Review of Disposal, Reprocessing and Reuse Options for Acidic Drainage Treatment Sludge

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EXECUTIVE SUMMARY

Sludge management is an ever-increasing issue as the inventory of sludge continues to grow through perpetual pump and treat. Current sludge management practices, in general, are ad hoc and frequently do not address long-term storage, and in some cases, long-term stability issues. While there are a variety of sludge disposal practices that have been applied, many have not been fully investigated and monitoring data on the performance of these technologies is limited and not readily available. Further research is required into disposal options that can recover metal, densify existing sludge or safely dispose of the material in a way such that it can be either easily reclaimed or disposed in mine workings. Promising options must be both technologically feasible and also cost effective. In addition, sludge management options must be able to meet increasing environmental standards and regulatory pressures.

This report contains a review of technologies related to the management of acidic drainage treatment sludges. The bulk of the report assesses technologies available for sludge management including conventional disposal technologies, reprocessing options for metal recovery, novel sludge reuse technologies and reclamation of sludge areas. The sludge management toolbox is limited. The knowledge gaps are identified and discussed, and recommendations are made for further work.

With such limited data available on sludge characteristics, standardized methods, and long-term laboratory and field performance, it is important to focus efforts to address some of these gaps in the knowledge base. Best practices for sludge management and standard testing methodologies need to be defined. The development of Sludge Management Guidelines is fundamental in ensuring that appropriate management options for sludges are implemented.

RÉSUMÉ

La gestion des boues est une question qui prend de plus en plus d'importance parce que le pompage et le traitement des boues en perpétuité continue d'en augmenter les quantités. Les pratiques courantes de gestion des boues sont en général ponctuelles. Dans certains cas, elles n'assurent pas la stabilité à long terme, et il arrive souvent qu'elles ne prévoient pas l'entreposage à long terme. Bon nombre des méthodes d'élimination des boues en usage n'ont pas été examinées à fond et les données sur leur efficacité sont peu nombreuses et difficiles d'accès. Il faut poursuivre la recherche dans le domaine de l'élimination des boues pour cerner des options qui permettent de récupérer le métal, de densifier les boues existantes ou d'éliminer les boues de façon sécuritaire de sorte qu'elles puissent être restaurées facilement ou déversées dans des galeries de mine. Les options prometteuses doivent être réalisables au plan technologique et efficaces en termes de coûts. De plus, les options pour la gestion des boues doivent respecter des normes environnementales et des règlements sans cesse plus exigeants.

Ce rapport renferme un examen des techniques liées à la gestion des boues de traitement du drainage acide. Le gros du rapport constitue une évaluation de techniques disponibles dans le domaine de la gestion des boues, notamment des techniques classiques d'élimination des boues, des options de retraitement permettant de récupérer le métal, de nouvelles techniques de réutilisation des boues et des techniques de restauration des bassins. La boîte à outils de la gestion des boues n'est pas très bien garnie. Les lacunes dans le savoir sont identifiées et examinées dans ce rapport, qui contient aussi des recommandations à l'égard de la poursuite des travaux.

On dispose de très peu de données sur les caractéristiques des boues, les méthodes normalisées et leur efficacité à long terme, tant en laboratoire que sur le terrain. Il est donc important de tenter plus que tout de remédier à certaines des lacunes présentes dans la base de connaissances. Il faut définir les pratiques exemplaires dans le domaine de la gestion des boues ainsi que les méthodes d'essai normalisées. Nous devons absolument disposer de lignes directrices sur la gestion des boues pour pouvoir mettre en œuvre des options appropriées dans ce domaine.

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INTRODUCTION

The treatment of acidic mineral effluents, such as acidic drainage (AD), acid mine drainage (AMD), acid rock drainage (ARD) and process water, is commonly accomplished through lime neutralization. This centuries old technology is effective in raising the pH of the water and precipitating the metals to below regulatory limits. However, one of the drawbacks with simple lime neutralization and chemical treatment in general is the production of a voluminous, hard to settle, metal laden sludge. The two principal challenges regarding acidic drainage treatment sludges are the volume of sludge generated and long-term chemical stability. As such, the management and disposal of these mining wastes requires careful consideration and planning. Unfortunately, limited data is available on sludge management practices and performance.

