

RESEARCH PAPER

Desorption of Molybdenum from Purolite A-100 by Ammonium Hydroxide: Towards Technical-Grade MoO₃

Bagdaulet Kenzhaliyev¹, Almagul Ultarakova¹, Nina Lokhova¹, Arailym Mukangaliyeva^{*1}, Azamat Yessengazyev¹, Kaisar Kassymzhanov¹, Azamat Toishybek¹, Nurzhan Sadykov¹

¹ Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty 050013, Kazakhstan; bagdaulet_k@satbayev.university (B.K.); a.ultarakova@satbayev.university (A.U.), n.lokhova@satbayev.university (N.L.), a.mukangaliyeva@satbayev.university (A.M.), a.yessengazyev@satbayev.university (A.Y.), k.kassymzhanov@satbayev.university (K.K.), azxoff@gmail.com (A.T.), namad2003@mail.ru (N.S.)

* Correspondence: a.mukangaliyeva@satbayev.university; Tel.: +7-777-3934621; Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty 050013, Kazakhstan

Received: 01.06.2026

Accepted: 04.06.2026

ABSTRACT

This study addresses the desorption of molybdenum from the Purolite A-100 macroporous weak-base anion-exchange resin using ammonium hydroxide solutions, followed by the recovery of technical-grade molybdenum trioxide from the concentrated eluate. Sorption from a model sulphuric acid solution (0.396–0.408 g/L Mo) was carried out at 80°C for 30 minutes, achieving a recovery of 48.7% with a static exchange capacity of 15.8–16 mg/mL. Under standard single-stage saturation, the degree of desorption with 12% NH₄OH did not exceed 27.2%, regardless of contact time (15–240 min) or temperature (20–40°C). A multi-cycle saturation strategy – 25 consecutive sorption cycles – produced a linear increase in resin capacity up to 182.27 mg/mL and brought subsequent molybdenum recovery into the eluate to 94%, at a final concentration of 3.63 g/L (120 g/L NH₄OH, 40°C, 120 min). Thermodynamic modelling of the Mo–H₂O system in HSC Chemistry 8.0 confirmed that pH 1.5 falls within the stability field of MoO₃·H₂O, justifying the chosen precipitation conditions. Acidification of the eluate to pH 1.5 with co-precipitation using ammonium sulphate, followed by calcination at 600°C, yielded 6.21 g of technical-grade molybdenum trioxide identified by XRD as molybdate MoO₃ (PDF 00-035-0609, 100%) with total impurity content below 0.14%.

Keywords: molybdenum; ion exchange; Purolite A-100; desorption; ammonium hydroxide

INTRODUCTION

Molybdenum is one of those metals whose absence would bring entire industrial sectors to a standstill [1]. Superalloys in aircraft turbines, hydrotreating catalysts in petroleum refining, thin-film electronics – the element is functionally irreplaceable across all of these [2, 3]. Global consumption reached 304,700 tons in 2025, with engineering and stainless steels alone accounting for over 60% of demand, and chemical applications accounting for a further 13% [4]. According to the latest USGS estimates, global mine production in 2024 stood at 260 kt, supported by reserves of 15 Mt [5].

Behind these figures, however, lies a pressing metallurgical challenge that is geological at its root. Molybdenum is a dispersed element in the Earth's crust (crustal abundance ~1.2 ppm) and does not occur in native form; its principal industrial mineral, molybdenite (MoS₂), is genetically associated with copper, tungsten, and rhenium within giant porphyry copper systems. As a consequence, the majority of global molybdenum supply – including the entire Kazakhstani output from the Balkhash ore belt (Aktogay, Bozshakol) – is recovered as a by-product of copper concentrate processing, which couples Mo production to the dynamics of the copper industry [6]. As high-grade sulphide zones are progressively depleted, operators are increasingly forced to process oxidised ores from supergene weathering zones, where molybdenum occurs as powellite (CaMoO₄) and ferrimolybdate (Fe₂(MoO₄)₃·nH₂O). These secondary minerals do not respond to sulphide flotation – they dissolve and migrate into the highly acidic sulphate heap-leach raffinate streams generated during copper recovery [7]. The metal is effectively lost. At concentrations typically in the tenths of a gram per litre, conventional precipitation is of little use: the driving force for nucleation is simply insufficient for complete and selective product recovery.

This pattern of valuable-component losses in process liquors is not unique to molybdenum and has motivated diverse recovery strategies across non-ferrous hydrometallurgy. Mechanochemical pre-treatment has been shown to substantially improve zinc extraction yields from refractory secondary raw materials [8]. Oxidative leaching of copper smelter wastes from the Balkhash plant has demonstrated the feasibility of recovering metal values from solid residues that conventional flowsheets discard [9]. Bioleaching of copper flotation tailings [10, 11] further illustrates the broader industry trend toward intensification and circular processing schemes.

Solvent extraction using tertiary amines and organophosphoric acids has historically been the method of choice for molybdenum recovery from such dilute, compositionally complex streams [12–15]. The approach is technically sound under idealised conditions but exhibits well-documented vulnerabilities in high-sulphate matrices: the organic phase tends to coagulate, stable emulsions form [16], and a persistent third phase develops [17–19]. Co-extraction of iron is substantial, necessitating additional stripping stages, while the obligatory use of flammable hydrocarbon diluents introduces environmental and operational hazards that are difficult to justify at active processing facilities [20].

