Getting More Out of Your Copper SX Plant

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Abstract

A significant economic consideration for concentrate producers is by-product credits. What if this concept could be applied to a copper solvent extraction (SX) operation as well? Due to large solution inventories, a number of copper SX operations contain significant minor metal values within the leach liquor. These metals values tend to build up in the leach solution over time until an equilibrium is reached. It may be possible to recover these metals economically since they exist in the solution 'for free' (no additional mining or leaching costs) [1]. Cytec has an active development project for the recovery of certain of these trace metals via SX or alternative routes – without negatively affecting the primary copper recovery process. This paper will review a solvent extraction and crystallization route for the recovery of molybdenum from copper SX liquors (patent pending).

Background

The recovery of Mo is practiced in the catalyst industry through solvent extraction from an acidic sulfate leach solution [2,3]. Solvent extraction has also been studied for the recovery of Mo from acid leach solution of molybdenite (MoS_2) concentrate [4,5,6]. The process presented here based on solvent extraction with a formulated phosphinic acid extractant is a flowsheet that concentrates the Mo from a Cu SX raffinate solution and resolves a number of practical physical, chemical and kinetic operating issues. With appropriate modifications the process is also applicable to the recovery of Mo from other industrial processes.

Solvent Extraction and Process Development

A modified phosphinic acid reagent formulation was developed for the molybdenum extraction process. A common problem for recovering molybdenum from these streams in the past has been finding a formulation which would have the right selectivity and kinetic properties to allow the low Mo concentration to be efficiently extracted without altering the standard Cu SXEW process. Due to the unique properties of the formulation it is possible to selectively remove molybdenum while leaving the majority of the impurity elements behind in the leach liquor. Ideally the recovery process would take place downstream of the standard copper SX plant, removing the molybdenum from the acidified copper raffinate stream.

Figure 1 shows the loading characteristics of the phosphinic acid formulation for Fe, Al, and Vanadium. Due to the extremely strong complex formed between the formulation and molybdenum, molybdenum loading is nearly stoichiometric even at a pH of 0.1. As shown, the Fe, Al, and Vwould also be extracted from solutions at typical Cu raffinate pH values (pH 1.2 – 1.6), however their loading is significantly reduced at higher acidities or lower pH values. Therefore, molybdenum may be separated from these other common impurities by increasing the raffinate acidity prior to the Mo recovery stage.