This report contains a review of technologies related to the management of acidic drainage treatment sludges. The detailed background section presents information on treatment processes, sludge characteristics and factors affecting sludge stability. The bulk of the report, contained in the section on options for sludge management, assesses technologies available for sludge management from conventional disposal technologies, to thought provoking reuse options. This is followed by a discussion on knowledge gaps and conclusions.

BACKGROUND

Acidic drainage and other acidic metalliferous effluents are commonly treated in the mining and metallurgical industries using lime neutralization. Upon neutralization, metals precipitate out of the effluent as hydroxides. This neutralization produces voluminous hydroxide sludges typically with low solids content (frequently < 5%). Despite recent improvements to the traditional neutralization method (Aubé, 1999;

Demopoulos et al., 1995; Dinardo et al., 1991; Flynn, 1990; Kuit, 1980; Kuyucak et al., 1991; Vachon et al., 1987), it is estimated that as much as 6.7 million cubic metres of lime treatment sludge is produced annually in Canada (Zinck et al., 1997) and this rate is expected to increase.

Basics of Chemical Treatment

Although many different biological and chemical technologies exist for treatment of acidic drainage, lime neutralization remains by far the most widely applied method. This is largely due to the high efficiency in removing dissolved metals through neutralization, combined with the fact that lime costs are low in comparison to alternatives. Lime treatment essentially consists in raising the pH of the acidic drainage to a point where the metals of concern are insoluble (Aubé and Zinck, 2003).

The principle of lime neutralization lies in the insolubility of heavy metals in alkaline conditions. By adjusting the pH to a typical set point of about 9.5, metals such as iron (Fe), zinc (Zn), and copper (Cu) are precipitated (Figure 1). The final pH set point can be higher or lower than 9.5 depending on the metal contaminants and concentrations in the water.

Lime dissolution is the first step of the neutralization process. For large treatment systems, quicklime is used. This lime must first be hydrated (slaked) and is fed to the process as a slurry. Occasionally dry lime is added directly to the waste stream, however this is the exception. Hydrated lime reacts or dissociates to increase pH. The following two equations illustrate these reactions:

$$CaO + H_2O \; ? \; Ca(OH)_2 \qquad (1)$$

$$Ca(OH)_2 \; ? \; Ca^{2+} + 2OH^- \qquad (2)$$

Hydrolysis reactions occur causing the metals present to precipitate as hydroxides. The following reaction shows the precipitation reaction with Zn as an example:

$$Zn^{2+} + 2OH^{-} \text{ ? } Zn(OH)_2 \quad (3)$$

Ferrous iron is among the metals to precipitate as per the above equation. Unfortunately, ferrous hydroxides are not as stable as ferric hydroxides when the sludge is exposed to acidic waters or natural precipitation. For this reason, aeration is often applied to oxidize the iron to the more stable form, as per the following equation:

