Acid Mine Drain (AMD) Treatment to Achieve Very Low Residual Heavy Metal Concentrations

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ABSTRACT

Mount Emmons mine wastewater treatment plant currently treats on average around 450,000 gallons per day of acid mine drain (AMD) water collected into several collection ponds. The plant uses standard lime hydroxide precipitation process at pH 10.7 to precipitate heavy metals and remove AMD contaminants with the subsequent flocculation - dissolved air flotation (DAF) and sand filtration.
Possible opening of the new molybdenum mine at the same site would require replacement of the current large DAF and sand filters with the small footprint equivalents. The pilot studies with the small footprint, hybrid centrifugal - dissolved air flotation (GEM System) and walnut filters have been performed. The results of the pilot study are described in this manuscript. GEM System and the walnut filters can be used as a replacement for current technologies.

KEYWORDS: acid mine drain treatment; precipitation, flocculation-flotation; filtration, walnut vs. sand filters

INTRODUCTION

Mount Emmons mine (i.e. "client") wastewater treatment plant currently treats large amounts of acid mine drain (AMD) water collected into several collection ponds. The treatment plant currently operates 5 days per week, approximately 9 hours per day, to treat water that is collected throughout the previous day. The total flow of water varies seasonally, but on average the plant treats about 450,000 gallons per day.

The plant uses standard lime hydroxide precipitation process to precipitate heavy metals and remove AMD contaminants. The process occurs at a pH of 10.7 in order to provide waste stream with an environment (approximately 14-20 minutes residence time) that will maximize the precipitation and eventual removal of cadmium, with good removal of zinc, iron, manganese, lead, silver and aluminum.

After pH adjustment with lime in AMD reactor, the wastewater stream with the precipitated metal hydroxides is pumped into a Sand Trap, where cationic granular high molecular weight flocculants are injected to the stream to begin the flocculation of precipitated particles prior to DAF treatment. An anionic surfactant is also injected to the stream while in the Sand Trap to help produce hydrophobic surfaces and more bubbles to enhance flotation in the DAF tank.

After addition of chemicals in Sand Trap, the flocculated wastewater is pumped to the client's DAF Systems. Currently, client operates two out of their 3 existing DAF systems at one time, leaving one extra system in case repairs or tank cleanings are being performed. The DAF Systems each operate at approximately 400-500 gallons per minute. The flow varies depending on the level in the collection ponds, and client uses a Variable Flow Drive pump to pump necessary amount of water to DAF while pond influent level changes.

The current DAF Systems are very large systems that rely on a tank with only 0.6 GPM/ft2 HRT, and consequently high amount of retention time for flotation. The DAF systems also rely on anionic surfactant chemicals added to the stream for the formation of bubbles. Plant personnel explained that the main reason they need 3 DAF's is because there are many heavy metal hydroxides particles that sink to the bottom of the tank, and tanks periodically need to be shut off and drained to remove sludge sediment from the bottom of the tanks.

The floated solids are skimmed from the surface and drop into an auger system which transfers the sludge to large tanks. The sludge contains approximately 2-3% solids to water ratio, and is processed through client's filter press for sludge thickening. Because the DAF sludge is difficult to dewater, client adds approximately 400 ppm of flocculant to the sludge to allow it to dewater properly. After filter press, sludge has approximately 16% dry solids. Because the sludge contains high concentration of zinc, manganese, and cadmium which are all environmentally hazardous, client mixes sludge into cement, which are eventually hauled away to be disposed safely.

Client's DAF effluent is processed through four (4) large Sand Filters. In addition, tests are currently performed with a Walnut Filter, which is similar to a standard industrial sand filter. Client has problems using existing sand filters because there are still traces of manganese and ferrous hydroxide and other particles that end up in the DAF effluent and foul the sand filters to the point where it becomes very difficult to backwash, often requiring maintenance or shut down. These instances will result in plant effluent water being out of compliance.

From the sand filters, wastewater is stored and eventually flows into the Coal River. The nearby town of Crested Butte, CO is directly downstream from the Mount Emmons Mine. The mine is heavily monitored by state and city agencies, to make sure the mine eliminates heavy metals that are hazardous to aquatic life. In 2010 prior to this pilot study local environmentalist agencies and groups argued that the permits for opening a new molybdenum mine will be granted only if a superb modernized wastewater treatment facility is available.

Upcoming plant modernization – goals

1) If possible replace large DAF units with smaller footprint system for solid/liquid separation; space will be needed if new molybdenum mine opens

2) Replace sand filters with walnut filters to save on backwash water
3) Test for possible use of high density sludge (HDS) process to achieve higher solids in sludge and save on sludge disposal costs
4) Improve on current process (identify why after 2 days of no operation at start up more heavy metals are present in the wastewater

