

Crystallization of Ammonium Heptamolybdate for Reduction to Mo Metal

Chemical and Fuel Cycle Technologies Division

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by

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1 INTRODUCTION

The ¹⁰⁰Mo/⁹⁸Mo recycle process developed by Argonne National Laboratory in collaboration with Oak Ridge National Laboratory (ORNL) and supported by the U.S. Department of Energy (DOE) National Nuclear Security Agency's (NNSA's) Office of Material Management & Minimization (M3) is vital to sustaining the economic production of ⁹⁹Mo [1]. The high-yield molybdenum solution extraction (MOEX) process recovers enriched Mo by acidifying spent generator solutions, extracting Mo using tri-n-butyl phosphate (TBP), and stripping Mo into ammonium hydroxide, where it is later converted to solid (NH₄)₆Mo₇O₂₄ (ammonium heptamolybdate or AHM) by crystallization. It is important to produce the AHM product with consistent particle size and morphology before its thermal treatment and reduction to Mo metal in a furnace. AHM particles that are too small (< 50 µm) result in Mo metal powder that is much too fine to properly fabricate into targets with optimum properties [2,3].

Although commercial producers of ammonium heptamolybdate use a cold crystallization process to produce several-kg quantities of AHM per batch, this method is not ideal for smaller batches (~600 g) of enriched material because of low yields (~40% per batch cycle) [4]. Argonne has made previous attempts to produce 600-g batches of AHM by cold crystallization, but XRD analysis showed that the product was not AHM, nor were its properties suitable for target manufacturing [2]. The approach taken by the MOEX process is rotary evaporation at high temperature (70°C–90°C) and low pressure to quickly evaporate the solution and produce AHM at high yield (~98%) [5]. Initial demonstration of the rotary evaporation process showed excellent particle size distribution and particle morphologies, but the results were inconsistent between batches and operators.

Since the types of solids formed in crystallization processes depend on the chemical speciation of the recovered solute immediately before precipitation, the speciation of Mo in solution during evaporation is key to understanding the production of AHM. Several literature sources indicate that AHM is unstable in solutions at higher temperatures, where (NH₄)₂Mo₂O₇ (ammonium dimolybdate or ADM) begins to dominate (around 80°C–120°C and higher) [6,7].

One study demonstrates the dramatic temperature-dependence of Mo speciation *in situ* using Raman spectroscopy during the heating of AHM solutions (0.2 M) from 20°C to 190°C [6]. Their results showed that the relative abundance of AHM species in solution reduces approximately linearly with temperature, suggesting that ambient or colder temperatures would be more effective for AHM crystallization. However, crystallization by rotary evaporation occurs at much higher Mo concentrations (>1.5 M AHM) when solubility at the given temperature is exceeded and where the formation of polymolybdates in saturated solutions should be promoted.

This report seeks to clarify the temperature, pressure, pH, and concentration dependences of Mo speciation in ammoniacal solutions during evaporation and the influence of these parameters on particle size distribution, morphology, and speciation. We use Raman spectroscopy to probe Mo speciation in saturated solutions of AHM from pH 5.5 to 8 and 30°C–90°C.

2 EXPERIMENTAL METHODS

2.1 Method: Cooling Crystallization at Atmospheric Pressure

A beaker was filled with a portion of a Mo solution and placed on a hot plate with magnetic stirrer set to a temperature of 350°C. A thermocouple and pH probe were placed in the solution while it was stirred, and the temperature, pH, and approximate volume of the solution were recorded at regular intervals as the solution evaporated. The remaining Mo solution was added to the beaker in increments after the solution had evaporated enough to accommodate the added volume.

If the solution reached a volume small enough that the thermocouple and pH probe could not be submerged but no solids were evident, it was transferred to a smaller beaker for the final stage of the evaporation. The hot plate was turned off once very fine specks of white solid were visible in the solution, which was then allowed to cool to ambient temperature (21°C) with stirring.