$$Fe(OH)_2 + ½\, H_2O + ¼\, O_2 \text{ ? } Fe(OH)_3 \quad (4)$$

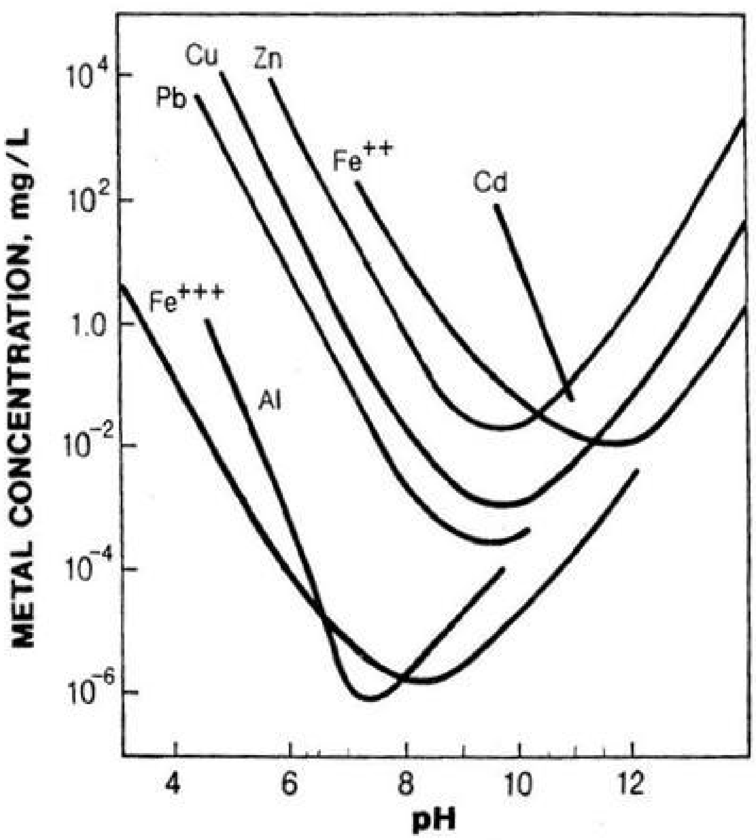


Figure 1 - Metal hydrolysis solubility curves.

A common by-product of lime neutralization is gypsum (calcium sulphate bihydrate). Gypsum precipitation occurs as acidic drainage is often rich in sulphate and the calcium added from the lime will bring the solubility product well above saturation. This reaction is often responsible for gypsum scaling in treatment processes. Gypsum is a major sludge component and contributes significantly to the volume of sludge generated.

$$Ca(OH)_2 + H_2SO_4 \; ? \; CaSO_4{\cdot}2H_2O \qquad (5)$$

Another common by-product of lime neutralization is calcium carbonate. The inorganic carbon for this reaction can either come from the AMD itself or be a result of carbon dioxide from air, which is dissolved during aeration. This carbon dioxide converts to bicarbonate and then partially to carbonate due to the high pH. The carbonate fraction will precipitate with the high calcium content of the slurry to form calcite (calcium carbonate). This calcite can play an important role in the stability of the final sludge product as it provides neutralizing potential to the sludge, as it is stored. It is also an indicator of the process lime efficiency: more efficient neutralizing processes will produce less calcite (Aubé and Zinck, 2003).

$$Ca(OH)_2 + CO_2 \; ? \; CaCO_3 + H_2O \qquad (6)$$

Treatment Processes

Three typical lime treatment processes are used in the industry and have been described in detail in the literature (Vachon et al., 1987, Zinck et al., 1997):

Basic. The basic lime treatment involves the addition of lime to a waste stream followed by solid/liquid separation in a settling pond (Figure 2). The lime is added to attain a pH suitable for precipitation of the heavy metals from the waste stream. Kidd Metallurgical Division (Timmins, Ontario) and Hudson Bay Mining and Smelting (Flin Flon, Manitoba) apply this type of treatment process. A higher pH setpoint is often necessary to ensure complete precipitation of metals throughout the pond. A low density sludge (LDS) is generated with 1-5% percent solids).

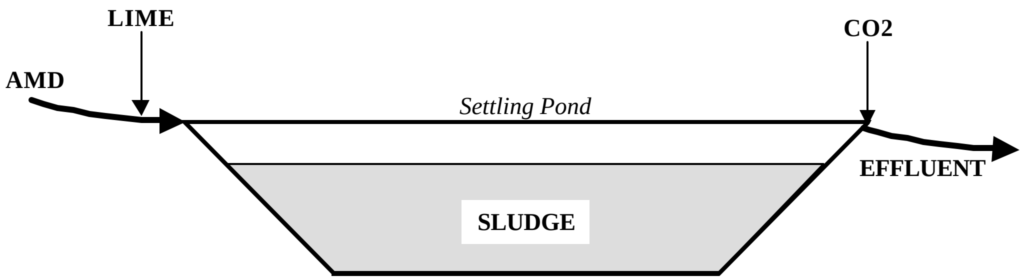


Figure 2 - Basic lime treatment process (Aubé and Zinck, 2003).

Conventional. Mechanically agitated reactors are used and lime addition is controlled by pH. The process provides good effluent quality. Reactor discharge is sent to sludge settling ponds or tailings ponds for solid/liquid separation. Percent solids generated range from 3-10%. This type of process is used at INCO (Sudbury, Ontario).

