Protection of ecosystem and human health via silica micro encapsulation of heavy metals

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Abstract: This paper briefly reviews the need for new technologies to address metal contamination and pollution and overviews some of the pathways linking contaminant sources and ecosystem and human targets. The principal focus of the paper is "inertisation" technologies in particular KEECO's Silica Micro Encapsulation (SME) process. This technology has been designed for the cost-effective remediation of metal, organic and radioactive contamination in solid and liquid phases. Through the silica encapsulation of metals and radioactive elements and oxidation of organic contaminants, SME produces clean water and an easily separable sludge that is chemically stable and leach-resistant. Similarly, soils, sediments and other wastes can be treated to destroy organic contaminants and render metals inert and non-leachable, usually in a single-pass treatment. Both liquid and solid media can be typically treated at a significantly lower total project cost when compared to standard technologies. Through the "inertisation" of metal-contaminated wastes, SME offers the prospect of breaking the pathways between contaminants sources and ecosystem and human targets, and this is explored in more detail using case studies describing SME treatment of acid rock drainage – an ongoing and major environmental and financial burden to the base, precious and coal mining sectors.

1 CONTAMINATION AND POLLUTION BY HEAVY METALS

A number of metals produced by industry (as valuable commodities or as by-products and wastes) have the potential to cause both short- and long-term impacts on human and ecosystem health. Impacts on human, faunal and floral populations result most often from exposure to metals dispersed into the natural and built environment. The regulated and unregulated chronic (long-term) and acute (short-term) release of metals from anthropogenic activity, alongside releases resulting from natural processes tends to result in their concentration in environmental media with a corresponding risk of increased bioavailability. Soils and sediments are both significant "sinks" for metals, while water and air represent important pathways for the dispersion of metals over extremely large areas and the most common direct cause of impacts on human and ecosystem health. Contamination and pollution by metals remains a widespread and growing problem in natural and built environments in industrialised and developing countries alike. Given that metals cannot be destroyed, the most appropriate form of environmental protection must ultimately consist of minimising their release (via regulated or unregulated routes) and their bioavailability.

In the absence of a continuous source, local air and water contamination by metals tends to be short-term, with concentrations generally returning to background levels via dilution, deposition, and dispersion pathways. In effect, these pathways form an indirect route to the contamination of soils and sediments in addition to the direct disposal or release of metal-bearing solids. Soils and sediments are prone to long-term contamination (in the absence of human intervention) via the physico-chemical fixation of heavy metals. However, while the "fixing" of metals is sufficient to retain metals for extended periods (e.g. decades, centuries or millenia) it is not perfect, and contaminated solids may give rise to contamination of surface and groundwaters long after the original contaminant source has ceased to exist.

Despite changes to industrial practices to prevent or minimize the quantity or toxicity of metals released there remains a need for effective removal of metals from contaminated and polluted waters, gaseous emissions and solid wastes. To prevent direct impacts and reduce pathways to sediment and soil contamination will therefore require the continuing development and implementation of new and improved in-process and end-of-pipe technologies. In water treatment it is anticipated that there will be a trend towards decontamination with use/reuse of the resultant clean water, both as a route to zero discharge, reduced costs and improved compliance with environmental regulations and to meet regional shortfalls in water as population growth continues. With respect to metals, few conventional water treatments meet the tenets of sustainable development or the concept of inter-generational equity (i.e. the policy of not passing environmental burdens from present to future generations). There is a large volume of available literature on the impacts of heavy metals on ecosystem and human health, but it is not the purpose of this paper to undertake a review of that literature. More germane is an overview of the direct and indirect *pathways* that link form links between contaminated media and human or ecosystem targets. From this, it is then possible to assess the opportunities to "break" these pathways and minimise and control the impact of heavy metals on ecosystem or human health.

2 PATHWAYS BETWEEN CONTAMINANT SOURCES AND HUMAN-ECOSYSTEM TARGETS

In broad terms, pathways can be subdivided into categories, with each category assigned principal targets, as shown in Table 1.

