CHARACTERIZATION OF MOLYBDENUM INTERFACIAL CRUD IN A URANIUM MILL THAT EMPLOYS TERTIARY-AMINE SOLVENT EXTRACTION*

Bruce Moyer and W. J. McDowell

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830
U.S.A.

MASTER

DISCLAIMER

CHARACTERIZATION OF MOLYBDENUM INTERFACIAL CRUD IN A URANIUM MILL

THAT EMPLOYS TERTIARY-AMINE SOLVENT EXTRACTION

Bruce Moyer and W. J. McDowell

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830
U.S.A.

A study has been undertaken to elucidate the nature and causes of interfacial crud in solvent extraction hydrometallurgy. In the present work, samples of a molybdenum-caused green, gummy interfacial crud from an operating western U.S. uranium mill have been physically and chemically examined. Formation of cruds of this description has been a long-standing problem in the use of tertiary amine solvent extraction for the recovery of uranium from low-grade ores (Amex Process). The crud is essentially an organic-continuous dispersion containing ~10 wt % aqueous droplets (50 μm to >1 cm) and ~37 wt % greenish-yellow, crystalline solids (5 to 100 μm) suspended in kerosene-amine process solvent. The greenish-yellow crystals were found to be a previously unknown double salt of tertiary amine molybdophosphate with three tertiary amine chlorides, having the empirical formula $(R_3NH)_3[PMo_{12}O_{40}] \cdot 3(R_3NH)Cl$, where the alkyl groups contain an average of 8.9 carbons per chain. To confirm the identification of the compound, a pure trioctylamine (TOA) analog was synthesized. In laboratory extraction experiments, it was demonstrated that organic-soluble amine molybdophosphate forms slowly upon contact of TOA solvent (0.05 $\underline{M}$ in $\underline{n}$-nonane modified with 0.05 $\underline{M}$ $\underline{n}$-dodecanol) with dilute sulfuric acid solutions containing low concentrations of molybdate and phosphate. If the organic solutions of amine molybdophosphate were then contacted with aqueous NaCl solutions, a greenish-yellow precipitate of $(TOAH)_3[PMo_{12}O_{40}] \cdot 3(TOAH)Cl$ formed at the interface. The proposed mechanism for the formation of the crud under process conditions involves build up of molybdenum in the solvent, followed by reaction with extracted phosphate to give dissolved amine molybdophosphate. The amine molybdophosphate then co-crystallizes with amine chloride, formed during the stripping cycle, to give the insoluble double salt, which precipitates as a layer of small particles at the interface. The proposed solution to the problem is the use of branched-chain, instead of straight-chain, tertiary amine extractants under the expectation that branching would decrease the stability of the crystal and thereby increase the solubility of the double salt.

Moyer

Introduction

Interfacial "crud" is a serious limitation in the application of solvent extraction methods to hydrometallurgy, having a costly impact on plant design and operation. Characterized by the accumulation of particulate solids at the aqueous/organic interface in the extraction and stripping circuits, crud problems may be attributed to mineral particles suspended in the aqueous feed or to internal precipitation of insoluble matter during processing (1). Despite preventive measures to remove the solids and precipitate-causing impurities from the system, crud formation is often not completely circumvented, leading to lower efficiency. In the extreme case, crud and emulsion problems may be so severe that they render an otherwise good solvent system unsuitable for certain applications. At present, the nature of the various interfacial cruds encountered in hydrometallurgical processing and the basic causes of their formation are poorly understood. Hence, there has been little recourse but to treat the symptoms of the problem. We have recently initiated studies of the underlying phenomena associated with interfacial cruds, emulsion formation, and phase separation to provide a rational basis for predicting and controlling these phenomena. In our first effort, we studied the interaction of aqueous colloidal silica with amine sulfate solvent systems (2), and we are extending this work to include situations in which crud is caused by precipitated material.

Tertiary amine solvent extraction of uranium from sulfuric acid leach solutions (Amex uranium extraction process) is an important commercial hydrometallurgical process for the recovery of uranium from low-grade ores (3-6). Although very selective for uranium over many commonly present elements, tertiary amines strongly extract molybdenum, a potential co-product which may typically occur in western U.S. uranium ore leach solutions in the concentration range 1 to 100 ppm (7). To avoid molybdenum contamination of the yellow cake uranium product, chloride stripping is often used because, in addition to good economics, it offers high selectivity in removing the uranium cleanly from the extracted molybdenum (5,6,8). Stripping of the molybdenum remaining in the solvent is then accomplished by means of relatively expensive alkaline solvent scrubbing, often used on only a portion of the solvent stream. Despite the advantageous selective stripping offered by this type of flowsheet, a serious difficulty associated with it has been the formation of insoluble "green, gummy precipitates" at the interface. Containing high concentrations of both amine and molybdenum, these interfacial cruds interfere with smooth processing and withdraw amine from useful service. Although the problem has been widely recognized since the development of the Amex processes 30 years ago (5-7,9), the difficulty has still not been adequately resolved.

The chemistry of the extraction of molybdenum and its eventual precipitation as crud is not well understood. Extraction studies indicate that the organic-phase molybdenum species are polynuclear, although there is disagreement about their identity (10). Precipitation of the extracted molybdenum as crud is known to be a function of various process variables, including redox potential, method of stripping, amount of solvent scrubbing, amine structure and concentration, diluent type, and type and concentration of diluent modifiers (5,9). Since molybdenum crud has been found to contain phosphate and sometimes vanadium, heteropolymolybdates have generally been suspected of causing or contributing to the problem (9). In one case, partly reduced molybdophosphate was identified as a major constituent of mill crud (11). However, discreet chemical compounds and formation mechanisms are generally unknown. In this paper, we present the results of our investigation of the chemical and physical characteristics of an interfacial crud occurring in a uranium mill that employs tertiary amine solvent extraction. We are currently investigating the chemistry of formation of the principal component of the crud in the laboratory. The first set of results, which are presented here, identify the chemical reactants that are involved and suggest the probable sequence of steps leading to the formation of the crud in the uranium mill.