Ion-exchange sorption on macroporous anion-exchange resins offers a route around these limitations and has gained traction as a cleaner technical alternative [21, 22]. The chemical rationale is straightforward. In sulphate media at pH < 2, Mo(VI) speciation shifts decisively toward anionic sulphato-complexes of the type [MoO₂(SO₄)₂]²⁻; these bulky anions are selectively captured by weak-base anion-exchange, while competing cationic impurities – Fe³⁺, Cu²⁺, Al³⁺ – pass largely unretained [23]. The body of evidence accumulated to date indicates that molybdenum recovery from sulphate leach solutions on resins of various types routinely reaches 90–99%, with results that are highly reproducible across different feed compositions [24–28].

A clear imbalance has emerged in the published literature: while sorption itself has received exhaustive treatment, the desorption step – examined in terms of elution completeness, kinetics, and the influence of resin loading level – remains only fragmentarily described. Yet it is desorption that ultimately governs the economics of the entire process. The molybdenum concentration in the eluate, the purity of the final product, and the number of regenerations cycles a resin can sustain without capacity loss all hinge on this stage. The choice between alkaline (NaOH) and ammonia-based (NH₄OH) eluents is therefore far from trivial. Ammonia elution delivers ammonium molybdate in a single step – a direct precursor for technical-grade molybdenum trioxide – whereas the use of sodium hydroxide introduces ballast Na⁺ that persists in the product after calcination.

The inherent difficulty of desorbing molybdenum from anion-exchange resins traces back to the polymorphism of its anionic forms across the pH scale. In an alkaline desorbing solution, Mo(VI) exists as the monomeric MoO₄²⁻ ion, but on a resin loaded from acidic sulphate media, it is held as a bulky polynuclear species – the heptamolybdate Mo₇O₂₄⁶⁻ – together with sulphato complexes of the [MoO₂(SO₄)_n]⁻⁽²ⁿ⁻²⁾ family. Con- version between these forms demands not only the rupture of ion-exchange bonds with the resin's functional amino groups, but

also structural reorganisation of the anion itself, and this slows elution kinetics appreciably. Sulphate retained within the pores of the loaded resin adds a second complication: upon introduction of the ammonia eluent, SO_4^{2-} competes with MoO_4^{2-} for active sites and erodes the driving force for ex-change. These factors together account for the characteristically low single-contact elution yields obtained with dilute NH_4OH solutions, and they explain why both eluent concentration and the degree of resin pre-saturation must be optimised in tandem. Three classes of eluents dominate the published literature on molybdenum desorption from anion-exchange resins: NaOH solutions, NH_4OH solutions, and mixed NH_4OH – NH_4HCO_3 systems. Sodium hydroxide delivers high elution yields – typically 95–98% –but produces sodium molybdate (Na_2MoO_4) in the eluate, and additional purification steps are then required to remove Na^+ before the final product can be recovered [29, 30]. Several groups have advocated ammonium-carbonate systems in which NH_4HCO_3 functions simultaneously as a buffer and as a precipitating agent: during eluate evaporation the carbonate decomposes, simplifying the subsequent isolation of ammonium molybdate [31]. Ammonia elution with aqueous NH_4OH in the 5–15% concentration range has been studied for resins such as Amberlite IRA-400, D296, and related grades, with single-stage molybdenum recoveries of 60–85% and a strong re-ported dependence on resin loading level and phase volume ratio. Systematic data on how multiple pre-saturation cycles affect the completeness of subsequent desorption are essentially absent from the literature, and this gap defines the scientific novelty of the present study.

The work reported here addresses the desorption of molybdenum from the Purolite A-100 anion-exchange resin using ammonium hydroxide solutions. We examined the influence of eluent concentration, temperature, and contact time on the elution yield, and tracked how the completeness of desorption depends on the number of pre-saturation cycles applied to the resin. Operating under the optimised conditions identified, we obtained technical-grade molybdenum trioxide, which was subsequently characterised by X-ray diffraction and X-ray fluorescence analysis.

MATERIAL AND METHODS

Materials

The test medium was a model sulphuric acid solution containing molybdenum, prepared by dissolving ammonium molybdate in sulphuric acid. Molybdenum concentration in the feed solution ranged from 0.396 to 0.408 g/L, corresponding to the typical metal content found in barren liquors from heap leaching of copper–molybdenum ores.

The ion-exchange material employed was Purolite A-100 (King of Prussia, PA, USA), a weak-based macroporous anion-exchange resin built on a polystyrene matrix with tertiary amine functional groups. Prior to use, the resin underwent the following conditioning sequence: rinsing with distilled water, treatment with 4% NaOH solution ($\geq 98\%$, analytical grade, Almaty, Kazakhstan), repeated rinsing with distilled water until the wash water reached neutral pH, conversion into the sulphate form by contact with 5% H_2SO_4 (95–98%, reagent grade, Almaty, Kazakhstan), and a final water rinse.

Aqueous ammonium hydroxide (NH_4OH , reagent grade, Almaty, Kazakhstan), of analytical purity grade qualification, served as the desorbing agent at two concentrations – 12 wt.% and 120 g/L. The rationale behind selecting an ammonia-based eluent rests on its dual functionality: NH_4OH not only elutes molybdate ions from the active sites of the resin, but simultaneously forms ammonium molybdate ($(\text{NH}_4)_2\text{MoO}_4$) in the eluate – a direct precursor for downstream precipitation of the final product.

