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TECHNICAL COMMUNICATION

Copper Removal from Mine Effluents: From Lab to Field Evaluations

**Lucas R. Moore · Jean Robert Durand ·
Forrest Strickland**

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Abstract The removal of metallic contaminants can be very complex due to intricate 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 its discharge criterion was being decreased to 25 µg/L. This evaluation explored a wide range of process variations such as pH, temperature, treatment dosage, and removal kinetics. The recommended chelant package was able to achieve levels below the ICP detection limit of 5 µg/L; levels of 7 µg/L were achieved at the mine site.

Keywords Copper chelation · Metal removal · Water treatment

Introduction

Mine effluents can pose significant environmental concerns given the potential impact of inorganic contamination on the aquatic biota (Jiménez-Rodríguez et al. 2009; Peleka et al. 2007; Young and Bohling 1981). Copper (Cu) is one of the contaminants of concern due to its bioaccumulative effect and level of toxicity. The US Environmental Protection Agency (US EPA) lists Cu in at least 906 of the 1,647 sites on the National Priority list (ATSDR 2012; US EPA 2012). Though there are many routes into the environment, the major sources of Cu contamination are through mining and manufacturing operations. Copper is often present in the waste stream of Cu and lead (Pb) smelting, as well as Cu and Pb refining (Ramachandran 2003). Globally, Cu is one of the most widely used metals, with operations in the electrical industry, batteries, construction, and industrial machinery (e.g. heat exchangers, alloys). Though much of the Cu lost to the environment during the various processes remains immobile in the ground near the processing facility, a large amount remains soluble. This can negatively affect biota, including human health, by causing liver and kidney damage from long-term exposure. The World Health Organization (WHO) states that the acute lethal dose for an adult is 4–400 mg of Cu ion per kg of body weight (WHO 2012). Copper can also affect plant life either directly or indirectly. Only a limited number of species can survive in Cu-rich environments.

The fate of Cu in aqueous systems depends on a number of factors including dissolved oxygen/oxidizing agents, coordinating ions (monodentate, or more), and pH. Precipitation of metal hydroxides is the most common method for removal of metal contaminants from process waters or effluents. Many metal hydroxides are amphoteric, which means they are soluble at both high and low pH; in between, there is a point where the metal hydroxides have minimal solubility and can be forced to precipitate (Coulton et al. 2004). The pH range of precipitation varies by metal and as such, can be used as either a tool for purification or as a means of selective contaminant removal from process waters. Besides the stringent pH requirements, a second major issue with metal hydroxide precipitation is the voluminous secondary waste generated (Bullen et al. 2008).

Chemical precipitation 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 2012a). Coagulants and

L. R. Moore (✉) · J. R. Durand · F. Strickland
Kemira Minerals and Metals, 387 Technology Circle,
Suite 300, Atlanta, GA, USA
e-mail: Lucas.moore@kemira.com

sequestering agents are the most commonly applied methods to achieve chemical precipitation through the ion conversion process. Coagulants are substances that cause particles, colloids, or dissolved contaminants in a liquid to destabilize, thus forming small suspended aggregates (Britannica 2012b). These are often inorganics, such as ferric or ferrous salts, and aluminates. Sequestering is the ability of a molecule to remove or separate metal ions from solution (Britannica 2012c). Sequestering agents are typically organic ligands, molecules that can coordinate or complex to a metal ion. In both cases, a flocculant is commonly applied to increase particle size of the precipitate as well as increase settling rates of the precipitate.

An understanding of 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 for optimal precipitation. In general, the stability of a metal complex can be predicted by comparing the size of a metal’s radius. This is a very useful tool, for 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 much stronger coordination strength than a monodentate ligand, with one ligation site (Clapp et al. 2006; Greenwood and Earnshaw 2001; Huheey et al. 1993; 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 ligands, and the available ligation sites on the metal.

The most widely used chelant is ethylenediamine tetraacetic acid (EDTA; Edocs 2012; Fig. 2). EDTA can potentially form 5 × 5-membered chelate rings, which in turn is a very strong complex. Though EDTA is a powerful chelant, it does not possess metal selectivity, nor is it expected to form a precipitating complex. The main reason for this lack of selectivity is its complex acid–base equilibrium. Among the concerns are its actual ligation to the metal, and the possible deprotonation of the coordinating functional groups.