The significance of each pathway is dependent on the metal, its speciation, presence or proximity of targets, and other site-specific factors that may mitigate or aggravate any potential impact. Of great significance is the sensitivity of particular biotic species and detoxification mechanisms. Examples of pathways are shown in Table 2. It is important to note that multiple targets can be affected by a single source, and that humans are often not the ultimate target or "sink" for the metal. This list is by no means exhaustive and a large number of permutations, combinations and cycles are possible, for which the likelihood must be reviewed by use of appropriate risk assessment methodologies.

Many of the ecosystem and human health impacts of heavy metals result from the presence of metals in a bioavailable form (e.g. as simple dissolved or complexed aqueous species, or compounds liable to form such species). Therefore, the presence of heavy metals is not sufficient alone to cause potential health impacts – the *bioavailable* concentration is far more significant than the *total* metal concentration. Therefore, in dealing with heavy metal contaminants - whether in solid or liquid media - control of the bioavailability of the target metal of concern is the foundation upon

Table 1 Pathway categories and principal targets

Category	**Target**	**Example**
Soil ingestion	Children Livestock Adults Other fauna	Pica (deliberate soil eating) Soil consumption during grazing Consumption of unwashed root vegetables Consumption of roots
Pasture herbage	Livestock	Grazing cattle, sheep
Foodstuffs	Vegetables Cereal crops Meat and fish products	Surface contamination, uptake in tissue Uptake by shoots Bio-concentration in specific organs
Water	Human consumption Livestock consumption Vegetative uptake Other fauna/flora	Potable water Potable water Uptake from pore water Ingestion
Dust ingestion	Human Livestock	} Ingestion of airborne particulates
Dust inhalation	Adults Children Livestock Other fauna	} Inhalation of airborne particulates
Dermal absorption	Humans Other fauna	} Contact with contaminated water

Table 2 Examples of target/pathway interactions

Source	***Pathway***	**Target**	***Pathway***	**Target**	***Pathway***	**Target**
Soil	*Porewater*	Vegetation	*Consumption*	Herbivores	*Milk /meat*	Humans
Water	*Ingestion*	Herbivores	*Milk/meat*	Humans		
Soil	*Porewater*	Vegetation	*Consumption*	Humans		
Water	*Consumption*	Humans				
Air	*Inhalation*	Humans				
Soil	*Ingestion*	Humans				

which design of remedial action should be based (while the other foundation is the prevention of potentially harmful metal releases through the implementation of cleaner technologies and environmental management). In a world where the concept of sustainable development is becoming integrated with other business activities, any remedial action must consider the ultimate fate of the metals (e.g. are metal contaminants merely transferred from one site to another, or from one environmental medium to another, such as land disposal of metal-bearing water treatment sludges). To genuinely promote inter-generational equity today's environmental issues must be addressed today - it is no longer acceptable to create clean water or land by transfer of contaminants to other environmental compartments in a form that will remain or become a problem for future generations.[1] The dominant water and solid phase metal treatment technologies (lime-based precipitation and landfill disposal respectively) do not meet the needs of future generations, and offer only a limited scope for "breaking" the pathways between contaminant sources and ecosystem or human targets.

As an alternative, "inertisation" technologies seek to address the limitations of current treatment systems - the key concept that unifies a broad range of approaches is that of placing the heavy metal(s) of concern in a form where the long-term bioavailability is controlled or minimised. A number of technologies exist at conceptual, research and development, pre-commercial and commercial stages, based on changing the chemical or physical form of the metal. These include physical solidification or stabilisation using cementitious or pozzolanic materials, high temperature vitrification, and chemical treatment (oxidation, reduction, precipitation or formation of specific mineral phases) to alter the toxicity or mobility of the metal.

However, KEECO's *Silica Micro Encapsulation* technology is unique in that it uses silica - one of the most inert natural substances - to minimise the bioavailability of heavy metals in waters, soils, sediments and other solid and liquid phases, and it is on this technology that the rest of the paper will focus.

