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Selective Recovery of Molybdenum from Steelmaking Dust Leachate Using Cyanex 600

Ilyes Mahti, Léa M. J. Rouquette, and Martina Petranikova

Department of Chemistry and Chemical Engineering, Nuclear Chemistry and Industrial Materials Recycling, Chalmers University of Technology, Gothenburg, Sweden

ABSTRACT

Steelmaking dust generated by steelmaking processes contains significant concentrations of heavy metals, classifying it as a hazardous waste that industries must handle. Among these, molybdenum (Mo) plays a critical role in modern technologies. Its increasing demand, coupled with concerns about long-term resource sustainability, has driven growing interest in recovering Mo from secondary sources. Selective Mo leaching was first achieved using 0.05 M NaOH, retaining Fe and Zn in the solid residue while partially dissolving Cr. Subsequent solvent extraction with Cyanex 600 enabled selective Mo extraction over the pH_{eq} range 2–4. Investigation of the extraction mechanism revealed that phosphine oxide impurities in the extractant enable neutral extraction of Mo and Cr. Given the versatility of steelmaking dust composition, the presence of Zn in real-life leaching solutions cannot be neglected, and another Zn-containing feed was evaluated. With Zn present, selective Mo extraction was possible under the following conditions: [Cyanex 600] = 0.1 M, t = 10 min, pH_{eq} = 1.4, and T = 20°C. McCabe-Thiele (MCT) analysis revealed that 3 countercurrent stages would be necessary to extract 99% of Mo at an organic to aqueous ratio (θ) = 0.25. Finally, a solution containing 1.4 g/L Mo could be produced after stripping with 0.15 M NH_4OH.

KEYWORDS

Molybdenum; steel making dust; solvent extraction; Cyanex 600; mechanism

Introduction

As with most industrial activities, the steel industry generates many by-products. Steelmaking dust generated by steelmaking processes contains numerous heavy metals. In Europe, approximately 30 kg of steelmaking dust is collected per tonne of steel produced.[1] The dust contains mostly iron (Fe) and zinc (Zn), as well as other heavy elements in lower amounts, such as chromium (Cr), tungsten (W), nickel (Ni), lead (Pb) or molybdenum (Mo).[2–5] The elemental composition can vary significantly depending on regional raw material sources, individual steel producers, and the

CONTACT Ilyes Mahti mahti83@gmail.com; mahti@chalmers.se Department of Chemistry and Chemical Engineering, Nuclear Chemistry and Industrial Materials Recycling, Chalmers University of Technology, Gothenburg SE-412 96, Sweden

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steelmaking technologies used.[2] Due to its composition, the electric arc furnace (EAF) dust is classified as hazardous waste by major environmental agencies, including the United States Environmental Protection Agency (US EPA), the European Waste Catalogue, and the Australian EPA.[6,7] The legislation prevents the improper disposal of this waste, which could cause environmental damage due to its toxicity and solubility; as a result, steel producers are required to dispose of EAF dust in industrial landfills, which entails substantial costs.[8,9] Consequently, actions to recycle and incorporate steelmaking wastes are currently undertaken by the industrial sectors to minimize environmental impact, meet the growing demand for resources, and establish a circular economy for valuable metals. To date, research has largely focused on Zn recovery (primarily via pyrometallurgical methods) or on downcycling the material into construction products, a practice that leads to the loss of valuable heavy metals contained in the waste.[10–13]

This work overlooks the potential Mo recovery from steelmaking dust. Molybdenum is widely used in the steel and aerospace industries as an alloying element. Given the growing scarcity of Mo primary resources, the development of extraction processes for Mo recovery from secondary sources is becoming increasingly important.[14,15] Hydrometallurgical processes have advantages over pyrometallurgy, such as lower energy requirements (low temperature), simplicity, and efficient selective recovery of small quantities of valuable metals with high purity.[16–19] In Petranikova *et al.* work, leaching experiments were successfully performed to selectively recover Mo and W from Zn and Fe from steelmaking dust using low concentrated NaOH solutions.[20] In their work, the final leachate contained mostly Mo along with other heavy metals such as W and Cr. The presence of Zn in the leaching solution was very limited (about 2% relative to Mo when the NaOH concentration was fixed at 0.05 M), but higher NaOH concentrations increased the extent of Zn leaching (up to 16% when the concentration was increased to 0.5 M). It was highlighted that the presence of these impurities in the solution will greatly depend on the EAF dust fed into the reactor.

Once Mo is in the solution, selective recovery and purification become the critical next steps. Solvent extraction processes are a promising option due to their commercial viability, high purity yields, and selectivity.

The nature of the metal ion species (cationic or anionic) present in the leachate or aqueous feed solution plays a crucial role in the recovery process. Molybdenum exists as Mo (VI) in solution, and its aqueous chemistry is complex due to its strong affinity for oxygen, various oxo-complexes can co-exist in solution. In alkaline solutions (pH > 6), Mo primarily forms mononuclear anionic species, such as the molybdate ion (MoO_4^{2-}). As the pH decreases, Mo ions begin to polymerize into higher molecular weight protonated species such as $HMo_2O_5^{3+}$, $Mo_8O_{26}^{4-}$, $HMo_8O_{26}^{3-}$, $H_2Mo_7O_{24}^{4-}$, or

$Mo_7O_{24}^{6-}$ and in strong acidic solution (pH < 1), these species convert into mononuclear species, MoO_2^{2+}.[21–25]

In recent years, many researchers have studied the recovery of Mo with various amines, chelating agents, and phosphoros extractants like Alamine 366,[26,27] Aliquat 336,[28] LIX 63,[29,30] DEHPA (di(2-ethylhexyl)phosphoric acid),[31,32] and Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid).[33,34] The Syensqo group has developed a novel phosphonic acid-based extractant, Cyanex 600, for Mo recovery from acidic solutions originating from both low- and high-grade Mo sources. According to Syensqo, Cyanex 600 is a new alternative to amine-based extractants with higher selectivity to Mo, lower base consumption, and better physical performance. Cyanex 600 is a purified version of Cyanex 272, containing a higher concentration of the active extractant compound. Cyanex 600 is highly selective against anionic species, including sulfate, chloride, arsenic, or metals like Fe, Al, Mn, Cu, Co, Ni, Cr, and Rh, at low pH (under 2). Extraction kinetics are fast, and the extractant exhibits excellent stability. Furthermore, Cyanex 600 offers potential cost reduction benefits and demonstrated strong physical performance during pilot-scale testing with commercial concentrate leach feeds, with no emulsion formation observed.[35] There are very few studies on Mo extraction with Cyanex 600. L. Karimova *et al.* investigated the hydrometallurgical processing of Mo from copper-molybdenum ore.[36,37] After leaching the ores with acidic solutions, Mo was selectively recovered with the Cyanex 600 extractant from the leachate. B. Dutta evaluated the extraction behavior of Cyanex 600 toward Mo in sulfuric acid medium.[21] An extractant concentration of 0.1 M was sufficient to extract ~97% of 0.04 M Mo (VI) at pH < 2, and the predominant extracted species was the molybdenyl cation, MoO_2^{2+}.

