Metals Removal from Mine Effluents –
Understanding the Chelant is Key

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Abstract Though dissolved metals can be a contaminant in mine effluents, the discharge criteria may vary from site to site. Removal of metallic contaminants can be difficult due to complex variations in coordination properties. Chelation is a useful tool that can be engineered to be more specific to a series of metals. A chelant treatment package was developed for the successful removal of copper from a mine effluent where the discharge criterion is being decreased to 25 µg/L on the upcoming permit renewal. This evaluation explores a wide range of process variations such as pH, temperature, treatment dosage, and removal kinetics.

Keywords metals removal, water treatment, copper chelation

Introduction

Mine effluents are of significant environmental concern when considering the potential impact of inorganic contamination on the aquatic biota (Jiménez-Rodríguez 2009; Peleka 2007; Young 1981). Copper is one of the contaminants of concern due to its bioaccumulative effect, negative effects on the olfactory systems in aquatic biota, and level of toxicity (ATSDR 2012; Hara 2011; US EPA 2012). The fate of copper in aqueous systems depends on a number of factors including dissolved oxygen/oxidizing agents, coordinating ions, and pH.

A common technique for inorganic contaminant removal is by chemical precipitation. This is achieved by either chemically altering the solvent matrix to decrease/diminish the solubility of the substance or by conversion of the substance to an insoluble form (Britannica 2012). An understanding of the metal/ligand stability is critical when designing a metal contaminant treatment system. It is important to understand the strength or 'desire' of a ligand to coordinate to a metal and the stability of the resulting complex to allow for optimal precipitation. This is a very useful tool, and it is possible to coordinate many different kinds of ligands to metals, but the key to a successful application is getting them to remain ligated and become labile only when desired.

One way of maintaining coordination is through chelation. Chelation is the ability of a ligand, in this case a sequestering agent, to coordinate to a single metal ion through two or more ligation sites. Generally speaking, a chelating ligand has a much stronger coordination strength than a monodentate ligand with one ligation site (Clapp *et al.* 2006; Huheey *et al.* 1993; Greenwood and Earnshaw 2001; Fig. 1). This strength is mainly due to the proximity of the chelating ligand to the metal while labile. Consider ethylenediamine (B); even if one portion becomes labile, it can only get a few hundred picometers away from the metal, while amine (A) can come and leave. However, the level of chelation depends not only on the ligand, but also the oxidation state and charge of the metal, the presence of other
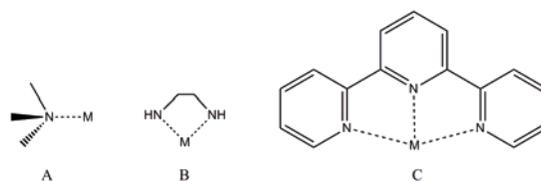
***Fig. 1** Examples of coordination. A) Monodentate, B) Bidentate, C) Tridentate*

Element	Ba(II)	Ca(II)	Mg(II)	Fe(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Hg(II)	Cd(II)	B	C	Si
Atomic Radii (pm)	134	99	66	74	69	72	74	72	110	97	23	16	44
Open Sites	2	2	2	6	4	4	2	4	2	2	N/A	N/A	N/A

Table 1 *Crystal ionic radii (pm)*

ligands, and the available ligation sites on the metal.

The ring size, formed during chelation, can also play a significant role in the stability of a metal complex. Generally, a 5 membered ring is more stable than a 6 membered, which is more stable than a 7 membered. Of course, this can change according to the size of the metal, vacant coordination sites, and other ligands coordinated to the metal (Wiki 2013; Weast 1988; Webelements 2013;Table 1).

The major difference, contributing to the stability of a 5-membered ring over a 6-membered ring is mainly the bite angle or steric strain caused by chelating to the metal. (Hancock 1992; Fig. 2) A 5-membered ring has a much larger bite, thus can more easily "bite" many metals. In order for a 6-membered chelate ring to be more stable, a metal similar in size to a carbon must be used. For example: a Cu-N bond is about 2.3 angstroms, which would suggest a copper atom would be most stable in a 5-membered chelate ring, while Mg-O bond is 1.75, which would make a stable 6 membered chelate ring. This trend is also seen when a 4-membered ring is considered. The larger atoms, like calcium, form a very stable complex with 4-membered rings, which is observed in carboxylates that are often found in calcium scale inhibitors and many dispersants. In complexes that form larger than 6-membered rings, the metal size is no longer the dominating factor in the stability of a chelate ring. The stability of such large chelate rings depends on the ability of both coordinating ligands to find the metal. Applying rigidity to the backbone of the chelant could assist in forming such 7 member ringed complexes.