2.1.1 Trial #1: AHM Cooling Crystallization at Atmospheric Pressure (Final pH 7.7)

A 0.32 M Mo (as AHM) solution was prepared by dissolving 28.3 g AHM in concentrated NH₄OH (20%–22% free NH₃) to a volume of 500 mL. The first stage of the evaporation was performed in a 400 mL beaker until the total solution volume reached approximately 75 mL. At that point, the pH of the solution was adjusted with concentrated NH₄OH to a pH₂₅ of 7.7 (pH₈₀ 6.9), and the solution was allowed to cool to 30°C. No solid precipitation was observed, so the solution was transferred in part to a 50 mL beaker for further evaporation and data logging. The hot plate was turned off once the total volume of solution had reached 40 mL. The solution was left to sit overnight, and then the solid was filtered and washed with 80% reagent alcohol.

2.1.2 Trial #2: AHM Cooling Crystallization at Atmospheric Pressure (Final pH 6.7)

A 0.32 M Mo (as AHM) solution was prepared by dissolving 5.65 g AHM in concentrated NH₄OH (20%–22% free NH₃) to a volume of 100 mL. The evaporation was performed in a 50 mL beaker until the total solution volume reached approximately 20 mL, when 5 mL deionized water was added to the beaker to allow submersion of the pH probe, and the pH of the solution was adjusted with approximately 1.25 mL concentrated HCl to pH_{25} 6.7 (pH_{80} 5.4). At that point, the pH and temperature could no longer be measured due to the small volume of liquid. The hot plate was turned off once the total volume of solution had reached 15 mL, and the solution was allowed to cool to ambient temperature. The solid was filtered and washed with 80% reagent alcohol.

2.1.3 Trial #3: AHM Cooling Crystallization at Atmospheric Pressure (0.05 M HCl; final pH 7.3) A 0.32 M Mo (as AHM)/0.05 M chloride solution was prepared by dissolving 28.3 g AHM and 2.05 mL concentrated HCl in concentrated NH₄OH (20%–22% free NH₃) to a volume of 500 mL. The first stage of the evaporation was performed in a 400 mL beaker until the total solution volume reached approximately 40 mL (the pH probe and thermocouple could not be submerged below 75 mL). The solution was then transferred in part to a 50 mL beaker for further evaporation and data logging. The hot plate was turned off once the total volume of solution had reached 35 mL, and the solution was allowed to cool to ambient temperature. The solid was filtered and washed with 80% reagent alcohol.

2.2 Method: Rotary Evaporator Crystallization

The evaporation flask on a rotovap was filled with a Mo solution, and the solution was evaporated at high or low vacuum until a small amount of solid was visible. The vacuum control knob on a Welch 2027 vacuum system was tightly closed for all high vacuum evaporations, and the rotovap water bath was set to 80°C. For all low-vacuum evaporations, the vacuum control valve was opened and adjusted to maintain a pressure of 250 torr, and the water bath was set to a temperature of 95°C. The solution was then allowed to crystallize by cooling, or the remaining liquid was evaporated under high vacuum until a thick paste was formed in the evaporation flask.

2.2.1 Trial #4: AHM Crystallization Hybrid Method (Low Vacuum)

A 0.32 M Mo (as AHM) solution was prepared by dissolving 14.1 g AHM in concentrated NH_4OH (20%–22% free NH_3) to a volume of 250 mL. The solution was evaporated under low vacuum (250 torr) with a 95°C water bath until the first solids appeared in the solution. The vacuum pump was turned off, and the evaporation flask was raised out of the water bath and allowed to cool to ambient temperature at a slow rotation speed. The resulting solid and remaining solution were filtered, and the solid was washed with 80% reagent alcohol.

2.2.2 Trial #5: AHM Crystallization Hybrid Method (High and Low Vacuum)

A 0.32 M Mo (as AHM) solution was prepared by dissolving 14.1 g AHM in concentrated NH₄OH (20%–22% free NH₃) to a volume of 250 mL. The solution was evaporated under high vacuum until the vapor pressure dropped below 100 torr, after which the vacuum control valve was opened and the pressure adjusted to 250 torr. The rotovap water bath temperature was increased from 80°C to 95°C, and the solution was evaporated until the first solids appeared in the solution. The vacuum pump was then turned off and the evaporation flask was raised out of the water bath and allowed to cool to ambient temperature at a slow rotation speed. After cooling, the remaining solution was evaporated under high vacuum until a thick paste formed. Then, 80% reagent alcohol was added to the evaporation flask and the resulting loose solid was filtered on a medium porosity frit.

