TREATMENT AND PREVENTION OF ARD USING SILICA MICRO ENCAPSULATION

by

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Abstract. In response to the known drawbacks of liming and the ever-increasing regulatory demands on the mining industry, KEECO has developed a silica micro encapsulation (SME) process. SME is a cost-effective, high performance reagent that is utilized in conjunction with simple chemical delivery systems. By encapsulating metals in a silica matrix formation and rapidly precipitating them into a sand-like sludge, it offers all the advantages of liming without the negative drawbacks. Utilizing an injection technique via a high shear mixing device, a slurry form of the SME product called KB-1™ was applied to ARD at the Bunker Hill Mine in Idaho and to ARD pumped from collection ponds at a remote mine site in the Sierra Nevada Mountains. Flow rates at both sites ranged from 500 to 800 gallons per minute. Treated water from the Bunker Hill Mine operation achieved the site's NPDES criteria for all evaluated metals and U.S. Drinking Water quality for arsenic, cadmium, chromium, lead and zinc with a dosage rate of 1.34 grams KB-1™ per liter. Treated water from the Sierra Nevada project focused on the control of aluminum, arsenic, copper, iron and nickel. All water samples displayed a >99.5% reduction in these metals, as well as an 84% - 87% reduction in the concentration of sulfate. Testing on sludge generated from both operations achieved TCLP Action Limits. The SME process is currently under evaluation as a means to coat the pyrite surfaces of newly generated mine tailings to prevent oxidation and future acid generation.

Additional Key Words: Bunker Hill Mine, K-250 injection unit, KB-1™, KEECO, silica matrix

The Problem: ARD

Acid rock drainage (ARD) is one of the largest and most intractable problems facing the non-ferrous metal and coal mining sectors. Once initiated, the cycle of chemically and biologically mediated and catalyzed reactious that lead to ARD generation is often difficult – and sometimes impossible – to stop. While there is evidence to suggest that the degree of contamination of ARD will decrease rapidly within a relatively short time, experience in historic mining regions of the world indicates that the problem may persist for centuries at certain sites.

The recent and continuing creation of a number of high-level national and international initiatives demonstrates the growing concerns of industry, government and other stakeholder groups. ARD is considered one of the most serious potential environmental impacts caused by mining by a broad range of stakeholders, amongst which are a large number of industry commentators and experts. Understandably then, there is considerable pressure on the industry to rise to the technical challenge represented by ARD.

Continuing global depletion of non-acid generating oxide ore deposits and the increasing dominance of sulfide ores can only lead to an increased potential for ARD incidents unless improved preventative and treatment options are developed.

Current best practice in dealing with ARD places the emphasis firmly on prediction and prevention planned from the outset of the operation and integrated with each phase of the mine site life cycle. The elements that constitute best practice are becoming more clearly defined and as this process of clarification continues, industry will undoubtedly accelerate the process of best practice implementation, putting behind it at last the image of mining as an unequalled despoiler and polluter of landscapes. In its place a new image is beginning to develop – that of a sustainable industry operating in relative harmony with the environment, and producing the materials that underpin much of today's culture and society.

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However, it is equally clear that despite the best efforts of industry, regulators and other stakeholder groups, many sites will continue to generate ARD during operation and following closure – in many cases a legacy of ARD has been derived from operational and strategic decisions made decades ago, before the risks and impacts of the self-sustaining cycle of ARD generation were properly understood. Add to this ARD generation from poorly managed operations and from historic and abandoned sites and it becomes clear that the treatment of ARD will be required for the foreseeable future to protect water quality, and ecosystem and human health.