This study focuses on the selective extraction and separation of Mo from the leach liquor of steelmaking dust using Cyanex 600, an acidic phosphorus-based extractant. The extraction mechanisms are elucidated through slope analysis and speciation diagrams. Subsequently, the impact of Zn in the leachate is investigated to assess whether Cyanex 600 retains its Mo selectivity in zinc-containing solutions, as Zn presence can vary from one feed to another. Optimal extraction parameters are established for each feed composition, with and without Zn, and process-scale considerations, including stripping and McCabe–Thiele analysis, are discussed.

Materials and methods

Materials

The steelmaking dust samples, used throughout the study, were supplied by Uddeholm AB. The elemental composition of the dust has been determined in a previous work and is reported in Table 1.[20] The metal dust composition was

Table 1. Metal content (in weight) of the major elements from the steelmaking dust Uddeholm ab. Standard deviations (STD) are given based on triplicate measurements.[20]

Element	[wt%] ± STD (%)
Mo	0.61 ± 0.01
Zn	35.9 ± 0.1
Fe	19.8 ± 0.1
W	0.06 ± 0.01
Cr	1.1 ± 0.1
Mn	1.4 ± 0.1
Ca	0.63 ± 0.01
Ni	0.06 ± 0.01

obtained after digesting 0.2 g of the dust in 50 mL of aqua regia (HCl/HNO_3: 3/1 volume ratios) and HF, performed at 80°C under magnetic stirring. Once dissolved, the liquid samples were diluted with 0.5 M nitric acid solution, and the metal content was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and inductively coupled plasma-mass Spectroscopy (ICP-MS).[20]

Leaching

The first step in the selective Mo recovery is leaching the solid material. The leaching experiment was performed according to our previous research. Mo is present in steelmaking dust as MoO_3, as demonstrated in our previous work.[20] During alkaline leaching, MoO_3 reacts with NaOH to form Na_2MoO_4, a soluble species in aqueous solutions, the reaction is given in Equation (1).

$$MoO_{3(s)} + 2NaOH_{(aq)} = Na_2MoO_{4(aq)} + H_2O_{(l)} \quad (1)$$

The leaching experiment was performed in a 3 L jacketed glass reactor equipped with a cap and a head stirrer. The influence of leaching parameters has been previously studied, suggesting that optimal Mo recovery can be achieved at 50°C, a leaching time of 30 minutes, a solid/liquid ratio of 1:3 (g/mL), and a NaOH concentration of 0.05 M.[20] Once the leaching was complete, the liquid phase was filtered using a vacuum system. Then, the concentrations of major metals in the leaching solution were measured using ICP-OES. Uncertainties in the resulting concentrations were obtained from triplicate measurements.

Solvent extraction

Solvent extraction experiments were carried out by mixing the organic phase (Cyanex 600 diluted in Solvent 70) with a certain volume of the aqueous phase (alkaline leachate). During the extraction, the target metals are transferred

from the aqueous phase to the organic phase. Acid phosphorus extractants extract cations by an ion-exchange type extraction, according to the following equilibrium from Wu *et al.*[33]:

$$M^{2+}_{(aq)} + \overline{2(HA)_2} = \overline{MA_2 2HA} + 2H^{+}_{(aq)} \quad (2)$$

where M^{2+} represents the metal cation, and HA and $(HA)_2$ represent the monomer and dimer forms of the acid phosphorus extractants, respectively, since these extractants are present as dimers in aliphatic diluents.[38] The overbar indicates that the species is present in the organic phase.

The extraction tests were carried out by mixing 1 mL of the organic phase with 1 mL of the aqueous phase in a 3 mL glass shaking vial. A shaker (IKA VIBRAX VXR Basic) was used to mix the two phases at a speed of 1000 rpm. The liquid-liquid settlements after mixing time were very short (typically <1 min) and no centrifugation was needed. After extraction, the aqueous phase is collected, and the concentration of the different metals is measured by ICP-OES. The pH of the collected phase is also measured to determine the equilibrium pH (pH_{eq}). The extraction rate depends on several fundamental parameters, including the extractant concentration, the contact time, the temperature, the pH_{eq} of the aqueous solution, the organic to aqueous volume ratio (θ), etc. A temperature control system was installed, and experiments were conducted at 20, 40, and 60°C. Extractions were performed for durations ranging from 1 to 30 minutes, using extractant concentrations between 0.01 and 1 M (dilution of Cyanex 600 in Solvent 70 to reach the desired concentration) and θ ranging from 0.1 to 1. The pH of the aqueous phases was measured with a pH electrode (Metrohm 827 pH Lab, Metrohm 6.0234.100, Switzerland) calibrated with pH buffers at 2, 4, and 7 at 20°C (Merck, Germany). All the experiments were performed in triplicate to obtain the standard deviation.

To study Mo's selectivity toward Zn, additional experiments were conducted by adding Zn to the feed solution. Two Zn sources were tested: standard Zn nitrate solution (1000 ppm $Zn(NO_3)_2$ in HNO_3 2–3%, ICP standard), and ZnO. $Zn(NO_3)_2$ solution was directly added to the leachate solution to get a final concentration of Zn of 40 ppm (~10% of the Mo concentration), while ZnO was first dissolved in 2.5 M of H_2SO_4 before being added to the solution, also at 40 ppm.

A UV/Vis spectrometer (Lambda 25, Perkin Elmer) was used to measure the absorbance over the 900 to 300 nm range in order to identify and characterize the chemical species of the elements present in the aqueous phase before the extraction.

The extraction of a generic metal M by an acid extractant can be generalized as shown in Equation (3). To quantify the extraction, the distribution coefficient (D_M) and the extraction yield are calculated using Equations (4) and (5), respectively. The metal concentration in the organic phase is determined by

mass balance: subtracting the final aqueous phase concentration (after extraction) from the initial aqueous phase concentration (before extraction). The selectivity of the extraction toward Mo can be quantified by the separation factor ($SF_{M/N}$) defined in Equation (6).