Another way of maintaining coordination is by applying the Hard/Soft Acid/Base theory. This theory is a method of predicting the affinity of a ligand towards a specific metal, and in conjuncture with chelation, can aid in making the "perfect" complex. Hard acids are alkali metals, alkaline earth metals, and lighter transition metals in higher oxidation states (*e.g.* Ti, Cr, Al, Zn, Mn, B, Fe^{3+}). Ligations of hard acids are preferred with hard bases, which are small and difficult to polarize, meaning electrons are donated from the ligand to the metal. Hard bases are ligands that contain the lighter elements with electron donating abilities (*e.g.* N, O, F, PO_4, SO_4, RC=OO-). (Fig. 3A)

Soft acids are the heavier transition metals and those of lower oxidation states (*e.g.* Rh, Ir, Pd, Pt, Ag, Au, Hg, Ni, Cu). As hard acids prefer hard bases, soft acids coordinate preferentially with soft bases. Soft ligands are large and easily polarized, meaning electrons from both the metal and ligand readily engage in bonding. Most often the ligand will donate σ electrons to the metal's empty d orbitals and the metal will back donate electrons into an empty π* orbital on the ligand. (*e.g.* ex. phosphines, carbenes, thioethers, conjugated organics, mercaptans). (Fig. 3B)
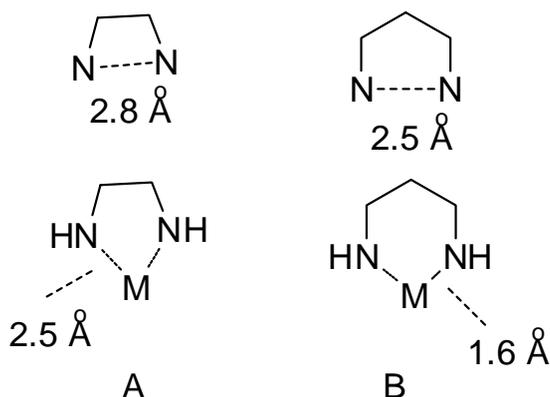
Fig. 2 *Bite angle comparisons between a 5 and 6 membered complex*
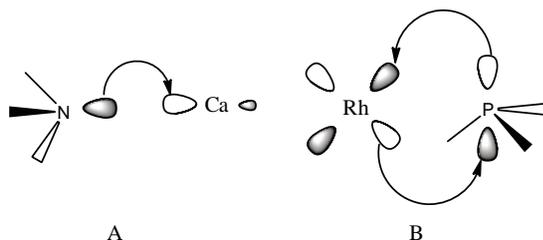
Fig. 3 *A) σ-donation of electrons from a hard base to a hard acid B) Interactions between a soft base and a soft acid.*

Fig. 4 *KemMet 1140 dosage demand over the customer specified process conditions (Temperature 49 °C, pH 3–4)*

Results and Discussion
Copper Removal

A chelant, KemMet 1140, was designed with a superior ability to remove metal ions from aqueous systems. KemMet 1140 applies a bidentate coordination of sulfur containing substituents that provide the hard base requirements and the ring size that makes it a perfect candidate for complexing to copper. Altering the backbone of the system allows for low solubility once the complexation occurs. This chelant was applied towards water that was obtained from a mine site located in the United States and was stored in a cooling unit at 1 °C prior to use (Table 2). In this case the objective was to reduce the total copper at the existing operational conditions (pH and temperature) with minimal impact on production. Copper, which was present at an average concentration of 172 μg/L, was released during the processing of the ore while in an acidic environment.

KemMet 1140 is efficient over a wide range

IC Analysis	Concentration	ICP Analysis	Concentration
Fluoride (mg/L)	2	Copper (μg/L)	172
Chloride (mg/L)	10	Arsenic (μg/L)	40
Sulfate (mg/L)	850	Selenium (μg/L)	283
Bromide (mg/L)	ND	Cadmium (μg/L)	1
Nitrate (mg/L)	ND	Sodium (mg/L)	120
Phosphate (mg/L)	ND	Magnesium (mg/L)	6
Conditions		Aluminum (mg/L)	170
pH	3	Calcium (mg/L)	27
Turbidity (NTU)	4800	Manganese (mg/L)	260
Total dissolved solids (ppm)	970	Iron (mg/L)	6
Hardness (as CaCO3)	94	Nickel (μg/L)	73
Conductivity (μS/cm)	1500	Molybdenum (μg/L)	9
Total suspended solids	2	Barium (μg/L)	230

Table 2 *Effluent (raw water) analysis*

of pH. It can be either continuously fed or applied via a batch treatment process. It was evaluated in the above mentioned effluent towards the removal of copper under the customer-specified process conditions of 49 °C and pH 3 (Fig. 4). While the minimum dosage required to achieve the desired < 25 μg/L discharge criterion was 1 mg/L total solution, 10 mg/L yielded copper levels less than the instrument detection limit of 5 μg/L. Interestingly, the addition of a flocculant alone yielded a 27 % reduction in the copper concentrations, which could be due to the presence of a suspended copper salt.