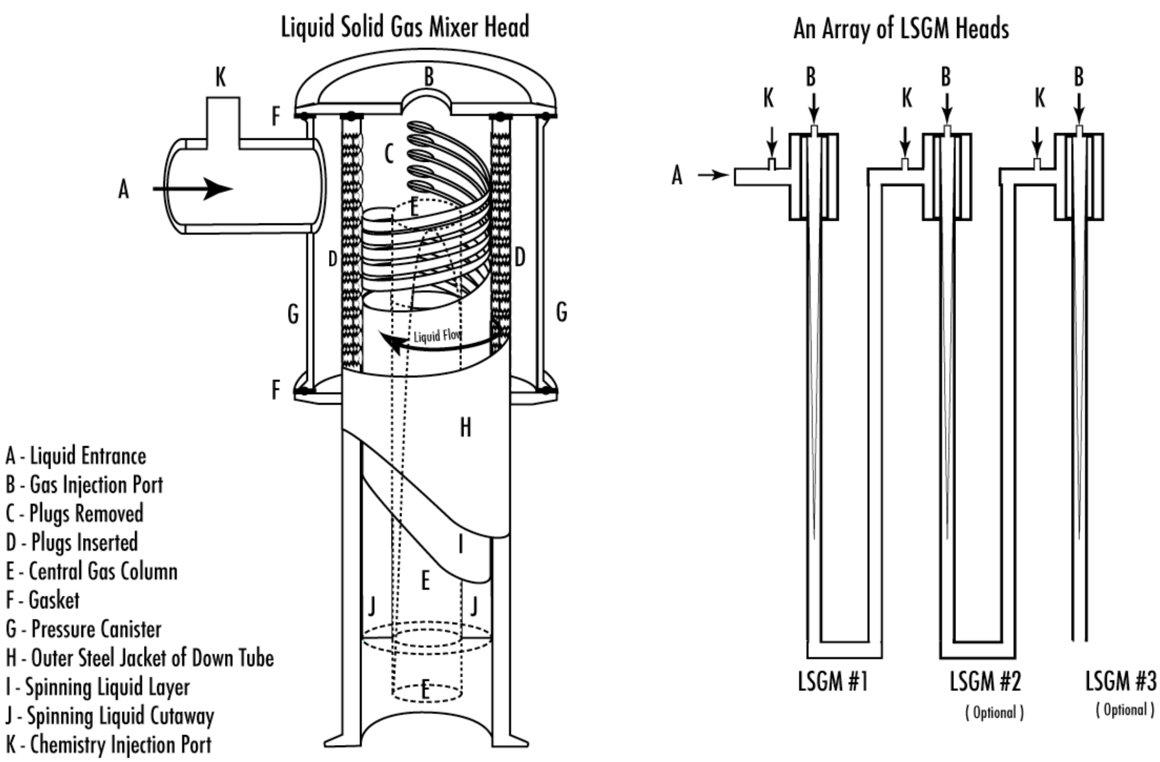
PILOT TESTS WITH THE GEM SYSTEM

A small footprint GEM hybrid centrifugal – dissolved air flotation was tested as a replacement for the bulk DAF Systems. GEM System would take only 10% of space needed to achieve same solid/liquid separation efficiency. Walnut filters were tested as a more efficient solution than current sand filter. Also HDS process modification was tested in the laboratory GEM unit to estimate improvements in sludge solids content.

THE DESCRIPTION OF THE HYBRID CENTIRFUGAL-DISSOLVED AIR FLOTATION SYSTEM

We proposed that a more efficient flotation system could be developed by combining high-energy centrifugal mixing of a liquid cyclone system (we termed it the liquid cyclone particle positioner, LCPP) with dissolved air as a source of flotation . Coagulants and flocculants can be delivered *in situ* directly into the flotation hydrocyclone unit. Pressurized air can be delivered to

Figure 1 – Schematic Presentation of the LCPP/LSGM



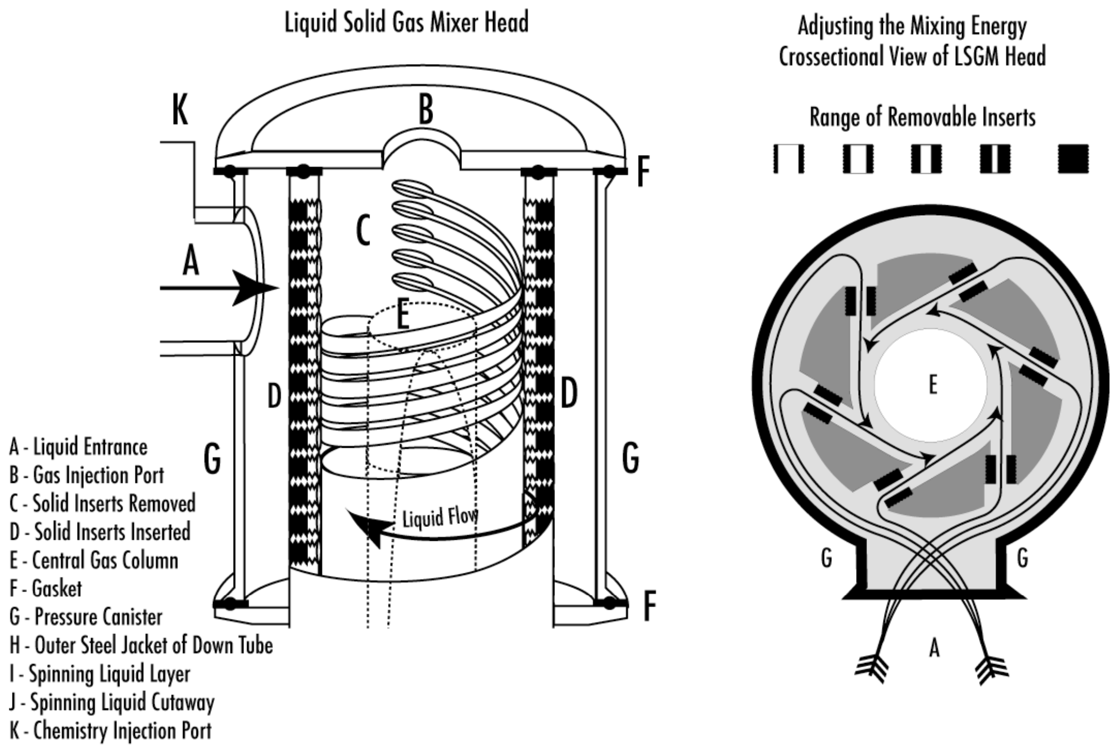
LCPP heads at the same time as flocculants. Such a procedure results in flocs, which are very porous and loaded with entrained and entrapped air.

As shown in Figure 1 the LCPP also acts as a liquid-solid-gas mixer (LSGM). Replacing the classical hydrocyclone head with the LCPP provides extremely energetic mixing by sequentially transporting liquid and entrained particles and gas bubbles throughout a centrifugally rotating liquid layer. Microturbulence in such vortices results in all particles and bubbles down to colloidal and molecular size acting as little mixers. Axial and radial forces inside the LCPP help mix coagulants and flocculants with the particles. Uncoiling of polymer and better mixing of ultrahigh-molecular-weight polymers (and more concentrated emulsions) is achieved in the LCPP. Such efficient mixing is important for proper flocculation of suspended particles. Centrifugal mixing also results in less floc breakage than with commonly used impeller or floc tube mixers.

Further modification of LCPP heads, as opposed to hydrocyclone heads, introduced multiple holes with plugs inside the LSGM heads, as shown in Figure 2. By changing the number of plugs, we can modify the mixing energy and head pressure from very low to very high. In this way, we can mix low-molecular-weight coagulant at relatively high energy and high-molecular-weight flocculants at relatively medium and low mixing energy to promote final large floc formation.

Hybrid centrifugal – dissolved air flotation technology (The GEM System developed at CWT [see Figure 3]) provides the best of both centrifugal and dissolved air systems: efficient continuous flow mixing and in line flocculation with the nucleation and entrainment of fine dissolved air bubbles. This development has resulted in systems with very efficient removal of particulate contaminants, a small footprint, drier sludge, durable long lasting flocs, fast response