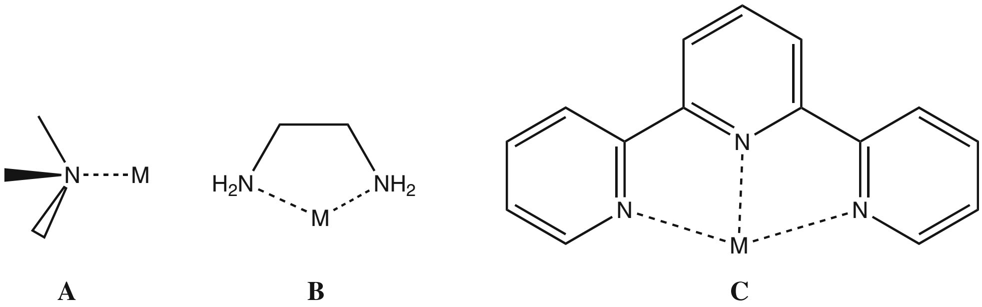
Experimental Details

A sample of 500 mL of raw water 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 temperature 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 agitated at 400 rpm for 2 min, which should provide a vortex that extends 50 % down the solution. At the end of 2 min, 2 mL of 0.05 % of a flocculant (Superfloc A130HMW) was added and allowed to agitate for 1 min at 400 rpm. Then the agitation was decreased to the point that the vortex only extended 15 % down the solution volume and allowed to agitate for 5 min, at which time the precipitate was allowed to settle for 10 min. The solution was then filtered through a 0.45 µm Millipore filter and the filtrate was n submitted for ICP analysis.

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 ions such as arsenic, selenium, and various metals in the water samples. Low detection limits (5 µg/L for Cu) 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.

To further understand the water chemistry and potential process limitations due to competing ions or other process

Fig. 1 Examples of coordination. **a** Monodentate, **b** bidentate, **c** tridentate



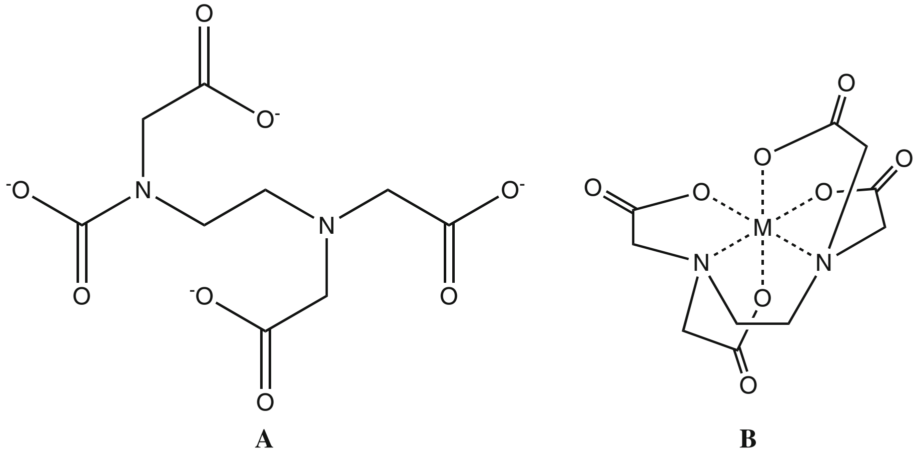


Fig. 2 **a** EDTA uncomplexed, **b** EDTA chelated to a metal through 6 ligation sites

Table 1 Raw water analysis; *ND* none detected with IC unit with a detection limit of 1 mg/L

IC analysis	Concentration	ICP analysis	Concentration
Fluoride (mg/L)	2	Copper (µg/L)	170
Chloride (mg/L)	10	Arsenic (µg/L)	40
Sulfate (mg/L)	850	Selenium (µg/L)	280
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)	4,800	Manganese (mg/L)	260
Total dissolved solids (ppm)	970	Iron (mg/L)	6
Hardness (as $CaCO_3$)	94	Nickel (µg/L)	73
Conductivity (uS/cm)	1,500	Molybdenum (µg/L)	9
Total suspended solids	2	Barium (µg/L)	230

interferences, a complete water analysis was performed prior to treatment evaluation. A Dionex ion chromatography system, equipped with an autosampler, was used to determine mg/L levels of multi-analyte ionic solutions. The IC was used to measure both cations and anions, but required a column change. Interfering ions could be competing ligands for the metal of interest such as oxyanions (sulfate, nitrate, phosphate) or ions that could lead to a potential for fouling throughout the process (sulfate, carbonate).

