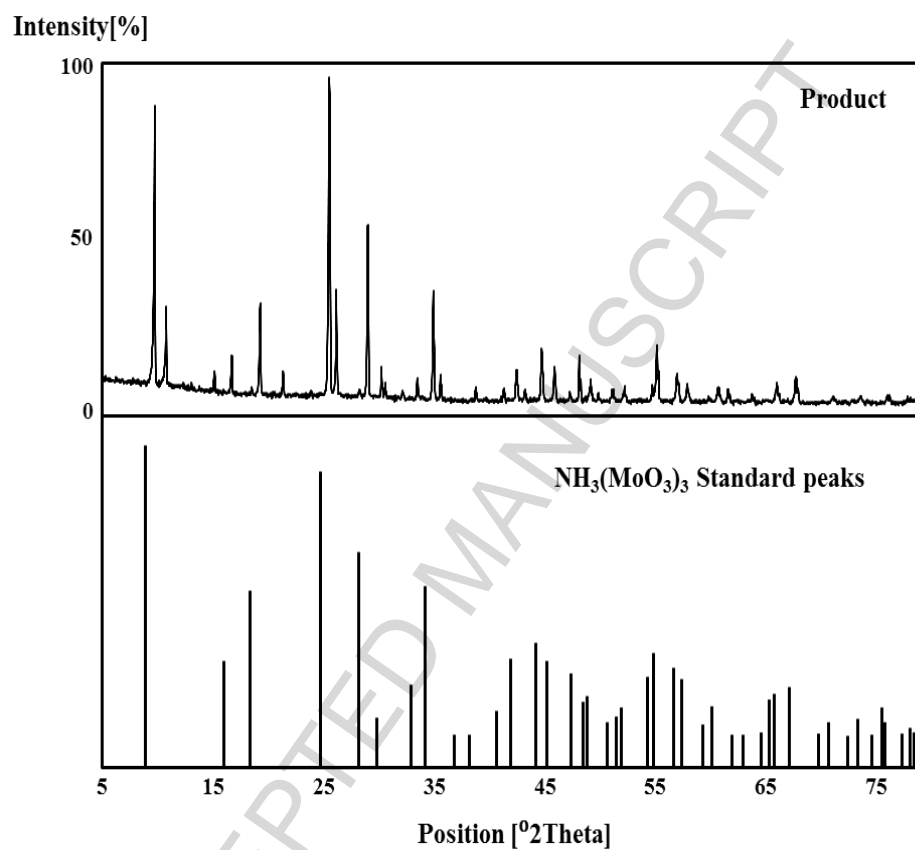
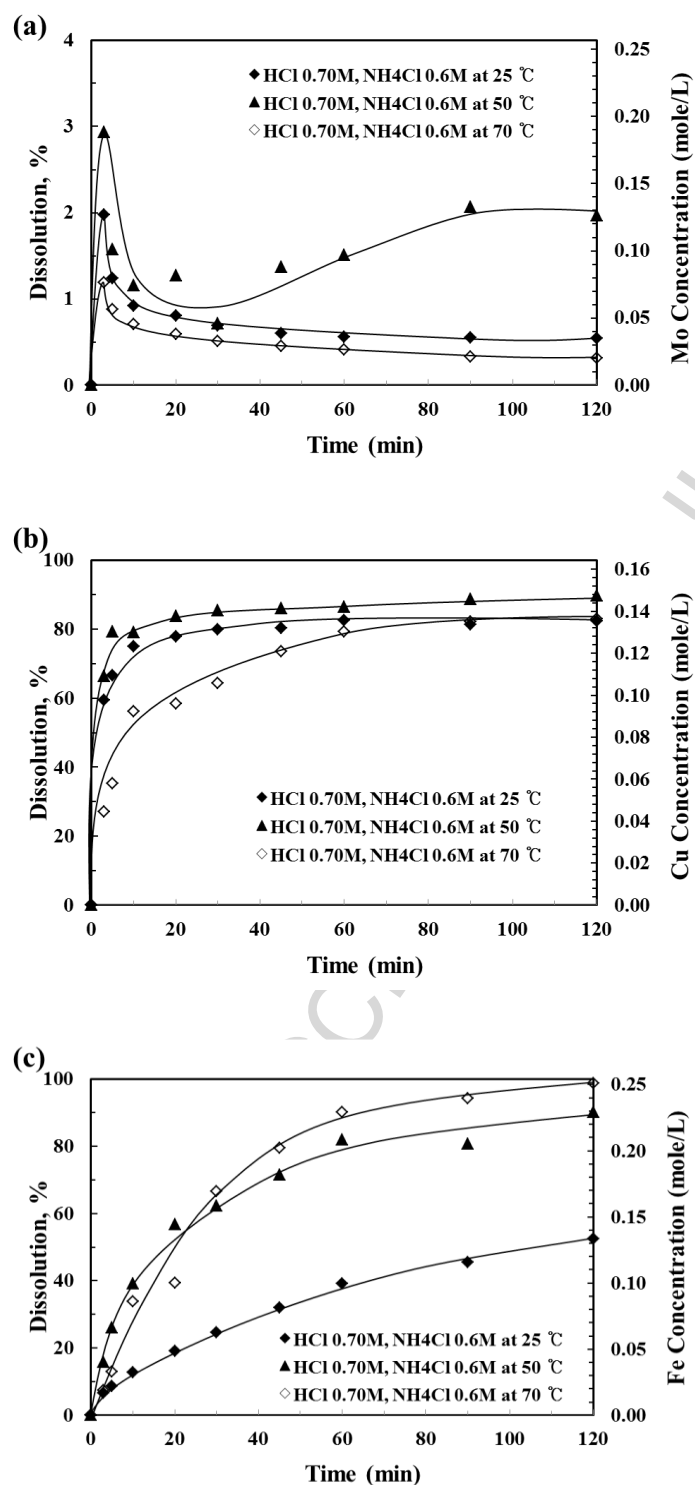


