Treating Tailings Waters From Moly Operations—A Review

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Removing pollutants from tailings water is a prime concern at Climax's Henderson mine.

Tailings water from primary flotation concentrators usually contains minor amounts of pollutants such as heavy metals, cyanide and solubilized molybdenum, which are solubilized in the flotation process. A review of various techniques to reduce pollutants to acceptable levels is presented.

Generally, molybdenite ores are processed by conventional size-reduction techniques, followed by flotation to produce a metallurgical-grade concentrate of 88% to 92% MoS_2. Reagents commonly used in the milling process include: vapor oil (collector); pine oil, MIBC (frother); Dowfroth 250 (water-soluble frother); lime (rougher pH control); and sodium cyanide (Fe and Cu depressor). For lead depression, Nokes reagent is stage-added to the regrind mills and cleaners. Flocculant is added to obtain clear overflows in the intermediate thickeners.

What's Needed to Treat Moly Tails Waters

About 2120 L (560 gal) of water or 2.33 st are required to process one short ton of ore; if 80% recycle is practiced, the fresh water usage will be 420 L (112 gal) or 0.47 st per ton of ore processed. In areas where there are significant quantities of rainfall, bleeding a part of the tailings pond decant water prior to discharge is essential to maintain water balance.

The flotation process tends to solubilize small amounts of heavy metals such as molybdenum, copper, manganese, and zinc. Low levels of cyanide are also present in the water; this can usually be attributed to the use of sodium cyanide in the milling circuit. If clarification is inadequate, total suspended solids content in the tailings pond decant water may increase.

Most of the flotation collector normally reports into the final concentrate. The balance of the collector is adsorbed in the tailings with very little reporting in the decant water. The same comments are valid for water-insoluble frothers like MIBC and pine oil; but the amounts of frother used are significantly smaller compared to the collector level. If the tailings pond decant water is visually frothy, it is an indication that excessive levels of frother are being used. The obvious solution would be to lower frother use in the mill.

Close control of the usage of water-soluble frothers like DF 250 in the mill will alleviate visual frothing of tailings

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ponds decant water. This is also applicable to surfactants like Syntex L.

In general, pollutants that may require treatment are the heavy metals, including molybdenum and cyanide.

Treatment of tailings water is done for two reasons; minimize heavy metal pollutants so as to meet pollution control requirements, and minimize the effect of MoS_2 recovery loss upon water recycle. However, the constituents of the recycle water that contribute to MoS_2 losses in the flotation circuit are not clearly defined.

Molybdenum Reduction

The Mo level of tailings water is in the range of 2 to 4 ppm and 7 to 10 ppm Mo with water recycle. The levels after treatment will depend upon the water flow since the discharge limit is usually in pound per day. With no recycle, these concentrations are expected to be below 1.0 ppm and 2.0 ppm with the recycle. A review of the important techniques follows.

Coprecipitation with hydroxides of Al and Fe—Molybdenum can be removed from aqueous solution by sorption or coprecipitation with flocculant hydroxides of iron (III) and aluminum (III). However, the quantity of dissolved aluminum required is greater than iron. For this reason, testwork with aluminum has been limited.

The chemistry of the Mo removal process with ferric iron is fairly straightforward. The optimum pH is between 3 and 4 and the Fe/Mo ratio controls the degree of Mo removal with the residual Mo concentration dependent upon the initial[5] concentration. The Fe/Mo ratio required for optimum removal is in the range of 6 to 10.

The technology for removal of the Fe-Mo complex is more complicated. Conventional solid-liquid separation of the complex by thickening may not be practical in view of the slow settling characteristics of the Fe-Mo precipitate. The use of flotation techniques for its removal has been investigated by the USBM and the Moly Project at the University of Colorado for solid-liquid removal.[6,7]