3 SILICA MICRO ENCAPSULATION

KEECO developed the Silica Micro Encapsulation technology to do precisely what the name implies – it encapsulates metal-bearing species in an impervious microscopic silica matrix that prevents the metals from migrating or otherwise adversely affecting human health or the environment by minimising bioavailability. SME is achieved by the addition of KEECO's proprietary reagents - KB-1™ for liquid phases and KB-SEA™ for solid phases. These are calcium/silica-based powders composed of several chemically active groups, chemisorbed into an inert matrix, which activate on exposure to moisture. They

[1] Clearly pollution prevention and waste minimisation also have a major role to play in achieving sustainable development goals, but do not address contamination and pollution that has already occurred, and do not totally prevent the discharge of metals in many sectors (of which mining is a principal example).

are introduced to solid and liquid phases as either dry powder or slurry, depending on site-specific factors and the nature of the medium being treated.

SME normally achieves the control of heavy metals in a single step in both solid and liquid phases, without the need for pre-treatment or post-treatment. The reaction begins with pH adjustment that initiates the precipitation of heavy metals from water (including pore water in solid media) and conditions metal-bearing surfaces in solid phases. Once the metal species have been precipitated or conditioned, three-dimensional encapsulation by silica follows. The microscopic encapsulating silica matrix contains no fissures or fractures, completely isolating the metal species from the surrounding environment. The encapsulated metal is environmentally benign and resistant to degradation under even extreme environmental conditions.

SME is a very robust technology that has been demonstrated to work effectively on heavy metals (e.g. chromium, copper, lead, mercury and zinc), metalloids (e.g. arsenic), and radionuclides (e.g. uranium). It can be applied to surface and groundwaters (including acid rock drainage), wastewaters, sediments, sludges, soils, mine tailings, and other complex solid and liquid media. In addition to the control of metals, SME chemicals reduce dissolved solids (such as sulphates) and degrade hydrocarbons (e.g. petroleum derivatives) and certain other organic chemicals through a high-energy oxidation process.

Figure 1 shows an example of the Silica Micro Encapsulation process, following the addition of KB-1™ to a synthetic copper-contaminated water at pH 3 under laboratory conditions (i.e. ambient temperature and pressure, mixing by magnetic stirrer).

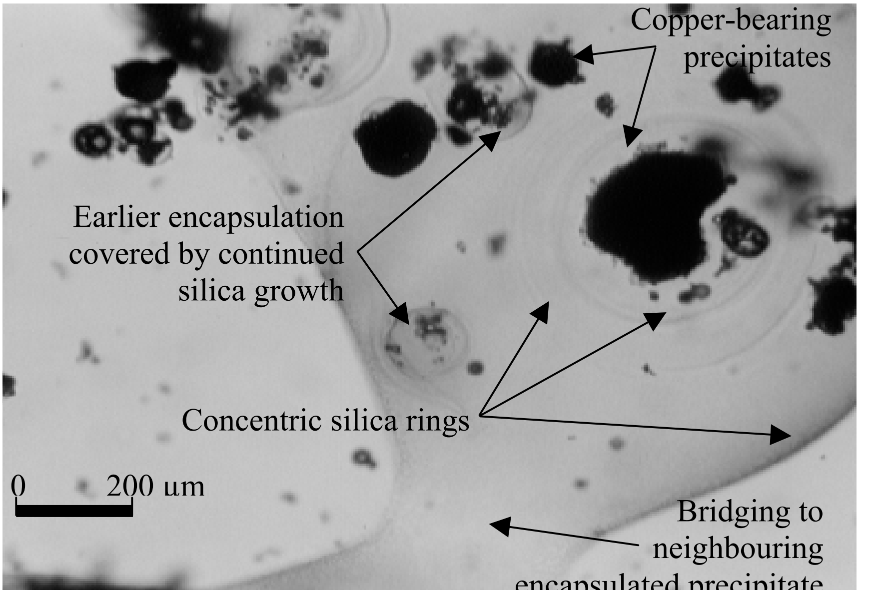

Figure 1 Silica Micro Encapsulation of precipitated copper species (optical microphotograph)

With regard to the pathways linking contaminant sources and human and ecosystem targets, SME causes "breaks" to occur via the production of leach-resistant solids (from the treatment of contaminated solid phases) and clean water and an inert metal-bearing sludge (from the treatment of contaminated aqueous phases). It can also contribute to the control of inhaled and ingested particulates by facilitating revegetation of previously phytotoxic wastes and soils.