Figure 2 – Schematic Presentation of the LSGM Heads

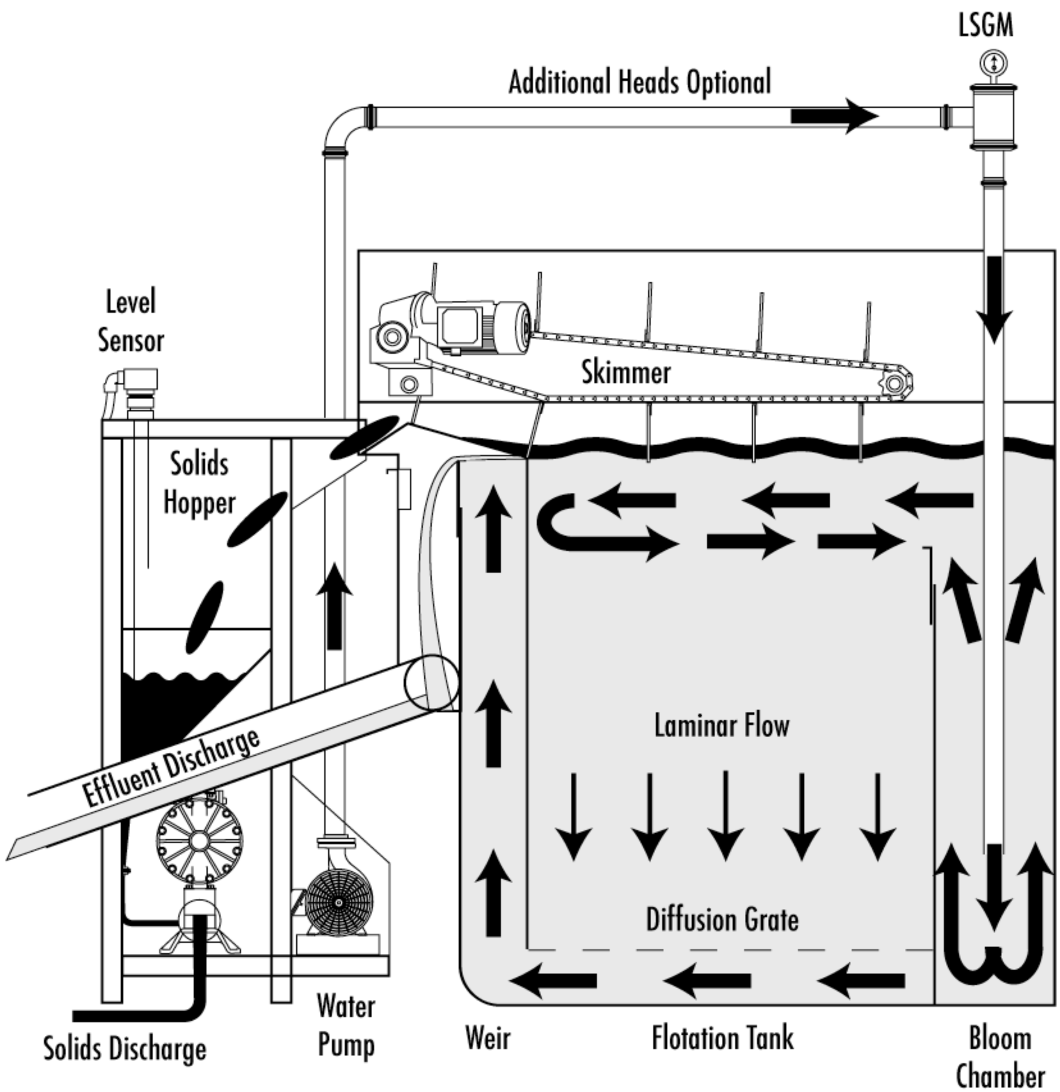


and treatment of the total wastewater stream (no recycling characteristic for DAFs). The design of on-line turbidity or fluorescence driven sensors for automatic control of coagulant and flocculant dosage is also underway. Computational fluid dynamics (CFD) has been used to design better flotation tanks with a vortical flow pattern that results in the formation of a dense air bed inside the tank . Such fine bubble layers prevent sedimentation of already floated heavier particulates, which results in significantly higher flotation rates.

SYNERGISM OF CHEMICAL AND MECHANICAL ASPECTS OF THE SOLID/LIQUID SEPARATION SYSTEMS

Solid/liquid separation processes are only as efficient as the weakest "link in a chain". New generation of high performance flotation units can only deliver if appropriate chemicals are used to coagulate and flocculate particles and emulsions in wastewater.

Figure 3 – Schematic Presentation of the Hybrid Centrifugal – Dissolved Air Flotation System



Coagulation, flocculation and flotation are among the most effective approaches to remove fats oils and grease, suspended solids and colloidal materials (even some proteins and macromolecules) from any industrial wastewater, such as for instance food processing. Solids, colloids and macromolecules present in food processing wastewater are generally charged. Charge stabilization often produces very stable colloidal suspensions. Solids and colloids that are charge stabilized repel each other and produce systems that have a tendency to "swim" within the wastewater bulk, rather than sediment or float. Surface charge has to be neutralized in order to get particles close together so that other attractive forces such as hydrophobic or van der Waals forces result in formation of larger aggregates that either sediment or attach to bubbles and float. Most colloids, macromolecules and solids in food processing wastewater are of organic nature. Ionization of carboxyl and amino groups from fatty acids or proteins produces some charge. Oil and grease particles are often emulsified and charge is present in the surfactants used as emulsifying agents. Many neutral colloids will preferentially adsorb hydroxyl ions and become negatively charged.

Most colloids present in any food processing wastewater are negatively charged, probably due to preferential adsorption of hydroxyl ions and widespread surface availability of carboxyl groups. The surface charge/dissociation of such groups is pH dependent. It is possible to find a pH at which total surface charge is zero (point of zero charge). At such pH colloids are quite unstable. However, coagulants and flocculants are designed so as to promote even faster, more efficient destabilization of colloids with growth of large, stable aggregates. The pH, therefore, should be adjusted close to the point of zero charge, in order to save on dosage of coagulants and flocculants needed to neutralize the surface charge. If surface charge is fully neutralized, the performance of flocculants is low.

Once the pH is adjusted, coagulation and flocculation process follow. Coagulation is addition of oppositely charged ions or molecules in order to neutralize surface charge and destabilize colloidal suspensions. Inorganic coagulants such as sulfate or chloride salts of trivalent iron (Fe[III]) or aluminum (Al[III]) have been quite popular in food processing wastewater treatment. However, such salts hydrolyze as part of coagulation process and produce oxohydroxyde sludge that is bulky and difficult to dewater. Prehydrolyzed –inorganic polymeric aluminum reagents such as polyaluminum chloride (PAC) or aluminum chlorohydrate (ACH) are more efficient in charge neutralization. Such salts also produce less bulky sludge. Cationic polyelectrolytes (organic low molecular weight polymers) such as quaternary polyamines produce less sludge that is easier to dewater. Such reagents are also much more efficient in charge neutralization. Therefore, the dosages needed to neutralize surface charge with polyelectrolytes are often more than order of magnitude lower compared to dosages of aluminum or iron salts. However, ferric salts have to be used if blood clarification is to be achieved. Precipitation of phosphate or sulfide ions also can be achieved only with inorganic ions. Finally some proteins can be removed with proper pH adjustment and use of inorganic coagulants.