2.2.3 Trial #6: Rapid AHM Evaporative Crystallization

A 0.32 M Mo (as AHM) solution was prepared by dissolving 14.2 g AHM in concentrated NH₄OH (20%–22% free NH₃) to a volume of 250 mL. The solution was evaporated under high vacuum until a thick paste formed, 80% reagent alcohol was added to the evaporation flask, and the resulting loose solid was filtered on a medium porosity frit.

2.2.4 Trial #7: AHM Crystallization Hybrid Method (High and Low Vacuum) Large Tests

A 0.32 M Mo (as AHM) solution was prepared by dissolving AHM in concentrated NH₄OH (20%–22% free NH₃) to a volume of 2, 3, or 6 L (corresponding to 110 g AHM, 160 g AHM, and 340 g AHM, respectively). The solution was evaporated under high vacuum until the first solids were visible in the solution, after which the vacuum control valve was opened and the pressure adjusted to 250 torr. The rotovap water bath temperature was increased from 80°C to 95°C, and the solution became clear with further heating. The solution was evaporated at 205 torr (low vacuum) until the first solids appeared in the solution. The vacuum pump was then turned off and the evaporation flask was raised out of the water bath and allowed to cool to ambient temperature at a slow or fast rotation speed. After cooling, the remaining solution was evaporated under high vacuum until a thick paste formed. Then, 80% reagent alcohol was added to the evaporation flask and the resulting loose solid was filtered on a medium porosity frit and allowed to dry overnight. The dry solid was sieved into extra-small (<45 μ m), small (between 45 μ m and 180 μ m), medium (between 180 μ m and 250 μ m), large (between 250 μ m and 425 μ m), and extra-large (>425 μ m) fractions and weighed. Where possible, the extra-large fraction was ground into smaller particles using a mortar and pestle.

2.3 pH–Temperature Compensation

The pH of AHM solutions decreases with increasing temperature, which could in turn affect the speciation of Mo in solution. To better understand this effect, and to help draw other correlations from the data when necessary (discussed in the following sections), we report temperature-corrected pH values that are calculated in reference to a standard temperature (25°C) using a measured pH-temperature coefficient.

The pH-temperature coefficient of the AHM solutions was determined by plotting the pH against the temperature of an AHM solution near its solubility limit as it was cooled from boiling (Figure 1). The slope of the resulting line (-0.0154 pH/°C) is the temperature coefficient, which was used to adjust all pH measurements to the value that would be measured at 25°C (pH₂₅) using Equation 1, where pH_{meas} is the pH observed at the process temperature, T is the process temperature, and C_{pH} is the system-specific pH temperature coefficient.

$$pH_{25} = pH_{meas} + (25 - T) * C_{pH}$$
(Equation 1)



Figure 1. pH values measured in solutions above ambient temperature were adjusted using the pH temperature coefficient of the AHM solutions used here.

2.4 Mo Solubility Measurements

The solubility of AHM at different temperatures and pHs was determined by measuring the Mo concentration in solution in the presence of excess AHM solid. First, a large excess of AHM (i.e., beyond the solubility point) was placed in a glass vial, which was then half-filled with deionized water. The vial was then either kept at ambient temperature (21°C) or submerged to the liquid level in a silicone oil bath at 50°C, 65°C, 80°C, or 95°C and allowed to temperature-equilibrate with mixing for at least 1 hour. After 1 hour, the pH of the solution was adjusted to reach approximately 6, 7, or 8, and the solution was allowed to equilibrate for an additional hour. The final pH was then measured and a sample taken for Mo analysis by inductively coupled plasma mass spectrometry (ICP-MS).