For the precipitation of molybdenum from the acidified eluate, ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ of chemically pure grade was used. Acidification of the eluate to pH 1.5 was carried out with concentrated sulphuric acid (chemically pure grade). All solutions were prepared using distilled water.

Equipment and Analytical Techniques

Batch sorption and desorption experiments were carried out on a KS 3000 i control orbital shaker (Staufen im Breisgau, Germany). Temperature control during desorption runs was maintained using an LOIP LT-100 liquid-circulation thermostat (Saint Petersburg, Russia). Suspension agitation during precipitation operations relied on an ES VELP overhead stirrer (Usmate Velate, Italy) and IKA RW16 basic (IKA-Werke, Staufen, Germany). pH measurements were taken with a benchtop HI 2213-02 pH/ORP meter (Hanna Instruments, Shelton, CT, USA),

calibrated by a three-point procedure across the –2.00 to 16.00 pH range, with automatic temperature compensation in the range of –20 to +120°C. Resin aliquots, reagents, and precipitates were weighed on a Shimadzu analytical balance (Kyoto, Japan). Drying of samples took place in a SNOL drying oven (Utena, Lithuania), while calcination at 600°C was performed in a SNOL 7.2/1300 muffle furnace (Almaty, Kazakhstan). Distilled water for the preparation of all solutions was produced using an AE-14 "Ya-FP" laboratory distiller (Ferroplast Medical, Moscow, Russia).

Molybdenum concentrations across all process stages were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) on an Optima 8300 DV spectrometer (PerkinElmer, Shelton, CT, USA).

The phase composition of the obtained product was established by X-ray diffraction analysis (XRD) on a D8 ADVANCE diffractometer (Bruker, Ettlingen, Germany), with Cu-K α radiation and phase identification against the PDF-2 database (ICDD, Swarthmore, PA, USA).

Elemental composition of the samples was characterized by X-ray fluorescence spectrometry on a PANalytical Venus 200 instrument (PANalytical, Almelo, The Netherlands).

Thermodynamic modelling and the construction of Pourbaix diagrams for the Mo–H $_2$ O system were performed using the HSC Chemistry 8.0 software package (Outotec, Espoo, Finland).

Experimental Methodology

Prior to each experimental series, the Purolite A-100 anion-exchange resin was conditioned through the following sequence: rinsing with distilled water, treatment with 4% NaOH solution, repeated rinsing with distilled water until the wash water reached neutral pH, conversion into the sulphate form by exposure to 5% H_2SO_4 , and a final rinse with distilled water. Resin volume in all experiments was measured using a graduated cylinder while the resin was swollen.

Sorption experiments were conducted in batch mode at three distinct solid-to-liquid (S:L) ratios corresponding to three experimental series. In Series 1: 4 mL of Purolite A-100 was contacted with 240 mL of model sulphuric acid solution containing 0.396 g/L Mo (S:L = 1:60). In Series 2: 16 mL of resin was contacted with 320 mL of model solution containing 0.408 g/L Mo (S:L = 1:20). In Series 3 (multi-cycle saturation): 60 mL of resin was contacted sequentially with 100 mL aliquots of feed solution (0.4 g/L Mo) per cycle, corresponding to S:L = 1:1.7 per individual cycle and a cumulative solution-to-resin contact ratio of 1:41.7 over 25 saturation cycles. In all series, sorption was performed at 80°C for 30 minutes on a KS 3000 i control orbital shaker. Once sorption was completed, the resin was separated by paper filtration, and the filtrate was analysed for molybdenum content by ICP-OES. The degree of molybdenum recovery onto the resin (R, %) and the static exchange capacity (SEC, mg/g) were calculated from standard mass balance equations.

Desorption experiments were carried out in three consecutive series to clarify the effects of contact time, temperature, and resin saturation level on elution completeness. In the first series, the molybdenum-loaded resin (4 mL) was transferred into conical flasks containing 100 mL of 12% NH_4OH solution and shaken at room temperature for 15, 20, 30, 40, and 60 minutes, respectively. The second series employed a larger resin volume (16 mL), an elevated desorption temperature of 40°C, and contact times in the 120–240-minute range; temperature was held constant using the LOIP LT-100 circulation thermostat. After each run the resin was filtered off and the eluate was analysed for molybdenum.

A third series was undertaken with the aim of producing a more concentrated eluate by subjecting the resin to repeated pre-saturation. Aliquots of 60 mL of resin were placed into conical flasks together with 100 mL of feed solution (0.4 g/L Mo). Sorption proceeded at 80°C for 30 minutes, after which the solution was decanted and the cycle repeated. Saturation was performed in successive blocks of five cycles – running from cycles 1–5 through to cycles 21–25 – with a resin sample taken after each block to determine the accumulated capacity. Desorption from the loaded resin (160 mL) was carried out in 200 mL flasks using 120 g/L NH_4OH at 40°C over 120 minutes.

The resulting eluate (1200 mL, 3.63 g/L Mo) was acidified with concentrated sulphuric acid to pH 1.5. Molybdenum precipitation was achieved by introducing 5 g of ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$ under continuous stirring for 4 hours. The precipitate was separated by filtration, dried at 100°C for 2 hours in a SNOL drying oven, and subsequently calcined in a SNOL 7.2/1300 muffle furnace at 600°C for 2 hours. The obtained product was characterised by X-ray diffraction and X-ray fluorescence analysis.

RESULTS AND DISCUSSION

Desorption of Molybdenum from the Purolite A-100 Anion-Exchange Resin

The desorption process was investigated through three consecutive experimental series, with elution conditions varied stepwise to achieve a technologically acceptable degree of molybdenum recovery in the eluate.