Flocculation is a process of formation of large stable flocs that either sediment or float. Flocculants are reagents that achieve flocculation. Flocculants are large polymeric molecules that bind together smaller flocs produced by coagulation. Synthetic high molecular weight polyacrylamides are the most commonly used flocculants. Cationic polyacrylamides can neutralize residual negative surface charge and also bind smaller flocs together. Flocs may also be overcharged with coagulants and cationic flocculants, with subsequent use of anionic polyacrylamide. Such approach, termed dual flocculants approach, will be described in detail later in this manuscript (also see Figure 4).

Several steps are involved in the coagulation and flocculation processes. First, coagulants are added to the wastewater with the precise dosing pumps. Then coagulants are mixed with the particles in the high energy mixing process in order to uniformly distribute adsorbed coagulant molecules or ions. Upon initial charge neutralization, flocculants are added. Even more precise dosing is needed in order to avoid under or overcharging of particles. Flocculants are mixed with less energy in order to avoid breakup of formed flocs or even polymer molecules, which are large delicate chains. On the other hand, enough mixing intensity is needed to achieve uniform distribution of polymer and adsorption on all particles, rather than over - absorption on nearby particles only. (Mixing is also needed to activate polymeric flocculants. Such giant molecules are coiled into the tight coils. Linearization is needed to achieve polymer configuration that can bind numerous smaller flocs together (see Figure 5).

Wastewater samples tested while developing the system described in the manuscript were coagulated and flocculated at numerous pHs ranging from 3 to 11. For most samples, best flocculation can be achieved at pH between 5 and 6. Removal of fine emulsions and proteins is also most efficient in this pH range. Some wastewater samples had a very small amount of TSS and colloidal materials. For such samples, the pH was adjusted between 7 and 9. Similar approach was used for samples with colloidal materials that are almost neutral. Increasing pH above 8 results in higher surface charge and stronger adsorption of flocculants. At pHs below 5, performance of flocculants was found to be sub optimal with smaller, weaker flocs and more carryover in laboratory flotation tests. At pHs above 9, consumption of coagulants and flocculants was very high.

Numerous inorganic, organic and blend coagulants were tested with food processing wastewater. Ferric (FeIII) and aluminum(III) sulfate require the highest dosages and produce sludge with the lowest % solids that is most difficult to dewater and dry. As wastewater becomes loaded with TSS and FOGs, the necessary dosages to achieve coagulation can be as high as 6,000 mg/l. These two coagulants also interfere with the performance of flocculants, producing "pinpoint" floc with very small particles and high amount of carryover (often over 200 mg/l) in laboratory flotation tests. However, if water is rich in blood proteins, small amount of ferric coagulant (10-60 ppm) is needed to clarify wastewater and reduce foaming problems.

Prepolymerized inorganic coagulants suffer from similar deficiency, namely large dosages needed, carryover after flotation produced, and sludge with low % solids produced. Needless to say, dosages are lower than that of monomeric ferric or aluminum ions based coagulants. The most popular reagents from this group are polyaluminum chlorides, (PAC) with various basicity and aluminum chlorohydrate (ACH). Also, inorganic coagulants produce sludge with tendency to sediment, rather than to float.

Organic polyelectrolyte coagulants are the most advanced new generation of coagulant reagents. Usually, those are small cationic polymers with 100% backbone charge. Polyethyleneimines were the first reagents used for such purpose. Modern quaternary polyamines, epiamine, and polydyallyldymethyl chlorides (polyDADMAC's) are most often used in wastewater treatment applications. Such reagents do not interfere significantly with the performance of flocculants. They also produce sludge with high solid % and dosages needed to coagulate the wastewater can be an order of magnitude lower than that of inorganic reagents. Total cost of wastewater treatment is actually lower when using such reagents rather than inorganic coagulants. Low molecular weight epiamines and quaternary polyamines (10,000 – 25,000 D) coagulated food processing wastewater with the lowest dosages and least interference with the performance of flocculants downstream. Higher molecular weight and crosslinked polyamines (weight over 50,000 D) interfered with the performance of flocculants, and surprisingly were less efficient in coagulating wastewater colloidal contaminants. If combination of ferric and polyamine coagulants are needed, it is often better to add them separately then as a blend. Blend coagulants contain fixed ratio of ferric to polyamine coagulants. However, when treating changing wastewater influents, the ratio of amount of ferric and polyamine ions can vary quite significantly. From economic standpoint, blend coagulants are also very expensive.

Flocculants are the key component of any successful flotation wastewater treatment. We tested granular, emulsion, direct dispersion and brine flocculants. Flocculants with molecular weight between 1,000,000 D and 70,000,000 D were tested. Flocculants with charge (mole%) between 2 and 100% were tested and the effects of ionic strength (salinity, temperature, pH and surfactant present were studied). In all cases studied, granular high molecular weight, high charge polyacrylamides performed best. Such reagents yielded best flocs, sludge with the highest % solids, and least amount of TSS in the effluent. Dual flocculant approach in which addition of cationic flocculant is followed by addition of anionic flocculant always yielded the best performance (Fan et al., 2000). Emulsion flocculants produced smaller flocs, sludge with less solids and more TSS in the effluent. The higher the % active polymer in the emulsion, the better the performance. The same applies for brine and direct dispersion flocculants. Granular high charge (50% or more), high molecular weight (5,000,000 D or higher), cationic polyacrylamides were always the cheapest solution, with the best performance, and lowest dosage needed for efficient flocculation. At high temperature (over 40^{o} Celsius) or high salinity (over 10, 000 micromhos/cm) cationic flocculants could not flocculate colloidal components anymore. Cationic polayamine coagulants were then used to overcharge colloids with the subsequent addition of granular or emulsion ultrahigh molecular weight polyacrylamides. Medium charge mole % (20-30%) or very high charge % flocculants (100%) were needed to achieve flocculation at high salinity.