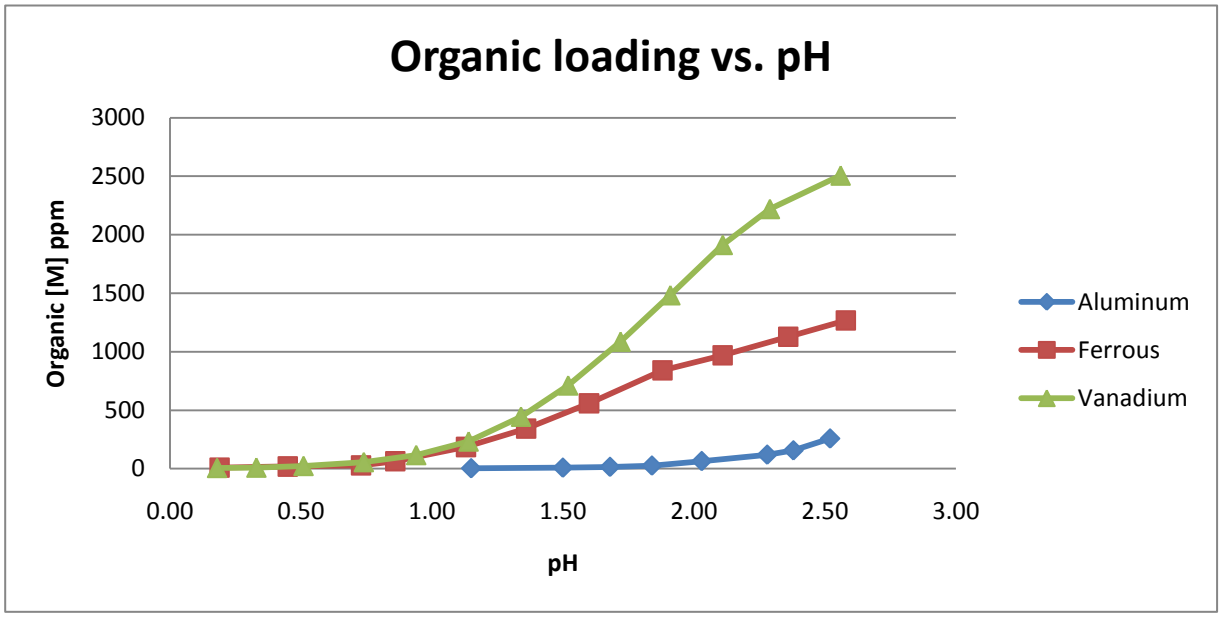

Figure 1: Impurity Loading as a Function of pH

The majority of other elements which would typically be present in the leach liquor (Cu, Zn, Mg, Si, etc…) are only extracted at much higher pH's than normally encountered in copper SX processing (pH >3).

Once the molybdenum has been extracted from the aqueous leach solution the next step was to develop a process for the recovery of the molybdenum from the organic phase. Although known that Mo could be removed from organics by utilizing a basic media for stripping, previous processes failed in part due to third-phase formation / physical separation difficulties.

In order to avoid or minimize third-phase formation, the new formulation contains a phase modifier which enhances the phase separation characteristics. In addition the stripping solution and stripping conditions are closely controlled to maximize Mo stripping while minimizing the formation of the basic salt of the phosphinic acid.

Molybdenum Extraction

Molybdenum extraction is believed to proceed according to the equation below:

$$MoO_2^{2+} + 2(H_2R_2)_{org} \rightarrow MoO_2(HR_2)_{2\ org} + 2H^+ \quad (1)$$

The reaction is largely non-reversible due to the strength of the molybdenum ligand complex. The kinetics of extraction are surprisingly fast. In a dynamic rig run (3 minute mixer retention time) greater than 90% recovery of molybdenum was achieved from a real raffinate solution initially containing <10 ppm Mo.

Figure 2 shows a Mo extract isotherm along with a McCabe Thiele diagram. The isotherm was generated using a copper raffinate solution containing 40 ppm Mo and an initial acidity of 20 gpl H_2SO_4. The organic was made up to a 10 vol% solution of the extractant formulation in diluent.

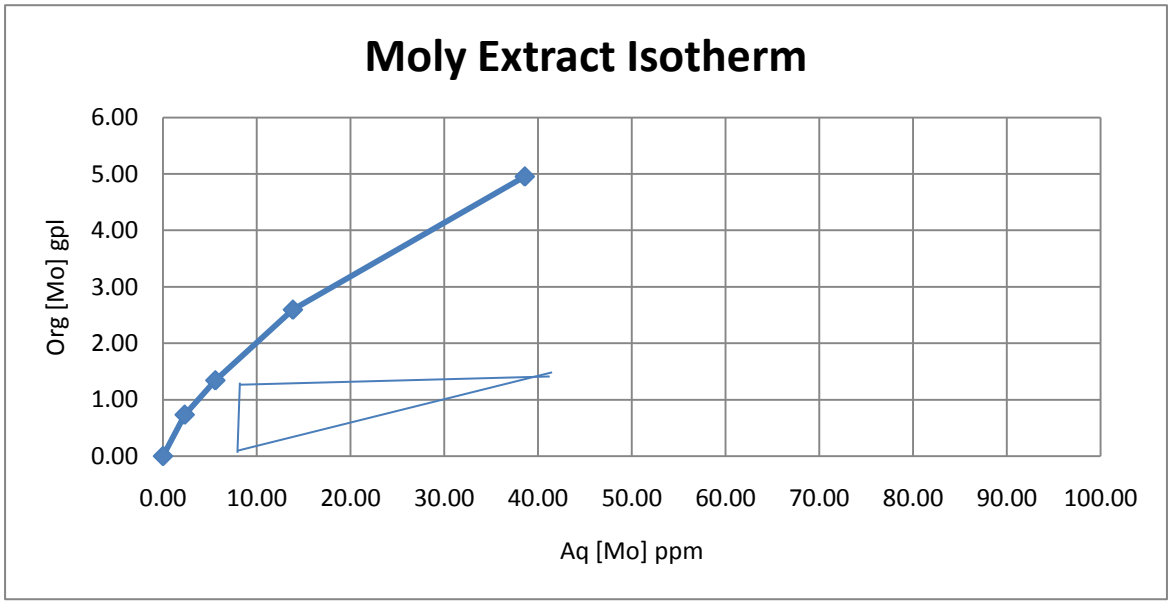

Figure 2: Molybdenum Extraction Isotherm

As shown, the extractant formulation could theoretically load up to 5 gpl Mo from the 40 ppm feed. Due to the low feed pH, the loading of impurities into the organic phase was minimal.