2.5 Correlation of Vapor–Liquid Equilibrium Data by Raoult's Law

The relationship between temperature, pressure, and composition can be correlated from experimental data in the ternary water-ammonia-molybdenum system investigated here using Raoult's law and assuming a pseudobinary system consisting only of water and ammonia. This approximation is used because the temperatures, pressures, and pHs measured in the ternary system during solution evaporation appear to be independent of the Mo concentration. Correlation allows for the determination of the approximate system pH from experimentally accessible temperature and vapor pressure measurements. The measurement of pH in a rotovap is difficult because it requires submerging a pH probe into a process solution contained in a rotating flask. In contrast, the vapor temperature and pressure can be directly measured in the rotovap headspace using standard equipment.

Raoult's law for the pseudobinary water-ammonia system is given in Equation 2, where P_{mix} is the experimental vapor pressure of the Mo solution as it is being evaporated, P_{H2O} and P_{NH3} are the vapor pressure of pure water and ammonia at the system temperature, respectively, and x_{H2O} and x_{NH3} are the pseudobinary mol fractions of water and ammonia, respectively. The data were correlated by calculating P_{mix} for each data point using Equation 2 and a fitted ammonia mol fraction determined by minimizing the sum of the squared errors between calculated and experimental values of P_{mix} . Pure component vapor pressures at different temperatures were calculated using the Antoine equation, Equation 3, where P_{vap} is the vapor pressure of the pure component (in bar), A, B, and C are component-specific parameters, and T is the system temperature in Kelvin. The Antoine parameters used here are given in Table 1.

$$P_{\text{mix}} = P_{\text{H2O}} x_{\text{H2O}} + P_{\text{NH3}} x_{\text{NH3}}$$
 (Equation 2)

$$\log_{10} P_{\text{vap}} = A - \frac{B}{T+C}$$
 (Equation 3)

 Table 1. Antoine equation parameters used to estimate water and ammonia pure component vapor pressures at varying temperatures [8].

Component	Α	В	С
Water	4.6543	1435.264	-64.848
Ammonia	4.86886	1113.928	-10.409

2.6 In situ Raman Spectroscopy of the Heating of Molybdenum Solutions

Raman spectra were acquired using a custom-built fiber-coupled Raman spectroscopy system. The system is pumped using a 785 nm diode laser. Spectra were collected on a low-shift (~ 0-1300 cm⁻¹) fixed-grating QE Pro OceanOptics CCD spectrometer. Each spectrum presented is the average of 8 scans taken with 32 s integration time. Approximately 10 mL of solution was added to a glass scintillation vial with a magnetic stir bar, and the vial was sealed with a cap containing a septum and thermocouple to record the temperature. The vial was placed on a stirring hot plate such that the solution was approximately 25 mm from the laser output. Spectra of the solution were acquired in a 90° geometry through the side of the glass vial with Raman scattering detected at the same angle as excitation. An empty glass vial was used for background subtraction. The solutions were heated using the controls on the hot plate. The final spectra were smoothed using a Savitzky-Golay filter with a window length of 7 and a polynomial order of 3.

3 RESULTS AND DISCUSSION

3.1 Temperature and pH Effects on Molybdenum Solubility

The feasibility of using a cooling crystallization method to produce AHM particles was evaluated by measuring the Mo solubility in the ammonium-molybdenum system at three different pH values and five different temperatures. Solubility was measured by determining the solution Mo concentration in a two-phase solid–liquid system. As seen in Figure 2, only a weak dependence of Mo solubility on pH was observed for the different temperatures tested. The only exception was at 65°C, where a 50% decrease in Mo solubility was observed when the pH₂₅ was increased from approximately 6 to 8.



Figure 2. The solubility of Mo in the ammonium-molybdenum system was not strongly dependent on pH for most temperatures tested, except for samples at 65°C, which displayed a negative dependence of solubility on pH₂₅.

When a solution consisting of AHM dissolved in concentrated NH_4OH is evaporated, the final pH_{25} of the system just prior to precipitation is approximately 7. The corresponding temperature-dependent Mo solubility curve is given in Figure 3. There is a 60% decrease in Mo solubility as a pH_{25} 6.9 solution is cooled from 80°C to 20°C.



