OPTIONS FOR THE STABILIZATION OF SLUDGES FROM ACID MINE DRAINAGE WATER TREATMENT PLANTS

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1.0 Introduction

Acidic metalliferous effluents produced as a result if mining activities have been treated in a variety of ways in order to minimize pollution of local surface and ground waters. Treatment techniques range in complexity and cost from methods such as simple dilution or sedimentation, coagulation or flotation of particulates, control of pH by lime addition, aeration or ozone oxidation, thickening, implementation of passive wetland systems, reverse osmosis or ion exchange, to chemical fixation and physical encapsulation. Depending on the site characteristics, chemistry of the effluent to be treated and disposal options available, one or a combination of these techniques may be utilized. These treatment techniques have proven quite successful for treating acidic, metalliferous effluent (ARD), however many of the techniques create another waste form, or sludge.

2.0 Water Treatment Sludges

Water treatment sludges typically consist of amorphous hydroxides, gypsum, and absorbed metals in an alkaline slurry which are much more manageable in comparison to ARD. Typically, sludge is dewatered whereby the alkaline, metal-poor solution can be decanted and released into local streams or recycled to the mill if it is still operating, but the solids content of the sludge must be disposed of or further treated. In other words, the sludge produced during water treatment must be stabilized to prevent its re-release to the environment. A review of water treatment sludge characteristics and alternatives for sludge stabilization are presented in this paper.

The Mining and Mineral Sciences Laboratories at CANMET have studied the characteristics of water treatment sludges produced by the Canadian Mineral Industry (Zinck, 1997). They determined that water treatment sludges in Canada typically range between 2% to 32% solids, range in pH from 8.2 to 10.8 and in dry density between 1.8 and 3.3 g/cm^3. They are comprised of one or two dominant hydrated amorphous phases that collect metals present in the effluent, they contain calcium in the form of gypsum, calcite, and/or bassanite, and often contain minor detrital silicates and/or sulfides. The stability of these sludges depends on the stability of the amorphous phases within them, and both the stability and the density have been found to improve somewhat with age.

There are various treatment systems employed by the mining industry to treat ARD, these systems range from relatively simple systems to more complex treatment methods. A typical Canadian system is illustrated by that at the Equity Silver Mine in British Columbia, where a lime slurry is added to the mine effluent in order to raise the pH to levels around 8.0 to 8.5. The neutralized slurry is then discharged to settling ponds where metals precipitate as metal hydroxide sludges. The treated supernatant is decanted to holding ponds and the dewatered sludge is ultimately disposed of in their Main Zone Pit (Aziz and Ferguson, 1997).

Many of the recently designed treatment systems have gone from methods such as that described above to ones that produce a High Density Sludge (HDS). These methods involve mechanical thickening and/or sludge recycling. An advantage to this technique is that less volume of sludge is produced which in many areas is a major consideration.

A high density sludge is produced at the Iron Mountain Mine in California, USA where topographic relief is such that large dewatering ponds are not feasible.

At the Geco Mine in Ontario, Canada, a treatment system has been developed to produce a high density, low viscosity sludge. In this process, the ARD effluent comes in contact with recycled sludge, this promotes both precipitation of metals onto the surface of the recycled solids and densification of the slurry. A lime slurry is then added and aeration provided to precipitate ferric hydroxides. The treated slurry is put through a clarifier with a flocculent added in order to separate the liquid from the sludge. At Geco, the sludge is pumped over 2 km for disposal in the abandoned underground workings of the mine thereby necessitating low viscosity sludge characteristics (Aubé and Payant, 1997).

The GYP-CIX process is a desalination water treatment technique that uses counter current ion exchange resins to remove metals, radionuclides and sulfate from lime treated ARD effluent (Robertson et al., 1993, Robertson and Rohrs, 1995, Gussman, these proceedings). The process involves fluidized cation and anion ion exchange technologies whereby the ion exchange resins can be regenerated easily and inexpensively. The sludge produced is gypsum-based.

The same company that developed the GYP-CIX process has also developed a GYP-MET process also based on ion exchange resins. This process can be used to remove metals from acidic waters as a separate, low volume sludge for disposal or for sale for additional revenue (Gussman, these proceedings). Once the metals are removed, the remaining sulfate-rich effluent can be treated via the GYP-CIX system producing an inert gypsum sludge that may also be of resale value.