Materials

Leach solution and interfacial crud samples were obtained from Kerr McGee Nuclear Corp., Grants, NM. The crud proved to be light sensitive (i.e., turns blue-green, then black), and it was therefore stored in the dark. Trioctylamine (TOA) purchased from the Aldrich Chemical Co. was recrystallized three times as the HCl adduct from acetone and passed through activated silica in order to remove ultraviolet-absorbing impurities to a tolerable level. Spectrograde acetonitrile and n-nonane were obtained from Burdick and Jackson Laboratories. n-Dodecanol (Eastman) was fractionally distilled under vacuum on a Perkin-Elmer 36-in. Adiabatic Spinning Band Still and fractionally crystallized once. All other chemicals and solvents were reagent grade and used as received.

Preparations

Standard Preparations. Molybdophosphoric acid ($H_3PMo_{12}O_{40} \cdot 15H_2O$) was prepared by a standard procedure (12), and the waters of crystallization were determined by thermogravimetric analysis on a Mettler TA2000 balance. It was made anhydrous as needed by heating at $170^{\circ}C$ for 5 min. (TOAH)Cl was prepared by shaking neat TOA with 1 $\underline{M}$ HCl and recrystallizing three times from acetone in a dry ice/isopropanol bath.

$(TOAH)_3[PMo_{12}O_{40}] \cdot 3(TOAH)Cl.$ TOA, 0.28 g (0.79 mmole), (TOAH)Cl, 0.31 g (0.79 mmole), and anhydrous $H_3PMo_{12}O_{40}$, 0.48 g (0.27 mmole), were added to 10 mL of chloroform and stirred 5 min (until all dissolved). The greenish-yellow crystals that formed upon addition of 10 mL of carbon tetrachloride were filtered and redissolved in 8 mL of chloroform containing 0.1 g of (TOAH)Cl. A 3-mL aliquot of carbon tetrachloride was added and slow (3 days) crystallization was effected by vapor-phase equilibration of the solution with 7 mL of carbon tetrachloride in a closed chamber. The crystals were then filtered off and washed with 6 mL of a 2:1 (by volume) carbon tetrachloride/chloroform mixture, followed by 40 mL of petroleum ether. Upon air drying, 0.74 g of a yellow powder was obtained (69% of theoretical). Ultraviolet spectophotometry and elemental analysis support the formulation of the compound as the double salt $(TOAH)_3[PMo_{12}O_{40}] \cdot 3(TOAH)Cl$ (see Tables IV and V, respectively, in the Results and Discussion Section).

$(TOAH)_3[PMo_{12}O_{40}].$ $H_3PMo_{12}O_{40} \cdot 15H_2O$, 0.70 g (0.33 mmole), and TOA, 0.36 g (1.02 mmole), were dissolved together in 10 mL of acetone, and the resulting solution was added dropwise to 100 mL of petroleum ether with stirring to form an insoluble, heavy green oil. The oil solidified upon decanting the petroleum ether and adding 50 mL more petroleum ether to the beaker. The oil was taken up in 10 mL of acetone and precipitated from petroleum ether as before to give 0.84 g of a green powder (88% of theoretical). Table IV gives the UV analysis.

Procedures

Physical Properties and Separations. Crud samples smeared on microscope slides were examined by visible light microscopy on a Nikon Apophot Microscope calibrated with a stage micrometer. The aqueous component of the crud was found to be present as oddly shaped droplets which shriveled on prolonged exposure to stage lighting. The droplets deformed when probed mechanically and did not take up the organic-soluble dye, aniline blue. Conductivity measurements were made using a Radiometer Conductivity Meter Type CDM 2d.

Crud samples were broken down by collecting the solids on a medium-frit glass filter (10- to 15-μm pores) and centrifuging the filtrate in a laboratory centrifuge until two clear layers appeared. The solids were washed with petroleum ether to remove the solvent and suspended in a carbon tetrachloride/petroleum ether mixture (4:1 by volume) with the aid of ultrasonic agitation. Using centrifugation, the greenish-yellow particles were then floated away from a small amount of heavier gray solids, and the density of the greenish-yellow solid was concomitantly determined by varying the carbon tetrachloride/petroleum ether ratio. The greenish-yellow powder was found to be soluble in polar solvents such as acetone and chloroform, but insoluble in nonpolar solvents such as hexane, petroleum ether, and carbon tetrachloride. It was, in fact, possible to recrystallize the solid with retention of its X-ray powder pattern (Table IV) by the same procedure described above for the recrystallization of $(TOAH)_3[PMo_{12}O_{40}]\cdot3(TOAH)Cl$. X-ray powder patterns (Table IV) were obtained on a Norelco XRD Powder Diffraction Unit equipped with a copper anode.

Chemical Analyses. Liquid phases listed in Table III (see Results and Discussion Section) were analyzed for molybdate, phosphate, sulfate, and chloride by the ORNL Analytical Chemistry Division. Amine values were measured by nonaqueous titration (13).

X-ray fluorescence spectra of the greenish-yellow solid in acetone solution were obtained by the ORNL Analytical Chemistry Division. Infrared spectrophotometry was carried out on a Perkin-Elmer 421 IR Spectrophotometer using mineral oil mulls or evaporated (from acetone) thin films on KBr plates. A Cary 219 Spectrophotometer was employed to make ultraviolet and visible spectral measurements ($\pm5\%$ precision). Using $H_3PMo_{12}O_{40}\cdot15H_2O$ as a standard, molar extinction coefficients for the two absorption maxima (14) of the molybdophosphate anion at 309 and 216 nm were measured (ϵ = 22,900 and 98,500, respectively, in acetonitrile) and then used to assay the $\%PMo_{12}O_{40}^{3-}$ in solid samples dissolved in acetonitrile (Table IV). Beer's Law was obeyed in the concentration range, 0.3 to 5 x 10^{-4} $\underline{M}$.