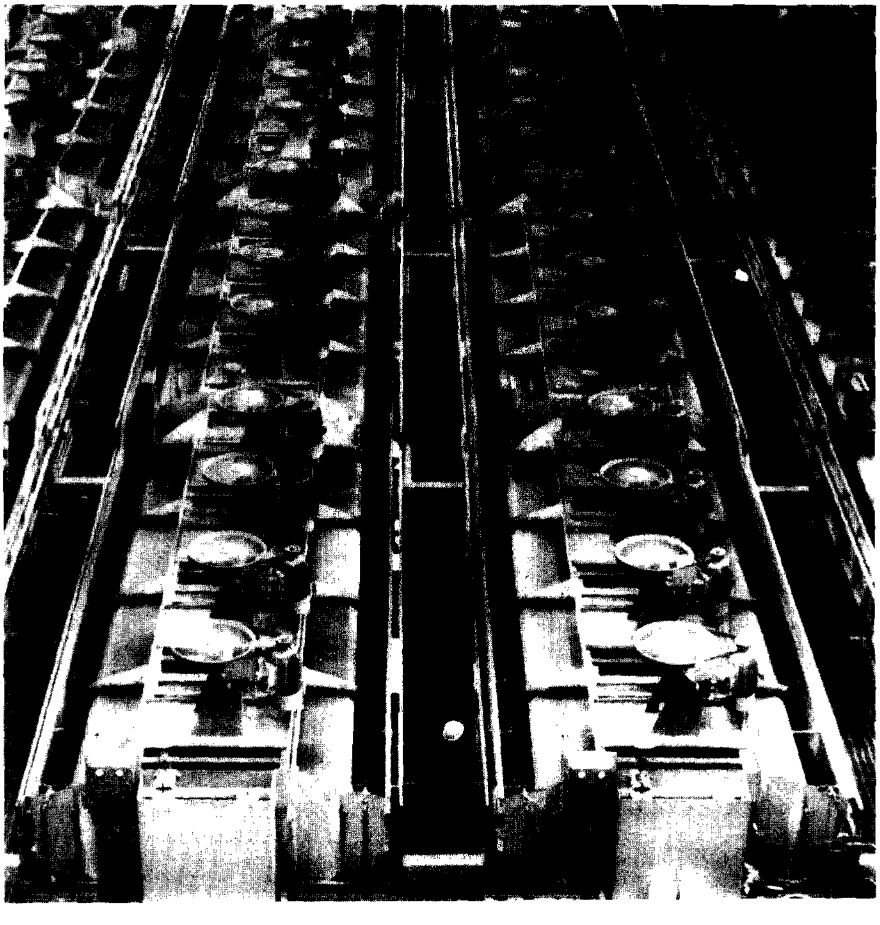
The Bureau of Mines has investigated the technique of dissolved air flotation (DAF) for removal of the Fe-Mo complex. An Fe/Mo ratio of 6 was found to reduce the Mo level from 4.0 to 0.5 ppm on synthetic solutions. Further testwork simulating recycle liquors with higher levels of Mo is continuing.[6]

Small-scale pilot testing using a specially designed DAF unit has been conducted by Jordan and coworkers at the University of Colorado under the sponsorship of the "Molybdenum Project."[7] The overflow rates were in the range of 122 to 367 L/min per m^2 (3 to 9 gpm per sq ft). Available commercial units usually operate at lower rates of 41 to 82 L/min per m^2 (1 to 2 gpm per sq ft).

Both the USBM and Jordon et al used a surfactant like sodium lauryl or capric sulfate to promote the flotation of the Fe-Mo complex.

While the technique appears to be feasible, several problems remain, including: (1) Will the treated water meet regulations for total iron and total suspended solids levels; (2) Will there be a further need for polishing of the treated effluent by filtration techniques; and (3) What about the handling and disposal of the Fe-Mo sludge? Finally, the overall question of the process economics remains, as the technical problems are solved.

Ion exchange—The literature has many references on the chemistry of Mo removal by ion exchange techniques. The removal of Mo is most efficient in the pH range of 3.0 to 4.0; amine-type anion exchange resins are used. Weak



In moly mills, the flotation process tends to solubilize small amounts of heavy metals such as molybdenum, copper, manganese, and zinc. Low levels of cyanide are also present in the water, owing to the use of sodium cyanide in the milling circuit.

base amine types were selected by Climax due to their higher Mo absorption capacities and smaller alkaline requirements for elution. Plus, the resin in the bisulfate or chloride form had a greater capacity to load Mo compared with the free form.