Figure 3. The solubility of Mo at a pH₂₅ of approximately 7 increases with temperature until reaching a maximum around 80°C, when it then decreases.

These data suggest that a viable AHM crystallization process could be based on heating the solution to between 60°C and 80°C, then allowing the solution to precipitate by cooling to ambient temperature. This conclusion relies on the assumption that the Mo in solution at these temperatures is found in the heptamolybdate form, rather than the other molybdate species that dominate at higher temperatures [6].

3.2 Evolution of AHM Solution Conditions During Solution Evaporation

The types of solids formed in crystallization processes depend on the chemical speciation of the recovered solute immediately prior to precipitation as well as the experimental conditions (such as cooling rate, degree of supersaturation, stirring, etc.) under which the crystals are formed. The former controls the chemical form of the solid, while the latter controls its bulk physical characteristics. Due to the diversity of molybdenum species found in aqueous solutions under varying conditions of temperature, pH, and solution environment, tight control over the nature of the solids produced in a Mo crystallization process requires a thorough understanding of changing experimental parameters and solution thermodynamic quantities with time and their impacts on the chemical form, particle size, and morphology of the solids.

In all crystallization processes tested, the temperature and vapor pressure of the Mo solution being evaporated were found to depend only on the ammonia concentration, as indicated by the pH. The measured pH plotted versus temperature and pressure defines a smoothly varying surface in the presence of excess ammonia. The temperature and pressure of the solution at boiling remained on this pH surface independent of the Mo concentration and the timing of the addition of ammonium hydroxide to the system. Once the excess ammonia in the system was evaporated, the temperature and pressure of the solution were observed to reach constant values before precipitation of the ammonium molybdate solid. Increasing Mo concentration with ongoing evaporation did not impact these values, which remained constant and in nearly quantitative agreement with the temperatures and vapor pressures of pure water. This behavior is shown for trial #3, AHM cooling crystallization, in Figure 4, where the boiling solution reaches a constant pH_{25} of 7.3 and temperature of 100°C, the boiling point of water at atmospheric pressure, after the final addition of the initial Mo solution to the evaporation beaker.



Figure 4. The temperature, vapor pressure, and pH₂₅ of a Mo solution being evaporated were highly correlated and independent of Mo concentration.

When a pseudobinary formulation of Raoult's law accounting only for water and ammonia was used to correlate the temperature, vapor pressure, and pH of the evaporating Mo solutions, a logarithmic relationship between the experimentally measured pH_{25} of the solution and the fitted pseudobinary NH₃ concentration (x_{NH3} in Equation 2) was observed (Figure 5). This correlation, given in Equation 4, can be used to relate experimentally measured temperature and vapor pressure to the solution pH_{25} and track the progression of a batch AHM evaporation process.

$$pH_{25} = 0.8244 \times ln \left[\frac{P_{mix} - P_{H2O}}{P_{NH3} - P_{H2O}} \right] + 13.425$$
 (Equation 4)

In Equation 4, P_{mix} is the measured vapor pressure, P_{H2O} is the vapor pressure of pure water at the measured temperature, and P_{NH3} is the vapor pressure of pure ammonia at the measured temperature. These quantities were calculated using Equation 3 as described in the methods section.



Figure 5. Raoult's law for a pseudobinary water-ammonia system was used to correlate temperature, vapor pressure, and pH₂₅ to yield the relationship shown between experimental pH₂₅ and fitted pseudobinary NH₃ mol fraction.

3.3 Impact of Processing Parameters on the Solution and Solid Phase Chemical Form of AHM

The temperature, pressure, and pH dependences of Mo chemical speciation in solid and liquid phases were probed by Raman spectroscopy. Raman vibrations of expected Mo species are shown in Table 2. Saturated solutions of approximately ~1.7 M Mo (AHM) dissolved in water have pH value of 5.8 ± 0.2 at 25°C. These solutions contained a mixture of Mo₇O₂₄^{6–} (indicated by the 895 cm⁻¹ band) and MoO₄^{2–} (939 cm⁻¹ band) which is consistent with the literature [9]. Dissolution of AHM in excess NH₄OH yields a solution around pH 12 in which the MoO₄^{2–} species dominates.