Nonaqueous titrations (13) were used to analyze the greenish-yellow solid for amine content (Table V). The solids were dissolved in chloroform, and the resulting solution was equilibrated with dilute aqueous Na_2CO_3 to liberate the free amine, which was then titrated with a p-dioxane solution of $HClO_4$. The remaining elemental analyses in Table V were performed by Galbraith Laboratories, Inc., Knoxville, TN. From the results of the analyses, the empirical formula for the greenish-yellow solid was deduced by adjusting the stoichiometric parameters X and Y (defined in Table V) to obtain the "best fit" between calculated and experimental values according to the least-squares criterion

$$Q = \Sigma(1/\sigma_i)^2(\%i_{calc} - \%i_{exper})^2 \tag{1}$$

where σ_i is the analytical error for determination of element i (see Table V). The computation made use of the MARQUARDT program (15) on the ORNL computer facility.

Extraction Experiments. Equilibrations were done at room temperature by shaking or slow stirring. The organic phase, consisting of 0.05 $\underline{M}$ TOA and 0.05 $\underline{M}$ dodecanol in nonane, was always preequilibrated with 0.1 $\underline{M}$ H_2SO_4 to give the amine sulfate salt. In initial experiments (e.g., Fig. 2 in the Results and Discussion Section), the aqueous phase contained 0.0002 $\underline{M}$ Mo(VI) [prepared from $(NH_4)_6Mo_7O_{24}\cdot4H_2O$] in 0.1 $\underline{M}$ H_2SO_4 with or without 0.01 $\underline{M}$ H_3PO_4. Molybdenum(VI) distribution coefficients ($\pm10\%$) were determined spectrophotometrically (ϵ_{215} = 5300 for dilute molybdate in 0.1 $\underline{M}$ H_2SO_4). Ultraviolet spectra of the organic phases were run against carefully prepared blanks in which Mo(VI) was excluded so that the absorbance due to solvent impurities would be cancelled, and the appearance of molybdophosphate was indicated

by the growth of an absorption peak at 309 nm. The aqueous:organic volume ratio was normally 10:1. However, in one run made with a 1:1 ratio the observed molybdophosphate formation was very slow, requiring 56 days to reach 32% completion. The maximum organic-phase concentration of molybdophosphate (as the amine salt) that could be tolerated under chloride-free conditions without formation of a green liquid third phase was found to be approximately 1.5×10^{-4} $\underline{M}$ at room temperature.

Green interfacial solids formed upon contacting the organic phases containing molybdophosphate with aqueous NaCl solutions (0.03 to 1 $\underline{M}$ in 0.1 $\underline{M}$ H_2SO_4). These solids were removed by filtration, washed with petroleum ether, air dried and analyzed (Table IV). The organic molybdophosphate solutions were prepared by 1) extracting Mo(VI) and phosphate as described above and allowing the solutions to stand several weeks, 2) adding ($H_3PMo_{12}O_{40}\cdot15H_2O$) dissolved in dodecanol directly to the organic phase, or 3) dissolving (TOAH)$_3$[$PMo_{12}O_{40}$] directly into the organic phase.

Results and Discussion

Physical Characterization

Samples of green interfacial crud from both the extraction and the stripping circuits were obtained from an operating western U.S. uranium mill which processes sandstone ores. Both molybdenum and amine were reported to be concentrated in the crud, which is routinely treated with base to recover the amine and molybdenum for reuse and sale, respectively. The process employed at the mill is a representative application of the Amex uranium extraction process (3-7,9), and some relevant operating data for the mill are given in Table I.

Table I.   Typical Uranium Mill Process Data

Organic solvent	0.07 equiv/L Alamine 336 (8- and 10-carbon straight chain tertiary amines); 3% isodecanol modifier; Kermac 627 kerosene diluent		
Aqueous feed	40-60 g/L SO_4^{2-} 0.5-1.0 g/L U	1.5-1.7 g/L Cl^- 0.03 g/L Mo	pH = 1
Strip solution	88 g/L NaCl	20 g/L SO_4^{2-}	pH = 2
Solvent cycle	Four extraction stages and four stripping stages, each with a 4:1 effective aqueous/organic phase ratio; organic-continuous mixing; 25% of solvent stream to NH_4OH scrub		

The nature of the extraction- and stripping-circuit crud samples proved to be similar in most essential respects, and therefore, only the extraction-circuit crud was examined in detail. Filtration and centrifugation easily separated the samples into aqueous, solvent, and solid fractions as quantified in Table II. The solvent and solid fractions formed the bulk of the samples, while the aqueous fraction was a relatively minor constituent. As shown in the table, the very low conductivity of the extraction-circuit crud corresponds to that of the kerosene solvent itself, implying that the solvent forms the continuous phase in the crud.

Microscopic examination showed that the crud is essentially a dispersion of greenish-yellow crystalline particles and aqueous droplets in the organic solvent, as can be seen in Fig. 1. Ranging in size from 0.005 to >1 cm, the aqueous droplets were highly irregular in shape, and under high magnification appeared to be "armored"

5

(i.e., coated with very fine particulate matter) (2). Some of the larger aqueous droplets were sampled and found, in themselves, to contain a dispersion of organic droplets and a variety of crystalline and fibrous solids. The greenish-yellow particles comprising the bulk of the crud ranged in size from 5 to 100 μm, and the crystalline appearance of the particles suggested that a discrete compound was present. The greenish-yellow particles were completely wetted by the organic solvent and showed no tendency to adhere to the aqueous droplets.