Results and Discussion

Copper Removal

Water was obtained from a US mine site and shipped in 20 L (5 gal) buckets to the Atlanta (GA) R&D center, where it was subsequently stored at 1 °C (Table 1). The objective was to reduce total Cu at the existing operational conditions (pH and temperature) with minimal impact on production. Though the water contains other common contaminants such as selenium (282.7 µg/L) and arsenic (39.7 µg/L), Cu was the contaminant of concern. Copper was being released at an average concentration of 172.4 µg/L during ore processing due to an acidic environment.

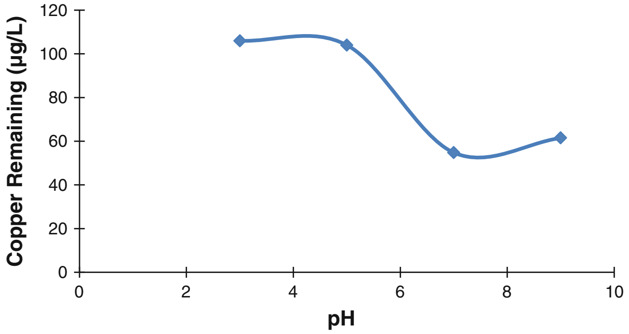
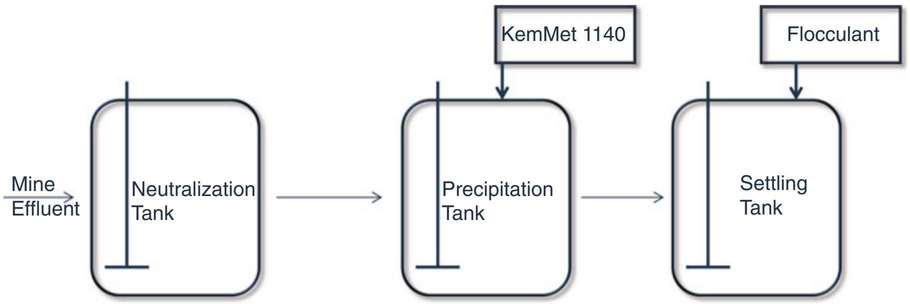


Fig. 3 EDTA evaluation towards copper removal from the mine effluent

Fig. 4 Generic treatment process



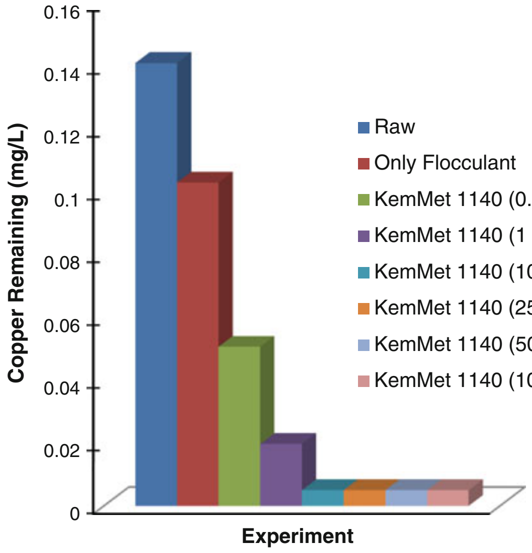


Fig. 5 KemMet 1140 dosage demand over the site-specific process conditions (temperature 49 °C, pH 3–4)