 Table 2. Molybdenum species expected in this system and their characteristic Raman vibrations. Numbers in parentheses refer to Raman peak relative intensities reported in reference.

Species	Raman vibrations	Reference
MoO4 ²⁻	895	[6]
$(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$	939	[9]
MoO ₃	820 (1), 995 (0.3)	[6]
$(NH_4)_2Mo_2O_7$	697 (4), 853 (4), 846 (8), 906 (20)	[10]
Mo ₂ O ₇ ²⁻	932	[6]
Mo ₈ O ₂₅ ⁴⁻	956	[6]

The Raman spectra for solutions in the pH range 5.5–7.9 are shown in Figure 6, where only 939 cm⁻¹ and 895 cm⁻¹ peaks are apparent in the whole collected range. As pH increases, the equilibrium between mono- and heptamolybdate species shifts to the right in the fully reversible Equation 5.

$$Mo_7O_{24}^{6-} + 4H_2O \leftrightarrow 7MoO_4^{2-} + 8H^+$$
 (Equation 5)

This equilibrium prevails in saturated solutions from ambient to high temperatures $(20^{\circ}C-90^{\circ}C)$ between pH 5 and 7. At a pH value of 7.2 and above, the only species in solution is the MoO₄²⁻. Our findings can be contrasted with those of Noack et al., who performed a similar experiment at 0.2 M AHM [6]. At pH 5.4 and 30°C, they found an appreciably larger 895 cm⁻¹ peak than we collected under the same conditions at higher Mo concentration (1.7 M Mo), indicating that AHM is favored over molybdate as Mo concentration increases. Furthermore, this species distribution in saturated Mo solutions appears to be largely temperature-independent, as shown in Figure 6 (top and bottom) where the spectra of solutions at 30°C are nearly identical when heated to 90°C. Note that the slight redshifting of Raman peaks upon heating is attributable to the increase in bond lengths of the Raman scattering molecules which is expected with increasing temperature [11]. These results indicate that care should be taken to keep the solution pH below ~7.2 during the evaporation process to help promote the aqueous formation of AHM.



Figure 6. Raman spectra of saturated (1.7 M Mo) AHM solution at different pH₂₅ values and at near-ambient temperature (30°C) and at the temperature achieved during rotary evaporation (90°C). The dotted lines indicate characteristic Raman peaks for AHM (939 cm⁻¹) and MoO4²⁻ (895 cm⁻¹) species. Redshifting of peaks is due to thermal effects.

Another notable exception to the findings of Noack et al. is that no peaks for $Mo_2O_7^{2-}$ (932 cm-1) or $Mo_8O_{25}^{4-}$ (956 cm⁻¹) were seen at any point in the thermal range 30°C–90°C. Figure 7 shows the Raman spectra of a pH 6.1 AHM solution collected across the temperature gradient and confirms that there is no

visible change in Mo species in the saturated solution. We can conclude that the tendency for Mo to form AHM in evaporating ammoniacal solutions (at pH 6.1) increases as the solution becomes more concentrated, even at elevated temperatures up to 90°C.



Figure 7. Raman spectra of a saturated (1.7 M Mo) AHM solution during heating from 35°C to 89°C. The dotted lines indicate characteristic Raman peaks for AHM (939 cm⁻¹) and MoO₄²⁻ (895 cm⁻¹) species. Redshifting of peaks is due to thermal effects.