The extraction equilibrium constant at a given temperature T ($K_{ext}(T)$) can be represented by Equation (7). The slope method is an analytical technique used in solvent extraction to determine the n and y values of Equation (3) and, therefore, the reaction that occurs during the extraction process. The method is based on the relationship between metal distribution and extractant or hydrogen ion concentration. By constructing logarithmic plots and computing the slopes with linear regression tools, key parameters can be determined: plotting Log(D) versus $\mathrm{Log}\left(\overline{\left[(\mathrm{HA})_2\right]}\right)$ yields the number of extractant molecules coordinated to the metal, while plotting Log(D) versus $-\log([\mathrm{H}^+])$ reveals the number of protons released during the extraction, as seen in Equation (8). The regression analysis was performed on the mean values for data sets studied, and the associated uncertainties were computed (R^2, and standard error on the slope) to support the robustness of the stoichiometry assessment.

$$M^{n+} + \left(\frac{n}{2} + y\right)\overline{(HA)_2} \rightarrow \overline{MA_n 2y(HA)} + nH^+ \tag{3}$$

$$D_M = \frac{\overline{[M]}}{[M]} \tag{4}$$

$$Extractionyield(\%) = \frac{D}{D+1/\theta} \cdot 100 \tag{5}$$

$$SF_{M/N} = \frac{D_M}{D_N} \tag{6}$$

$$K_{ext}(T) = \frac{\overline{[MA_n 2y(HA)]}[H^+]^n}{[M^{n+}]\overline{\left[(HA)_2\right]^{\left(\frac{n}{2}+y\right)}}} = \frac{D_M[H^+]^n}{\overline{\left[(HA)_2\right]^{\left(\frac{n}{2}+y\right)}}} \tag{7}$$

$$Log(D_M) = Log(K_{ext}(T)) - n\log([H^+]) + \left(\frac{n}{2} + y\right)Log\left(\overline{\left[(HA)_2\right]}\right) \tag{8}$$

Results and discussion

Extraction of Mo from the original leachate

Impact of the pH on the distribution coefficient

First, the steelmaking dust was leached with an alkaline solution ([NaOH] = 0.05 M) to selectively recover Mo. The metal concentrations obtained are shown in Table 2.

Table 2. Metal composition of the leachate solution (conditions: T = 50°C, t = 30 min, S:L ratio = 1:3, and [NaOH] = 0.05 M). Standard deviation of triplicate measurements is given.

	Mo	Zn	W	Fe	Cr
Concentration (ppm)	480 ± 10	<LOD	<LOD	<LOD	87 ± 5
Concentration (10^{-3}M)	5.0 ± 0.1	–	–	–	1.7 ± 0.1

The leaching process is effective and initiates the separation of Mo from the other elements, although a small amount of Cr remains in the solution. After the leaching experiment, the solution pH was measured at 12.3.

Then, the leachate was used as the feed solution for solvent extraction. As seen in Table 2, the feed solution contains mostly Mo but also Cr. The aim here is to selectively recover Mo from the leachate. To investigate the impact of pH_{eq} on the extraction and the selectivity, different pH_{eq} values were screened by adding droplets of H_2SO_4 to the feed. According to the literature, extraction equilibrium is reached in 3–10 min for Mo with Cyanex 600 and 10–20 min for Cr with Cyanex 272.[21,37,39,40] In this work, the contact time has been set to 30 min to ensure reaction equilibrium. The results are presented in Fig. 1a. The equilibrium pH was measured and found to be lower than the initial pH, as shown in Fig. 1b, indicating that the pH decreases during the solvent extraction process. This can be explained by the release of protons occurring during the extraction reaction (3).

The results presented in Fig. 1a reveal three distinct extraction behaviors for Mo across different equilibrium pH ranges: pH < 2, 2 < pH < 4, and pH > 4. Table 3 presents the extraction yields of Mo and Cr at pH_{eq} = 0.6 and 4, and the separation factors for Mo against Cr.

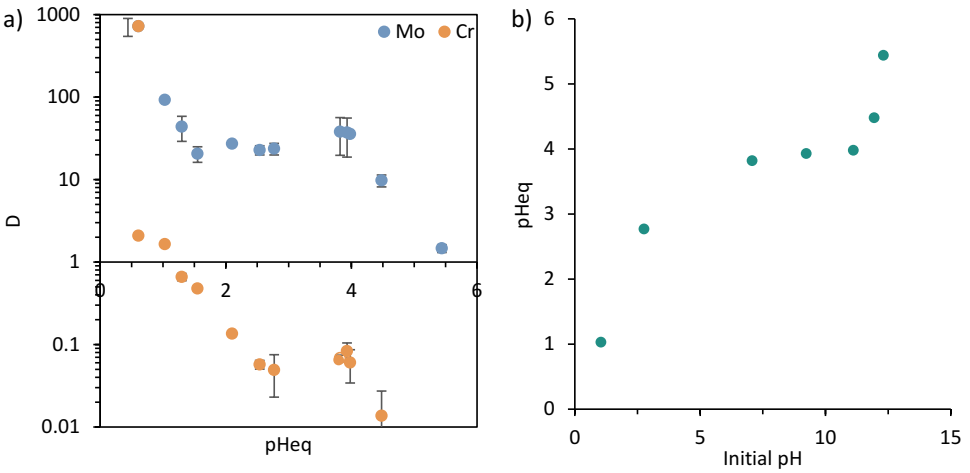

Figure 1. a) Distribution coefficient of Mo and Cr at different equilibrium pH. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C. Uncertainties of triplicates are given. b) pH before and after the solvent extraction. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C.

Table 3. Extraction yields and separation factors of Mo and Cr at different equilibrium pH. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C. Uncertainties of triplicates are given.

	pH_{eq} = 0.6		pH_{eq} = 4	
	Mo	Cr	Mo	Cr
Extraction (%)	99.86 ± 0.03	67.6 ± 0.7	97.27 ± 0.02	5.69 ± 2.23
$SF_{Mo/Cr}$	/	375 ± 96	/	684 ± 284

When the solution is acidified at pH_{eq} below 2, D_{Mo} sharply increases, reaching values up to 1000 with $SF_{Mo/Cr}$ of 375. Between pH_{eq} 2 and 4, Mo is extracted from the feed with high and constant D_{Mo} (>10). Above pH_{eq} 4, D_{Mo} begins to decline progressively, dropping from values exceeding 10 to $D_{Mo} = 1.5$ at pH_{eq} 5.4. Cr presents two behaviors: elevated D values when $pH_{eq} < 2$ ($D > 1$) and low D values at $pH_{eq} > 2$ ($D < 0.1$).

To understand these different extraction trends observed for Mo and Cr, we need to investigate the extraction mechanisms and the speciation of the elements.

Investigation of the extraction mechanisms

Molybdenum speciation highly depends on pH and Mo concentration. Molybdenum mainly exists as molybdate (Mo(VI), MoO_4^{2-}) species in alkaline media (pH > 6).[14,26] Due to its anionic nature, molybdate is preferentially extracted by amine-based extractants. D.M. Imam *et al.* have shown that molybdate can be extracted by Aliquat 336 through an anionic exchange mechanism at pH ≈ 12, forming $(R_3CH_3N)_2MoO_4$ in the loaded organic phase.[41]

Between pH 2 and 6, the mechanisms involved in the solvent extraction of Mo are quite complicated to describe because of the rich speciation of Mo in the aqueous phase in this pH range.[28] Indeed Mo, at a concentration above 10^{-3} M, tends to form numerous polynuclear species such as $Mo_7O_{24}^{6-}$ or $Mo_8O_{26}^{4-}$[42–44] Within the pH range of 1–4.5, molybdenum can also exist as hydromolybdate species $HMoO_4^-$ and H_2MoO_4. Sastre *et al.* have studied the solvent extraction of Mo in acidic sulfate media with LIX 622 extractant.[45,46] They concluded that the overall extraction mechanism of Mo (VI) by LIX 622 seems to be much more complicated than the simple 1:2 (Mo:extractant) stoichiometry and that a solvation reaction may be involved. The molybdate species formed in the extraction of Mo with LIX 622 according to Sastre *et al.* were MoO_4H_2HA, $MoO_4H_3HA{\cdot}HSO_4$.[45] Based on these observations, we suggest that hydromolybdate species can also be extracted into the organic phase through a solvation reaction with Cyanex 600.