Since Mo is typically present in these leach liquors at very low concentrations (5 – 100 ppm), it is advantageous to extract the Mo while utilizing a very low flow O/A ratio. Organic recycle may be utilized to maintain proper mixing characteristics. By concentrating Mo in the organic within the extract circuit, the downstream equipment required for organic processing is minimized.

As shown by the McCabe Thiele diagram, using an extract O/A ratio of 0.025 and a single extraction stage, the Mo recovery would be expected to be ~80% while concentrating the Mo in the organic phase from 40 ppm to ~ 1200 ppm (30 times concentration). In order to maintain the organic loading in extract constant, the organic flowrate for the downstream scrubbing and stripping operations would be ~30 times lower than the initial raffinate flowrate into the extraction section.

Impurity Scrubbing

Acidification of the raffinate stream prior to molybdenum extraction, can greatly reduce the co-extraction of impurities, depending on the final molybdenum product purity required a scrub stage may also be necessary. Acidified water may be used to remove any co-extracted impurities and the process may be optimized to achieve the desired metal separation.

Molybdenum Stripping:

Due to the very strong Mo extractant complex, Mo can only be partially back extracted with acid. Molybdenum stripping is best achieved using a base. Molybdenum stripping with ammonium hydroxide is believed to involve a speciation change reaction according to equation 2. Equation 3 then shows the possible stripping reaction.

Speciation Change:

$$MoO_2^{(+2}{}_{org)} + 2NH_4OH_{aq} \leftrightarrow MoO_4{}^{(-2)}{}_{aq} + 2H^+{}_{org} + 2NH_4{}^+{}_{aq} \quad (2)$$

Stripping Reaction:

$$MoO_2(HR_2)_{2\ org} + 2NH_4OH \leftrightarrow (NH_4)_2MoO_4 + 2H_2R_{2\ org} \quad (3)$$

Under these conditions, the formation of the ammonium salt of the phosphinic acid formulation is minimized. However the choice of the base and the ratio of base to ligand / metal must be carefully controlled to prevent third phase formation. Under proper conditions, the Mo may be

successfully stripped from the organic minimizing the circulating load of Mo and maximizing extraction.

In the pilotings completed to date, the Mo was stripped from the organic phase using a strip solution containing ammonia and ammonium carbonate. Presence of ammonium carbonate greatly enhanced the physical separation between the phases and minimized the transfer of base back with the organic into extract.

In order to produce a concentrated strip liquor it is advantageous to run a high flow O/A ratio within strip. Aqueous recycle may be used to achieve the necessary mixing conditions. Concentrated base should be utilized to achieve the optimum stripping conditions while minimizing dilution effects.

Crystalization

Molybdate crystals in different forms may be produced from the concentrated strip liquor utilizing multiple methods such as distillation, cooling, selective solubility, etc. In the trials run to date, the molybdenum was recovered from the strip liquor by adjusting the pH of the concentrated solution using sulfuric acid. This was done on a batch basis but could also be achieved continuously by taking a small bleed stream from the aqueous strip liquor. Ammonium molybdate can also be produced in situ through adjustment of the strip liquor pH.

Pilot plant Results

Molybdenum was recovered, concentrated and purified from a real leach liquor in a 3 week long continuous pilot plant run. The configuration utilized a single extract stage and a single strip stage separated by coalescors to minimize impurity transfer. Figure 3 shows the basic flowsheet.