Since water treatment techniques often necessitate a high cost to mining companies for long periods of time, it is advantageous to try to treat the effluent so as to recover some of the metals and offset the cost of treatment. Therefore, for both economic and environmental reasons, systems that can recover the metals from the effluent are attractive to the mining industry. Another example of a system used whereby economic metal recovery is possible has been proposed at Mount Lyell in Western Tasmania, Australia. A solvent extraction/electrowinning (SX/EW) process has been proposed for this site to recover copper. This process would be used in conjunction with a conventional neutralization technique to treat the ARD effluent. The SX/EW recovery of copper would therefore help offset the cost of lime requirements (Miedecke et al., 1997).

Relatively recently, biotreatment technologies have also been developed to treat ARD effluent and recover metal. These techniques utilize sulfate reducing bacteria to convert sulfate to sulfide. For example, NTBC Research in British Columbia, Canada has developed a combined biological-chemical treatment process to remove copper, zinc and cadmium as metal sulfides (Rowley et al., 1997). A similar process was developed at the Royal School of Mines in London, UK that uses a consecutive hydroxide sulfide precipitation technique with biogenerated hydrogen sulfide to precipitate metal sulfides from the effluent (Diaz et al., 1997).

Uranium producers have the added task of radionuclide removal from their ARD effluent. Radionuclides can be removed from effluent by ion exchange (as seen in the GYP-CIX process) or via chemical treatment. For instance, at Wismut, barium chloride is added to the effluent during treatment to induce the precipitation of barium sulfate and subsequent removal of radium as $Ba(Ra)SO_4$. Uranium is also removed during treatment by the addition of a specific polymer that binds the uranium at a controlled pH (Robertson GeoConsultants Inc., 1997). The resultant sludge, as with many water treatment sludges, must be further stabilized and/or disposed of as a hazardous waste.

3.0 Sludge Stabilization Alternatives

Most sludge stabilization techniques are based on the same general principles as water treatment techniques, such as neutralization reactions, oxidation/reduction reactions, physical entrapment, chemical fixation, binding, and disposal. These general principles must be adapted to the specific waste and site specifications that are dependent on chemical and physical characteristics of the waste, locale, and waste disposal requirements established by law, regulations and economics.

The term stabilization has been used in various ways throughout the literature with respect to waste treatment. Sometimes it has referred to a particular process, sometimes only to chemical stabilization and other times has been used as a general word for the overall "fixation" of a waste. In this paper, stabilization has been used in the general sense to define an overall procedure whether physical, chemical, or both. Stabilization immobilizes heavy metals and radionuclides present in a waste, decreases the surface area and permeability of the waste being treated and/or involves safe disposal or placement of the waste. The objective of stabilization, regardless of the specific method chosen, is to "fix" the waste so that it remains at its location of deposition and migration from there into the environment is minimized. The environment has a finite assimilative capacity for any contaminant and the objective of minimization is to maintain long term releases to levels less than this value.

Stabilization may be either physical or chemical. Physical stabilization is required to prevent particular (solid) transport of contaminants into the environment and may be used to prevent water flow, which provides a soluble contaminant transport mechanism to, from or through the sludge. Chemical stabilization prevents dissolution, hence water transport, of contaminants from sludges subjected to surface or groundwater leaching.

3.1 Chemical Stabilization Methods

Chemical stabilization methods involve the addition of a reagent, or binder, to the waste, in this case sludge. These methods must be tailored to the specific chemical and physical characteristics of the sludge as well as site conditions. The quantity of binder to be added is crucial, as is the compatibility or reactivity of the sludge and the binder, the level and character of contamination that might be introduced to the binder, the possible interferences present in the sludge and the chemical binding properties of specific contaminants. There are six major groups of stabilization methods, as defined by the U.S. EPA, that can be adapted for site specific waste forms (Cullinane et al., 1986, Robertson GeoConsultants Inc., 1997).

3.1.1 Sorption Techniques

Sorbents are commonly applied to semisolid materials such as sludges to produce a low strength solid. Common sorbents are nonreactive materials such as celite, clays and zeolites that interact with and immobilize small, polar molecules like water or other ions. The sorbents chemically bind these ions by incorporating them into the sorbents atomic structure, absorption onto the sorbents surface, or retention in the sorbents pore spaces

3.1.2 Lime-based (Pozzolanic) Techniques

Another stabilization method involves the use of a combination of finely divided, noncrystalline silica (pozzolanic materials), for example fly ash, cement-kiln dust, diatomaceous earth, chert or certain tuffs, and calcium, in the form of hydrated lime. When the silica and calcium are added to the sludge, the result is a solid mass of calcium silicate and aluminum hydrate bonds that act to entrap the sludge creating a pozzolan-concrete-waste mixture.