At lower pH, the solvent extraction mechanism of Mo is better known.[47–49] The main species at pH < 1 is molybdenyl, MoO_2^{2+}. The equation below presents the mechanism of Mo extraction in acidic

media.[48] The stoichiometry of the Mo:Cyanex 600 complex was found to be 1:2 which indicates that 2 moles of dimeric Cyanex 600 was required to extract one mole of Mo ion.

$$MoO_{2(aq)}^{2+} + \overline{2(H_2A_2)} \leftrightarrow \overline{MoO_2A_2 2HA} + 2H^+ \quad (9)$$

The pH decrease reported in Fig. 1b is attributed to two mechanisms: the extraction reaction itself (Reaction (9)) and the deprotonation of the extractant upon contact with the aqueous phase (Reactions (10) and (11)). According to the literature, the pKa of Reaction (11) is equal to 3.73.[50] This value could explain the buffering effect observed in Fig. 1a,b, where the pH_{eq} remains around 3.8 even when the initial pH is decreased by multiple units. It could also explain why the pH does not change after the solvent extraction when the initial pH is below 3. Under this value, the extractant does not deprotonate and therefore does not acidify the aqueous solution. The low concentration of Mo compared to the extractant present in the solution might explain why the release of protons in Reaction (9) does not acidify the solution. Reaction (11) is the prevalent reaction for the acidification of the aqueous solution.

$$\overline{(HA)}_2 \leftrightarrow 2(HA) \quad (10)$$

$$(HA) \leftrightarrow H^+ + A^- \quad (11)$$

Results show that Mo is efficiently extracted up to pH 4 (>95%). However, at this pH, molybdenyl does not exist, and therefore, Reaction (9) cannot occur. As mentioned previously, a solvation reaction may occur with the extractant. Below pH 2, Mo is quantitatively extracted (extraction yield up to 99%) through Reaction (9), but both Mo and Cr are extracted.

Concerning chromium, Cr(+VI) is not supposed to be extracted by Cyanex 272, and Cr(+III) is fully extracted at pH 5.[39] Our results do not match any of these behaviors. To have a better understanding of the mechanism occurring during the extraction reactions, a UV-Vis spectrophotometry analysis has been performed on the feed at different pH (Fig. 2).

The spectra show an intense band at 370 nm for the leachate solution. A shift and decrease of this band from 370 nm to 345 nm is observed when the solution is acidified. This phenomenon is characteristic of the presence of Cr(+VI) and more specifically, chromate anions, CrO_4^{2-}, which explains the yellow color of the feed solution. At low pH, formation of hydrogen chromate: $HCrO_4^-$ is observed (pKa = 6.4). At even lower pH, chromic acid, H_2CrO_4, is supposedly formed (pKa = 0.74).[51]

According to the literature, only Cr(+III) is extracted by Cyanex 272. However, studies have shown that Cr(+VI) can also be extracted at highly acidic pH.[39] This is due to the phosphine oxide impurities present in the

Cyanex 272 solution, which can extract H_2CrO_4 and $Cr_2O_7^{2-}$[52] The extraction of neutral metal species by bis(2,4,4-trimethylpentyl) phosphinic acid is not generally accepted. However, Cyanex 272 contains a significant amount of phosphine oxide impurity. Indeed, according to the product's safety data sheet, Cyanex 272 can contain 7–13% phosphine oxide. In our case, Cyanex 600 contains 1–2.5% of phosphine oxide. This amount is equivalent to 5–15.10^{-3} M, which is enough to extract Cr.

The speciation diagram for CrO_4^{2-} anion has been calculated using the Medusa software (Fig. 3). Above pH 7, CrO_4^{2-} is the major species, and below, it is the hydrogen chromate, $HCrO_4^-$. Below pH 2, chromic acid begins to appear, which is one of the species that can be extracted by the phosphine oxide impurities. This observation is consistent with the extraction trend (Fig. 1a), which shows an increase in the distribution coefficient for Cr below pH 2. A very low amount of $Cr_2O_7^{2-}$ is also observed between pH 0 and 7, which can explain the low D values for Cr observed in Fig. 1a.

As mentioned previously, Mo is not supposed to be extracted by acidic extractant at pH higher than 2 because MoO_2^{2+} is not present. However, as Mo and Cr are in the same column in the periodic table, they share similar properties. Therefore, the speciation diagram for MoO_4^{2-} was also calculated

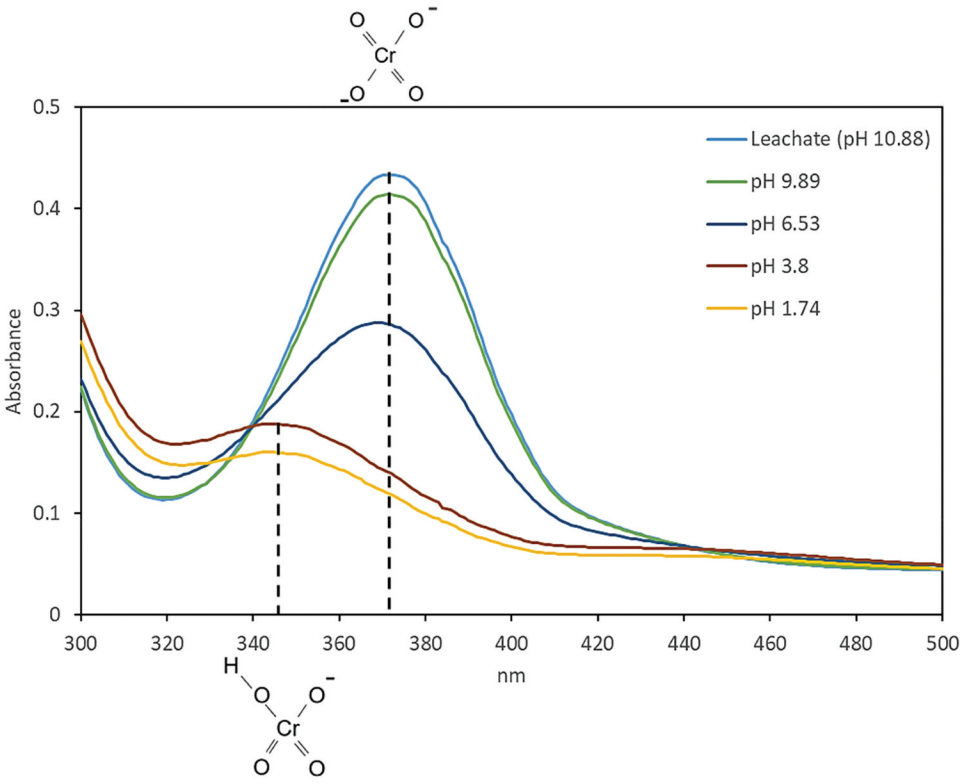

Figure 2. UV-Vis spectra of the feed at different pH. Condition: [Cr] = 8.5.10^{-4} M.