Lime and the Treatment of ARD

Despite recent advances in predictive and preventative measures, treatment technologies have been stuck in something of a rut for several years, and remain dominated by the application of lime in a number of basic and more sophisticated guises. Although the drawbacks and deficiencies of lime-based systems are well known, the absence of cost-effective alternatives has ensured that it remains the treatment of choice at the majority of sites. Although the negative aspects of lime-based systems vary according to site-specific factors, it is possible to draw up a generic list that includes:

- Relatively high capital cost;
- Chemical instability of treatment sludges leading to possible classification as hazardous wastes that require high-cost disposal at designated sites;
- Poor handling characteristics of treatment sludges, which may require extensive land areas for dewatering or expensive mechanical dewatering;
- High pH required to remove metals such as manganese which may in turn cause other metals (e.g., zinc and aluminum) to resolubilize, necessitating a multi-stage treatment to reduce all metals to acceptable concentrations;
- Long-term liability associated with sludge disposal sites as a result of the potential for contaminant redissolution.

While lime is widely accepted by the mining industry at present on the basis of operational costs and a proven capacity to treat ARD, it is becoming increasingly clear that these drawbacks will continue to undermine its monopolistic position in the next century and contribute to the overturning of industry hesitance in taking up alternative innovative techniques.

Silica Micro Encapsulation

In response to the known drawbacks of lime-based treatment systems, KEECO has developed a cost-effective and high performance reagent and associated delivery technology that has all the positive characteristics of liming systems but none of the drawbacks. The reagent – KB-1™ – is based on a unique proprietary calcium/silica-based formulation, manufactured as a powder and applied in either a dry or slurried form.

The Formulation

KB-1™ contains three major components. The first is a pH adjuster that initiates the precipitation of heavy metals from the water. The second component undergoes condensation polymerization, chemisorbing the metals into a three-dimensional structure, or matrix, composed primarily of silica (the process of silica micro encapsulation or SME). The microscopic matrices contain no fissures or fractures, completely surround the metal precipitates and continue to strengthen with time. The bound metal precipitates are in the form of a fast-settling, sand-like substance that is resistant to degradation under naturally occurring environmental conditions. Due to the coarse size and high density of the particles (relative to precipitates resulting from liming), no flocculant is required to induce settling, which occurs naturally at a high rate. The third component of KB-1™ acts as a support structure for the pH adjuster and polymerizer components, increasing the available surface area and maximizing reactivity.

Key advantages offered by the SME technology as compared to liming include the following:

- Provides pH control and neutralization;
- Eliminates the need for precipitants and flocculants;
- Reduces or eliminates the need for hazardous waste disposal;
- Reduces the volume of generated sludge materials and associated costs of handling and disposal;
- Meets or exceeds regulatory/discharge requirements;
- Reduces or eliminates long-term liabilities.

KB-1™ and its associated reagent delivery systems may well represent the first serious alternative to lime that delivers reliability in its performance, a high level of environmental protection, and a waste management tool that meets the wider requirements of sustainable development at low capital and operating cost. Its application as a dry powder or as a slurry means that there is no need for major reinvestment in terms of plant for those sites already using lime, removing one very significant obstacle often seen in the uptake of innovative technologies. Its position as a serious contender with lime is being confirmed recently by an upsurge in field trials and commercial contracts. Some of those include the following projects:

- Bunker Hill Mine
- Mine in the Sierra Nevada Mountains (confidential client).

The projects were both completed on a field-scale at a treatment rate of 500 – 800 gallons per minute (gpm), after initial bench-scale test work was completed. Each scenario involved the application of KB-1™ to control a variety of heavy metals contained in acidic mine drainage.

KEECO Field Operations – Chemical Delivery Technique and Project Summaries

Due to the unique nature of the KB-1™ product and its high reactivity, KEECO developed specialized systems to properly apply KB-1™ and maximize its efficiency and reactivity. To date, the company has developed two delivery systems; one involving injection of an activated KB-1™ slurry (the K-250 System) and the other the delivery of the dry chemical directly iuto the waste stream (the K-500 System). Althongh both techniques have been successfully demonstrated in field operations, the Bunker Hill and Sierra Nevada projects relied on the use of the slurry injection technique.