Basic and conventional treatment processes are commonly referred to as low density sludge (LDS) processes.

*High Density Sludge Process***.** Figure 3 describes the conventional High Density Sludge (HDS) process. The acidic drainage is generally fed into a Rapid Mix Tank (RMT), where it is contacted with a lime/sludge slurry to bring the pH of the combined slurry to 9.0 or 9.5. The RMT is often used to offer better pH control in the process, but is not necessary. The retention time in this vessel varies normally from 2 to 10 minutes. The Lime Reactor (LR) has a retention time typically ranging from 30 to 90 minutes. It should be noted that there are lot of different configurations of the HDS process. The flowsheet selection is governed by a lot of factors including acidity of the feed, flowrate, cost, etc. The flowsheet in Figure 3 was the original CESL (Cominco Engineering and Services Limited) design (Kuit, 1980) that has been modified.

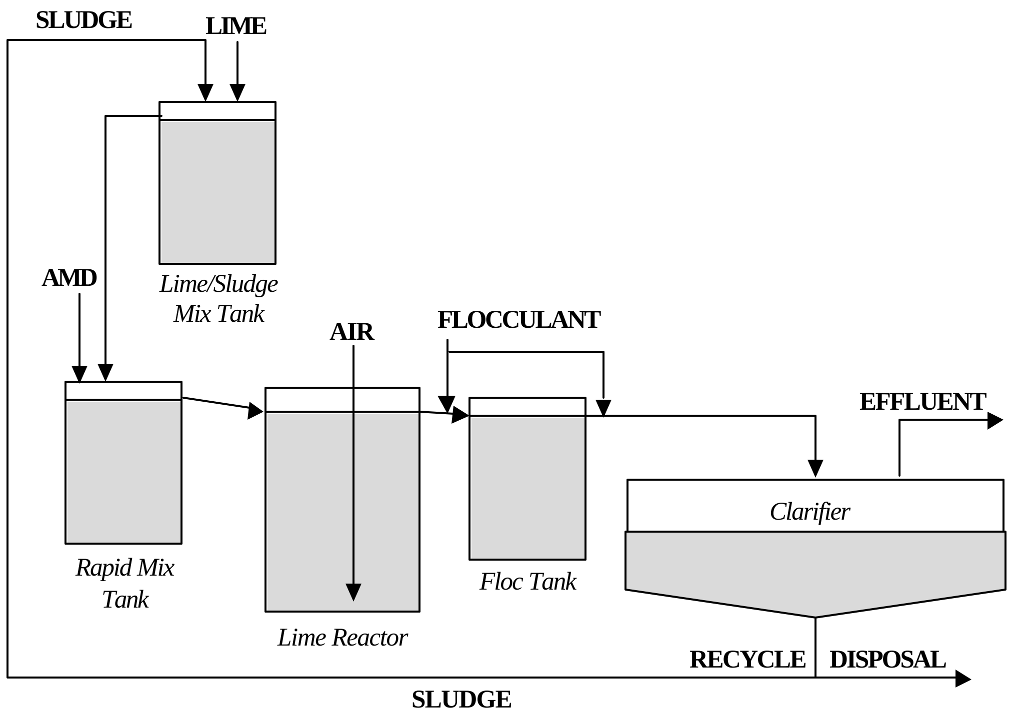


Figure 3 - Conventional high density sludge process (Aubé and Zinck, 2003).

Air is normally sparged in the LR for ferrous iron oxidation. The Floc Tank (FT) is used to contact the polymer to the precipitates for floc formation. A portion of the sludge from the clarifier underflow is recycled to the lime/sludge mix tank (L/S).

The feed rate and a pre-determined ratio of solids recycled to solids formed control the sludge recycle rate. The lime addition is controlled to keep pH at the desired setpoint, measured either in the RMT or the LR. Percent solids generated range from 15-30%. The High Density Sludge technology is used at various sites in Canada including Teck-Cominco's Sullivan site (Kimberley, British Columbia), Cambior's La Mine Doyon (Rouyn-Noranda, Quebec) and Noranda's Brunswick and Heath Steele mines (Bathurst, New Brunswick). Figure 4 presents some HDS treatment plant operations.