Amberlite XE 299 was chosen for development work. Laboratory loadings of up to 192 kg of Mo per m^3 (12 lb per cu ft) of resin at a cumulative percent recovery of 90.8 were obtained. Resin moly elution efficiencies in excess of 98% have also been obtained.

Ion exchange on a commercial scale is performed in several ways. A brief reference to these follows:

- Fixed Bed Downflow Ion Exchange—It is essential to present a clarified liquor as free of solids as possible to the fixed bed column. Feed liquor is clarified by filtration; if the slimes are ultra-fine, coagulation and flocculation precede filtration. When this is done, care must be exercised in the use of flocculant; an excess may be deleterious to the resin.

If algae is a problem, addition of an algicide would be recommended. If this is not done, fouling of resin will probably occur. Chlorination could also be used to destroy the algae.

- Resin in Pulp (RIP) Process—The process was developed to handle turbid liquors by ion exchange from U_3O_8 leach liquors. High maintenance costs and excessive resin losses have made the process obsolete.
- Chemseps Countercurrent Ion Exchange (CCIX)—Pioneered by Climax for Mo removal in tailings water, the fully automated system operates by continuous cycling between a "service" mode and a "pulse" mode. During the service mode, loading regeneration, elution, pulsing and resin storage are performed in five separate sections in a continuous loop. The resin is moved from one section to another by sonic pulsing. Backwashing removes suspended solids and fine resin.

This system attempts to minimize the problem of TSS while maintaining high flow rates; it requires less resin inventory. An average Mo concentration of 2.0 ppm could be obtained from feed concentration ranging from 2 to 24 ppm. Average resin loadings were 59 kg/m^3 (3.66 lb per ft^3) of resin.

- Fluid Bed Ion Exchange—Several designs have been described in the literature, including the Cloete and Streat, the USBM design by Rosenberg and Ross, Ritchey et al, Haines et al,[18] and the Himsley Contactor.[19] All of these have potential application in moly removal from wastewater streams.

Removal of Heavy Metals

The effluent guidelines are noted in Table 1. Data on Climax are found in Reference 2; information on other operations is not generally available. The levels of heavy metals in the feed will vary depending on the degree of recycle and the solubilities of the different metals in the tailings waters. The heavy metals to be found in molybdenum milling water are usually inorganic in nature.

The chemistry of the removal of heavy metals from process wastewater has been reviewed.[20] Technology available for heavy-metal removal is varied; e.g., the chemical precipitation of heavy metals by pH adjustment followed by flocculation and clarification, activated carbon adsorption, reverse osmosis, ion exchange, and cementation.[2] Conventional lime precipitation is not generally useful due to the poor settling nature of the metal hydroxides. The solids content is also low due to the relatively low levels of pollutants in the recycled water. Cation exchange does not appear to be feasible, as noted by Climax.[2] Cementation is not generally applicable since it is done in acid solutions.

Table 1—Effluent Guidelines for the Ferroalloy Ore Mining and Dressing Industry

	Effluent 24 hr. (max.*)	Effluent 30 day (average*)
F^-	3.0	—
T. Fe	0.6	—
Mn	1.0	1.0
As	1.0	0.5
Cu	0.1	0.05
Mo	2.0	1.0
Zn	0.2	0.10
Cd	0.10	0.05
CN	0.04	0.02
TSS	30.00	20.00
pH	6-9	6-9
COD	50.0	25.0

* All values in mg/L except pH.

In addition, the more active metal used as the cementing agent will dissolve in the process and may need to be removed. Reverse osmosis as noted by Lenouette[21] is still in the development stages.

The use of ferric chloride or sulfate as a coagulant followed by lime to pH 8.6 was attempted by Climax with little success;[2] solids settling was not improved.

Several flotation techniques are available. These include Dissolved Air Flotation (DAF), Induced Air Flotation (IAF) and the Swift Lectroclear process.

Dissolved air flotation (DAF)—Primarily used in the removal of oils and grease from industrial wastewaters, the process saturates wastewater under air pressure. When the pressure is reduced, excess air is released, forming bubbles of 30 to 120 microns in diameter. These bubbles attach themselves to the suspended matter or oil and are floated to the top of the flotation basis since the average density of the aggregates is less than that of water. Chemical coagulants and flocculants are usually added to ensure good separation. The DAF process as a means of heavy metals removal (except molybdenum) does not appear to have been evaluated.