The K-250 Slurry Injection Technique. KB-1™ , in its raw state, is in the form of a powder. For purposes of efficient delivery to the water stream, a slurry of the product is generated and pumped through a shearing mechanism to an injection manifold that is placed directly in the acid stream. The shearing mechanism provides maximum reactivity of the KB-1™ and the injection manifold accomplishes effective mixing with the waste stream. The water utilized to generate the chemical slurry is taken from a bleed line off the mine acid flow or from the treated effluent.

The sheared KB-1™ slurry is extremely reactive and is dispersed through the chemically resistant, ventilated plastic manifold to facilitate rapid dispersion of the reagent throughout the stream. This process results in an immediate reaction between the dissolved metals and KB-1™, rapidly precipitating then encapsulating them in the silica matrix.

Applying the SME Technology at the Bunker Hill Mine

The Bunker Hill Mine (part of the Bunker Hill Mining and Metallurgical Complex) was one of the largest lead and zinc mines in the United States and has been in virtually continuous operation for over 100 years. With 31 levels, over 150 miles of drafts, 6 miles of major inclined shafts and a total volume of disturbed ground reaching approximately 5 cubic miles, the mine is an archetypal example of the difficulties of retrospectively implementing preventative measures in underground workings once the process of acid generation is underway. Preventative measures have also been hindered by the infiltration and percolation of incipient rainfall through several thousand feet of sulfide-bearing rock overlying the mine workings.

In 1991, the mine was purchased by The New Bunker Hill Mining Company, the owner of which, Mr. Bob Hopper, requested that KEECO undertake trials at the mine to treat the acid stream flowing from the underground workings which discharges from the site at an average flow of 800 gpm. Standard treatment processes had proved unsuccessful or uneconomic (including the use of lime-based systems). At the time of the trials, an acid stream of approximately 500 gpm at a pH of 1.96 was emanating from the underground workings.

At the request of Mr. Hopper, KEECO positioned its treatment system 2 miles underground and injected a slurry of the SME product KB-1™ into the acid stream. Previous laboratory tests had indicated that a dose rate of 3 – 4 grams KB-1™ per liter would be required to reduce metal concentrations to acceptable levels. However, enhanced chemical reactivity through the shearing mechanism reduced the chemical demand in the field application to 1.34 grams KB-1™ per liter. At this dosage rate, the treated water achieved discharge criteria and satisfied U.S. Drinking Water Criteria for arsenic, cadmium, chromium, lead and zinc (see Table 1; all metals are mg L^{-1}).

Table 1 – Bunker Hill Mine Water Quality Analyses

Parameter	Untreated Water	Treated Water	DW Standard
pH	2.0	9.0	6.5-8.5
As	0.585	0.027	0.050
Cd	0.401	<0.001	0.005
Cu	0.555	0.002	0.150
Fe	146.029	<0.001	-
Pb	1.291	0.004	0.015
Zn	199.645	<0.001	5.000

Applying the SME Technology to an Abandoned Site in the Sierra Nevada Mountains

Utilizing the same method of slurry injection described above for Bunker Hill Mine application, the company executed an emergency response water treatment project at an abandoned mine site located in the Sierra Nevada Mountains of California. The project was completed for a client who was obligated under a Consent Order by the U.S. Environmental Protection Agency to treat several million gallons of ARD. The waters collected throughout the winter and spring in lined containment ponds which, upon overflow, would discharge into an adjacent freshwater stream. The purpose of the emergency response actiou was to preclude the occurrence of untreated overflow.

The site posed significant logistical challenges that made the possibility of mobilization and execution of traditional active treatment approaches unfeasible. The site lacked infrastructure and power supply, offered only limited access roads and staging areas for chemical storage and system layout, and presented extremely harsh weather conditions.

Due to the compact size of the KEECO K-250 slurry injection unit and the small footprint of the water treatment and sludge handling system, the SME technology offered a viable alternative to active chemical treatment at a site that previously had few options to economically accomplish such treatment objectives.