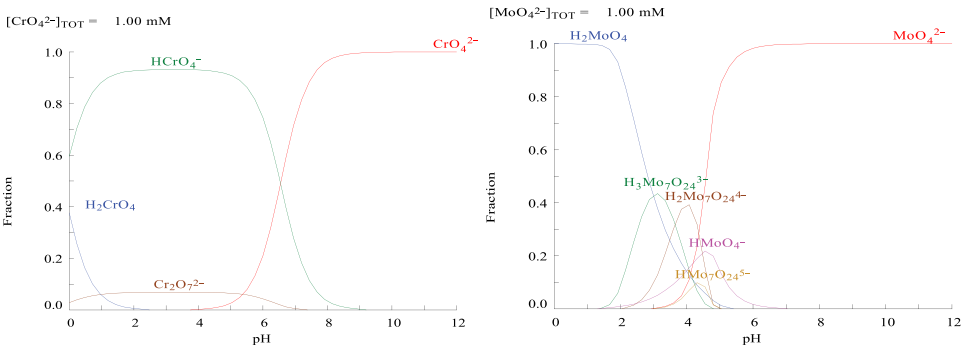

Figure 3. Speciation diagram for 1 mM of CrO_4^{2-} (left) and for 1 mM of MoO_4^{2-} (right) using Medusa software.

using the Medusa software (Fig. 3). Similarly to Cr, above pH 5, the mono-anion form, MoO_4^{2-}, is the major species in solution. This species is not extracted by Cyanex 600, consistent with the decline in extraction yields and D_{Mo} values observed after pH 5 in Fig. 1a. Between pH 2 and 5, a lot of polymeric species are present, but also H_2MoO_4 and $HMoO_4^-$. Several studies have reported the existence of these species in this pH range, with pKa1 values of 3.61–4.0 and pKa2 values of 3.89–4.37.[53,54]

We therefore propose that, between pH 2 and 4, Mo extraction proceeds through a mechanism analogous to that of Cr (VI), involving solvation by phosphine oxide impurities, which is consistent with the extraction trends shown Fig. 1a. This hypothesis is further supported by the work of C. Marie *et al.* who studied Mo extraction by HDEHP (di-2-ethylhexyl phosphoric acid) and observed that, by increasing the pH, the extraction mechanism evolves from a cationic exchange mechanism to a solvating mechanism with $HMoO_4^-$ being the Mo species involved in the reaction.[55] We suggest that the same phenomenon is occurring here with Cyanex 600. Extraction mechanisms for Cr and Mo are shown in Equations (12) and (13), respectively, according to the literature.[39,52,55] The formation of the $\overline{H_2MoO_4.HX}$ species is in good agreement with the results obtained in the study of Sastre et *al.*, where they observed the same species with LIX 622.[45]

$$HCrO_4^- + H^+ + \overline{HX} \rightarrow \overline{H_2CrO_4.HX} \tag{12}$$

$$HMoO_4^- + H^+ + \overline{HX} \rightarrow \overline{H_2MoO_4.HX} \tag{13}$$

where HX, is the phosphine oxide impurity of the Cyanex 600.

To confirm our hypothesis, the slope method was used to estimate the number of protons involved in the extraction reactions. A plot of pH_{eq} vs. Log (D) is given in Fig. 4. The slopes obtained for Mo and Cr are equal to -0.94 ± 0.07 and -0.98 ± 0.09, respectively. These results indicate that, in the

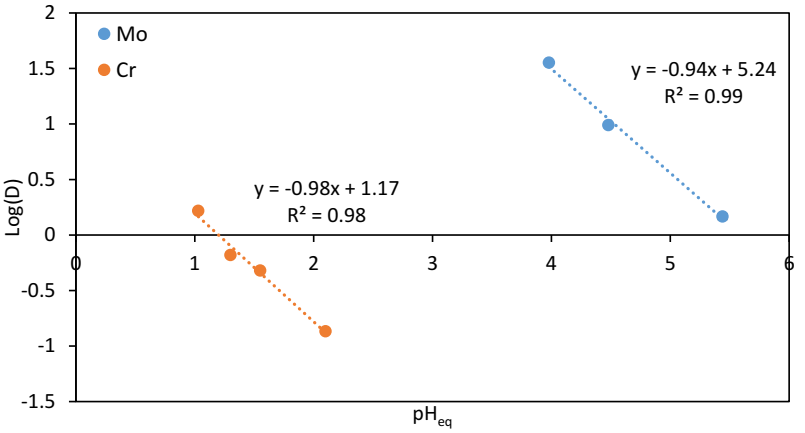

Figure 4. Slope method used for calculation of the number of protons involved in the extraction reaction. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C.

extraction reactions for both elements, one proton is consumed, which is in agreement with Equations (12) and (13).

Influence of zinc into the feed solution

Impact of the pH on the distribution coefficient

To determine the selectivity of Cyanex 600 for Mo over Zn, the same experiments were repeated as before using a new feed solution containing Zn. The first feed solution studied contained a standard solution of zinc ($Zn(NO_3)_2$). The new feed solution contains approximately 480 ppm Mo and 40 ppm Zn.

The impact of the pH_{eq} on the distribution coefficients was investigated. Results are reported in Fig. 5.

The results showed that adding Zn inside the feed solution compromises the selective extraction of Mo at pH > 2 as Zn is also being highly extracted by Cyanex 600. A similar observation was reported by Salgado et *al.* in the context of zinc recovery from spent alkaline batteries using Cyanex 272.[56] Below pH = 2, Zn is not quantitatively extracted.[57,58] This may be due to the protonation of the extractant at low pH, preventing metal extraction.[59] The slope method used for the calculation of the number of protons plotted in Fig. 5b indicates that two protons (2.06 ± 0.04) are involved in the extraction of Zn, which is consistent with the literature and Equation (2).