Figure 4 - Examples of treatment operations, high density sludge plants on the left and a basic lime treatment system on the right.

The metal precipitates created during all processes are wastes typically identified as sludge. This sludge must be disposed of in an environmentally acceptable manner. As sludge disposal costs can be significant the most advanced processes minimize the waste volumes by creating a higher-density sludge. The sludge disposal and lime costs over the long-term usually justify a higher capital investment due to significant savings in operating costs (Zinck and Aubé, 2000).

Sludge Management

Sludge management is an ever more challenging issue. As with all waste management strategies, detailed characterization of the waste is required. Sludges are difficult to characterize, as they are amorphous products of hydrolytic precipitation. In a recent MEND study, samples of sludge from across Canada were characterized (Zinck, 1997).

Sludge characteristics

A summary of sludge characteristics at various mine sites in Canada is presented in Table 1.

Table 1 - Characterization of typical metal hydroxide sludge. (N=22)

Physio-Chemical Characteristics		
Parameter	Range	Average
pH	8.2 - 10.8	9.5
Eh (mv)	58 - 315	236
Particle size, D_{50} (µm)	2.89 - 42.5	11.2
Solids (%) - fresh	2.4 - 32.8	3.4 (LDS) 24.1 (HDS)
Chemical Composition		
Assay	Range	Average
Al (%)	0.1 - 11.2	2.7
Ca (%)	1.8 - 26.6	9.3
Cd (%)	<0.0001 - 0.13	0.015
Cu (%)	0.001 - 1.48	0.41
Fe (%)	1.5 - 46.5	11.2
Zn (%)	0.003 - 22.0	3.9
S_{total} (%)	0.8 - 11.3	3.3
NP (kg $CaCO_3$eqv./tonne)	62 - 725	253

NP - Neutralization Potential

In several studies, samples of sludge from across Canada were characterized (Zinck, 1997; Aubé and Zinck, 1999; CANMET, 2004). The pH values for various lime treatment sludges sampled in Canada ranged from 8.2 to 10.8. In most cases aged sludges showed a lower pH than their fresh counterparts. Eh values of these sludges ranged from 58 to 315 mV with the aged sludges commonly recording the lower values. The mean particle size for lime sludges varies from 3-43 µm. Denser sludges, generally produced using the HDS process, display both smaller median particle sizes and narrower particle size distributions (Aubé and Zinck, 1999). Many of the sludges produced from LDS processes exhibit bimodal particle size distributions. Typically, particle size increases with sludge aging due to recrystallization.

The solids content of fresh lime sludges ranges from 2% to 33%. Aging serves to further densify the sludge, in some cases doubling or tripling the solids content of the sludge. However, the degree and rate of densification obtained is not the same for all sludges and tend to be better for high density sludges (Zinck et al., 1997).

Neutralization potential, or the measure of available excess alkalinity, ranges in lime sludges from 62 to 725 tonnes $CaCO_3$ equivalent per 1000 tonnes of sludge. Higher values (over 900 $CaCO_3$ equivalent per 1000 tonnes of sludge) have been observed for some neutral drainage sludges, where effective metal removal is often a challenge without sufficient ferric iron present. While low neutralization potential (NP) values are attractive in terms of plant efficiency, sludges with high NPs have more neutralization capacity, which directly impacts sludge stability as discussed further in the next section.

Mineralogical analyses of sludge samples show a major amorphous phase. Readily leached metal species such as zinc are commonly associated with this phase, which appears to be effective in scavenging metal species (Al, Cu, Fe, Mg, Na, Ni) during precipitation. Calcium is present as calcite, gypsum and bassanite, which occur both as individual grains and in the amorphous phase. Calcium content in the sludges varied from 2 to 27%. Figure 5 present a scanning electron microscope (SEM) photomicrograph of typical sludge.

Zinc concentrations in lime treatment sludges ranges from 0.003% to as much as 22%. Copper and nickel are generally less than 1%. Aluminum ranges from 0.1% to 11%. Boron, chromium and mercury occur only in trace amounts, generally less than 0.01%. Iron ranges from 1.5 to 47% in the sludges.