The complete system layout, in addition to the K-250 injection unit, consisted of a piping network, through which the influent water was pumped and treated with the KB-1™ slurry via an injection portal. After treatment with the KB-1™, the treated water continued discharged into a sequence of three 20,000-gallon FRAC tanks. The FRAC tanks served as retention zones for sludge settling and were connected to allow the treated decant water to weir over from tank to tank, providing a total of approximately 45 minutes retention time measured from the inflow point on tank 1 to the exit portal on tank 3. Water sampling occurred at tank 3.

The process of acid generation has beeu occurring at this site for decades and its environmental impact on the surrounding area have come under a great deal of scrutiny by the public, the local tribes, regulatory officials and other stakeholders. The acid waters collected within the lined pouds are generated from a number of sources including underground workings, seeps and surface runoff. Although they contain a host of metals and metalloids, in addition to a significant concentration of sulfate, the metals of focus for the project included only aluminum, arsenic, copper, iron and nickel. Furthermore, the stability of the sludge generated from the treatment process was of significant concern to the client as the expense of transporting the sludge off-site was prohibitive.

The results of the KEECO treatment process are listed in Table 2 for the regulated metals (dissolved conceutrations are shown). In addition, for those analytical runs that included testing for sulfate, the resulting data sets are reported as well.

Table 2 – Sierra Nevada Site Water Quality Analyses

Parameter	Raw Water Quality (mg L^{-1})	Sample #1 (mg L^{-1})	Sample #2 (mg L^{-1})	Sample #3 (mg L^{-1})
pH	2.5	9.5	8.8	7.5
Aluminum	1000	1.1	4.6	4.2
Arsenic	38	0.019	0.017	0.018
Copper	8.4	<0.02	<0.02	<0.02
Iron	2100	<0.1	<0.1	0.27
Nickel	22	<0.1	<0.1	<0.1
Sulfate	14,000	NA	NA	NA

The data clearly show that the treatment process successfully reduced the concentrations of the key metals by over 99.5%, most below detectable limits. Furthermore, the sulfate concentration was significantly reduced by as much as 87%.

The sludge generated from the treatment application was pumped from the FRAC tanks to lined containment vessels on-site. Several sludge samples were collected from each containment vessel. Each sample passed the TCLP Action Limits for all regulated metals, thereby offering the client a number of disposal options that are fiscally reasonable, eliminating the requirement to transport the sludge out of state for disposal at a hazardous waste repository.

SME as a Preventative Tool for ARD

At the request of a newly developing mining company in California, the SME technology is presently being evaluated for use as a preventative measure in mine tailings where the potential for ARD generatiou exists. This is considered theoretically possible through the addition of small amounts of the SME product to the tailings as they are produced, prior to waste deposition. Conceptually it should be possible to target and encapsulate the pyritic content before oxidation, preventing the autocatalytic cycle of acid generation. In addition, based on previous test work, SME product application to the tailings will further enhance soil fertility through the release of essential plant nutrients and provide a substrate more conducive to plant growth and a rolling programme of revegetation and eventual mine closure. The capacity to eliminate the potential for ARD from the outset offers a unique benefit to planning for closure and may substantially reduce potential risks and related bond requirements. Further trials utilizing the SME process to treat newly generated mine tailings will reveal the cost benefit and overall advantages of this technique as a preventive measure.

Conclusions

Understandably, the mining industry is relatively conservative when investing funds in new technologies or approaches. This reflects in part the low profit margin of many companies. However, as more stringent regulatory criteria are imposed and public awareness of environmental impacts of mining operations is increased, new technology must be incorporated into mine design and closure plans as it becomes available. Evidenced by the results of several mine water treatment projects, such those outlined from the Bunker Hill and Sierra Nevada Mine sites, it appears that the opportunity to utilize this technology to achieve the required criteria of an ever-increasing demand for better water treatment is a viable one. At the very least, it represents a substantive stepping-stone on the way to achieving new, more effective means to satisfy environmentally responsible mining practices.