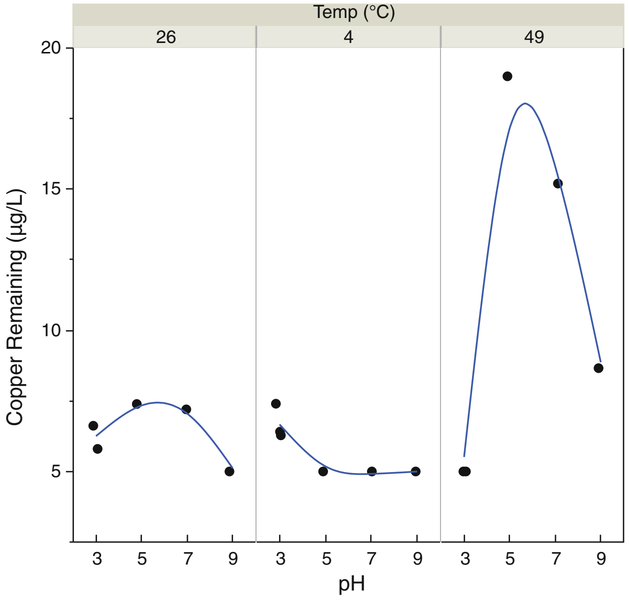


Fig. 6 Evaluation of KemMet 1140 over a broad range of process conditions

Understanding that EDTA is not efficient at actually precipitating metals, but is just a powerful chelating agent, it was tested with the raw water to provide a level of understanding of the effects of pH on chelation stability (Fig. 3). Applying 25 mg/L of EDTA over a range of pH, the Cu concentrations only appear to decrease at a high pH, presumably due to the precipitation of Cu hydroxide rather than EDTA-Cu.

A chelant, KemMet 1140, was designed with a superior ability to remove metal ions from aqueous systems. KemMet 1140 is efficient over a wide range of pH. It can be either continuously fed or applied via a batch treatment process (Fig. 4).

KemMet 1140 was evaluated in the above mentioned process waters towards the removal of Cu under the customer-specified process conditions of 49 °C and pH 3 (Fig. 5). While the minimum dosage required to achieve the desired <25 µg/L discharge criterion was 1 mg/L total solution, 10 mg/L yielded Cu levels less than the instrument detection limit of 5 µg/L. Interestingly, the addition of a flocculant alone yielded a 27 % reduction in the Cu concentrations, which could be due to the presence of a suspended Cu 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 water under a broad range of temperatures to simulate seasonal variations and pH and simulate other potential site-specific process requirements (Fig. 6). 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 Cu removal was observed as the pH was further increased to 9.

This trend continued as the temperature was increased to 49 °C. Reduced performance at elevated temperatures could have been due to increased rates of ligation-site oxidation of KemMet 1140. The performance was

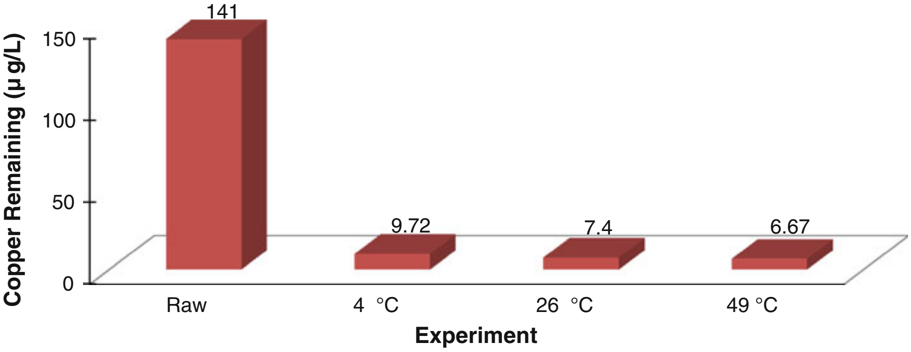


Fig. 7 Precipitation with sodium hydroxide (pH 9)

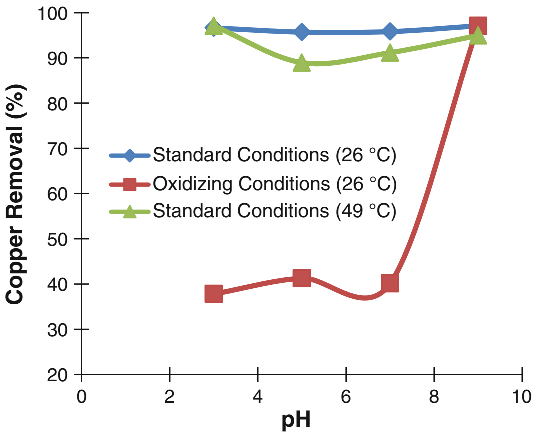


Fig. 8 Effect of oxygen-rich environment on the efficiency of the removal of copper by KemMet 1140

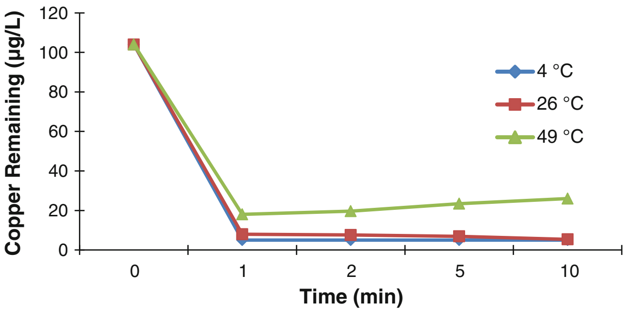


Fig. 9 Effect of temperature on the efficiency of KemMet 1140 on the removal of copper (pH 3–4, 1 mg/L dosage)