In the first series, the loaded resin (4 mL, SEC 15.8 mg/mL) was contacted with 100 mL of 12% NH_4OH solution at room temperature for 15–60 minutes. The data summarised in Table 1 show that molybdenum recovery into the eluate remained modest across the entire time range examined – from 18.1% at 15 and 20 minutes to 25.9% at 60 minutes.

Table 1 Desorption of molybdenum with 12% NH_4OH solution at room temperature

Sample	Mo content, g/L	Volume, mL	Resin, mL	Mo in eluate, g	Recovery, %
Sorbed onto resin	0.0193	—	—	—	—
Eluate, 15 min	0.035	100	4	0.0035	18.1
Eluate, 20 min	0.035	100	4	0.0035	18.1
Eluate, 30 min	0.04	100	4	0.004	20.7
Eluate, 40 min	0.047	100	4	0.0047	24.4
Sample	Mo content, g/L	Volume, mL	Resin, mL	Mo in eluate, g	Recovery, %

Notably, the same eluate concentration was recorded at 15 and 20 minutes (0.035 g/L Mo); further extension of the contact time produced only a gradual increase in concentration. This pattern points to a kinetic limitation of the process at ambient temperature, compounded by an insufficient driving force for elution at the chosen phase ratio.

The second series employed a larger resin volume (16 mL), an elevated desorption temperature of 40°C, and contact times of 120, 180, and 240 minutes. Despite the more aggressive operating conditions, the outcomes (Table 2) remained on par with those of the first series: peak recovery of 27.2% was registered at 120 minutes (0.0533 g/L Mo), while extending the contact period to 180 and 240 minutes failed to increase the eluate molybdenum concentration, which plateaued at 0.047 g/L (23.9%).

Table 2 Desorption of molybdenum with 12% NH_4OH solution at 40°C

Sample	Mo content, g/L	Volume, mL	Resin, mL	Mo in eluate, g	Recovery, %
Sorbed onto resin	0.0196	—	—	—	—
Eluate, 120 min	0.0533	100	16	0.00533	27.2
Eluate, 180 min	0.047	100	16	0.0047	23.9
Eluate, 240 min	0.047	100	16	0.0047	23.9

Reaching a plateau as early as 120 minutes indicates that the rate-limiting factor was not diffusional kinetics but rather the thermodynamic equilibrium of the resin–eluent system. With the resin only modestly loaded, the concentration driving force for desorption proved inadequate even at elevated temperature. This observation prompted a fundamentally different strategy. Rather than intensifying the elution conditions further, it was decided to substantially increase the resin saturation level through repeated sorption cycling.

In the third series, the resin (60 mL) was subjected to sequential saturation in blocks of five cycles each – proceeding from cycles 1–5 through to cycles 21–25. As shown in Fig. 1, the accumulated resin capacity increased almost linearly with cycle count: from approximately 25 mg/mL after the first five cycles to ~70 mg/mL after cycles 6–10, ~112 mg/mL after 11–15, ~148 mg/mL after 16–20, and 182.27 mg/mL upon completion of 25 cycles. The linear character of this dependence indicates that no irreversible deactivation of the active sites occurs during repeated use – the resin retains its exchange capacity throughout the entire experiment.

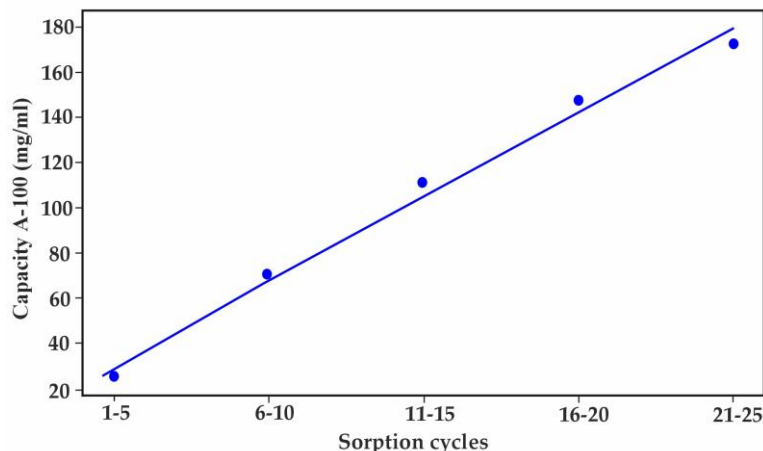


Fig. 1 Effect of the number of sorption cycles on molybdenum loading of the Purolite A-100 resin.

Desorption from the maximally loaded resin (160 mL) was performed in six 200 mL flasks using 120 g/L NH_4OH at 40°C over 120 minutes. Under these conditions, molybdenum recovery into the eluate reached 94%, with a final eluate concentration of 3.63 g/L Mo. A direct comparison of the three series demonstrates the decisive role of resin saturation: shifting from a lightly loaded resin (SEC ~15.8 mg/mL) to a heavily saturated one (182 mg/mL) – at the same desorption temperature of 40°C – raised the molybdenum recovery from 27.2% to 94%. The explanation lies in the sharp increase in concentration gradient between the resin phase and the solution, which shifts the desorption equilibrium toward the eluate and amplifies the mass-transfer driving force.