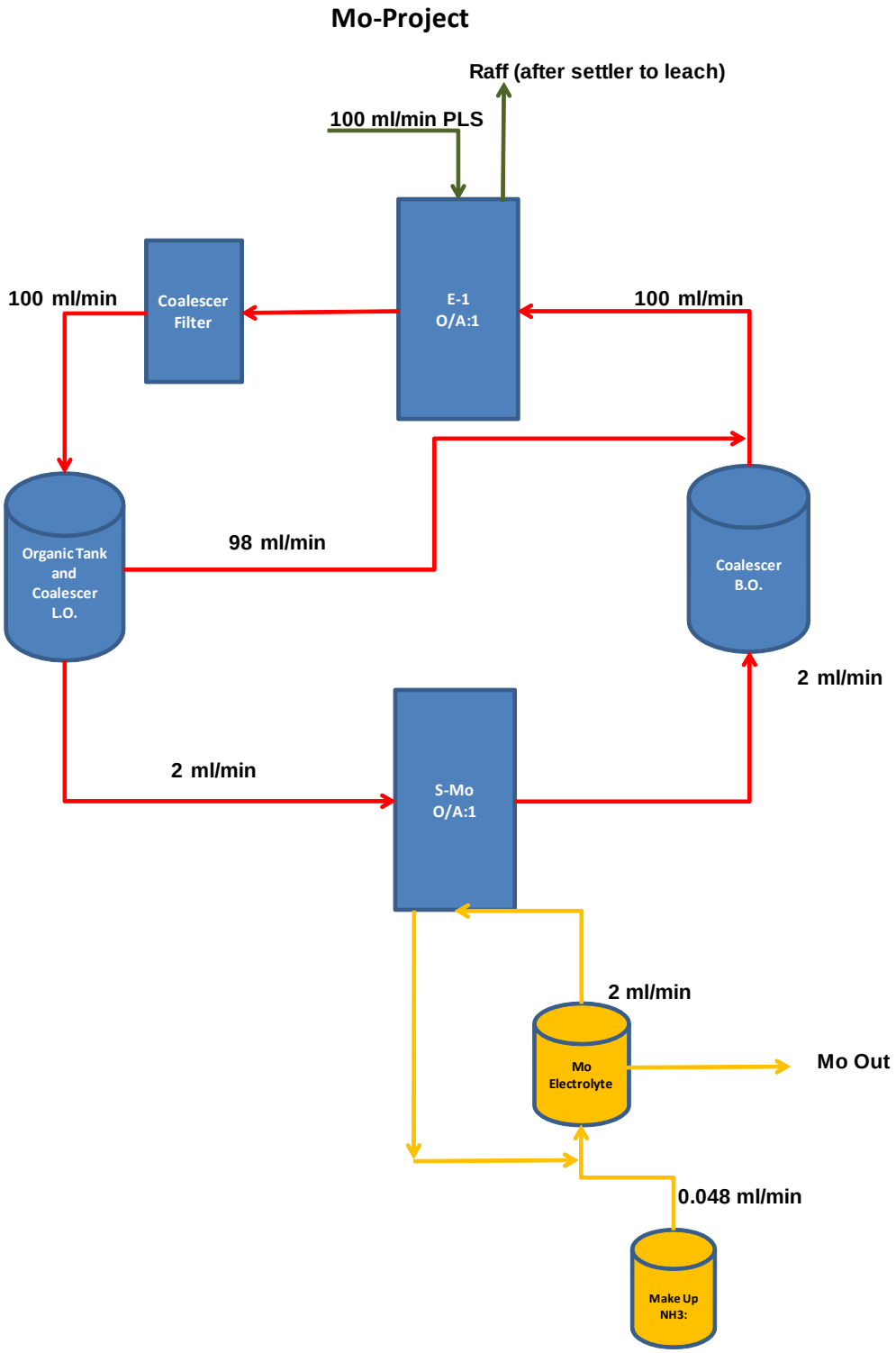

Figure 3: Mo circuit flow diagram

The raffinate solution obtained from the copper SX operation was adjusted to a total acidity of 40 gpl H_2S0_4 before being used as the feed to the Mo extraction circuit. Table 1 shows the composition of the Mo feed following the acidity adjustment.

Table 1: Feed Composition to Mo Extraction Circuit (ppm).