Effects of Process Conditions

Understanding process limitations would make transferring this technology to treatment processes at other mine sites much easier. Therefore, a dosage of 25 mg/L KemMet 1140 was evaluated in the above mentioned raw waters under a broad range of temperatures and pH values to simulate seasonal variations and other potential site-specific process requirements (Fig. 5). The optimal conditions were found at a temperature of 4 °C, at which point the instrument detection limit was met for a pH range of 5–9. Only a slight decrease in

performance was observed at pH 3. Increasing the temperature to 26 °C yielded a slight decrease in performance for those experiments carried out over the pH range of 5–7. An interesting increase in copper removal was observed as the pH was further increased to 9.

This trend continued as the temperature was increased to 49 °C. While operating at pH 3, a comparable level of copper reduction was achieved over the entire range of temperatures. The reduced performance at the elevated temperatures could have been due to the potentially increased rates of ligation-site oxidation of KemMet 1140.

The KemMet 1140 performance was consistent throughout the temperature range evaluated at pH 3, with a similar trend observed for those treatments carried out at pH 9, but there appeared to be a loss in performance at a pH range 5–7 at 49 °C. The reduced levels of copper at pH 9 can be explained by the precipitation of cupric hydroxide, though this does not explain the loss in performance at elevated temperatures at a pH of 5 to 7. To evaluate this inhibition in performance, the samples were analyzed for residual chelant (KemMet 1140) in both the samples treated with 0.625 mg/L KemMet 1140 at 26 °C and 49 °C. It was concluded that at 26 °C, a residual concentration of 180 µg/L remained in the effluent. The 49 °C treatment yielded nearly 100 % of the chelant as soluble, residual material in the effluent. One potential explanation would be an oxidizing effect on the nucleophilic sites as a competing reaction for the copper chelation, which can be evaluated by applying bleach to the water prior to treating, in efforts to increase the oxidizing conditions at a lower temperature (Fig. 6). This would also prove that it is not an effect of temperature as a means of decomposition, but rather the energy required to increase the rate of oxidation. During this evaluation, KemMet 1140 was greatly hindered at 26 °C, as the efficiency was decreased from 96 % removal to 40 % removal.

Even though the discharge criteria were met over the complete range of pH and tem-
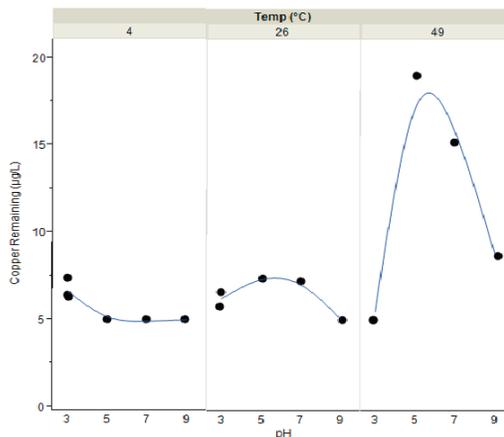
Fig. 5 *Evaluation of KemMet 1140 over a broad range of process conditions*
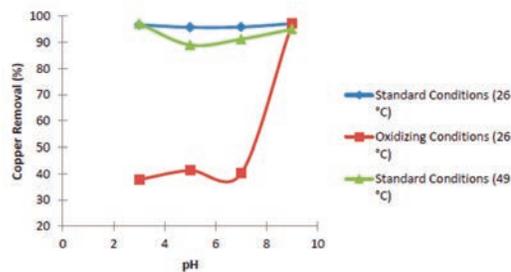
Fig. 6 *Effect of oxygen-rich environment on the efficiency of the removal of copper by KemMet 1140*

perature, clear sensitivities were observed during the KemMet 1140 evaluation when pH and temperature were varied. To further evaluate the treatment efficiency and requirements, the rate of removal was measured as a function of temperature (Fig. 7). At 4 °C, > 99 % of the copper was removed within the first minute and was maintained insoluble for the entire 10 minute contact time. The efficiency was slightly reduced as temperature was increased to 26 °C, which yielded 96 % removal of the copper within the first minute. Copper concentrations continued to decrease over time until 5.38 µg/L was reached after 10 minutes. Though the discharge criteria were met at 49 °C, only 86 % of the copper was removed within the first minute, which began to de-

grade and release copper over the remaining reaction time.