3.1.3 Cement-based Techniques

Cement-based techniques are similar to, but considered more durable than, the lime-based techniques described above. They consist of Portland cement, used as a binding agent, and fly ash or other pozzolanic materials mixed into and solidifying the sludge. The result is a stronger type of sludge/concrete composite with excellent strength and durability. This type of stabilization is considered to be the most versatile and adaptive technique.

3.1.4 Thermoplastic Techniques

Thermoplastic techniques involve the blending of fine particulate waste with melted thermoplastics such as asphalt, polyethylene, polypropylene, wax, bitumen or sulfur polymer, which when cooled will harden.

3.1.5 Polymeric Techniques

This is a three-step technique, firstly a monomer is added to the sludge and thoroughly mixed, then a catalyst is added and mixed, and lastly the entire mixture is transferred to a container where it hardens. Common polymeric materials used include polyethylene and paraffin based agents (Holcomb, 1979), polyester-styrene, styrene-trimethylol-propane trimethacrylate (TMPTA) (Heiser and Colombo, 1990) and a sulfur polymer cement (Darnell, 1994). The long chained polymeric molecules trap the waste.

3.1.6 Encapsulation Techniques

The encapsulation technique isolates larger masses of waste using a jacketing, or encapsulating material such as 280 L drums or powdered polyethylene that is fused over a block of waste by applying heat and pressure. This method is commonly used in conjunction with other stabilization techniques and serves to overcome the shortcomings other techniques may have.

3.1.7 Cost Comparison

A cost comparison of the primary methods of chemical stabilization is given first in terms of reagent costs and secondly in terms of treatment operations. The comparison is by necessity extremely general since specific site and/or waste characteristics may increase the cost severalfold.

The reagent costs include purchase cost, transportation of reagents, and storage and handling onsite. The greatest of these factors, and possibly most variable between methods, is the purchase cost. Table 1 gives the typical costs of chemicals used for various stabilization/solidification techniques. The costs have been escalated from 1983 U.S. dollars to 1997 U.S. dollars based on a 3% per annum rate of inflation.

Table 1: Common Reagent Costs.

Chemical	Cost Range (in 1997 U.S. dollars)
Portland cement[a]	\$60-\$100 /ton (bulk)
Portland cement[a]	\$105-\$130 /ton (bag)
Quick lime (CaO)[a]	\$70-\$85 /ton (bulk)
Hydrated lime ($Ca(OH)_2$)[a]	\$70-\$85 /ton (bulk)
Hydrated lime ($Ca(OH)_2$)[a]	\$90-\$115 /ton (bag)
Cement kiln dust[a]	\$8-\$38 /ton
Waste quick lime[a]	\$6-\$15 /ton
Fly ash[a]	\$0-\$60 /ton
Gypsum[a]	\$0-\$53 /ton
Sodium Silicate[a]	\$0.08-\$0.30 /pound
Concrete admixtures[a]	\$2.25-\$14.00 /gallon
Polyester resin[b]	\$9000-\$10,000 /ton

[a] From Cullinane et al. (1986)
[b] From Donato and Ricci (1990)

In 1986, the U.S. EPA calculated the cost estimates for five common S/S treatment alternatives on the basis of treatment procedures assuming the same reagent type, project duration, and mobilization costs for each technique. Although the costs are specific to waste characteristics, site characteristics, and disposal options, these estimates may be used as a comparison to each other. The overall costs for five common treatment methods are given in table 2, details of these cost estimations can be found in Cullinane et al. (1986). The assumptions made in all cases were: 2,850 tons of waste was treated with 30% Portland cement and 2% sodium silicate with onsite disposal; costs include only those operations necessary for treatment. As was done with the costs for reagents, these costs have been escalated from 1986 U.S. dollars to 1997 U.S. dollars based on a 3% per annum rate of inflation.

While the processing techniques and reagent usage may not be directly applicable or appropriate to acid mine drainage treatment sludge, it provides some idea of the relative costs of "batch" treatment by various techniques. Total costs per ton are all relatively high compared with physical stabilization methods reviewed in the next section of this paper and accounts for the tendency for the mining industry to seek more cost effective physical stabilization methods.

Table 2: Comparative Summary of Relative Costs for Treatment Alternatives.