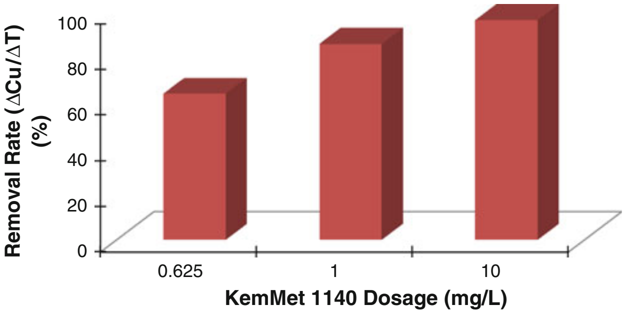


Fig. 10 Effect of KemMet 1140 dosage on the rate of copper removal (pH 3, 49 °C, data point is representative of 2 min of contact)

consistent throughout the temperature range 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 49 °C for the pH range of 5 to 7. To evaluate if this trend was due to the performance of the KemMet 1140 actually having a pH-dependent performance deficiency from 5 to 7 or if that observation was due to a separate mechanism, a series of treatments was carried out in the absence of any chemical precipitant, applying the knowledge of pH-driven precipitation over a similar range of temperatures (Fig. 7). Cupric hydroxide is believed to begin forming around pH 7 with the peak pH optimal precipitation around 9.5, as seen in Fig. 1. It was discovered that the total dissolved Cu could be reduced to 9.72 µg/L at 4 °C, and that this can be slightly improved by increasing the temperature.

The reduced levels of Cu 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. One potential explanation would be an oxidizing effect on the nucleophilic sites as a competing reaction for the Cu chelation, which was evaluated by applying bleach to the water prior to treating, to increase the oxidizing conditions at a lower temperature (Fig. 8). During this evaluation, KemMet 1140 was greatly hindered at 26 °C, as the efficiency was decreased from 96 % removal to 40 % removal. This indicated that the energy required to increase the rate of oxidation was the critical factor.

Even though the discharge criteria were met over the complete pH and temperature range, clear sensitivities were observed during the KemMet 1140 evaluation when the 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. 9). At 4 °C, >99 % of the Cu was removed within the minute and was maintained insoluble for the entire 10 min contact time. The efficiency was slightly reduced as temperature was increased to 26 °C, which yielded 96 %

Table 2 Evaluation of competing ions (pH 3–4, 49 °C, 2 min)

	Raw	Post-treatment
pH	3	4
Turbidity	4,800	1
TDS	970	970
Hardness	94	92
Conductivity	1,500	1,500
TSS (mg/L)	2	17
Fluoride (mg/L)	2	ND[b]
Chloride (mg/L)	10	8
Sulfate (mg/L)	850	700
Bromide (mg/L)	ND[a]	ND[a]
Nitrate (mg/L)	ND[a]	26
Phosphate (mg/L)	ND[a]	ND[a]

ICP analysis[d]	Raw	Post-flocculent	Post-treatment	Treatment efficiency (%)
Be	3	ND	1	NA
Na (mg/L)	120	130	150	−13
Mg (mg/L)	6	6	6	0
Al (mg/L)	170	4	4	0
Ca (mg/L)	27	27	27	0
Ti	6,800	ND[c]	1	NA
V	150	54	54	0
Cr	830	0.2	2	−1,000
Mn	260	250	270	−5
Fe	5,500	770	1,100	−30
Co	34	23	11	*52*
Ni	73	22	27	−22
Cu	170	170	10	*94*
Zn	300	430	150	*64*
As	40	39	39	0
Se	280	270	200	*27*
Sr	490	440	430	2
Mo	9	1	1	0
Ag	3	ND[c]	1	NA
Cd	1	ND[c]	1.0	NA
Sn	7	ND[c]	ND[c]	NA
Sb	1	ND	0	NA
Ba	230	49	72	−47
Pb	48	ND[c]	2	NA

Turbidity was measured in NTU, total dissolved solids (TDS) and total suspended solids (TSS) in mg/L, and concentrations were measured by ion chromatography (IC) in mg/L or ICP (in µg/L, unless otherwise specified), conductivity (cond.) was measured in uS/cm

Italic values appear to be competing ions

[a] *ND* none detected with detection limit at 1 mg/L

[b] Data obtained via Fisher Scientific Traceable™ meter

[c] *ND* none detected with detection limit at 0.5 µg/L

[d] Samples were diluted 100× before analysis

removal of the copper within the first minute. Copper concentrations continued to decrease over time until 5.38 µg/L was reached after 10 min. Though the discharge criteria were met at 49 °C, only 86 % of the Cu was removed within the first minute, which then began to degrade and release Cu.