Optimization of the extraction parameters

At acidic pH, Mo extraction selectivity is compromised by the co-extraction of Cr while at $pH_{eq} > 2$, Zn becomes the interfering element. Optimization of experimental parameters is therefore essential to enhance Mo extraction selectivity. Extraction yields at $pH_{eq} = 0.6$, 1.4 and 3.9 are presented in

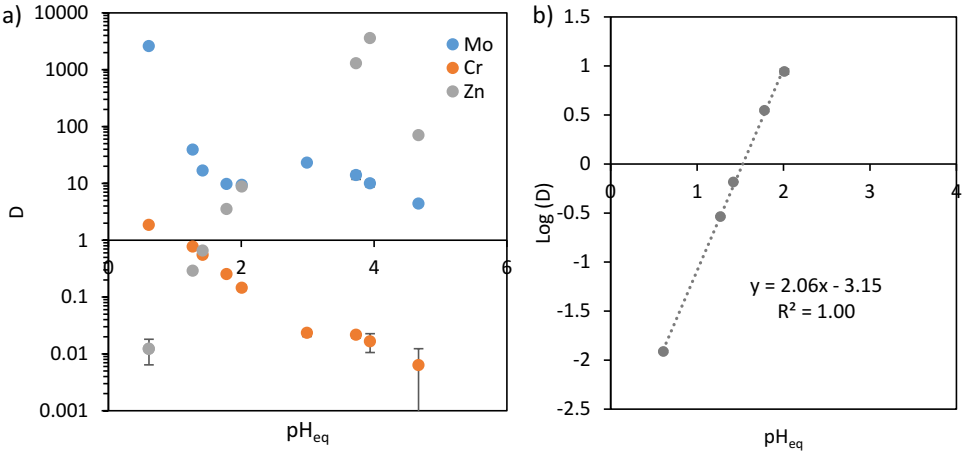

Figure 5. a) Distribution coefficients of the metals at different pH_{eq}. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C. Uncertainties of triplicates are given. Slope method used for calculation of the number of protons involved in the extraction reaction for Zn. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C.

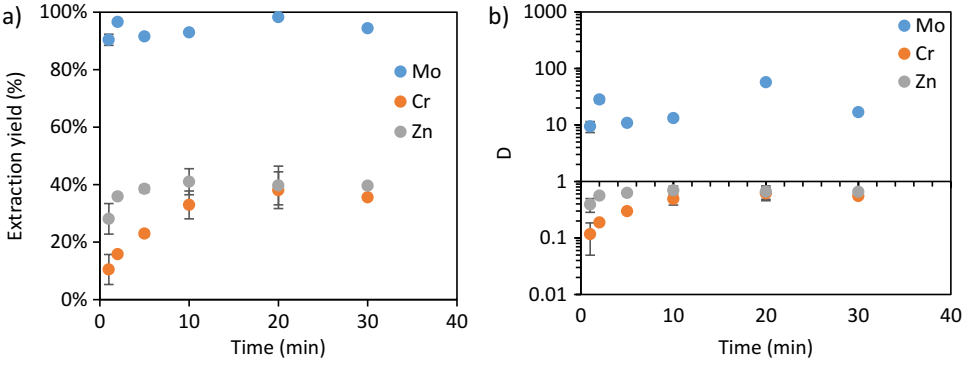

Figure 6. a) Extraction yields of metals and b) distribution coefficients at different contacting times. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C. Uncertainties of triplicates are given.

Table 4 along with the separation factors. The highest separation factors are observed at acidic pH, with values exceeding 900; however, 65% of Cr is co-extracted under these conditions, corresponding to approximately 50 ppm. At pH_{eq} 4, Mo is effectively separated from Cr (SF = 591 ± 234), but not from Zn (SF = 0.01 ± 0.01). Performing experiments at pH_{eq} ≈1.4 represents the optimal compromise, minimizing the co-extraction of both Zn and Cr (extraction yields <40%) while maintaining high Mo selectivity, with separation factors exceeding 20.

The temperature is an important parameter that can affect the kinetics and the yield of the metal's extraction. Thus, two additional temperatures (40°C and 60°C) were studied at pH_{eq} = 1.4. Results are presented in Table 5.

Table 4. Extraction yields and separation factors of Mo, Cr and Zn at $pH_{eq} = 0.6$, 1.4 and 3.9. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C. Uncertainties of triplicates are given.

	$pH_{eq} = 0.6$			$pH_{eq} = 1.4$			$pH_{eq} = 3.9$		
	Mo	Cr	Zn	Mo	Cr	Zn	Mo	Cr	Zn
Extraction yield (%)	99.96 ± 0.04	65.1 ± 0.6	1.2 ± 0.6	94.4 ± 0.4	35.6 ± 0.5	39.6 ± 0.3	91 ± 1	1.6 ± 0.8	99.97 ± 0.2
SF Mo/M	/	930 ± 87	+∞	/	31 ± 3	26 ± 2	/	591 ± 234	0.01 ± 0.01

Table 5. Extraction yields (%E) of Mo, Cr and Zn at 25°C, 40°C, and 60°C. Conditions: [Cyanex 600] = 1 M, t = 30 min, θ = 1, and T = 20°C at pH_{eq} = 1.4. Uncertainties of triplicates are given.

Temperature (°C)	%E (Mo)	%E (Cr)	%E (Zn)
20	94.4 ± 0.4	35.6 ± 0.5	39.6 ± 0.3
40	99.0 ± 0.6	50.4 ± 1.5	47.6 ± 3.8
60	99.0 ± 1.3	63.1 ± 4.2	48.5 ± 2.3

The results indicate that temperature significantly influences Cr extraction, whereas it has only modest effects on Mo and Zn. Indeed, Cr extraction increased considerably from 36% to 63% of extraction at 60°C, indicating the endothermic nature of these processes. According to the literature, temperature can impact solvent extraction by increasing both solute solubility and diffusion rates, leading to faster and more efficient extraction.[60] This effect likely explains the increased extraction efficiency observed in our system at elevated temperatures. Hence, as Mo extraction is already efficient at room temperature, all subsequent extractions were conducted at ambient temperature. This approach allows us to limit the extraction of Zn and Cr while maintaining selectivity for Mo, and offers the advantage of eliminating heating requirements, thereby reducing both energy consumption and operating costs.

As mentioned previously, many parameters can influence solvent extraction. A kinetic study was performed, at shorter times, to investigate the influence of the contacting time between the organic and aqueous phases. The results are presented in Fig. 6. The aqueous phase was collected after 1, 2, 5, 10 and 20 min of extraction time at pH_{eq} = 1.4. According to the results, Mo extraction reached equilibrium almost instantly. This observation is consistent with the literature, which shows that Mo extraction with Cyanex extractants (600, 272, 301, 923) is very fast in acid media (5 ~ 10 minutes).[21,61–63] Cr and Zn extraction reached equilibrium in 10 minutes. The fast kinetics in the system could be attributed to the excellent physical properties of Cyanex 600, which facilitate faster mass transfer. It can also be explained by the high extractant concentration compared to the metal concentration. The extraction time (t) was set to 10 minutes for optimal time and cost efficiency.

As the standard solution of Zn contains nitrates that could affect the solvent extraction, another source of Zn has been investigated, zinc oxide, ZnO.

Indeed, studies suggested that H_2O and NO_3^- molecules participate in the formation of extractable Mo species in nitric acid medium.[47,48,64] Next, experiments including Zn will be performed with ZnO.

As said previously, the extractant concentration in the system is high compared to the metal concentration. Different extractant concentrations were screened, from 0.01 to 1 M, to determine their impact on the extraction efficiency, distribution coefficients, and selectivity of Mo. Results are given in Fig. 7.