Precipitation and Production of Technical-Grade Molybdenum Trioxide

The aqueous chemistry of molybdenum is considerably more complex than a simple pH-dependent transformation scheme. Speciation is simultaneously governed by three interdependent parameters: pH, total molybdenum concentration, and electrochemical potential (Eh). At concentrations below 10^{-3} mol/L, the monomeric molybdate anion MoO_4^{2-} remains dominant even at mildly acidic pH, as the probability of polycondensation is low. By contrast, at concentrations characteristic of the concentrated eluate used in this study (3.78×10^{-2} mol/L), polycondensation proceeds significantly more readily upon acidification, thereby accounting for the high precipitation yields achieved at pH 1.5. With regard to electrochemical potential, all operational stages of the present process – sorption, desorption, acidification, and precipitation are conducted under aerated, oxidising conditions ($E_h \approx +0.2$ to $+0.5$ V), where molybdenum exists exclusively in its hexavalent state (Mo(VI)). The stability fields of tetravalent MoO_2 and metallic Mo are accessible only at strongly negative Eh values not encountered at any stage of the present work. These considerations are directly reflected in the Pourbaix diagram.

The chemical state of molybdenum in aqueous solutions is governed first and foremost by the acidity of the medium. The transformation of molybdenum-bearing anions across the pH scale follows the sequence MoO_4^{2-} (pH 14 → 6.5) $\rightleftharpoons \text{Mo}_3\text{O}_{11}^{4-}$ (pH 6.5 → 4.5) $\rightleftharpoons \text{Mo}_8\text{O}_{21}^{6-}$ (pH 4.5 → 1.5), while in strongly acidic sulphate media the metal converts into the neutral molybdenyl sulphate MoO_2SO_4 together with anionic complexes of the $[\text{MoO}_2(\text{SO}_4)_n]^{-(2n-2)}$ family. The eluate obtained at the preceding stage was an alkaline solution of ammonium molybdate $(\text{NH}_4)_2\text{MoO}_4$ with a pH of around 9–10, in which molybdenum exists as the highly soluble MoO_4^{2-} ion and is therefore not amenable to direct precipitation.

The thermodynamic justification for the chosen precipitation pH is supported by the Pourbaix diagram for the Mo-H₂O system, constructed at a molybdenum concentration of 3.78×10^{-2} mol/L and a temperature of 25°C (Fig. 2). The diagram reveals that across a broad pH window from 0 to 9, under oxidising Eh values (above +0.20 V) – conditions consistent with an aerated sulphate solution – the thermodynamically stable solid phase is MoO₃·H₂O, molybdic acid. Above pH 9, the metal shifts into the soluble molybdate ion MoO₄²⁻, which matches the state of the eluate obtained after ammonia stripping. Acidifying the eluate to pH 1.5 drives the system out of the soluble MoO₄²⁻ field and deep into the stability domain of MoO₃·H₂O, thereby securing thermodynamic completeness of molybdenum precipitation. Subsequent calcination at 600°C completes dehydration of the precipitate, yielding anhydrous MoO₃.

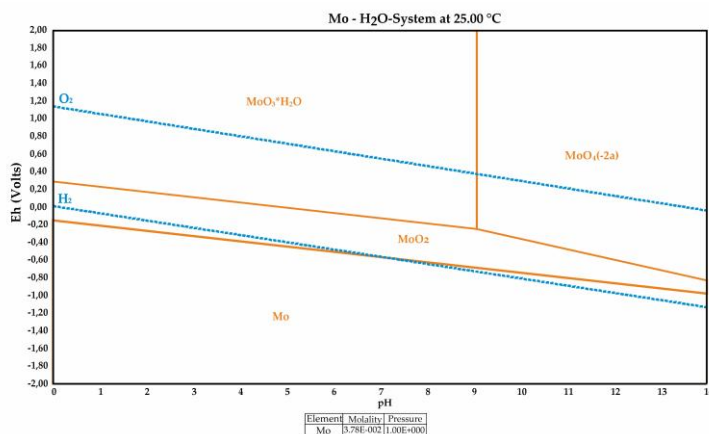
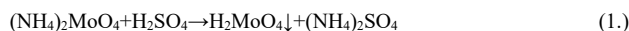


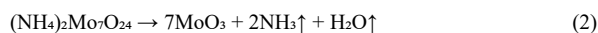
Fig.2 Pourbaix diagram (ϕ -pH) for the Mo-H₂O system at 25°C.

To convert molybdenum into an insoluble form, the 1200 mL eluate containing 3.63 g/L Mo was acidified with concentrated sulphuric acid to pH 1.5. As the pH decreases, the molybdate ion undergoes protonation and polycondensation, generating polymolybdates that become less soluble upon further acidification and precipitate as molybdenum hydroxide. The process can be described by the following reaction:



To improve the completeness of precipitation, 5 g of ammonium sulphate (NH₄)₂SO₄ was added to the acidified solution. The salting-out agent drives further deposition of molybdenum by raising the ionic strength of the solution and shifting the equilibrium toward the formation of insoluble ammonium polymolybdates. Precipitation was carried out under continuous stirring for 4 hours, with the molybdenum recovery from solution reaching 80–100%.

The precipitate was separated by filtration, dried at 100°C for 2 hours to remove free moisture, and then calcined in a muffle furnace at 600°C for 2 hours. During thermal treatment, the ammonium and sulphate groups decompose completely:



The procedure yielded 6.21 g of technical-grade molybdenum trioxide in the form of a pale-yellow powder.