Using acid rock drainage (ARD) as an example of contaminated water, the following section compares the SME technology with standard approaches on the basis of environmental and technical performance, and capital and operating costs, drawing on selected case study sites in the U.K. and U.S.A.

4 SME TREATMENT OF ARD - REAGENT DELIVERY AND MIXING SYSTEMS

SME was initially developed for the treatment of ARD in the early 1990s, and while the applications of the technology have widened to include many other contaminated solids and liquids, the treatment of ARD remains a major focus, particularly in the USA. SME offers all the positive characteristics of liming (e.g., the capacity to respond to variations in flow and target metals, degree of contamination, capacity to treat highly acidic waters, and performance that is independent of temperature) but none of the drawbacks. In general, SME will out-perform traditional precipitation in terms of: Lower capital costs.

- Lower operating costs due to less chemical reagent(s) required to achieve end results, lower power and operator time demands for the chemical delivery system and lower maintenance costs.
- Enhanced water quality, particularly evident at low-level metal concentrations.
- Elimination of aeration or other techniques typically required to achieve oxidation.
- Reduced volume of stable non-leachable sludge that settles quickly (without flocculents) reducing off-site disposal costs and potential long-term liabilities.
- Reduced health and safety risks, both from application and handling of the resultant treated materials.

High efficiency dosing and mixing of KB-1™ can be achieved using KEECO's patented K-series dosing systems based on dry chemical injection of KB-1 ™.

The K-10 ™ dosing system is a portable device designed to treat wastewater flows of approximately 10 gpm, while the K-500 ™ system is larger and treats flows of approximately 250 to 750 gpm. Both the K-10™ and the K-500 ™ consume very little energy (<0.4 and <2 horsepower, respectively) and, with minimal moving parts, require minimal maintenance. In both systems, untreated water enters the top of an inverted hemisphere mixing chamber through a spring-loaded valve, forming a thin film along the inner surface of the chamber (2-4 mm). Chemical is moved from the reagent hopper by a pH-controlled variable speed auger onto a rotating powder beater in the centre of the mixing chamber, projecting the chemical as a fine smoke-like dust into the thin film of water. With the high surface area and the fine pulverization of the chemical, contact between the contaminated water and SME chemical occurs immediately and the silica encapsulation process begins in the chamber. Upon leaving the unit, a retention time of only a few minutes is usually sufficient for the encapsulated metal-bearing precipitates to settle out before the treated water can be safely discharged. A schematic of the K-10 ™ is shown in Figure 2.

As an innovative technology competing with lime and other traditional precipitation methods for the treatment of ARD, SME has experienced the full range of obstacles associated with overcoming the reluctance to try a new and different approach. In addition, it has faced a number of challenges unique to the technology and the mining industry. For example, the available cost data on environmental projects is largely limited to soil and groundwater remediation technologies and does not address the treatment of surface drainage from mining activities. Also, since most conventional ARD treatment projects are conducted privately or with minimal regulatory oversight and control, publicly available data on liming costs is lacking. In addition, the data that is available usually fails to account fully for the capital costs, costs to run and maintain the treatment plant, and costs and liabilities associated with sludge handling, management and disposal.

However, despite these problems, SME has established a track record of performance – initially via laboratory treatability studies and then through pilot projects and commercial contracts. In the majority of situations, and when life cycle costs are considered, SME has proven more cost effective than lime or other traditional approaches to treating ARD and offers significant long-term advantages not available to standard treatment technologies.