DUAL POLYMER FLOCCULATION

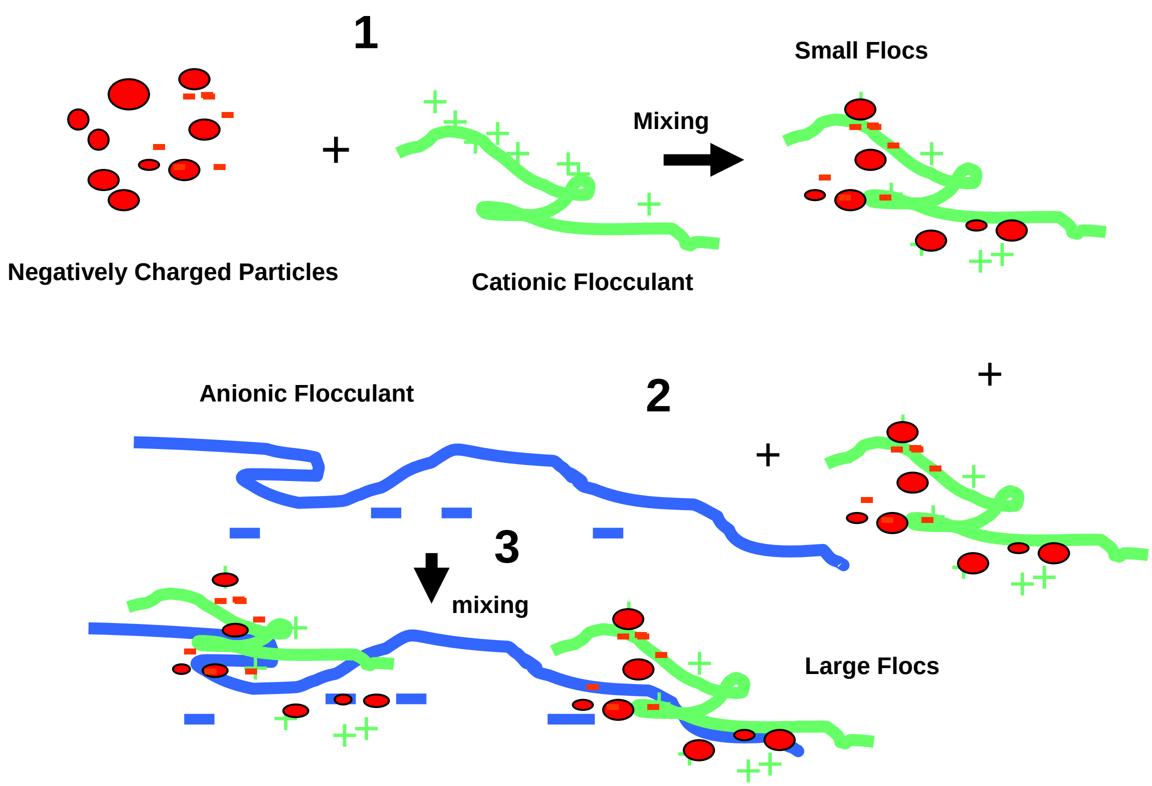


Figure 4. Dual polymeric flocculant approach.

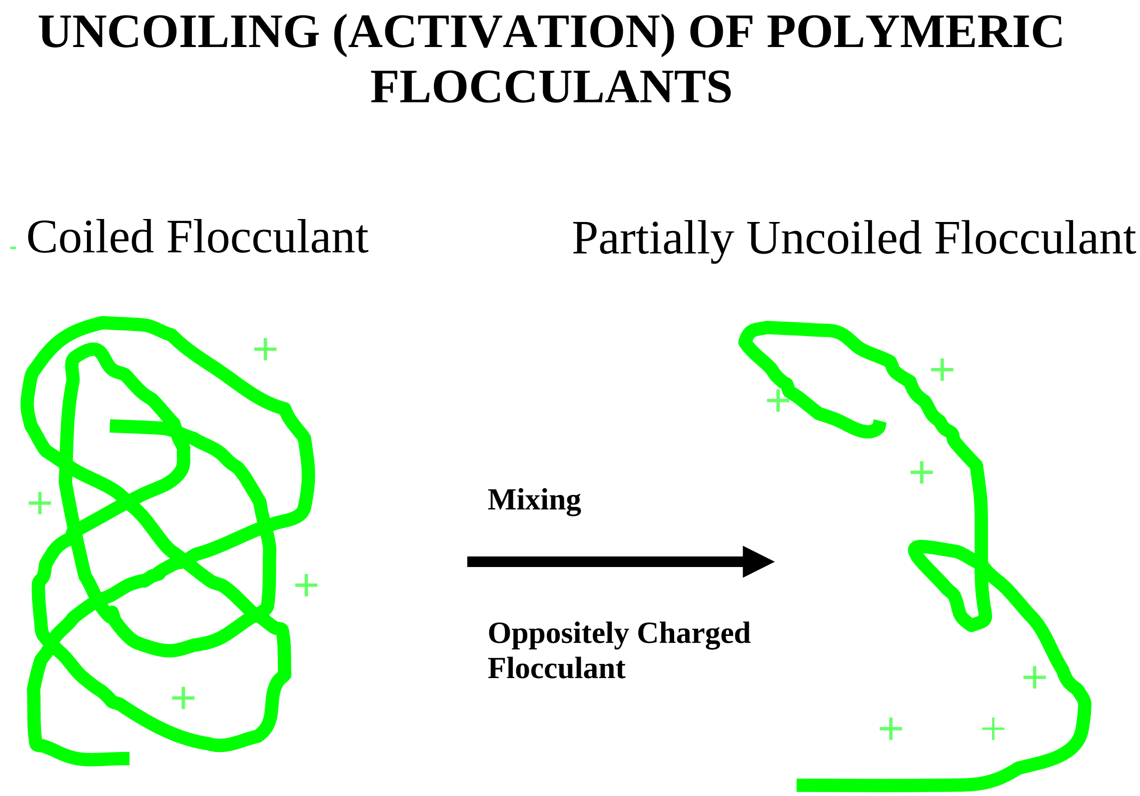


Figure 5. Uncoiling of high molecular weight polymeric flocculant molecules.

RESULTS OF THE PILOT STUDY

The primary goal of the pilot study was to demonstrate that the GEM System can successfully treat Mount Emmons' mine wastewater stream. Other goals included demonstrating how the GEM System will run with extremely low chemical dosages and finding the breaking point at which the GEM System begins to lose performance when the chemical dosage is too low. Additionally, client wanted to test dewatering capability of GEM Sludge without additional sludge thickening flocculants, when sludge is added to client's filter press.

To demonstrate the GEM System's effectiveness, we conducted onsite lab tests to measure the reductions of TSS, NTU (turbidity), and sludge solids percentage after water was treated by the GEM System.

During tests, we experimented to attain a complete analysis of values for optimal chemical usage, optimal chemical regimes, dryness of sludge, and sludge dewatering capacity.

The GEM System was operated at 10 GPM flow. Influent was taken ahead of sand trap where no other chemicals than lime have been added to the stream. Various dosages of cationic high molecular weight high charge polyacrylamide followed by anionic high molecular weight high charge polyacrylamide floculant were used, ranging from 20 mg/l to 1.5 mg/l of each. No anionic surfactants were used. Tables 1 - 8 summarize the results of the tests. After the GEM or DAF effluent was filtered with sand or walnut filters and residual heavy metal concentrations were measured.