Regarding the results, decreasing the extractant concentration increases the selectivity for Mo as less undesirable elements are extracted below 1 M of Cyanex 600, while Mo is still efficiently extracted. This is in good agreement with other studies, which show that Mo can be quantitatively extracted (>80%) with low concentrations (<0.5 M) of Cyanex (272, 301, 572) extractants in acid media.[21,34,65,66] At higher extractant concentrations, Zn and Cr are increasingly extracted, thereby affecting the selectivity. Below an extractant concentration of 0.1 M, Mo extraction yield begins to decline. At 0.01 M, only 36% of Mo is extracted, corresponding to a distribution coefficient of $D_{Mo} = 0.6$. Thus, for this feed solution, a 0.1 M concentration seems to be the most selective for Mo relative to Zn and Cr.

The effect of the phase ratio, θ, on Mo extraction was investigated. Decreasing θ offers two main advantages: it reduces the consumption of the organic phase, thereby lowering extractant costs, and it concentrates the target metal in the organic phase.

The distribution coefficients remain consistently high ($D > 10$) across all tested θ values (from 1 to 0.1), as shown in Fig. 8. However, extraction efficiency began to decline below $\theta = 0.25$, reaching 71% at $\theta = 0.1$, leaving 124 ppm of Mo in the raffinate. Based on these results, $\theta = 0.25$ was identified as the optimal ratio, under which a Mo concentration of 1.5 g/L was achieved in the organic phase.

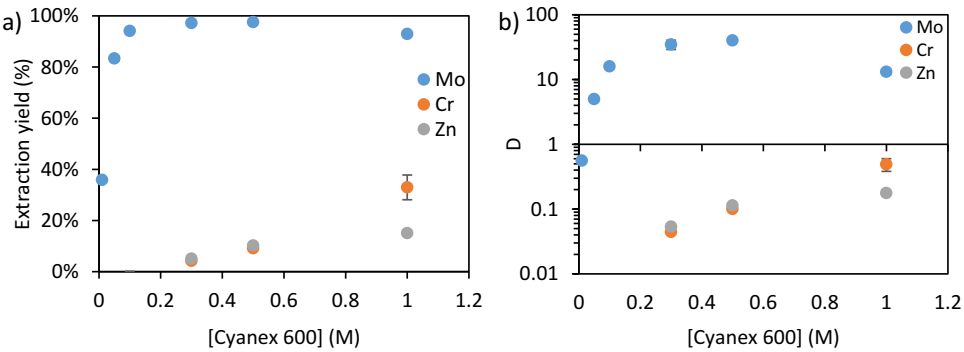

Figure 7. a) Extraction yields and b) distribution coefficients of metals at different concentrations of Cyanex 600. Conditions: $pH_{eq} = 1.4$, $t = 10$ min, $\theta = 1$, and $T = 20°C$. Uncertainties of triplicates are given.

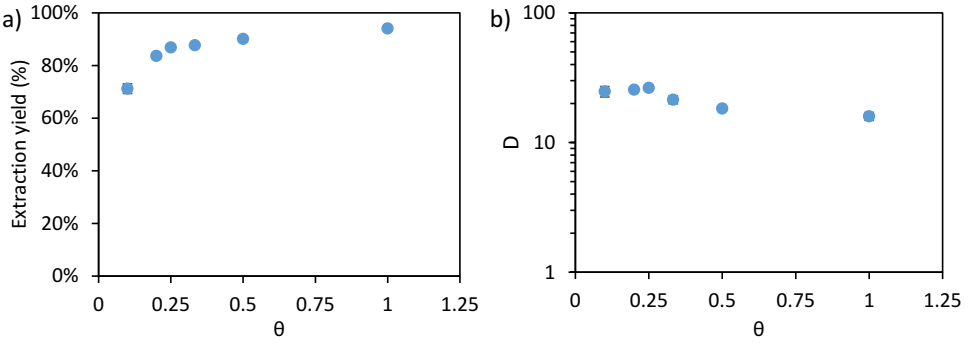

Figure 8. Mo extraction yields a) and distribution coefficients b) at different organic to aqueous ratios. Conditions: pH_{eq} = 1.4, [Cyanex 600] = 0.1 M, t = 10 min, θ = 1, and T = 20°C. Uncertainties of triplicates are given.

To determine the number of extraction stages required for maximum Mo recovery using 0.1 M Cyanex 600, a McCabe–Thiele diagram was constructed following the methodology reported in the literature.[67,68] Figure 9 shows the extraction curve obtained by contacting the feed and the extractant under the optimal extraction conditions (pH_{eq} = 1.4, [Cyanex 600] = 0.1 M, t = 10 min and T = 20°C) at different θ. The curve was extrapolated to the origin (dashed gray line), and two operating lines were drawn based on a target extraction efficiency of 99% and 95% at θ = 0.25.

The McCabe–Thiele construction indicates that three theoretical counter-current stages are sufficient to achieve 99% extraction of Mo into the organic phase at θ = 0.25, while two are sufficient to extract 95% of Mo.

Stripping

Complete transfer of Mo from the organic to the aqueous phase during stripping is essential to allow further processing and recovery of the final

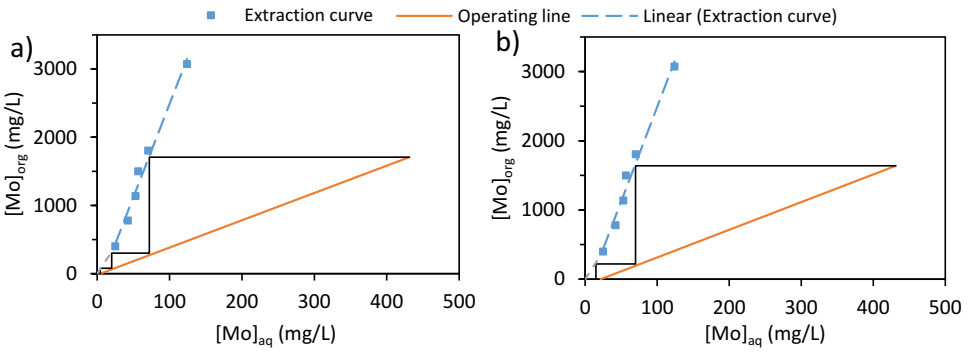

Figure 9. McCabe–Thiele diagrams for Mo extraction. a) Operating line for 99% extraction, b) Operating line for 95% extraction. Conditions: θ = 0.25, [Mo] = 430 mg/L, pH_{eq} = 1.4, [Cyanex 600] = 0.1 M, t = 10 min, and T = 20°C.

product. The strong association between Mo and Cyanex 600 observed, however, makes complete stripping challenging. Given the stability of the Mo-extractant complex formed at low pH, acid stripping yields only partial recovery. Since Mo loading weakens at higher pH, using a base is a more suitable alternative for effective stripping. Two stripping agents were therefore investigated and compared to confirm the theory: sulfuric acid (H_2SO_4), a commonly used reagent for stripping loaded organic phases, and ammonium hydroxide (NH_4OH), which has demonstrated promising performance for the stripping of Mo-loaded organic phases.[21,69] θ was kept to 1, and different stripped solution concentrations were tested (0.1 and 0.25 M for H_2SO_4, while 0.25, 0.1, 0.15, 0.2 and 0.25 M for NH_4OH).