Table II. Physical Characteristics of Crud Samples

| | Composition[a] | | Specific Conductance (Ω^{-1} cm^{-1}) | Density (g/cm^3) | Size Range |
	Extn.	Strip			
Bulk crud	---	---	1×10^{-7}	0.99	---
Solvent	59%	48%	1×10^{-7}	0.81	Continuous phase
Aqueous	7%	12%	1×10^{-2}	1.04	50 μm to >1 cm
Solids	34%	40%	---	1.37[b]	5 to 100 μm[b]

[a] Composition data are given for the extraction crud and stripping crud. All other data in the table pertain to the extraction crud.
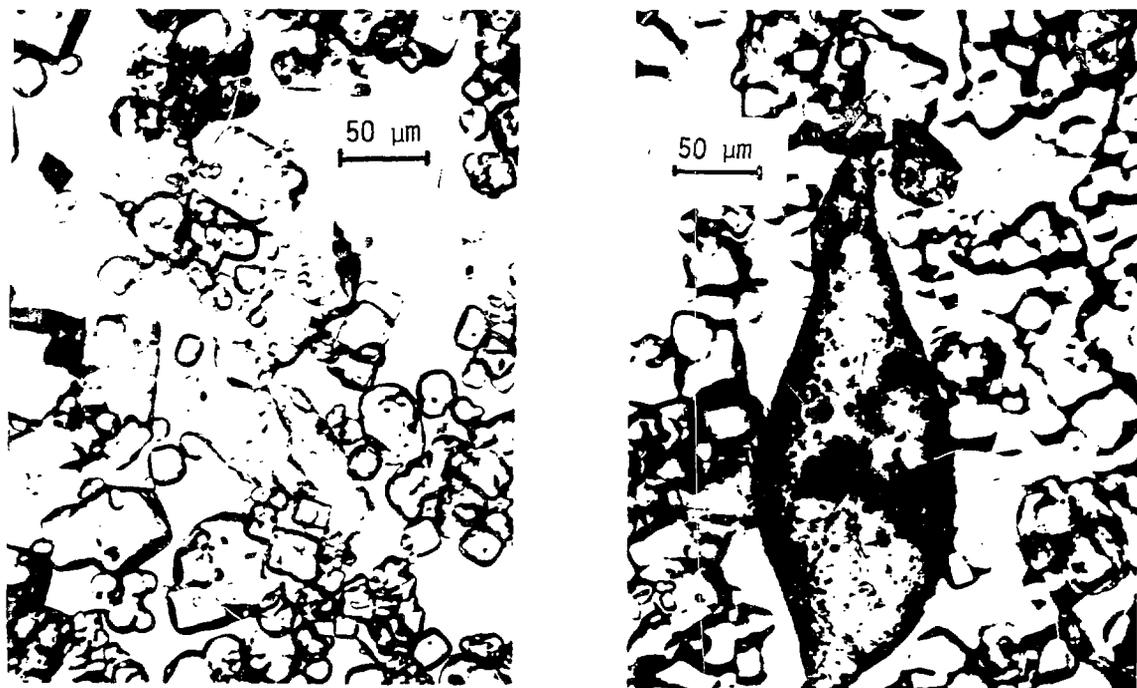
[b] Pertains to the greenish-yellow solids.

Figure 1 - Photomicrographs of molybdenum crud. The bulk of the sample was composed of 5- to 100-μm greenish-yellow crystalline particles (left) suspended in process solvent. Much less numerous were irregular aqueous droplets (right) scattered throughout the bed of greenish-yellow crystals.

In addition to the greenish-yellow solid particles, a minor amount of more dense material (4% of the total solids) was present in the form of gray, finely divided solids probably of mineral origin. The latter solids were probably the solids observed to be associated with the aqueous droplets in the microscopy experiments (Fig. 1), but we went no further to characterize them. Interestingly, the greenish-yellow solid material is actually more dense than the aqueous phase (see Table II). Since the solvent forms the continuous phase in the crud, the crud physically lies above the organic/aqueous interface, and the mechanical forces that restrain the particles must therefore be interfacial tension forces. As a whole, however, the layer of crud is slightly less dense than the aqueous phase and can therefore be expected to remain sandwiched between the organic and aqueous layers in the settler.

Chemical Characterization

Table III gives analytical data for a sample of leach solution and the liquid phases separated from the crud samples. The results indicate a high and low sulfate-to-chloride ratio, respectively, for the aqueous-phase fractions of the extraction- and stripping-circuit cruds, corresponding roughly to the bulk aqueous-phase compositions given in Table I. In addition, the amine concentration of the solvent fraction compares well with the concentration of amine reportedly used in the kerosene-amine process solvent. Thus, the chemical analyses corroborate the physical description of the crud given above, characterizing the crud as a multiphase dispersion primarily consisting of droplets of bulk aqueous phase and greenish-yellow crystals in kerosene-amine process solvent.

Table III. Composition of Aqueous and Organic Phases[a]

Phase		$[SO_4^{2-}]$	$[Cl^-]$	$[PO_4^{3-}]$	[Mo]	[Amine]
Aqueous feed		0.44	0.028	3.9×10^{-3}	2.5×10^{-4}	
Extraction crud	– aq	0.43	0.068	4.6×10^{-3}		
	– org		0.025	1.9×10^{-4}	9.4×10^{-4}	0.059
Stripping crud	– aq	0.28	2.01	6.5×10^{-5}		
	– org		0.080	1.4×10^{-4}	9.8×10^{-4}	0.061

[a] Units are in moles/L.

Since the crud appeared to be chiefly caused by the presence of the greenish-yellow precipitate, most of our subsequent effort focused on the analysis of the chemical composition of the precipitate and its probable formation mechanism. Molybdenum was the only abundant (>0.5%) metallic element detected in the greenish-yellow solid by X-ray fluorescence spectrometry, and infrared spectral correlations (16) further revealed that the molybdenum was present as the molybdophosphate anion $PMo_{12}O_{40}^{3-}$. Typical infrared absorptions characteristic of protonated tertiary amine (17) were also identified, as verified by recording the spectrum of (TOAH)Cl. The ultraviolet spectrum of the solid in acetonitrile solution exhibited characteristic intense absorptions due to molybdophosphate anion at 309 and 216 nm (14), matching well the spectrum of molybdophosphoric acid $(H_3PMo_{12}O_{40}\cdot15H_2O)$. Using molybdophosphoric acid as a standard, the amount of molybdophosphate in the solid was found to be 44% (Table IV).