Results

1) GEM System using lime precipitation at pH 10.7 and dual granular flocculant flocculation-flotation removed TSS to less than 10 ppm most of the time. Cadmium was removed to less than 10 ppb and zinc to less than 1 ppm. Ferric and aluminum were reduced to around 1.2 ppm most of the time. Lead, silver and copper were reduced close to nondetectable levels.
2) Walnut filters removed all heavy metals even further with cadmium to less than 0.5 ppb, zinc less than 0.3 ppm and ferric and aluminum to less than 0.5 ppm, and TSS to less than 1 ppm.
3) Only 5% of produced clean water had to be used for walnut filter washing, as opposed to 43% when using current sand filters
4) GEM system produced sludge with around 3% of dry solids, sludge could be filter pressed without any additional flocculant

Table 8 summarizes average heavy metal concentrations after sand and walnut filter filtrations. Table 9 compares the performance of the large footprint DAF and small footprint GEM System.

Table 1. Turbidity Reductions: Lab tests indicated that the GEM System reduced Mount Emmons Turbidity (NTU) by 99.5% on average.

		Turb/NTU	Turb/NTU		
Date:	**Time:**	**Influent:**	**Effluent:**	**% Reduction:**	**Cat/Ani/ppm**
9/14/10	3:30 PM	1000	7	99.30%	20/10
9/15/10	10:00 AM	1000	6	99.40%	20/10
9/15/10	11:45 AM	1000	7	99.30%	20/10
9/15/10	2:30 PM	1000	4	99.60%	10/5
9/15/10	4:30 PM	1000	5	99.50%	10/5
9/16/10	9:30 AM	1000	3	99.70%	5/5
9/16/10	11:00 AM	1000	5	99.50%	2.5/2.5
9/16/10	1:00 PM	1000	4	99.60%	2.5/2.5
9/16/10	2:30 PM	1000	9	99.10%	1.25/1.25
9/17/10	9:30 AM	1000	2	99.80%	3.75/3.75
9/17/10	11:00 AM	1000	2	99.80%	3.75/3.75
9/17/10	1:30 PM	1000	3	99.70%	3.75/3.75
9/17/10	4:30 PM	1000	3	99.70%	3.75/3.75
9/18/10	7:30 AM	1000	8	99.20%	4.25/4.25
9/18/10	9:00 AM	1000	9	99.10%	4.25/4.25

Table 2. TSS Reductions: Lab tests indicated that the GEM System reduced Mount Emmons TSS by approximately 98% on average:

Date:	**Time:**	TSS/ppm **Influent:**	TSS/ppm **Effluent:**	**% Reduction:**	**Cat/Ani/ppm**
9/14/10	3:30 PM	345	12	96.52%	20/10
9/15/10	10:00 AM	745	9	98.79%	20/10
9/15/10	11:45 AM	349	16	95.42%	20/10
9/15/10	2:30 PM	320	7	97.81%	10/5
9/15/10	4:30 PM	375	8	97.87%	10/5
9/16/10	9:30 AM	621	3	99.52%	5/5
9/16/10	11:00 AM	330	5	98.48%	2.5/2.5
9/16/10	1:00 PM	301	5	98.34%	2.5/2.5
9/16/10	2:30 PM	285	13	95.44%	1.25/1.25
9/17/10	9:30 AM	691	2	99.71%	3.75/3.75
9/17/10	11:00 AM	265	2	99.25%	3.75/3.75
9/17/10	1:30 PM	300	3	99.00%	3.75/3.75
9/17/10	4:30 PM	275	3	98.91%	3.75/3.75
9/18/10	7:30 AM	311	13	95.82%	4.25/4.25
9/18/10	9:00 AM	300	3	99.00%	4.25/4.25

Table 3. Cadmium Reductions: Lab tests indicated that the GEM System reduced Mount Emmons Cadmium by approximately 97.5% on average.

Date:	Time:	Cadmium/ppm Influent:	Cadmium/ppm Effluent:	% Reduction:	Cat/Ani/ppm
9/15/10	10:00 AM	0.36217	0.00875	97.58%	20/10
9/15/10	11:15 AM	0.36217	0.01149	96.83%	10/5
9/16/10	8:30 AM	0.36217	0.00746	97.94%	5/5
9/16/10	10:45 AM	0.36217	0.00778	97.85%	2.5/2.5
9/16/10	1:00 PM	0.36217	0.00626	98.27%	2.5/2.5
9/16/10	2:30 PM	0.36217	0.00810	97.76%	1.25/1.25
9/17/10	7:30 AM	0.36217	0.00874	97.59%	1.25/1.25
9/17/10	9:30 AM	0.36217	0.00729	97.99%	3.75/3.75
9/17/10	11:00 AM	0.36217	0.00940	97.40%	3.75/3.75
9/17/10	1:30 PM	0.36217	0.00991	97.26%	3.75/3.75
9/17/10	3:00 PM	0.36217	0.00954	97.37%	3.75/3.75
9/18/10	7:30 AM	0.36217	0.00883	97.56%	4.25/4.25
9/18/10	8:30 AM	0.36217	0.01599	95.58%	4.25/4.25

Table 4. Zinc Reductions: Lab tests indicated that the GEM System reduced Mount Emmons Zinc by approximately 97.5% on average.

Date:	Time:	Zinc/ppm Influent:	Zinc/ppm Effluent:	% Reduction:	Cat/Ani/ppm
9/15/10	10:00 AM	37.80290	0.85940	97.73%	20/10
9/15/10	11:15 AM	37.80290	1.18490	96.87%	10/5
9/16/10	8:30 AM	37.80290	0.78190	97.93%	5/5
9/16/10	10:45 AM	37.80290	0.80970	97.86%	2.5/2.5
9/16/10	1:00 PM	37.80290	0.65660	98.26%	2.5/2.5
9/16/10	2:30 PM	37.80290	0.86400	97.71%	1.25/1.25
9/17/10	7:30 AM	37.80290	0.97640	97.42%	1.25/1.25
9/17/10	9:30 AM	37.80290	0.82900	97.81%	3.75/3.75
9/17/10	11:00 AM	37.80290	0.99950	97.36%	3.75/3.75
9/17/10	1:30 PM	37.80290	1.06060	97.19%	3.75/3.75
9/17/10	3:00 PM	37.80290	1.04970	97.22%	3.75/3.75
9/18/10	7:30 AM	37.80290	1.00370	97.34%	4.25/4.25
9/18/10	8:30 AM	37.80290	1.72360	95.44%	4.25/4.25

Table 5. Iron Reductions: Lab tests indicated that the GEM System reduced Mount Emmons Iron by approximately 98% on average.