The settling time with the acid stripping was fast, and both phases were clearly separated. In contrast, alkaline stripping resulted in significantly longer settling times, requiring a centrifugation step to achieve phase separation. Even after centrifugation, stripping with 0.2 M NH_4OH and 0.25 M NH_4OH resulted in cloudy phases, and a white turbidity was observed in the aqueous phase. The stripping vials after alkaline stripping are shown in Fig. 10.

The stripping results are summarized in Table 6. Acid stripping proved ineffective for Mo recovery, with stripping efficiencies below 5% (<50 mg/L in the final product), consistent with the strong Mo-extractant complex formed at low pH. For alkaline stripping, only 0.1 and 0.15 M NH_4OH were

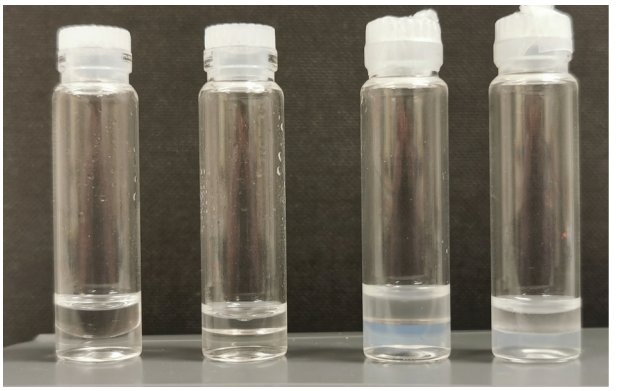

Figure 10. Stripping of Mo using different concentrations of NH_4OH, from left to right: 0.1 M, 0.15 M, 0.2 M, 0.25 M. Conditions: θ = 1, t = 30 min, and T = 20°C.

Table 6. Recovery of Mo into the aqueous phase achieved with acid and alkaline stripping agents. Conditions: θ = 1, t = 30 min, and T = 20°C.

	Mo stripping yield (%)	Mo product concentration (mg/L)	Mo product concentration (mM)	pH of the product solution
H_2SO_4 0.1 M	1.6 ± 0.05	24.2 ± 0.7	0.25 ± 0.01	0.5
H_2SO_4 0.25 M	3.3 ± 0.1	49.0 ± 1.4	0.51 ± 0.01	0.9
NH_4OH 0.1 M	68.9 ± 1.4	1071 ± 22	11.2 ± 0.2	5.3
NH_4OH 0.15 M	88.7 ± 1.8	1377 ± 27	14.3 ± 0.3	8.4

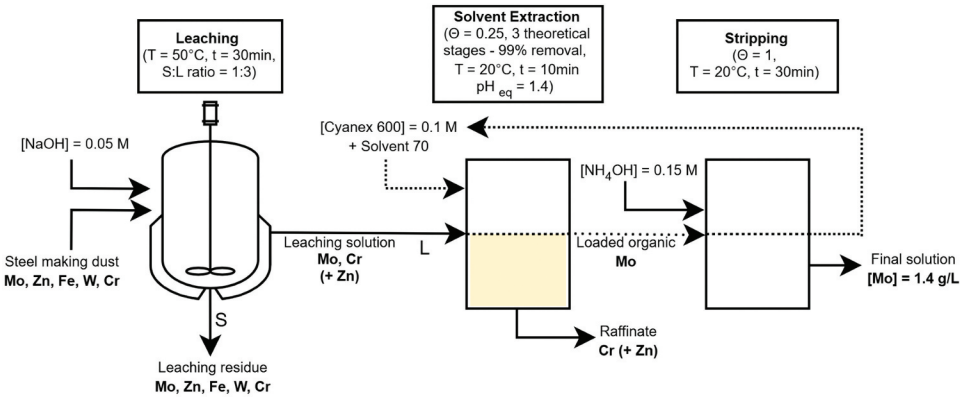

Figure 11. Flowsheet for the separation of Mo, Cr, and Zn from steelmaking dust alkaline leachate.

considered, as higher concentrations caused phase turbidity issues. Both conditions significantly outperformed acid stripping: 0.1 M NH_4OH achieved 69% Mo stripping (1 g/L in the final product), while 0.15 M NH_4OH yielded 89% recovery (1.4 g/L in the final product). These results identify 0.15 M NH_4OH as the optimal stripping condition for the recovery of highly pure and concentrated Mo.

A flowsheet for Mo, Cr, and Zn separation from the feed is presented in the figure below (Fig. 11).

Conclusion

This work contributes to the selective recovery of Mo from steelmaking dust via alkaline leaching and solvent extraction with Cyanex 600. Two feeds for the solvent extraction step were studied: the first contained only Mo and Cr (after leaching with 0.05 M NaOH), and the second was an identical solution enriched with 40 ppm Zn, as the versatility of the steelmaking dust could lead to Zn presence in the feed despite the first selective dissolution.

For the first feed, selective recovery of Mo was achieved in the pH range 2–4, with extraction yields exceeding 95% for Mo and below 10% for Cr, and a $SF_{Mo/Cr}$ approaching 600. The extraction mechanisms of both metals were investigated, revealing that phosphine oxide impurities play a critical role in the extraction process through solvation reactions.

For the second feed, extractant concentration was found to significantly influence the extraction selectivity. At low concentrations (≤0.1 M), Mo is efficiently and selectively extracted from the feed solution, and neither Cr nor Zn goes into the organic phase. The optimal extraction conditions were determined to be $pH_{eq} = 1.4$, [Cyanex 600] = 0.1 M, contact time of 10 min, and T = 20°C. Investigation of θ demonstrated that Mo can be concentrated in the organic phase at a $\theta = 0.25$ while maintaining high extraction yields.

McCabe–Thiele analysis indicated that three countercurrent stages are required to achieve 99% Mo extraction under optimal conditions. Stripping experiments identified 0.15 M NH_4OH as the optimal stripping reagent, yielding a highly pure and concentrated Mo solution of 1.4 g/L. These results demonstrate that Cyanex 600 is a top-of-the-line extractant for the selective recovery of Mo from steelmaking dust leachates.

This study contributes to the understanding of Mo recovery from steelmaking dust, an area with limited research, and demonstrates an effective approach. The work also provides a better understanding of the extraction mechanism and highlights the impact of the impurities present in the extractant.

Author contributions

CRediT: **Ilyes Mahti:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing; **Léa M. J. Rouquette:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing; **Martina Petranikova:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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ORCID

Ilyes Mahti http://orcid.org/0009-0007-1226-5005
Léa M. J. Rouquette http://orcid.org/0000-0003-0780-4020
Martina Petranikova http://orcid.org/0000-0002-0957-7768

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