The amount of amine in the solid was determined by nonaqueous acid-base titration to be one equivalent of amine per 690 (±14) g of solid. In combination with the spectrophotometric results, the titration results indicated 6.0 (±0.3) amines

Table IV. X-ray Diffraction and UV Analytical Data

Sample	% $PMo_{12}O_{40}{}^{3-}$ *		Prominent Reflections** (nm)				
	Exper.	Theor.					
Extraction crud solid	44.3	42.5	19.2	15.7	12.4		
Stripping crud solid	44.2	*	19.6	15.7	12.6		
Recryst. extr. crud solid	44.4	*	20.1	16.1	12.6		
TOA synthetic compound	46.2	44.9	19.6	15.5	12.8		
TOA extraction precipitate	47.0	*	19.2	15.5	12.4		
(TOAH)$_3$[PMo$_{12}$O$_{40}$]	65.7	63.1	13.6	9.8	4.4	4.0	3.4
(TOAH)Cl	---	---	20.5	7.0	4.5	4.2	

* Experimental values are calculated using ϵ = 22,900 at 309 nm; theoretical values for the double salts are calculated using X = 3 for the crud solids and Y = 8.0 for TOA double salts (see Table V).

** d spacings are calculated from angles of reflection using the Bragg equation.

per $PMo_{12}O_{40}{}^{3-}$, twice the number required to balance the negative charge. Elemental analysis (Table V) showed that chloride, suspected because of its use in stripping, accounted for the remainder of the negative charge, implying an empirical formula of the form

$$((C_YH_{2Y+1})NH)_3[PMo_{12}O_{40}]\cdot X((C_YH_{2Y+1})_3NH)Cl$$
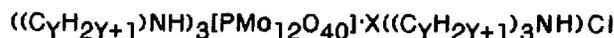
where X is the stoichiometric ratio of amine chloride to amine molybdophosphate and Y is the alkyl chain length of the tertiary amine. Using the value X = 3, indicated from the titration and spectrophotometric results, a least-squares optimization gave a good fit to the analytical data with Y = 8.9 (±0.1) as shown in Table V. This chain-length value coincides with the average chain-length of the extractant, Alamine 336, for which Y = 8.9 (2). Thus, the data may be reasonably interpreted in terms of a double salt composed of amine molydophosphate with three amine chlorides, wherein the amines evidently have 10- as well as 8-carbon alkyl chains. Slight ambiguity arises, however, if X is also allowed to vary in the least-squares calculation. In this case, we obtain a slightly better fit with X = 3.3 (±0.1) and Y = 8.5 (±0.1). Although the fractional value of X might be interpreted as an indication of a

Table V. Elemental Analyses*

Sample		% C	% H	% N	% Cl	% Mo	% P	X	Y
Extn. crud solid	– found	44.75	8.30	2.03	2.76	26.17	0.73		
	– theor.	44.92	8.10	1.96	2.48	26.87	0.72	3.0	8.9**
	– theor.	44.81	8.11	2.05	2.72	26.73	0.72	3.3[†]	8.5[†]
TOA analog	– found	42.97	7.57	1.98	2.66				
	– theor.	42.64	7.75	2.07	2.62			3.0	8.0
	– theor.	42.93	7.81	2.09	2.68			3.1[††]	8.0
Experimental uncertainty		±0.3	±0.3	±0.04	±0.2	±0.4	±0.1	±0.1	±0.1

* Experimental data are compared to the calculated values using the formula $((C_YH_{2Y+1})NH)_3[PMo_{12}O_{40}]\cdot X((C_YH_{2Y+1})_3NH)Cl$, where X and Y are adjustable stoichiometric parameters.

** Y determined by least-squares fitting.

[†] Both X and Y are determined by least-squares fitting.

[††] X determined by least-squares fitting.

molybdophosphate-to-chloride ratio of 3:10, for example, the analysis of the pure TOA analog (wherein Y = 8) described below tends to support a ratio of 1:3 in the pure double salt.

Since the molybdophosphate anion imparts a yellow color to its simple salts, the green color of the crud solids probably indicates the presence of reduced forms of molybdophosphate which are intensely blue [called "heteropoly blues" (18)]. A visible spectrum of an acetone solution of the solid showed that the green color is caused by an absorption at 790 nm, in the region where heteropoly blues typically absorb (18). In fact, reduced molybdophosphate has been identified previously in uranium mill crud where it was found to be a major fraction of the molybdophosphate present (11). Our sample, however, contained only a minor amount of heteropoly blue, less than 0.2% of the molybdophosphate present as estimated spectophotometrically (ϵ = ~5000 (16)). The presence of reduced molybdophosphate is understandable in terms of the mild oxidizing nature of molybdophosphate and the availability of potential organic reducing agents.

X-ray powder patterns were found to be an excellent tool for comparing the various solids isolated in this work since the samples were usually sufficiently crystalline to ensure sharp reflections. Prominent reflections are listed in Table IV. The fact that nearly identical diffraction patterns were obtained for the extraction crud solids, the solids similarly isolated from the stripping crud, recrystallized extraction crud solids, and TOA analogs implies that these materials are structurally equivalent.

Syntheses

To confirm the identification of the crud solids, a synthetic analog was prepared essentially by co-crystallizing (TOAH)Cl and (TOAH)$_3$[PMo$_{12}$O$_{40}$] (made in situ) out of chloroform/carbon tetrachloride solution as described in the Experimental Section. Elemental and UV analyses (Tables V and IV, respectively) support the formulation of the compound as the analogous double salt compound with X equal to 3. X-ray diffaction powder patterns indicated that this solid was equivalent to the solids isolated from the crud (Table IV). Thus, the crud solids do indeed appear to be co-crystallized amine molybdophosphate and amine chloride.

In the course of the work, (TOAH)$_3$[PMo$_{12}$O$_{40}$] was also isolated as a solid. Some X-ray and UV data are reported for this compound, along with (TOAH)Cl, in Table IV. None of the X-ray reflections for either of these two compounds was observed in the powder patterns for the double salt solids.