The phase composition of the product was confirmed by XRD analysis: the diffraction pattern of the sample (Figure 3) is fully identified as molybdate MoO₃ (PDF 00-035-0609, 100%), with no detectable impurity phases.

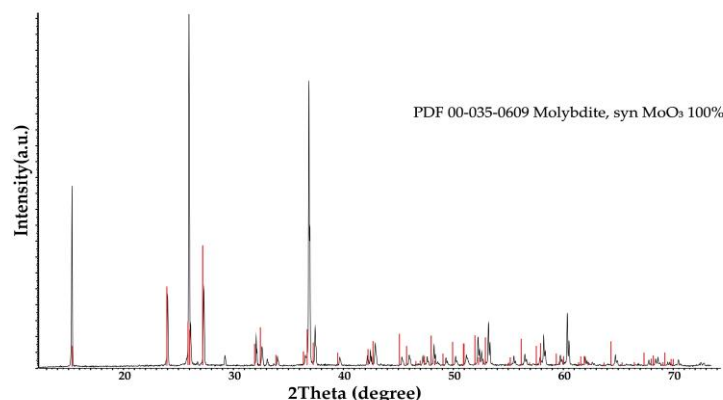


Fig.3 XRD pattern of the molybdenum trioxide product.

Analysis of the Impurity Composition of the Product

Alongside molybdenum, XRF analysis of the obtained trioxide detected trace amounts of copper (0.027%) and thorium (0.111%). The presence of these elements is not coincidental – it has a geochemical explanation tied directly to the nature of the source raw material.

Porphyry copper deposits, which include the principal molybdenum-mining operations of Kazakhstan, are characterised by a consistent geochemical association of Mo-Cu-Re-W, accompanied by dispersed traces of thorium, uranium, and rare-earth elements within accessory minerals such as monazite, thorite, and uranotorite. During acid leaching, these minerals undergo partial dissolution, releasing thorium into solution as Th⁴⁺ together with its sulphate complexes ThSO₄²⁺ and Th(SO₄)₂. Thorium concentrations in such solutions are usually modest – on the order of a few mg/L – yet under conditions of repeated concentration, as occurs during 25 consecutive saturation cycles of the resin, even background levels of impurities inevitably accumulate alongside the target metal.

The behaviour of Th(IV) on the macroporous weak-base anion-exchange resin Purolite A-100 cannot be described as classical anion exchange, since tertiary amine groups are only marginally protonated outside strongly acidic conditions. The trace accumulation of thorium observed in the present study (0.111% in the final product) is attributed to two complementary mechanisms operating throughout the 25 consecutive saturation cycles: partial uptake of [Th(SO₄)₃]²⁻ complexes on the limited fraction of protonated amino groups in the strongly acidic feed solution (H₂SO₄ > 50 g/L, pH ≈ 1), and physical entrapment of hydrolysed thorium species within the macroporous matrix of the resin. The marked difference between the distribution coefficients of Mo(VI) and Th(IV) under these conditions explains why thorium accumulates only at the trace level (~0.1%), while molybdenum is efficiently concentrated.

The copper content (0.027%) reflects the composition of the feed sulphate solution itself, which simulates a barren liquor from the leaching of copper-molybdenum ore – Cu²⁺ is naturally present as a background impurity. Although copper cations are not expected to sorb on a weak-base anionite under normal circumstances, minor physical adsorption within the macroporous structure of the resin cannot be ruled out at elevated concentrations and after repeated contact.

It should be emphasised that the total impurity content in the resulting product does not exceed 0.14%, fully consistent with the specifications for technical-grade molybdenum trioxide. The MoO₃ obtained is suitable for further conversion into commercial products such as ammonium paramolybdate or ferromolybdenum, with subsequent refinement by standard purification techniques. The presence of thorium, however, deserves careful attention in industrial process design: the accumulation of a radioactive element in recycling streams and on the resin over prolonged operation calls for radiation monitoring in accordance with the relevant regulatory standards.

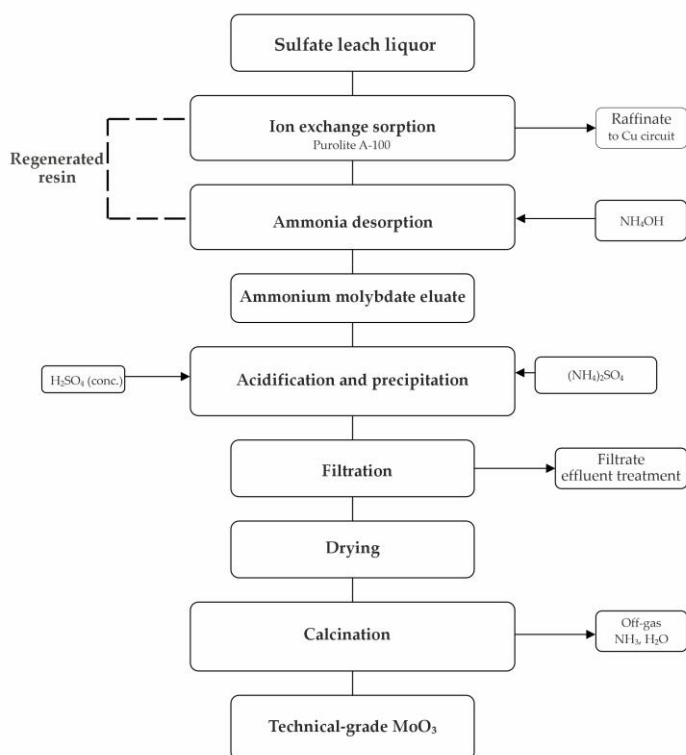
To place the obtained product within the context of established industrial specifications, the elemental composition of the molybdenum trioxide produced in this study was directly compared with the requirements of the principal commercial standards for technical-grade MoO₃, including ASTM A146 (West Conshohocken, PA, USA), ISO 5452 (Geneva, Switzerland) and GOST 17341 (Technical Molybdenum Trioxide, grades MO-2 and MO-3, Moscow, Russia).