Competing Ions

Understanding what the treatment is doing to the water is important prior to moving into field evaluations, as there could be competing ions that could lead to requiring increased dosages. In addition, it is also crucial to study what was being left behind (Table 3). During this evaluation, sodium appeared to be the only ion that increased, approximately 20 %, from the raw water analysis to the post-treatment analysis. When evaluating for competing ions, the analysis of the post-treatment water was compared to water treated with flocculant only. This would allow an accurate understanding of the KemMet 1140 performance instead of what was just being removed through the flocculation process. KemMet 1140 appears to have the strongest affinity for copper, but zinc and cobalt were also removed through the chelation/precipitation process.

Experimental
Procedure

A sample of 500 mL of raw water (untreated effluent) and a stir bar was added to a 600 mL beaker, which was then placed on a Thermo Scientific stir plate for agitation. The pH was adjusted to the desired range using nitric acid or 10 % sodium hydroxide. Once the desired pH was reached and controlled, the temperature was adjusted to the experiment-specific tem-
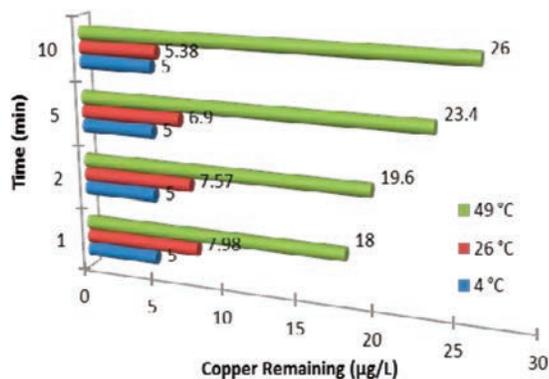
Fig. 7 *Effect of temperature on the efficiency of KemMet 1140 on the removal of copper (pH 3–4, 1 mg/L dosage)*

perature using an iced water bath or a hot plate. Once the temperature was stabilized, the KemMet 1140 was added at the experiment-specific dosage using a 10 – 100 μL precision pipette equipped with disposable pipette tips. The water was allowed to agitate on high (400 rpm) for 2 minutes. This agitation should provide a vortex that extends 50 % down the solution. At the end of the specific time, 2 mL of 0.05 % of a flocculant (Superfloc A130HMW) was added and allowed to agitate for 1 minute on high. Then the agitation was decreased to the point that the vortex only extended 15 % down the solution volume and allowed to agitate for 5 minutes, at which time the precipitate was allowed to settle for 10 minutes. The solution was then filtered through a 0.45 μm Millipore filter. The filtrate was then submitted for ICP.

	Raw	Post-treatment
Turbidity	4800	1
TDS	970	970
TSS (mg/L)	2	17
Sulfate (mg/L)	850	700

ICP Analysis4	Raw	Post-flocculent	Post-treatment	Treatment efficiency (%)
Mg (mg/L)	6	6	6	0
Ca (mg/L)	27	27	27	0
Fe (µg/L)	5500	770	1100	-30
Co (µ g/L)	34	23	11	52
Ni (µ g/L)	73	22	27	-22
Cu (µ g/L)	170	170	10	94
Zn (µ g/L)	300	430	150	64

Table 3. *Evaluation of competing ions (pH 3–4, 49 °C, 2 min); highlighted cells appear to be competing ions*

Instruments

In this study, a Thermo Scientific ICP-AES system model iCAP 6500 equipped with a charge injection device detector and a CETAC ASX-520 autosampler was used for determination of copper concentration following the EPA method 200.8. Low detection limits (5 μg/L for copper) were achieved by pre-concentration of 100 mL aqueous samples. Quantitative elemental analysis of trace elements was conducted on a Bruker S4 Explorer wavelength-dispersive x-ray fluorescence spectrometer.

Conclusions

That properly designing a chelant can provide somewhat metal selective coordination and can yield a desired level of solubility. It is evident by the required discharge criteria being met under the customer-specified processing conditions of pH ≈ 3 and operating temperature of approximately 49 °C on lab scale evaluations. The required ratio of ≈ 3/1 active Kem-Met/Copper ion was the minimum dosage to meet the discharge criteria in the lab. Due to potential increase in rate of ligand oxidation at elevated temperatures, the optimal process temperature for the application of the Kem-Met 1140 is 4 °C, but the discharge criteria can be met at temperatures as high as 49 °C. This was supported by the kinetics data, which also suggests a decrease in removal rate with an increase in temperature. The larger radii ions (*e.g.* Ca, Ba) were not a competing ion for this chelation. However, those ions with an atomic radii ≈ 72 pm, similar to that of copper, posed as a competing ion for chelation.

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