Parameter	In-drum mixing	In-situ mixing	Plant mixing: Pumpable waste	Plant mixing: unpumpable waste	Area Mixing
Metering and mixing efficiency	Good	Fair	Excellent	Excellent	Good
Processing days required	374	4	10	14	10
Cost/ton					
Reagent	$28.50 (9%)*	$28.50 (63%)	$28.50 (53%)	$28.50 (42%)	$28.50 (49%)
Labor and per diem	70.69 (23%)	1.88 (4%)	5.30 (10%)	9.59 (14%)	8.79
Equipment rental	51.41 (17%)	1.91 (4%)	5.44 (10%)	10.44 (16%)	5.63 (10%)
Used drums @$11/drum	66.69 (21%)	-	-	-	-
Mobilization/ demobilization	21.70 (7%)	2.19 (5%)	1.98 (4%)	3.12 (5%)	1.66 (3%)
Cost of treatment process	$238.99	34.48	41.22	51.65	44.58
Profit and overhead (%30)	71.59 (23%)	10.31 (23%)	12.33 (23%)	15.46 (23%)	13.33 (23%)
TOTAL COST/TON	$310.69	44.79	53.55	67.11	57.91

* % of total cost/ton for that alternative.
From Cullinane et al. (1986)

3.2 Physical Stabilization Methods

Physical stabilization techniques, similar to encapsulation techniques, can be used as the primary stabilization technique as well as to compensate for inadequacies of chemical stabilization methods. The more common of these methods are described in this section and have been classified as either "dry" techniques or "wet" techniques.

3.2.1 "Dry" Techniques

The physical stabilization methods that can be classified as "dry" techniques are those in which the waste is disposed of, or placed, above the water table. Dry Techniques are derived primarily from currently accepted and well understood landfill technologies. These techniques include the use of evaporation ponds, drying by means of mechanical drying or freeze drying and filtration. Once dried, sludges of this type are typically placed in a landfill, disposed of above the water table in an open pit, or underground, or placed with other forms of waste such as tailings or on top of waste rock.

Disposal above the water table provides isolation from groundwater leaching. If there is no existing natural geological liner in places where dry waste disposal is considered, then placement of a synthetic liner is mandatory. Deterioration of the liner is a fundamental concern in these environments. Liner degradation may result in contamination of local surface or ground waters. Advective flow is the primary transport mechanism whereby contaminants may be transported to either the surface water or groundwater whereas if the waste is disposed of underwater, the much slower diffusive flow is the primary mechanism.

Infiltration remains as a source of leach water, thus the permeability of the waste or the requirement of an "impermeable cap" become an essential part of the physical isolation. Over the very long term leaching of the waste is controlled by the cap or cover. Infiltration passing through the cap must inevitably be released to the environment, regardless of the quality of the liner, since "storage" above the liner is limited. The "stability" of the "system" is therefore dependent on the stability of the cap under the perpetual attack of wind and water erosion, burrowing activities of animals and man, frost, root action etc. Being located above the water table increases the potential for both erosion (of surface mounds) and increases the hydraulic gradient driving infiltration through the waste.

3.2.2 "Wet" Techniques

Wet Techniques are those in which the waste is disposed of below the water table and is a much more recent, and less widely accepted concept than that of "dry" technologies. Until relatively recently, waste disposal technologies aimed to isolate and contain the waste source as far away from groundwater or surface water as possible, however, these techniques often carry with them great risks if the system is flawed. These risks, in certain circumstances may be greatly reduced by disposal below the water table.

The objectives of "wet" techniques are to isolate the waste from physical effects of surface water erosion and hydraulic gradients, and from oxygen, all of which are difficult if not impossible via "dry" techniques. While solubility of contaminants in groundwater remains a concern, the potential for these contaminants to travel away from the source can be minimized by physical controls minimizing the hydraulic gradients.

It is therefore an objective of "wet" disposal to achieve site hydrologic controls which minimize the hydraulic head through the waste deposit. This can be achieved if the permeability contrast between the waste and the surrounding materials is sufficiently high.

This gives rise to the "permeable surround" design concepts that have been used to prevent contaminant migration from deposits such as the tailings in the Rabbit Lake in-pit tailings depository in Saskatchewan. The concept is shown in Figure 1.