Formation Mechanism

Molybdophosphate Formation. Molybdophosphate anion, PMo$_{12}$O$_{40}$$^{3-}$, is the condensation product of molybdate and phosphate (18), both of which occur at low levels in the uranium ore leach solution. (see Tables I and III). The condensation of molybdate and phosphate is given by the equation

$$12MoO_4^{2-} + PO_4^{3-} + 24H^+ \rightleftharpoons intermediates \rightleftharpoons PMo_{12}O_{40}^{3-} + 12H_2O \quad (2)$$

The reaction is best described in terms of a series of equilibria involving various intermediates. Since only minute equilibrium concentrations of molybdophosphate exist under dilute conditions, very little of the molybdate in leach solution is expected to exist as molybdophosphate. To verify this conclusion, crystalline molybdophosphoric acid was dissolved in 0.1 $\underline{M}$ H$_2$SO$_4$ over a range of concentrations. The

molybdophosphoric acid decomposed rapidly, presumably by the reverse of Eq. 2, and no molybdophosphate anion was detected spectrophotometrically using up to ten times the molybdate concentration found in the aqueous feed of the uranium mill. We therefore concluded that the molybdophosphate probably does not exist in any appreciable quantity in the aqueous feed but must form during or after the extraction step.

Extraction experiments were then conducted to look for the anticipated organic-phase formation of molybdophosphate using 0.05 $\underline{M}$ TOA in nonane modified with dodecanol as the organic phase. (Modifier is needed to increase the solubility of the TOA-sulfate salt in the diluent.) As shown by the spectrophotometric experiment depicted in Fig. 2, molybdophosphate does indeed build up in the organic phase subsequent to extraction of dilute solutions of molybdate and phosphate (0.0002 and 0.01 $\underline{M}$, respectively, in 0.1 $\underline{M}$ H_2SO_4). Whereas molybdophosphate could not be detected in dilute aqueous solutions of molybdate and phosphate, condensation of molybdate and phosphate
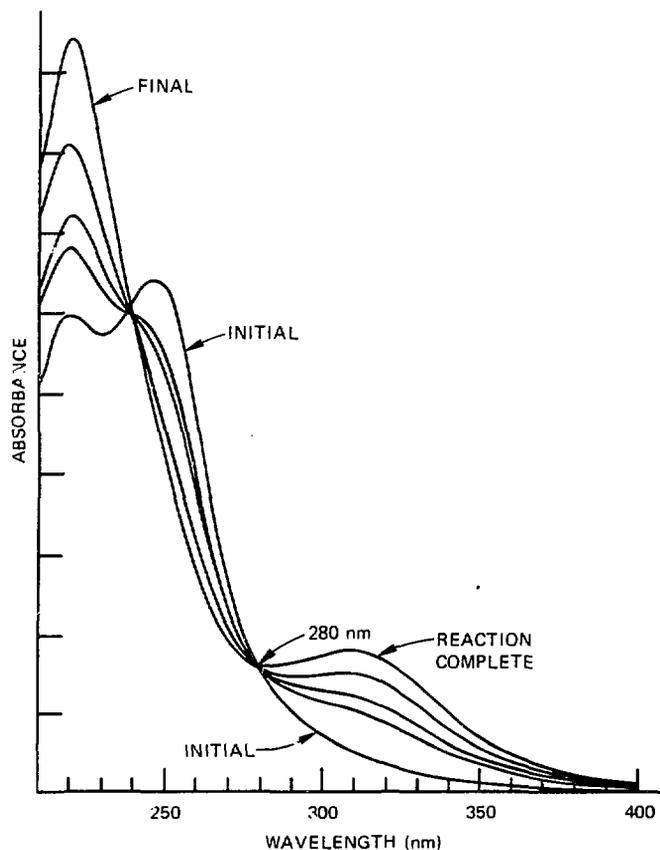

Figure 2 - Formation of molybdophosphate. TOA solvent was contacted with a tenfold volume equivalent of aqueous phase containing molybdate and phosphate. After a 16-hour contact time, the organic phase was removed and observed spectrophotometrically. The initial observation was made 1 day after the time of first contact, and the successive scans were made after 5, 8, 18, and 53 days, respectively. The formation of molybdophosphate anion is indicated by the appearance of the absorption peak at 309 nm.

(eq. 2) is apparently favored in the organic solvent to give the dissolved salt, $(TOAH)_3[PMo_{12}O_{40}]$. This should not be surprising since analytical chemists have for years taken advantage of solvent extraction techniques to drive Eq. 2 to completion for the analysis of phosphorus as molybdophosphate (14). The final spectrum is a good match with the spectrum of molybdophosphate either as $H_3PMo_{12}O_{40}$ or $(TOAH)_3[PMo_{12}O_{40}]$, and although the reaction takes weeks to reach completion, the expected stoichiometric amount of molybdophosphate eventually forms, based on the initial amount of molybdate used. The existence of the isosbestic point at 280 nm indicates the presence of only two detectable species at the higher wavelengths: an apparent intermediate with λ_{max} = 247 and 220 nm and the final product, molybdophosphate. No spectral changes above 250 nm occur when phosphate is omitted from the experiment.

The eventual conversion of molybdate to molybdophosphate did not appear to be affected by the extraction procedure. Molybdophosphate formation occurred regardless of whether the molybdate and phosphate were brought together by 1) simultaneous extraction of molybdate and phosphate together from the same solution, 2) sequential extraction from different solutions into the same organic solution, or 3) separate extraction from different solutions into different organic solutions followed by mixing of the separate organic solutions. Moreover, the reaction occurred even when the aqueous phase was removed soon after the initial contact between the two phases. However, removal of the aqueous phase did tend to decrease the reaction rate as measured by the time elapsed for 50% of the final amount of molybdophosphate to form (first half-life). The removal of the aqueous phase at 15 min, 16 hours, and 2 months (reaction complete) gave the following first half-lives: 7.2, 5.7, and 4.1 days, respectively. Since the condensation of molybdate and phosphate requires a large number of protons (see Eq. 2), the role of the aqueous phase during the reaction may be to serve as a buffered proton source, sustaining the reaction by preventing the depletion of available protons in the organic solvent. In the experiments described above, the molybdate was concentrated in the organic phase (by a factor of 9.4) by contacting the aqueous and organic phases in the volume ratio 10:1. Although precise kinetic measurements have not yet been made, it was noted that the reaction rate increases with molybdate loading; consequently, the formation of molybdophosphate is much slower with an aqueous to organic ratio of 1:1.