Though the optimal temperature for this application of KemMet 1140 was 4 °C, the customer-specific conditions were at pH 3 at 49 °C. An evaluation of rate as a function of dosage was conducted under these conditions (Fig. 10). The rate was measured by the change in Cu concentrations over the change in time as a function of dosage. At a dosage of 10 mg/L KemMet 1140, 96 % removal was observed after 2 min, which was the instrument detection limit; 86 % removal was observed after 2 min, with a dosage of 1 mg/L of KemMet 1140, which also met the discharge criteria of 25 µg/L.

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 a demand for increased dosages. In addition, it is also crucial to study what was being left behind (Table 2). During this evaluation, sodium appeared to be the only ion that increased, ≈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 allowed 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 Cu, but zinc, cobalt, and selenium were also removed through the chelation/precipitation process.

Field Evaluation

All of the data to this point were generated under lab scale evaluations with excellent control of the process conditions. After the recommendation was made for the optimal treatment package, KemMet 1140 was taken to the mine site for testing under more realistic conditions, and its performance was compared to standard coagulants (Fig. 11). Ferric coagulants (SO_4, Cl, etc.) and aluminum coagulants (polyaluminum chloride sodium aluminate, etc.) are commonly applied coagulants in the contaminant removal industry, but are primarily used for removal of oxyanions, such as phosphate and arsenate. While the dosage of KemMet 1140 was recommended at 1 mg/L, the optimal dosage in the field was 100 mg/L, which yielded 86 % removal at pH <3. Possible reasons for the loss in performance could have been due to the mixing capabilities, the different flocculent package applied at the time in the field, and the lack of a filtration step in the field. The last was later proven to not significantly affect the results when we compared water analyzed by atomic adsorption and ICP. Atomic adsorption does not require a prefiltration step, and thus is an accurate depiction of what would be observed in the field in the absence of a filter, while the ICP is much more sensitive and has a filtration step as part of the sample preparation. Having said that, ferric chloride actually increased the levels of Cu by more than 30 %, which would suggest that the coagulant actually contains some Cu. The polyaluminum chloride (PAX) also appeared to have some Cu, but a much lower concentration.

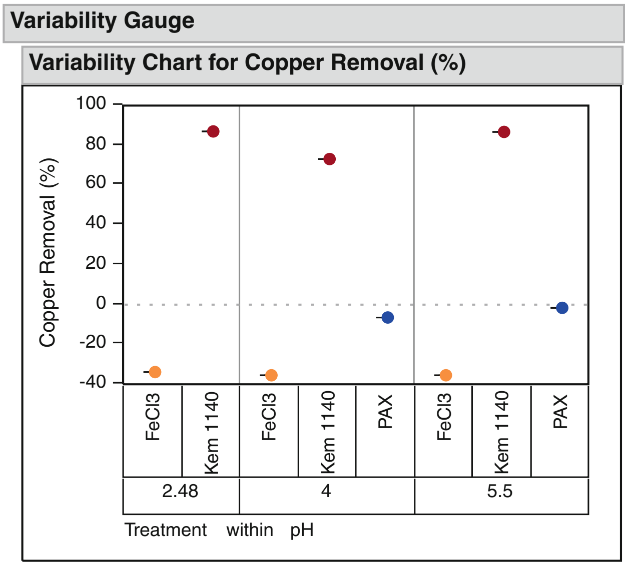


Fig. 11 Field evaluation of KemMet 1140 (43 °C, 2 min contact time)

Conclusions

The required discharge criteria were met under existing processing conditions (pH ≈3 and ≈49 °C) in lab scale evaluations. The success was repeated in the field, though the dosage demand did not transfer, possibly due to the lack of control of the mixing capabilities or a variation in the flocculant treatment package from that which was evaluated in the lab. A ratio of ≈3/1 active KemMet/copper ion was required to meet the discharge criteria in the lab. Due to potential degradation, the optimal process temperature for the application of the KemMet 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.

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