Al	*As*	*Ca*	*Cd*	*Co*	*Cu*	*Fe*	*Gd*	*K*	*Li*	*Mg*	
6115.3	13.2	422.6	3.3	21.0	2004.6	5879.1	1.4	812.8	7.3	3241.1	
Mn	*Mo*	*Nd*	*Ni*	*P*	*Sc*	*Si*	*Sr*	*Ti*	*U*	*V*	*Zn*
962.1	75.1	4.7	4.8	695.5	0.3	89.9	15.6	25.6	38.3	14.8	283.7

Operating conditions:

Configuration: 1E + 1S
Feed Solution: 75 ppm Mo and 40 gpl H2SO4
Aqueous feed flowrate: 100 mls/min
Organic flow rate: 2 mls/min
Aqueous strip flow rate: 0.045 mls/min
Extraction O/A ratio: 0.02:1 (1:1 including organic recycle)
Stripping O/A ratio: 45:1 (1:1 including aqueous recycle)

The extraction portion of the plant was initially started under 100% organic recycle to build the Mo concentration within the organic phase to a predetermined level. Once the organic Mo content had been reached, a bleed of the organic flow was then sent to the stripping circuit (for this piloting the alternative scrub stage was not utilized). The organic was stripped utilizing an ammonia/ammonium carbonate solution.

The piloting was run for three weeks (24hr/day operation) under operating temperatures of 10 – 15 degrees C. Due to the scale of the operation it was difficult to determine entrainment losses however there were no issues with the physical operation of the plant (dispersion bands, phase disengagement times were consistent and crud build up was negligible). Figure 4 shows a picture of the pilot plant equipment. A standard deep cell (500 ml mix box) was utilized for the extraction stage while a mini rig stage (100 ml mix box) was used as the stripping stage. Note in the picture the second mini rig unit was utilized as a coalescor to minimize aqueous in organic transfer to strip.

Figure 4: Picture of Pilot Plant Equipment / Mo Rig Run

During the run the molybdenum concentrations were monitored in the organic, raffinate, and the strip liquor. Figures 5 and 6 show the extraction and stripping efficiencies (Note: raffinate was reprocessed following 150 hrs of operation). Figure 7 shows the steady increase in the Mo concentration within the strip liquor over time.

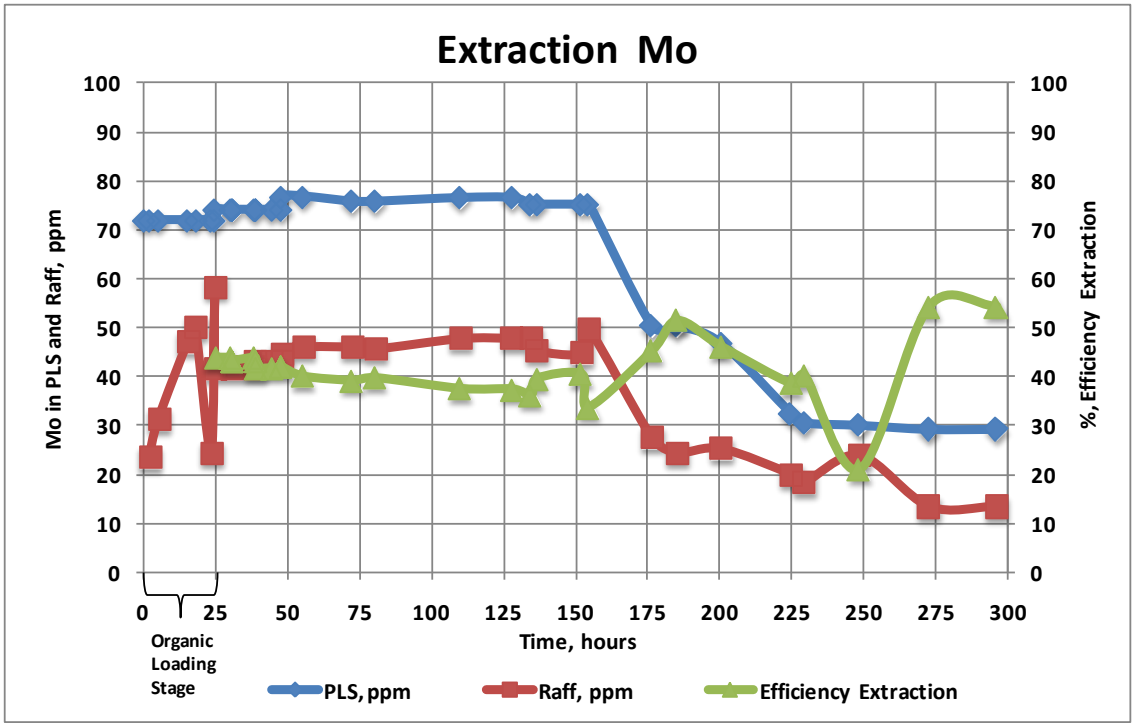

Figure 5: Extraction Efficiency

As shown, the extraction efficiency achieved was only ~40%. This was due to the configuration chosen (single stage extract), the targeted organic Mo concentration, and fairly low strip efficiency. Higher extraction efficiency could be achieved by utilizing additional extraction stages or reducing the Mo concentration in the organic phase (running a higher O/A ratio).