With new knowledge of Mo aqueous speciation, the effect of solution pH and evaporation conditions on the final molybdenum solid product was examined to better understand the connection between the solution speciation and the recrystallized product. The Raman spectra of solid material produced under different conditions are shown in Figure 8. The measurement of solid samples by Raman spectroscopy produces higher resolution spectra compared to dissolved material due to the increased density of Raman scattering sites, so these peaks are more well-defined. The top three spectra were collected from Mo solutions of pH 6.9 that were evaporated at different vacuum pressures (40 torr to atmospheric) in the rotovap. The lower three spectra were all evaporated at atmospheric temperature but at different solution pHs. At pH \leq 6.7, the collected spectrum is consistent with that of pure solid ammonium heptamolybdate. When the pH of the starting solution is increased to a value of 7.3 or greater, the distinctive peaks for ammonium dimolybdate dominate. Therefore, the aqueous phase speciation of Mo can be related to the solid phase, where the transition away from AHM occurs somewhere between pH 6.9 and 7.2. Our results show that when MoO_4^{2-} is the predominant species in the aqueous phase (pH > 7) the product crystallizes as the ADM dimer, whereas when AHM is predominantly in solution (pH < 7) the product crystallizes as AHM. The formation of solid-form AHM is mainly a function of solution pH, which is itself largely independent of evaporation rate and pressure, as demonstrated in earlier sections of this report.



Figure 8. The chemical form of the molybdenum solids produced by various precipitation processes was primarily dependent on pH. Characteristic Raman peaks for AHM (939 cm⁻¹) and ADM (906 cm⁻¹) species are present.

3.4 Impact of Processing Parameters on the Physical Form of the AHM Solid

The processing parameters of temperature, pressure, pH, and stir speed were examined for their effects on the particle morphology and size. Small-scale trials that achieved ideal particle characteristics were then investigated at larger scale.

3.4.1 Cooling Crystallization at Atmospheric Pressure

The AHM solids formed by rapid evaporative crystallization using cooling crystallization at atmospheric pressure (trials 1, 2, and 3) were predominantly fine powders. Figure 9 shows how the crystallization occurred quickly from the high temperature solutions after the removal of heat, resulting in the formation of a fine uniform powder in the beaker.



Figure 9. Crystallization occurs quickly when heat is removed, resulting in the formation of a fine uniform powder in the beaker.

Photomicrographs obtained from scanning electron microscopy (SEM) of the products (Figure 10) reveal that the AHM/ADM products resulting from cooling crystallization were amorphous rather than crystalline. Trials 1, 2, and 3 correspond to solutions adjusted at the start of their cooling cycle with the addition of NH₄OH or HCl to pH_{25} values of 7.7, 6.7, and 7.3, respectively. Based on our Raman analysis of these powders, the chemical form of the solid products formed during crystallization of solutions in this pH range were AHM (pH_{25} 6.7), AHM + ADM mixture (pH_{25} 7.3), and ADM (pH_{25} 7.7). All three products were similar in particle size and morphology.

The amorphous morphology of all three solids appears to be linked to the cooling crystallization process itself and not to the pH or Mo chemical form. It is likely that the relatively high cooling rate after turning the hot plate off led to rapid nucleation at many sites, leading to smaller grain sizes. Performing cooling crystallization at a much lower cooling rate, using a temperature-controlled vessel, should enable more accurate particle size control.

#1 ADM & AHM/atm/pH 7.7



#2 AHM/atm/pH 6.7



#3 ADM/atm/pH 7.3



Figure 10. SEM images of the solids produced in the three cooling crystallization tests described in the methods section (trials 1–3) showing that an amorphous solid material was produced in each test, regardless of solution pH and Mo chemical form.

3.4.2 Rotary Evaporator Crystallization

Trials 4, 5, and 6 correspond to solution evaporated at low vacuum (4), hybrid high/low vacuum (5), and high vacuum (6) evaporations at high temperatures (80°C–95°C) in a rotovap. The trials performed at low and hybrid high/low vacuum pressures (4 and 5) produced larger, more uniformly sized particles that were visibly faceted. Figure 11 shows the appearance of large single crystals and polycrystalline grains. Cooling of the solution to ambient temperature took place more slowly than in the cooling crystallization process at atmospheric pressure, due to the larger solution volume remaining and the lower initial temperature difference between the solution and ambient conditions, allowing for the more gradual formation of larger particles.

In trial 6, where rapid evaporative crystallization was performed without adjustment to vacuum pressure or temperature, the result was an amorphous solid similar in appearance to the solids obtained from the cooling crystallization method but with a few larger particles evident in the product.