5 COMPARISON WITH EXISTING TECHNOLOGIES

Sludge handling and disposal is perhaps the most cost-intensive aspect of ARD treatment. For a liming operation that often produces high volumes of characteristically low-density sludge, these costs can rapidly become unmanageable. Therefore, use of additional equipment and manpower is required to thicken, de-water and handle the sludge. As evidenced from a number of field-scale treatment projects, the sludge volume generated from the SME process is typically one-third of the volume generated from a liming application.

In addition, results of preliminary test work from both bench and field treatment of ARD with the SME reagent has indicated a potential for selected metal recovery from certain streams. In a field test using a two-stage application of SME reagent to treat a 400 – 500 gpm stream of ARD emanating from the Bunker Hill Mine in Idaho, the second stage sludge was subjected to SEM analysis. Results showed that the sludge carried a zinc concentration of 33% by weight, supporting the feasibility of offsetting water treatment costs via selective metal recovery.

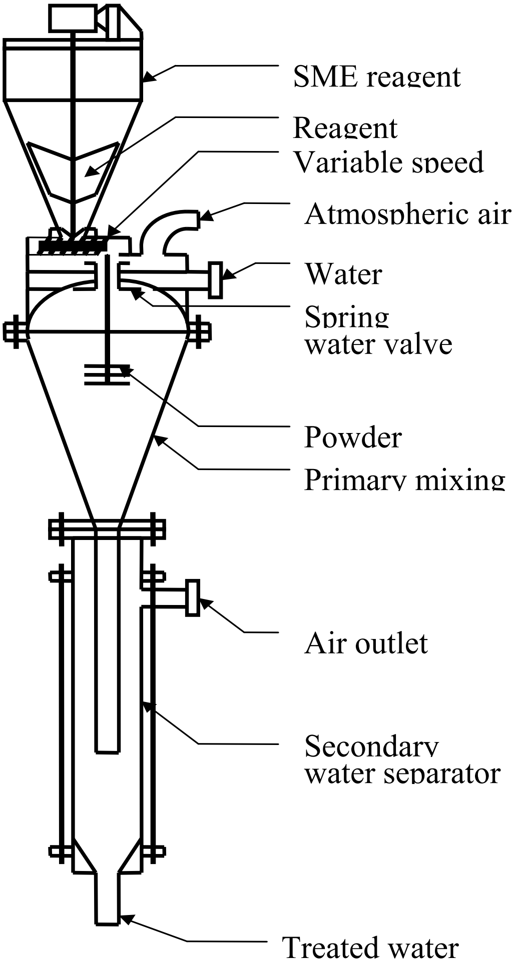

Figure 2 Schematic of K-10™

Retention time required for sludge settling using SME is significantly reduced relative to liming and does not require flocculants and/or polymers to achieve efficient separation. In past projects using SME chemical reagents to treat ARD at flow rates from 15 gpm to 800 gpm, retention time required for settling and clarification ranged from 4 to 22 minutes. Flocculants and polymers were not required. Sludge density ranged from 9 to 44 percent solids. The expense of flocculent and polymer reagents, associated labour, power and equipment capital and operating/maintenance associated with their delivery was eliminated.

In addition, the SME technology offers the unique advantage with respect to sludge stability and may reduce or eliminate potential liability related to future metal remobilisation. Such liabilities are difficult to quantify from site-to-site but are clearly evident in many well-documented and highly publicized examples. Perhaps the greatest cost of such liabilities is felt within the mining industry as a whole, as public perception of the industry is one of mistrust and fear of permanent ecological damage. The improvements offered by the SME technology such as enhanced water quality, lower sludge volumes, increased sludge stability and lower cost treatment systems are necessary steps towards improving the environmental practices of the industry and its public perception, while reducing the life cycle costs of achieving effective ARD treatment

Water quality has a direct impact on the costs of a selected water treatment system and its overall operation. For example, a broad range of metals contamination is typical of any ARD stream and often necessitates a multi-stage treatment process in order to precipitate some metals at a higher pH without re-dissolving those that precipitate at a lower pH. Incorporating multiple stages into any water treatment project has significant impacts on costs, and in particular, on labour expenses. Furthermore, precipitating metals at a high pH typically necessitates the use of additional chemicals for "end of pipe" pH adjustment prior to discharge.