Table 3 Comparison of the elemental composition of the obtained MoO₃ product with international industrial-grade specifications

Parameter	Technical grade MoO ₃	ASTM A146 / ISO 5452	GOST 17341 (MO-2)	Industrial MoO ₃ (typical)
Mo content (%)	43.68	≥ 57	≥ 66	≥ 60
MoO ₃ equivalent (%)	65.5	≥ 85.5	≥ 99	≥ 90
Cu (%)	0.027	≤ 0.5	≤ 0.05	≤ 0.5
Th (%)	0.111	not specified	not specified	not specified
Σ trace impurities (%)	0.14	–	–	–

As shown in table 3, the trace impurity levels of Cu (0.027%) and Th (0.111%) in the obtained product are within or below the maximum limits specified by ASTM A146 and GOST 17341 for technical-grade MoO₃. The lower total Mo content compared with the highest commercial grades is attributed to residual sulphur compounds from the (NH₄)₂SO₄ precipitating agent and adsorbed moisture, which account for the unmeasured fraction of the XRF spectrum (~25.5%). These can be effectively removed by a subsequent water-washing step followed by re-calcination at 700°C – a standard post-processing stage not included in the scope of the present study.

Drawing together the experimental findings of the present study, a conceptual flowsheet for the industrial implementation of the proposed scheme is presented in Fig. 4. The flowsheet integrates all unit operations investigated – sorption, ammonia stripping, acidification with precipitation, filtration, drying, and calcination – into a coherent technological sequence, providing a clear basis for further pilot-scale evaluation.

**Fig.4** Proposed industrial flowsheet for molybdenum recovery.

The proposed scheme is designed for compatibility with existing porphyry copper hydrometallurgical infrastructure and requires only standard equipment – ion-

exchange columns, agitated precipitation reactors, filter presses, drying ovens, and muffle or rotary calciners. Two closed-loop streams enhance the environmental and economic feasibility of the process: regenerated resin is returned to the sorption stage, and the depleted raffinate is recycled to the upstream copper circuit. Off-gases from calcination (NH₃, H₂O vapour) are directed to scrubbing for ammonia recovery, while the precipitation filtrate undergoes standard effluent treatment.

CONCLUSION

The decisive factor governing the completeness of molybdenum desorption from the Purolite A-100 anion-exchange resin with NH₄OH solution is the degree of resin saturation, not the elution parameters themselves. Under standard single-stage saturation (SEC ~15.8 mg/ml), molybdenum recovery did not exceed 27.2%, regardless of contact time (15–240 min) or temperature (20–40°C) – the process was constrained not by kinetics but by an insufficient concentration driving force across the phase boundary. The multi-cycle saturation strategy fundamentally changed the picture: 25 consecutive sorption cycles produced a linear increase in resin capacity up to 182.27 mg/mL, and the subsequent desorption under optimised conditions (120 g/L NH₄OH, 40°C, 120 min) delivered 94% molybdenum recovery at an eluate concentration of 3.63 g/L. The linear trend in capacity build-up confirms the absence of irreversible degradation of active sites during repeated use.

Thermodynamic modelling of the Mo-H₂O system in HSC Chemistry 8.0 substantiated the choice of pH 1.5 as the precipitation condition: the Pourbaix diagram shows that under oxidising potentials this pH falls within the stability field of MoO₃·H₂O. Acidification of the eluate with sulphuric acid to pH 1.5, combined with co-precipitation using ammonium sulphate, brought molybdenum recovery into the precipitate to 80–100%. Calcination at 600°C yielded 6.21 g of technical-grade molybdenum trioxide, identified by XRD as molybdate MoO₃ (PDF 00-035-0609, 100%) with no impurity phases. The total content of Cu and Th, as determined by XRF, did not exceed 0.14%, consistent with the specifications for technical MoO₃.

The findings demonstrate the viability of an integrated anion-exchange sorption ammonia stripping scheme for molybdenum recovery from dilute sulphate solutions – the type of liquor encountered in heap-leach circuits of copper-molybdenum ore processing. Further work should focus on scaling the process to column operation, establishing the resin's long-term regeneration capacity, and optimising the final purification stage to reduce thorium and copper contents to levels that meet the specifications for chemically pure MoO₃.

Acknowledgements: This research is funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan, under the targeted funding program BR24992757.