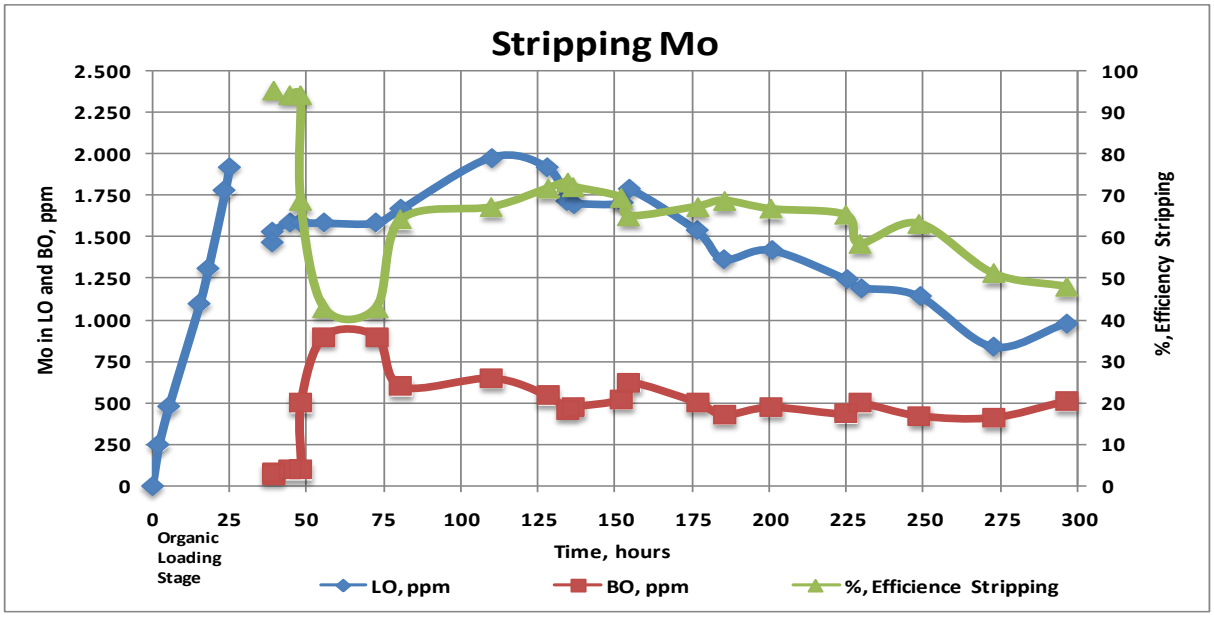

Figure 6: Stripping Efficiency

As shown the stripping efficiency achieved on the piloting was ~60% so molybdenum was recirculating back into the extraction stage. It is possible to achieve higher strip efficiencies – by tighter control of the strip liquor composition. The piloting was completed under overly conservative conditions due to concerns regarding formation of the ammonium salt. Salt formation would lead to phase disengagement and 3rd phase formation issues – which were completely avoided within the piloting. Subsequent testwork has shown higher strip efficiencies may be obtained by optimizing the strip solution composition and strip O/A ratio. This can be accomplished without forming the basic salt of the phosphinic acid.