As expected from earlier studies on related systems (3), molybdate is strongly extracted in the above TOA system, having distribution coefficients of 146 and 81, with and without 0.01 $\underline{M}$ phosphate, respectively. On the other hand, experience has shown that phosphate is extracted weakly from sulfate media, although no direct distribution measurements appear to have been reported. Sufficient phosphate apparently does extract along with molybdate, however, to support stoichiometric completion of the condensation to molybdophosphate (Eq. 2) in these experiments. Tracer experiments are presently being conducted to quantify the extraction behavior of phosphate and to investigate molybdate-phosphate complexation behavior in the solvent.

Solids Precipitation. Analogous to the chemistry employed in the synthetic preparation of $(TOAH)_3[PMo_{12}O_{40}] \cdot 3(TOAH)Cl$, the formation of double salt solids in hydrometallurgical amine extraction systems probably involves co-crystallization of amine molybdophosphate and amine chloride. Present in high concentration in the stripping solution and to some extent in leach solution (Table I), chloride exchanges readily for sulfate in the solvent, and appreciable concentrations of amine chloride are normally found in process solvent (3,7). In fact, analysis of the solvent fractions of the crud samples did show high chloride values (Table III). In the laboratory, it was thus a straightforward matter to cause precipitation of solids by stirring solutions of $(TOAH)_3[PMo_{12}O_{40}]$ (as before, in 0.05 $\underline{M}$ TOA, dodecanol-modified norane) over aqueous NaCl solutions (0.03 to 1 $\underline{M}$). The solutions of $(TOAH)_3[PMo_{12}O_{40}]$ were prepared, for example, by extracting molybdate and phosphate, but other methods were also used (see Experimental Section). The precipitated solids were identified by UV

spectrophotometry and X-ray diffraction as the double salt (Table IV). In stoichiometric terms, the precipitation reaction may be written as

$$\underdotted{(TOAH)_3[PMo_{12}O_{40}]} \;+\; \underdotted{3(TOAH)Cl} \;\rightleftharpoons\; \underline{(TOAH)_3[PMo_{12}O_{40}]\cdot 3(TOAH)Cl} \qquad (3)$$
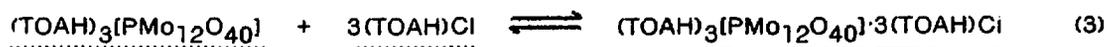
where dotted underlining denotes salts dissolved in the organic phase, and solid underlining denotes solid phase. Currently, solubility and precipitation experiments are being conducted over a wider chloride range to quantify the solubility of the double salt, investigate mass-action behavior and possible aggregation phenomena, and characterize other precipitates that may form. An initial indication from Table III is that the organic-phase solubility of the double salt is quite low, approximately 8×10^{-5} $\underline{M}$ or less. Thus, since extracted molybdate can be expected to eventually convert to molybdophosphate with sufficient phosphate present, only minute amounts of molybdate in the solvent are apparently required to cause crud.

Summary and Conclusions

As part of our study of interfacial crud and phase separation in solvent extraction, we have chemically and physically characterized an actual hydrometallurgical interfacial crud from a western U.S. uranium mill. The cause of the crud is the precipitation of a solid compound derived from the extractant and an extracted metal, molybdenum. The compound is exactly analogous to the pure TOA compound that we synthesized in the laboratory, having the empirical formula, $(TOAH)_3[PMo_{12}O_{40}]\cdot 3(TOAH)Cl$, except that the tertiary amines in the crud contain some 10- as well as 8-carbon alkyl chains. Apparently unknown until the present, the compound is a crystalline double salt of amine molybdophosphate with three amine chlorides.

From the results of our laboratory experiments, we propose the following mechanism for the formation of the crud: Molybdate is strongly extracted from the leach solution and builds up in the solvent to a level determined largely by the aqueous feed concentration of molybdate and degree of solvent scrubbing. Reacting with a small amount of extracted phosphate, the molybdate undergoes a slow, spontaneous condensation reaction in the solvent to form molybdophosphate as the organic-soluble amine salt. Although alkaline scrubbing partly removes the molybdophosphate from the solvent, sufficient levels of molybdophosphate apparently accumulate to co-crystallize with amine chloride, formed by anion exchange during stripping, giving the insoluble double salt. As the organophilic double salt crystals precipitate from the organic phase, they come to rest on the organic side of the solvent/aqueous interface, but they do not become wetted by the aqueous phase. The layer of particles begins to interfere with coalescence of aqueous droplets produced during the organic-continuous mixing, and small droplets may eventually become occluded in the crud layer, immobilized because of tight packing and insufficient density difference to propel the droplets downward.

Although our experiments are not yet complete, the proposed mechanism is consistent with the observations made thus far. Physically, the crud is a dispersion of small crystals of double salt and occluded aqueous droplets in process solvent. We have shown that the presence of low concentrations of molybdate and phosphate in dilute sulfuric acid leads to the spontaneous formation of molybdophosphate in the solvent subsequent to amine extraction. When organic-phase solutions of molybdophosphate were contacted with aqueous chloride solutions, the double salt precipitated. Since molybdate, phosphate, and chloride may be difficult to avoid in uranium ore processing, eventual precipitation of the double salt (and hence, crud formation) is likely when these species are present. Although molybdenum-caused cruds in amine extraction hydrometallurgy have been sometimes associated with other

chemical factors (such as vanadium, for example), these results may generally explain the often observed occurrence of molybdenum-related "green, gummy solids" in amine extraction hydrometallurgy (5,9,11).