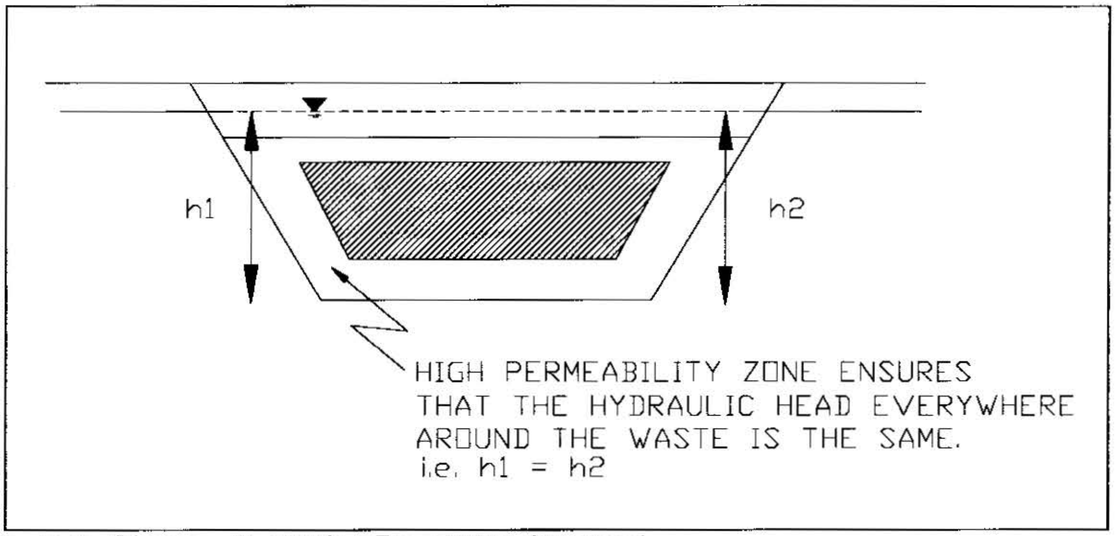

Figure 1: Diagram Illustrating Permeable Surround

Since acid mine drainage collection and treatment implies a very long term active interaction with the site, consideration is now also given to the maintenance of artificially induced hydraulic gradients to provide long term containment. This can be achieved by creating an inward gradient through the waste mass thus preventing outward migration of contaminants into the environment. The effect is illustrated in Figure 2. Pumping at relatively low rates may be adequate to establish such an inward flow and effectively producing a "hydraulic cage". Hydraulic cage techniques combined with permeable surround techniques can be used very effectively for contaminant migration control. Where initial placements of waste produce an initial "flush" of contaminants from the more readily leached perimeter of the deposit then the hydraulic cage effect may be required for only a period.

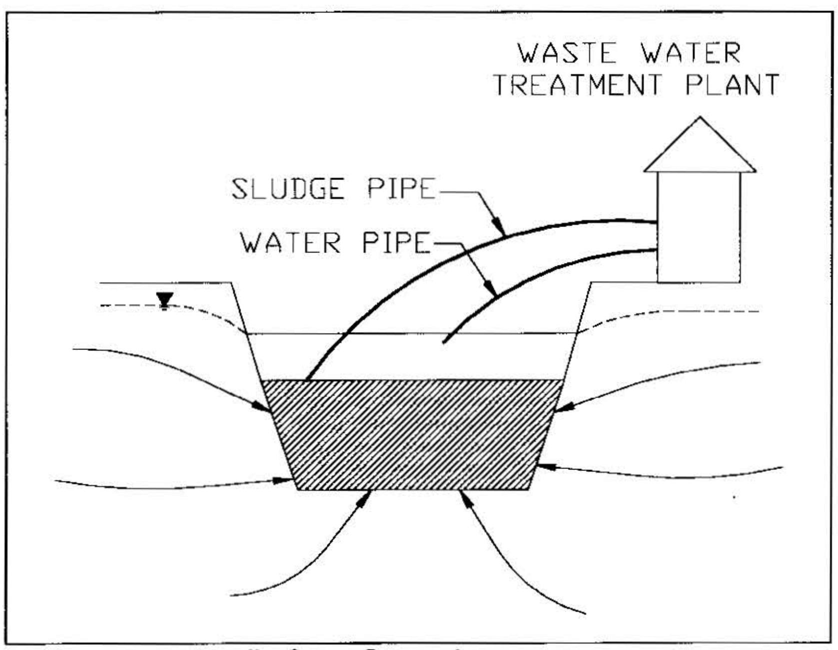

Figure 2: Schematic of Hydraulic Cage Scenario.

Determination of the leachability of potentially hazardous metals and radionuclides is typically done via two types of leaching tests. The first is the Toxicity Characteristic Leaching Procedure (TCLP) and the second is the ANS 16.1 method developed by the American National Standards (U.S. EPA, 1996). The leachability of soluble species such as chlorides, sulfates, and nitrates at some sites may also be important. Waste forms that have good metal leaching properties may exhibit poor containment of salts.

If advective flow, due to hydraulic gradient, is small, the primary flow mechanism of concern with respect to disposal underwater is diffusion transport of contaminants. In comparison to advective flow, diffusion results in low mobilization and slow transport of contaminants and in many cases can be controlled.

The placement of acid generating mine wastes in the Ronneburg open pit mine takes advantage of the effects of a natural permeable surround to reduce the effective rates of contaminant transport. Disposal of water treatment sludges (possibly in combination with chemical stabilization) in flooded open pit mines and underground mine workings is being considered and implemented more frequently as the advantages become more apparent.

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