Date:	Time:	Iron/ppm Influent:	Iron/ppm Effluent:	% Reduction:	Cat/Ani/ppm
9/15/10	10:00 AM	26.12000	0.02400	99.91%	20/10
9/15/10	11:15 AM	26.12000	0.76400	97.08%	10/5
9/16/10	8:30 AM	26.12000	0.54900	97.90%	5/5
9/16/10	10:45 AM	26.12000	0.54900	97.90%	2.5/2.5
9/16/10	1:00 PM	26.12000	0.41600	98.41%	2.5/2.5
9/16/10	2:30 PM	26.12000	0.48800	98.13%	1.25/1.25
9/17/10	7:30 AM	26.12000	0.67000	97.43%	1.25/1.25
9/17/10	9:30 AM	26.12000	0.55500	97.88%	3.75/3.75
9/17/10	11:00 AM	26.12000	0.65900	97.48%	3.75/3.75
9/17/10	1:30 PM	26.12000	0.65700	97.48%	3.75/3.75
9/17/10	3:00 PM	26.12000	0.63300	97.58%	3.75/3.75
9/18/10	7:30 AM	26.12000	0.67500	97.42%	4.25/4.25
9/18/10	8:30 AM	26.12000	1.22800	95.30%	4.25/4.25

Table 6._Manganese Reductions: Lab tests indicated that the GEM System reduced Mount Emmons Manganese by approximately 97% on average.

Date:	Time:	Manganese/ppm Influent:	Manganese/ppm Effluent:	% Reduction:	Cat/Ani/ppm
9/15/10	10:00 AM	16.83340	0.28120	98.33%	20/10
9/15/10	11:15 AM	16.83340	0.68240	95.95%	10/5
9/16/10	8:30 AM	16.83340	0.43220	97.43%	5/5
9/16/10	10:45 AM	16.83340	0.46860	97.22%	2.5/2.5
9/16/10	1:00 PM	16.83340	0.36490	97.83%	2.5/2.5
9/16/10	2:30 PM	16.83340	0.45330	97.31%	1.25/1.25
9/17/10	7:30 AM	16.83340	0.54630	96.75%	1.25/1.25
9/17/10	9:30 AM	16.83340	0.49410	97.06%	3.75/3.75
9/17/10	11:00 AM	16.83340	0.57130	96.61%	3.75/3.75
9/17/10	1:30 PM	16.83340	0.60860	96.38%	3.75/3.75
9/17/10	3:00 PM	16.83340	0.59090	96.49%	3.75/3.75
9/18/10	7:30 AM	16.83340	0.57670	96.57%	4.25/4.25
9/18/10	8:30 AM	16.83340	0.98540	94.15%	4.25/4.25

Table 7. Sludge (percentage solids): The GEM System produced sludge with approximately 3% solids off the beach. The GEM Sludge dewatered in client's filter press much easier than the DAF Sludge. The DAF sludge requires addition of approximately 400 ppm flocculants to help prepare sludge for thickening on the filter press. After filter press, the GEM Sludge averaged 16% solids with **no sludge thickening chemicals added**, resulting in significant cost savings.

GEM Sludge Date:	Time:	% Solids:	Cat/Ani/ppm		
9/14/10	3:30 PM	2.30%	20/10		
9/15/10	10:00 AM	1.80%	20/10		
9/15/10	11:45 AM	2.90%	20/10		
9/15/10	2:30 PM	2.80%	10/5		
9/15/10	4:30 PM	2.50%	10/5		
9/16/10	9:30 AM	3.50%	5/5		
9/16/10	11:00 AM	3.30%	2.5/2.5	avg.	2.83%
9/16/10	1:00 PM	2.50%	2.5/2.5		
9/16/10	2:30 PM	2.50%	1.25/1.25		
9/17/10	9:30 AM	3.10%	3.75/3.75		
9/17/10	11:00 AM	3.50%	3.75/3.75		
9/17/10	1:30 PM	3.30%	3.75/3.75		
9/17/10	4:30 PM	3.40%	3.75/3.75		
9/18/10	7:30 AM	2.50%	4.25/4.25		
9/18/10	9:00 AM	2.50%	4.25/4.25		

Table. 8 Heavy metal and TSS after sand and walnut filters

Parameter	Sand Filter Concentration/ppm	Walnut Filter Concentration/ppm
TSS	<1	<1
Cadmium	0.0007	0.00085
Zinc	0.0460	0.0520
Iron	0.25	0.35
Manganese	0.15	0.23
Copper	0.0060	0.0065
Aluminum	0.490	0.550
Lead	0.00050	0.00060

Table 9. Heavy metals and TSS after GEM and DAF Systems

Parameter	GEM Concentration/ppm	DAF Concentration/ppm
TSS	9	4
Cadmium	0.0091	0.0051
Zinc	0.65	0.48
Iron	0.55	0.38
Manganese	0.44	0.35
Copper	0.0095	0.0085
Aluminum	1.25	1.1
Lead	0.011	0.00085

DISCUSSION

Acid Mine Drain Stream

Influent heavy metal analysis shows that Mount Emmons Mine has a very unusual AMD Stream. The typical AMD stream contains approximately 300 ppm or more of iron and small amounts of other heavy metals such as manganese, zinc, cadmium, nickel, copper, etc. At this mine, however, the wastewater is dominated by zinc (50-60 mg/L in influent). Iron concentration is also lower than normal with levels ranging from 20 ppm to 70 ppm. Manganese concentration, which is usually significantly lower than Iron concentration, is almost equal to Iron concentration at this plant. A small amount of aluminum is present, and sulfate concentrations (700 mg/L at Mount Emmons) are lower in this mine than usual AMD streams.

Sludge Analysis

Sludge analysis indentifies that zinc hydroxide (around 140 grams/kg) and Iron hydroxide (around 130 grams/kg) are the main sludge components. Also present in the sludge are manganese hydroxide, aluminum hydroxide and gypsum (calcium sulfate), while also containing a hint of undissolved lime. The sludge produced from the Clients' DAF contains unusually low percentage solids (2-3%). A typical Acid Mine Drain Stream rich in ferric ions will produce sludge with 6% solids off the beach which can be decanted to 10% sludge solids to water ratio after GEM treatment. After filter press, a typical AMD stream will produce up to 40% solids. Due to the high amount of zinc and low amount of ferric in Mount Emmons stream, the sludge does not decant well because the heavy hydrophilic sludge fails to phase separate, and therefore can only be filter pressed to 16% solids. Although both the GEM Sludge and DAF sludge do not decant well compared to typical AMD water, the GEM sludge did filter press much easier than

DAF sludge, without requiring the addition of more cationic flocculants to properly dewater the existing DAF sludge.

DAF System vs. GEM

The primary goal of the existing DAF is to remove heavy metals through flocculation and flotation of metal hydroxide mixed precipitates. According to the results of tests performed by CWT and by Colorado Analytical Laboratories, both the DAF and the GEM Systems were very effective in removing heavy metals from the stream. The GEM will be able to achieve very similar results to the DAF, however, the GEM will require a much smaller footprint than the DAF. Furthermore, the GEM System can be engineered with a bottom Auger, which will remove any sludge sediment from the bottom of tank, eliminating the need for a third GEM System. Such implementation would allow client to create more floor space for future growth, in the event client begins to add other types of machinery when the mine is back in operation. Current DAF System did remove dissolved heavy metals somewhat more efficiently. It has 10 times longer tank residence time for effluent flotation. During this long period more iron (II) gets oxidized into iron (III) that is 10 times less soluble and precipitates fast out of solution. Other heavy metals such as cadmium and zinc then co-precipitate with iron (III) hydroxide. The best results with the GEM System were achieved with dosage of 2.5 ppm of cationic and 2.5 ppm of anionic polyacrylamide flocculants. Similarly, the best performance of the DAF System was achieved with dosage of 2.5 ppm of cationic polyacrylamide flocculant and 2.5 ppm of anionic surfactant.