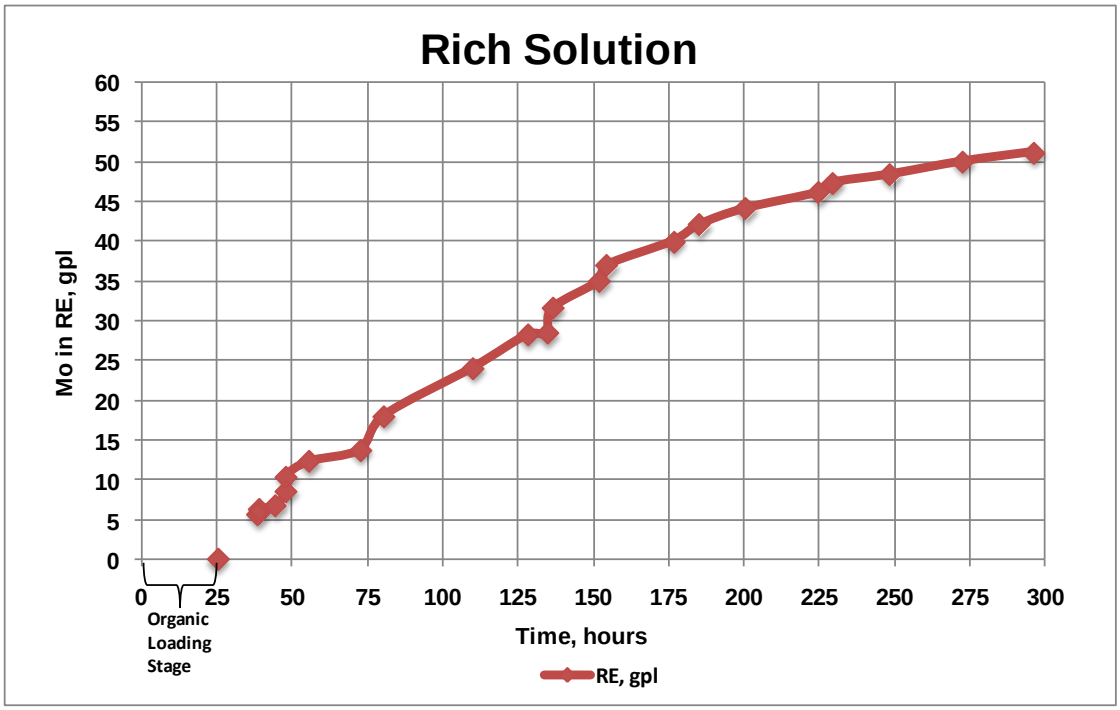

Figure 7: Rich Electrolyte Mo Concentration

As shown the Mo concentration in the electrolyte consistently increased despite the dilution effect of the ammonia/ammonium carbonate make-up into the strip liquor.

At the conclusion of the run, the strip liquor was analyzed for impurity elements (Table 2). As shown, even without operating the additional scrub stage the electrolyte purity was very high.

Table 2: Rich Electrolyte Impurities (ppm)

Al	As	Cd	Co	Cu	Fe	Gd	Mg	Mn
15.2	18.3	nd	nd	22.4	10.2	nd	29.5	nd
Ag	**Ba**	**Be**	**Bi**	**Cr**	**Ga**	**Ge**	**Hg**	**La**
0.1	nd	0.5	12.2	nd	nd	nd	nd	nd
Mo	**Ni**	**P**	**Sc**	**Sr**	**Ti**	**U**	**V**	**Zn**
44787.2	nd	30.0	nd	nd	nd	nd	nd	0.2
Na	**Pb**	**S**	**Sb**	**Se**	**Sn**	**Te**	**Th**	**W**
12.0	nd	694.0	nd	nd	nd	nd	nd	0.9

The strip liquor was then treated with sulfuric acid to generate a high quality mixture of ammonium molybdate hydrates and molybdenum oxide hydrate crystals. The major impurities found with the crystals were P, and S, while minor impurities were: As, Cu, Fe, Si, Zn, and Na. The crystal quality and purity could be improved with suitable washing of the filter cake.

Figures 8&9 show the strip liquor pre and post acid addition.

Figure 8: Strip solution Pre Acid Addition

Figure 9 Strip Solution Post Acid Addition

Conclusions

Mo was successfully extracted from copper raffinate liquor, concentrated and purified via an SX route. The molybdenum was extracted from a feed containing ~70 ppm, was concentrated within the organic phase to ~2 gpl, and was then stripped producing a strip liquor containing ~45-50 gpl Mo (>600 x concentration). High purity crystals were obtained from the rich liquor through pH adjustment. The piloting ran successfully with no major difficulties. Work is ongoing to optimize the extraction scrubbing and stripping stages to maximize Mo transfer while minimizing impurity transfer.

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