An obvious approach to reducing the formation of molybdophosphate crud is simply to increase the amount of alkaline scrubbing of the solvent. However, owing to the relatively high cost of alkaline scrubbing (6,8), this approach may not be attractive. Although we have not yet conducted any supporting tests, we suggest that the molybdenum crud problem could be dealt with in some cases by choosing a tertiary amine extractant with a higher molybdophosphate tolerance. Branched-chain amines appear promising, based on some limited Amex process-development data (7,9) and our general experience over many years that branched-chain extractants often give superior phase characteristics over their straight-chain analogs. A higher molybdophosphate tolerance would have an obvious beneficial effect on circuit operation, allowing for molybdenum recovery, reduction of the amount of alkaline scrubbing, smaller solvent inventory, and elimination of the awkward handling of the crud.

Acknowledgments

References

1. G. M. Ritcey, "Crud in Solvent Extraction Processing – A Review of Causes and Treatment," Hydrometallurgy, 5 (1980) pp. 97-107.

2. B. A. Moyer and W. J. McDowell, "Factors Influencing Phase Disengagement Rates in Solvent Extraction Systems Employing Tertiary Amine Extractants," Separation Science and Technology, 16(9) (1981) pp. 1261-1289.

3. C. F. Coleman, K. B. Brown, J. G. Moore, and D. J. Crouse, "Solvent Extraction with Alkyl Amines," Industrial Engineering Chemistry, 50(12) (1958) pp. 1756-1762.

4. K. B. Brown, C. F. Coleman, D. J. Crouse, C. A. Blake, and A. D. Ryon, "Solvent Extraction Processing of Uranium and Thorium Ores," pp. 472-487 in Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy held in Geneva, Vol. 3, United Nations Publications, New York, 1958.

5. R. C. Merritt, The Extractive Metallurgy of Uranium; Colorado School of Mines Research Institute, 1971.

6. G. M. Ritcey and A. W. Ashbrook, Solvent Extraction / Principles and Applications to Process Metallurgy, Part II, pp. 452-522; Elsevier, New York, 1980.

7. A. D. Ryon and R. S. Lowrie, "Experimental Basis for the Design of Mixer Settlers for the Amex Solvent Extraction Process," Report ORNL-3381, April 19, 1963, p. 20.

8. R. B. Coleman, "Uranium Milling Overview," Mining Congress Journal, 66(11) (1980) pp. 53-54.

9. D. J. Crouse and K. B. Brown, "Amine Extraction Processes for Uranium Recovery from Sulfate Liquors," Vol. 1, Report ORNL-1959, Oak Ridge National Laboratory, Nov. 18, 1955; H. M. McCleod, Jr., "Progress Report of Engineering Section, Raw Materials Process Testing, July-December, 1955," Report ORNL-2112, July 12, 1956; D. J. Crouse, K. B. Brown, W. D. Arnold, J. G. Moore, and R. S. Lowrie, "Progress Report on Uranium Extraction with Organonitrogen Compounds," Report ORNL-2099, May 14, 1957; K. B. Brown, C. F. Coleman, D. J. Crouse, and A. D. Ryon, "Progress Report on Raw Materials for February, 1957," Report ORNL-2269, May 31, 1957; K. B. Brown, C. F. Coleman,

D. J. Crouse, and A. D. Ryon, "Progress Report on Raw Materials for May 1957," Report ORNL-2366, Sept. 27, 1957; W. D. Arnold and D. J. Crouse, "Further Evaluation of Amines as Extractants for Uranium from Sulfate Liquors," Report ORNL-3030, Dec. 28, 1960.

10. A. S. Vieux, K. Bibombe, and M. Nsele, "Organic Phase Species in the Extraction of Molybdenum (VI) by Aliquat 336 from Chloride Media," Hydrometallurgy, 6 (1980) pp. 35-47, and references within.

11. E. Sialino, C. Mignot, P. Michel, and J. Vial, "Extraction and Selective Stripping of Uranium and Molybdenum in Sulfate Solution Using Amines," pp. 592-599 in Proceedings of the International Solvent Extraction Congress held in Toronto 1977, Vol. 2, The Canadian Institute of Mining and Metallurgy, Montreal, Quebec, 1979.

12. G. A. Tsigdinos, "Preparation and Characterization of 12-Molybdophosphoric and 12-Molyhdosilicic Acids and Their Metal Salts," Industrial Engineering Chemistry, Product Research and Development, 13(4) (1974) pp. 267-274.

13. J. Kucharsky and L. Safarik, Titrations in Non-Aqueous Solvents, pp. 169-179; Elsevier Publishing Co., New York, 1965.

14. C. Wadelin and M. G. Mellon, "Extraction of Heteropoly Acids," Analytical Chemistry, 25(11) (1953) pp. 1668-1673; H. So and M. T. Pope, "Origin of Some Charge-Transfer Spectra. Oxo Compounds of Vanadium, Molybdenum, Tungsten, and Niobium Including Heteropoly Anions and Heteropoly Blues," Inorganic Chemistry, 11(6) (1972) pp. 1441-1443.

15. D. W Marquardt, "Least-Squares Estimation of Nonlinear Parameters," Report SDA-3094, E. I. DuPont de Nemours & Co., Wilmington, Del., March 1964.

16. N. E. Sharpless and J. E. Munday, "Infrared Spectra of Some Heteropoly Acid Salts," Analytical Chemistry, 29(11) (1957) pp. 1619-1622; R. A. Nyquist and R. O. Kagel, Infrared Spectra of Inorganic Compounds, pp. 336,337; Academic Press, New York, 1971.

17. L. J. Bellamy, The Infra-red Spectra of Complex Molecules, Vol. 1, pp. 277-293; John Wiley and Sons, New York, 1975.

18. T. J. R. Weakley, "Some Aspects of the Heteropolymolybdates and Heteropolytungstates," pp. 131-176 in Structure and Bonding, Vol. 18, J. D. Dunitz, ed.; Springer-Verlag, New York, 1974; G. A. Tsigdinos, "Heteropoly Compounds of Molybdenum and Tungsten," pp. 1-64 in Topics in Current Chemistry;" Springer-Verlag, New York, 1978.