The SME process has a proven capacity to accomplish complete ARD treatment in a single stage on streams that require a multiple stage approach using traditional precipitation reagents. In addition, once the SME-treated decant waters are separated from the resulting sludge, the pH of the effluent naturally equilibrates to neutral levels. This was evident on the Leviathan Mine site in 1998 where pH 2.0 ARD water with a high concentration of arsenic was treated with the SME reagent in a single step to a pH approaching 10.0 in order to achieve precipitation of all target metals. At the high pH, the arsenic concentration did not exhibit any tendency to re-dissolve and, once separated from the sludge, the effluent waters equilibrated to a pH of 6.5 to 7.0. Treatment occurred at rates ranging from 300 – 600 gpm. Lime treatment on the Leviathan Mine waters requires a multi-stage introduction to achieve similar water quality.

6 CONCLUSIONS

As metals cannot be destroyed under normal circumstances, KEECO considers "inertisation" of wastes to a new chemically and physically stable form the most appropriate tool to complement the growing application of pollution prevention initiatives. The generation of a durable, inert waste aids the process of long-term ecosystem and human health protection by ensuring that the encapsulated metals remain non-bioavailable and effectively immobilised. Of the standard and "inertisation" technologies commercially available, KEECO's is the only process that uses silica – one of the least soluble natural materials. The SME technology is unique in its permanent encapsulation of metal contaminants, which greatly reduces or eliminates the need for costly hazardous waste disposal and the environmental liabilities associated with future remobilisation of metals. Under most conditions, the capital, operating and life cycle costs of SME treatment are lower – and sometimes by an order of magnitude or more – than conventional methods for addressing metals contamination.

The mining industry is relatively conservative when investing its funds in new technologies, which reflects in part the low profit margin of many companies in this sector. However, as more stringent regulatory criteria are imposed and public awareness of environmental impacts of energy and mining operations increases, new technology must be incorporated into project design and closure plans. Evidenced by the successful results of several large-scale field applications, the SME technology represents an opportunity to meet the ever-increasing demand for better treatment of metal-contaminated wastes. It represents a substantive stepping-stone for industry to use in the course of strengthening its commitment to more environmentally responsible mining and related waste management.

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Ochrona ekosystemu i zdrowia ludzkiego poprzez mikrokrzemową hermetyzację metali ciężkich

Paul Mitchell, Amy Anderson & Clive Potter

Streszczenie: Artykuł krótko omawia zapotrzebowanie na nowe technologie do walki z zatruwaniem i zanieczyszczeniem metalami, jak również związki między źródłami tych zatruć a ekosystemem i celami społecznymi. Artykuł skupia się głównie na technologiach „inercyjnych", zwłaszcza na procesie KEECO hermetyzacji krzemem (SME). Technologię tę opracowano dla celów zapobiegania - niskim kosztem - zatruciom metalami, związkami organicznymi i radioaktywnymi w ciałach stałych i płynnych. Dzięki krzemowej hermetyzacji metali i pierwiastków radioaktywnych oraz utlenianiu zanieczyszczeń

organicznych, SME produkuje czystą wodę i łatwo wydzielający się szlam, który jest stabilny chemicznie i odporny na wypłukiwanie. Podobnie postępuje się z glebami, osadami i innymi zanieczyszczonymi substancjami, w których niszczone są substancje skażające i wytrącane metale, zwykle w jednym procesie oczyszczania. Tą metodą oczyszcza się zarówno ciecze jak i ciała stałe, przy znacznie niższych kosztach w porównaniu z innymi technologiami. Przez zobojętnianie („inertyzację") odpadów zanieczyszczonych metalami, SME daje możliwość przerwania dróg przepływu pomiędzy źródłem zanieczyszczenia a ekosystemem i wpływem na organizmy ludzkie. Problem ten jest przedstawiony bardziej szczegółowo w przypadku kwaśnego drenażu skał, który stanowi główne środowiskowe i finansowe obciążenie dla górnictwa kruszcowego i węglowego.