All the sludges contain sulphate, in some cases greater than 30%. Quartz, silicates, sulphides and iron oxide particles present in minor amount in some sludges were present in the water prior to treatment and are detrital in origin.

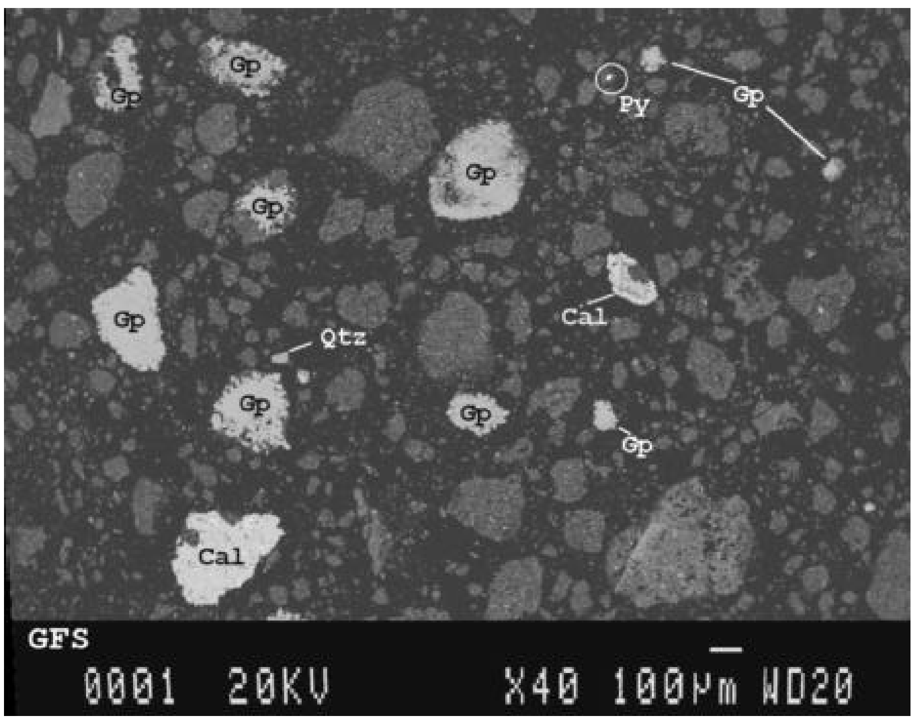


Figure 5 - SEM photomicrograph of typical sludge showing grains of gypsum (Gp) and calcite (Cal) in an amorphous phase.

Factors affecting sludge stability

Geochemical stability is a complex phenomenon in which many factors may influence the release of specific constituents from a material over prolonged time intervals. These factors include major element chemistry, pH, redox, complexation, liquid-to-solid ratio, contact time, available alkalinity, biological activity, permeability and water movement.

Several factors affect sludge stability. The key factors are outlined below (from Zinck, 1999).

Leachant pH. One of the most important factors affecting sludge stability is leachant pH (or the pH of which the water that the sludge might be exposed to). The lower the leachant pH the greater the expected level of metal mobility. All sludges will become unstable if exposed to enough acid. For example, if a zinc rich sludge (>10% Zn) is exposed to pH of 8.5 very little zinc leaching is expected. However, if the same sludge is exposed to a pH of 6.5 zinc mobilization could be in the range of 30 mg/L.

Treatment Process. The degree of sludge stability is indirectly related to the type of treatment process used. In basic or LDS treatment systems, the amount of lime consumed is high and this results in sludge with a high degree of excess alkalinity. The HDS systems have better pH control, which not only increases the lime utilization efficiency it also tends produce more crystalline sludge components as the precipitation mechanism is better controlled.

Sludge Crystallinity. Metal release from crystalline precipitates is generally lower than from amorphous or poorly crystallized material. In evaluating metal leachability with respect to sludge mineralogy, it appears that sludge stability depends on the stability of the amorphous phase rather than on the other sludge components.