Fig. 8: XRD of ammonium molybdate precipitates



Figs 9: Concentration and dissolution profiles for (a) Mo, (b) Cu and (c) Fe showing the effect of temperature (25, 50 and 70°C).

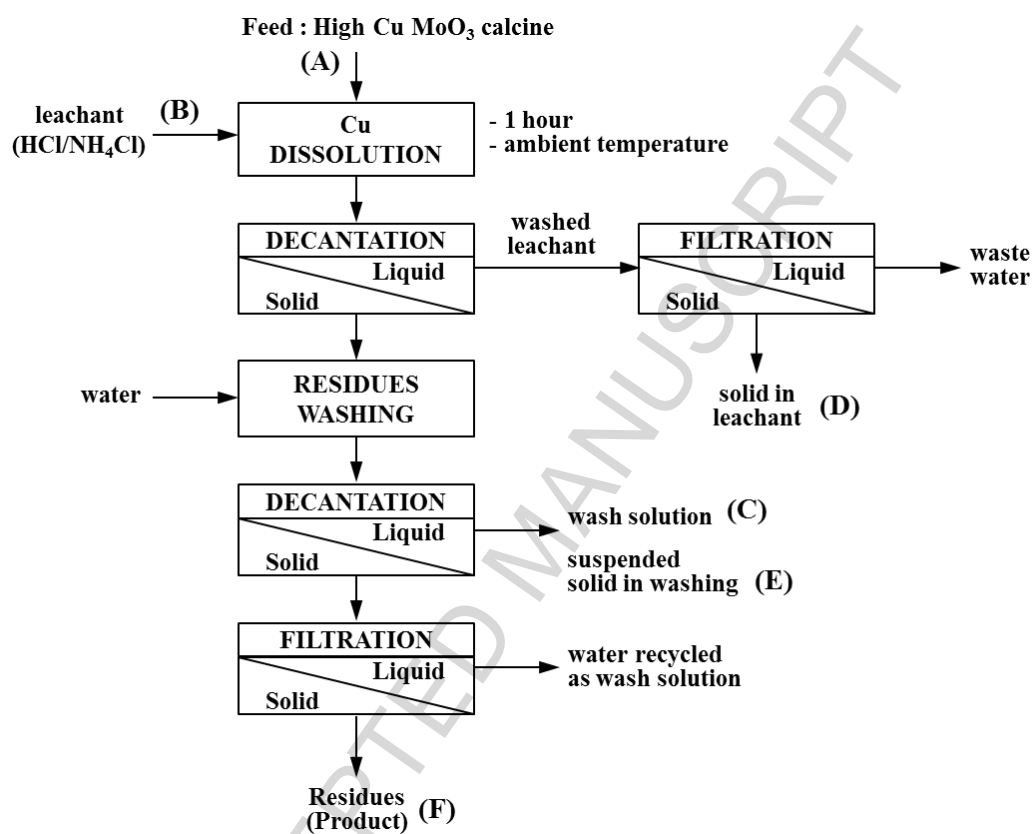


Fig. 10: Flowsheet of the treatment process used for removing Cu from MoO₃ calcines