Induced Air Flotation—The IAF system operates on the same principle as the pressurized DAF units with one difference; the gas is self-induced by a rotor-dispersed mechanism, and is dispersed in the water.

Swift Lectroclear Process—The process is applicable for solid-liquid separation when the total suspended solids (TSS) is below 8000 mg/L. It is especially valuable in separating solids which are easily destabilized by electrodes.[23] In the Swift process, the heavy metals are precipitated as hydroxides into lime. The hydroxide precipitate is electrolyzed in an electrocoagulation cell. Hydrogen and oxygen are produced in the process. These attach themselves to the slurry and render them lighter than water. Subsequently, a polymer flocculant is added to agglomerate the precipitate, which is then floated off in the electroflotation basin by electrolytically generated oxygen and hydrogen. The skim containing the hydroxides of the heavy metals and excess lime is disposed of, while the effluent from the cation removal process has to be filtered in a high-rate sand filter to remove the residual TSS.

Gott[2] has reported optimum results in the removal of heavy metals with the Lectroclear process at a pH of 10.5 on mine tailings wastewater at Climax, Colo.

Treating Cyanide

Several treatment techniques are available to lower cyanide to the target level of 0.02 mg/L.[24] The feed cyanide level can range from a low of 0.02 to a high of 0.50 mg/L. Chemical oxidation by alkaline chlorination is appropriate for these levels. The oxidant can be chlorine gas, sodium hypochlorite or calcium hypochlorite; cyanide is rapidly oxidized to cyanate. Retention times for oxidation are in the range of 0.5 to 2.0 hr; a pH of 10 or higher is necessary. Additional chlorine can be used to oxidize the cyanate further to nitrogen and carbon dioxide or to carbon dioxide and ammonia by acid hydrolysis at a pH of 2 to 3. This requires readjustment of treated water to a pH range of 6 to 9 prior to discharge.

Alternatively, excess chlorine can be added at pH 8 to 8.5 to oxidize the cyanate to nitrogen and carbon dioxide; retention time of 1 hr is essential. Excess chlorine is needed to prevent the formation of highly toxic cyanogen chloride.

Hydrogen peroxide plus formaldehyde has been used by DuPont in their Kastone process to oxidize cyanide to cyanate.[25] The major disadvantage of the process is its inability to oxidize cyanide below the level of cyanate. However, if the cyanide is present as "free" cyanide and not complexed, the process could be attractive since no problems of cyanogen chloride are encountered.

Hydrogen peroxide alone will probably by equally effective in lowering cyanide levels. The same comments on "free cyanide" will apply to this as those stated above for the Kastone process.

Climax has used hypochlorite in lowering cyanide to acceptable levels on the effluent from the Chemseps Ion Exchange unit used for lowering Mo levels in tailings water.[2]

Fluoride

Several approaches are possible; choice of a specific process depends on the effluent.[26,27]

The most widely used treatment consists of the addition of a soluble calcium salt to form insoluble calcium fluoride which is removed by liquid-solids separation. The optimum pH for precipitation is between 8 and 9. The fluoride levels after treatment vary from the theoretical solubility limit of 7.8 mg/L to about 30 mg/L. For lowering the fluoride levels even further, the most promising treatments are alum precipitation and adsorption on activated alumina.

Alum (aluminum sulfate) has been used to lower fluoride levels in potable waters in the pH range of 6.5 to 7.5. The quantity of alum needed depends on the initial fluoride level and the desired final level; this increases as the residual fluoride level decreases. Extensive amounts of sludge are produced in the process; settled sludge will amount to 18% to 40% of the volume treated.[26]

Activated alumina can reduce fluoride ion levels to less than 2 mg/L. Problems of handling regenerant and the effect of regenerant on overall effluent quality are yet to be resolved.[26]

In general it can be said that technology for fluoride reduction to low concentrations is not well established. An extensive development program will be essential to determine the applicability of the defluoridation techniques discussed earlier to the effluent in question. ☐

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