In the GEM System, the applied dual flocculant approach eliminated the need for surfactant chemicals used in flotation of particles. The dual flocculant approach also eliminates the need to add further chemicals to sludge before adding sludge to the filter press. The GEM sludge can be taken directly from the beach to the filter press without any additional treatment or costs therein.

Further observations:

Effluent Analysis after the GEM and DAF Systems showed very low amount of cadmium (around 5 ppb on average), zinc (less than 1 ppm), and very low traces of other metals such as copper, lead, silver and manganese. Such heavy metal removals are only achieved due to the presence of ferric (Iron III) hydroxide and oxidized manganese hydroxide, which are present in this stream. Most AMD streams contain much more ferric than this particular mine. Without co-precipitation with ferric hydroxide, cadmium and zinc could not be removed to such low concentrations with the hydroxide precipitation process.

Mount Emmons influent analysis over a 3 year period showed that the ratio of Iron II and Iron III can vary wildly from 400:1 all the way down to 1:1. In addition, manganese is present in both reduced and oxidized forms. We suspect that as the water sits over night and over the weekends when the pond water is stale, some ferric ions are probably lost due to hydrolysis and precipitation. Upon start-up, this type of stream is more difficult to treat than that of a typical AMD stream because the lack of overall ferric will leave a heightened amount of leftover Iron II in the effluent when these conditions fail to precipitate this version of Iron. If these levels of Iron II are not precipitated properly, they will remain in the stream and result in unwanted dissolved effluent carry over, since iron (II) slowly gets oxidized into iron (III) which is 10 time less soluble and precipitates much faster at the filter media or in the river.

Currently, at 9600 feet elevation, Mount Emmons Mine water lacks oxygen, therefore some iron and manganese ions remain in the effluent in reduced forms. Mount Emmons Mine does not oxygenate their influent prior or during precipitation process. Because iron and manganese forms are reduced in the first place, hydroxides precipitate much slower than normal and are not as efficient as co precipitants for cadmium and zinc. In addition, they produce sludge with a much lower solids loading than a typical AMD stream.

The GEM removed Cadmium below 10 ppb and zinc below 1 ppm (See Tables for detailed results). If additional walnut filters are installed and perform as advertised, there should not be any problems with heavy metals, removals, or backwash water usage. Removal efficiencies are usually worse after weekends and overnight because some ferric hydroxides precipitate outside in the ponds due to the lack of mixing.

After cement treatment of sludge there was slightly more cadmium and zinc in the effluent. Cement may react with Ferric producing ferric silicate and reducing the amount of available Iron III for co-precipitation.

The plant generally has problems with undetected amounts of materials that end up in the walnut filters and sand filters in spite of ultra low TSS in the effluent from DAF or GEM Systems. CWT believes that we understand why these materials are found in the filters.

After CWT collected some effluent samples from GEM and DAF on Friday Afternoon (September 17, 2010), results looked perfect. Water was crystal clear, turbidity and TSS were almost undetectable. However, approximately 48 hours later, a significant amount of precipitate (over 50 mg/L of TSS) appeared in both samples. The brownish color and noticeable heavy metal particles visible to the naked eye indicated that reduced forms of manganese and ferrous (Iron II) hydroxides are still present in the water, in addition to a trace of gypsum. These reduced iron and manganese ions slowly oxidize and precipitate less soluble higher valency metal hydroxides.

Oxygenation of the influent AMD would be a suitable solution for this problem. Standard Precipitation of these reduced forms of manganese and iron will typically take a few days to fully precipitate. However, oxygenation of the influent stream should increase the efficiency of the precipitation of reduced forms, and allow them to precipitate much faster, as any reduced ions of iron and manganese will almost completely be oxidized.

CONCLUSIONS

Through various tests resulting from the pilot demonstration, we have identified the following areas where Mount Emmons mine water treatment can be improved:

1) Currently, there is not enough iron in water to properly precipitate all heavy metals by co-precipitation with iron(III) hydroxide at all times
2) Currently not enough oxygen in water, which could accelerate precipitation of Iron II by oxidizing it to iron (III), which is 10 times less soluble and precipitates faster out of water.
3) DAF sludge does not dewater very well and requires addition of approximately 400 ppm of flocculant addition before filter press.
4) Client uses anionic surfactants for bubble formation; this can leave residue in the effluent

Instead of surfactants, we recommend the dual flocculant approach with high molecular weight high charge granular polyacrylamides, as used in the GEM System during entire pilot demonstration. Use of dual flocculants gives client an approach that also eliminates the need for additional flocculant injected to sludge for dewatering in filter press.

To oxygenate AMD influent prior to lime addition, we recommend using an LSGM hydrocyclone with compressor to oxidize manganese and iron(II) hydroxide stream completely. This energy efficient approach can reduce the retention time necessary to fully precipitate iron. This can prevent some solids carry over that is currently found in Mount Emmons effluent. Iron (II) ions slowly oxidize in the effluent and produce iron (III) hydroxide that coats sand or walnut shell filter media.

In order to add more iron to the influent, CWT recommends recycling the sludge into a lime-sludge mixing tank or directly into client's existing lime – AMD reactor. This way, there will be enough ferric (III) hydroxide added in contact with AMD influent without any chemical addition (ferric sulfate). In this environment, the appropriate increase in iron is present without any additional monthly chemical costs. After many rounds of sludge recycle, customer should also see an increase in sludge density, because typically the higher the iron concentration in the influent, the higher the sludge solids percentage coming out of the GEM System.
Sand filters should be replaced with walnut filters to save backwash water and energy. Sand filter use up to 50% of produced water for backwash, walnut filters 3-5 %. Removal of heavy metals is similar with sand filters performing slightly more efficiently, (15-20% better removals).

Both DAF and GEM Systems can be used for solid/liquid separation. DAF removes TSS and heavy metals somewhat more efficiently (around 10-45%). The GEM System has much smaller footprint (12% of that of DAF).

PROJECT UPDATE

US Energy Corporation is still running the Mount Emmons mine wastewater treatment plant. Local community environmental organizations strongly oppose an opening of new molybdenum mine. Other US Energy partners decided not to invest any further in the mine project. US Energy Corporation is considering federal land exchange for the Mount Emmons property. If this happens, the federal government will assign a third party to run the wastewater treatment plant. Until this situation is resolved no investments in plant upgrade will be made.