The formation of AHM requires that the solution pH is below 7. The pH of the solutions prior to crystallization was around 6.7 without pH-adjustment, resulting in crystallization of a pure AHM product as determined by Raman spectroscopy (Figure 8). From our measurements, saturated solutions of AHM dissolved in water have a pH₂₅ of 5.8 ± 0.2 , whereas solutions of AHM dissolved in excess NH₄OH that are evaporated at high temperature reach an equilibrium pH₈₀ of about 6.7–6.9. The exact pH of AHM solutions may vary from batch to batch based on the Mo concentration or other parameters, though this was not explored in-depth in the present study. Temperature-induced pH changes did not appear to cause significant changes in Mo speciation in the saturated solutions.

#4 AHM/250 torr/pH 6.7



#5 AHM/100 & 250 torr/pH 6.7



#6 AHM/40 torr/pH 6.7



Figure 11. SEM images of the solids produced in the six small volume crystallization tests described in the methods section (trials 1-6) show that the formation of larger crystals takes place when solids formed at higher temperatures.

3.4.3 Large Scale Hybrid Rotary Evaporation

The hybrid evaporation method (trial 5) combines initial rapid evaporation of solution with slower evaporation of concentrated solutions to obtain large crystals in a shorter overall processing time. This procedure was scaled up to 100–300 g AHM batches in trial 7 and the product characteristics were analyzed by SEM.

Figure 12 shows that the product obtained from the large-scale hybrid method differed from the smallscale trial (5) in both morphology and particle size distribution. The images show large grains of AHM coated in amorphous particles similar to those obtained in trials 1-3. It is not clear what caused the formation or agglomeration of particles at this large scale. We speculate that the initial cooling period in which the large grains formed may have been proceeded by a brief period of rapid cooling, causing the formation of finer, amorphous particles.



Figure 12. SEM images of the solids produced in large batch (100-300 g AHM) trials. Large grains of AHM are coated in an amorphous material similar to that obtained in trials 1-3.

The particle size distribution of varying mixing speeds (Figure 13) shows that primarily medium to large sized particles (45–425 μ m) formed under each tested condition. Based on our results, mixing speed and starting mass of Mo did not have clear impact on the size of the particles formed during evaporation, although it is predicted that slower rotation speeds would result in crystallization of larger particles. Therefore, slower mixing is recommended to obtain larger particle sizes.



Figure 13. Particle size distribution for AHM product obtained under different operation conditions.

4 CONCLUSION

The evaporation of molybdenum from ammoniacal solutions between pH 5 and 8 can produce either ammonium heptamolybdate (AHM) or ammonium dimolybdate (ADM) crystals, the speciation of which is primarily dependent on solution pH. AHM forms at pH \leq 7; ADM forms at pH \geq 7. The product formed during cold crystallization of a Mo solution at pH 7.3 comprised a mixture of AHM + ADM, as determined by Raman spectroscopy. All products that formed below pH 7 were pure AHM. Raman spectra of saturated AHM solutions showed that solutions from pH 7 to 12 contained only the simple molybdate (MoO₄²⁻) anion which dimerizes during crystallization to form solid ADM.

The pH of saturated AHM solutions is strongly temperature dependent and shifts almost an entire pH unit (7.3 to 6.6) upon heating to 95°C. Despite the change in pH, Mo solution speciation did not appear to change with increasing temperature, perhaps due to a temperature-dependent pKa shift in the Mo polymerization equilibrium (Equation 5). The chemical speciation of the solid formed during evaporation can therefore be related to the pH₂₅ of solution. *In situ* measurements of pH can be performed at high temperatures and corrected to pH_{25} via the measured pH–temperature correlation coefficient provided in Equation 4.

We can conclude that the main parameters affecting the grain size during crystallization by rotary evaporation are the evaporation rate and cooling rate immediately prior to crystallization. These rates are controlled by the changing either water bath temperature or vacuum pressure, and these must be changed prior to the point of crystallization. Failure to adjust either rate adequately results in rapid nucleation and formation of too-fine material. Rotary evaporation of AHM solutions followed by a decrease in temperature and/or vacuum pressure results in large crystalline and polycrystalline product ideal for the production of new Mo targets.

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