REFERENCES

1. D.R. Lide (Ed.): *CRC Handbook of Chemistry and Physics*, (104th ed., CRC Press: Boca Raton, 2023.
2. A. Panichkin, et al.: *Journal of Composites Science*, 7(12), 2023, 483. <https://doi.org/10.3390/jcs7120483>
3. A. Panichkin, et al.: *AIMS Materials Science*, 10(3), 2023, 517-540. <https://doi.org/10.3934/matricsci.2023029>
4. International Molybdenum Association (IMO). *Molybdenum Market Information: Global Production, Use and Price Data 2025*. IMO: London, UK, 2025.
5. U.S. Geological Survey. *Mineral Commodity Summaries 2025*. U.S. Department of the Interior: Reston, VA, USA, 2025; pp. 122–123. Available online: <https://pubs.usgs.gov/publication/mcs2025> (accessed on 18 May 2026).
6. A. Baibatsha, I. Vikentyev, D. Muratkhonov, K. Bulegenov: *Geology, Geochemistry, and Mineralogy, Geosciences*, 14(9), 2024, 237. <https://doi.org/10.3390/geosciences14090237>
7. B. Kenzhaliyev, et al.: *Materials*, 18(11), 2025, 2496. <https://doi.org/10.3390/ma18112496>

8. T. Sadykov, et al.: Journal of Chemical Technology and Metallurgy, 60(5), 2025, 17. <https://doi.org/10.59957/jctm.v60.i5.2025.17>
9. M. Sydykanov, Y. Bektay, G. Turysbekova, A. Baibatsha, G. Yalcin: International Multidisciplinary Scientific GeoConference: SGEM, 22(4.2), 2022. <https://doi.org/10.5593/sgem2022V/4.2/s18.03>
10. M. Sydykanov, et al.: *Method of bacterial leaching of non-ferrous metals from copper-containing tailings*. Utility Model Patent RK No. 9269, Official Bulletin No. 25, 21 June 2024, <https://doi.org/10.2139/ssrn.4873424>
11. X. Lin, F. Jiao, Q. Wei, Y. Wu: Separation Science and Technology, 59, 2024, 449–463. <https://doi.org/10.1080/01496395.2024.2319143>
12. J. Harvey, et al.: Mrs Energy & Sustainability, 9, 2022, 212–247. <https://doi.org/10.1557/s43581-022-00042-y>
13. J. Du, F. Wei, F. Zhang: ACS Sustainable Resource Management, 2(8), 2025, 1466–1475. <https://doi.org/10.1021/acssusresmg.5c00202>
14. T. Chepushanova, et al.: Chemical Methodologies, 10(1), 2025, 75–111. <https://doi.org/10.48309/chemm.2026.535012.1988>
15. R. Abdulvaliyev, A. Ultarakova, A. Mukangaliyeva, N. Lokhova, K. Kassymzhanov: Separations, 11(10), 2024, 288. <https://doi.org/10.3390/separations11100288>
16. T.A. Lasheen, M.E. El-Ahmady, H.B. Hassib, A.S. Helal: Mineral Processing and Extractive Metallurgy Review, 36(3), 2015 145–173. <https://doi.org/10.1080/08827508.2013.868347>
17. H. Shalchian, F. Ferella, I. Birloaga, I. De Michelis, F. Vegliò: Hydrometallurgy, 190, 2019, 105167. <https://doi.org/10.1016/j.hydromet.2019.105167>
18. R. Behmadi, M. Mirzaei, R. Afshar, H. Najafi: Fuel, 357, 2024, 129772. <https://doi.org/10.1016/j.fuel.2023.129772>
19. B. Paphane, B. Nkoane, O. Oyetunji: Journal of The South African Institute of Mining and Metallurgy, 113, 2013, 485–489.
20. L. Zhang, et al.: Colloids and Surfaces A, 687, 2024, 133508. <https://doi.org/10.1016/j.colsurfa.2024.133508>
21. B. Liu, et al.: Resources, Conservation and Recycling, 181, 2022, 106232. <https://doi.org/10.1016/j.resconrec.2022.106232>
22. F. Ogata, et al.: RSC Advances, 15, 2025, 24475–24482. <https://doi.org/10.1039/d5ra02921j>
23. Y. Fu, et al.: Transactions of Nonferrous Metals Society of China, 28(8), 2018, 1660–1669. [https://doi.org/10.1016/s1003-6326\(18\)64809-5](https://doi.org/10.1016/s1003-6326(18)64809-5)
24. B. Kenzhaliyev, A. Ultarakova, N. Lokhova, A. Mukangaliyeva, K. Kassymzhanov: Processes, 13(5), 2025, 1486. <https://doi.org/10.3390/pr13051486>
25. U.T. Ashrapov, S.S. Khujaev, S.R. Malikov: Machines, Technologies, Materials, 19(8), 2025, 292–295.
26. A. Ultarakova, et al.: Metals, 16(3), 2026, 298. <https://doi.org/10.3390/met16030298>
27. E. Kirillov, Z. Bochkareva, V. Semenishchev, S. Kirillov, G. Bunkov, V. Rychkov: Hydrometallurgy, 230, 2024, 106387. <https://doi.org/10.1016/j.hydromet.2024.106387>
28. P. Cyganowski, P. Pohl, S. Pawlik, D. Jermakowicz-Bartkowiak: International Journal of Molecular Sciences, 26(15), 2025, 7563. <https://doi.org/10.3390/ijms26157563>
29. B. Kenzhaliyev, A. Ultarakova, N. Lokhova, A. Mukangaliyeva, A. Yessengazyev, K. Kassymzhanov: Processes, 14(8), 2026, 1225. <https://doi.org/10.3390/pr14081225>
30. H.-Z. Liu, et al.: Rare Metals, 37, 2018, 707–715. <https://doi.org/10.1007/s12598-018-1077-z>
31. Z. Zheng, et al.: Asian Journal of Chemistry, 26(2), 2014, 393–395. <http://dx.doi.org/10.14233/ajchem.2014.15409>