Raw Water Composition. The composition and characteristics of acidic mineral effluents vary from site to site. As a result, what is effective for one site may not necessarily be effective at another site. However, general trends are apparent between various raw water components and their effect on sludge stability particularly for

Fe(II)/Fe(III) and sulphate. For example Zinck et al., (1998) found that a greater proportion of ferric iron in the raw water enhances sludge density and settleability. However, the amount of zinc leached from the sludges studied increased with increasing ferric iron concentration in the raw water.

Excess Alkalinity. It is clear that the amount of excess alkalinity present in the sludge serves to reduce metal leachability and subsequently increase sludge stability, at least in the short term. The excess alkalinity will buffer the pH in the alkaline or neutral region thus limiting the degree of metal leaching.

Sludge Aging. In both field and laboratory studies, it was evident that the degree of metal mobility from sludge decreases with aging. It appears that the aged sludges seem to have a somewhat lower propensity for metal leaching than fresh sludges as presented in Figure 6. This correlates with mineralogical data that indicates that sludge stability may improve with age.

Disposal Environment. The method of disposal will ultimately affect the long-term stability of lime sludge. The next section discusses in detail sludge disposal options and their effect on sludge stability.

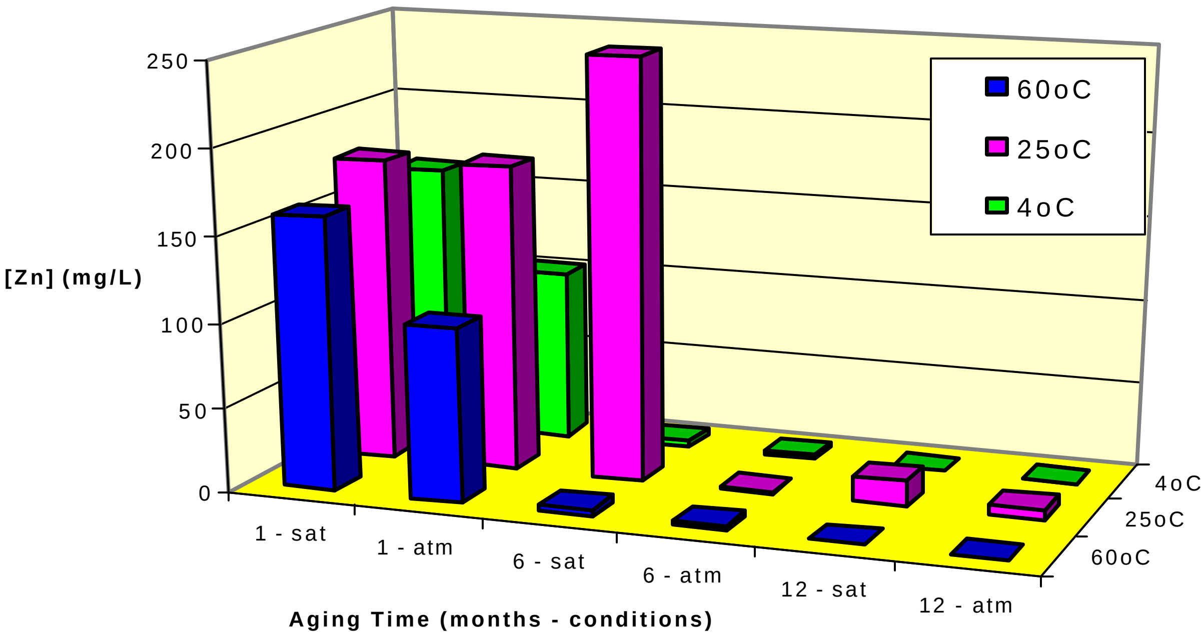


Figure 6 - Relationship between metal mobility and sludge aging. Samples of sludge were leached after aging under various conditions (saturated - sat, dry - atm,) and temperatures (4, 25, 60°C) for several months (1, 6, 12). (Data from Zinck et al., 1998).

OPTIONS FOR SLUDGE MANAGEMENT

Sludge Management Considerations

Before one can design the most appropriate sludge management strategy for a site, several factors need to be considered. The principle considerations in effective sludge management are mass of sludge produced, operating or closed mine, dewatering ability of the sludge, sludge density (moisture content), sludge volume, chemical and physical stability, sludge composition, disposal location availability and economics.

The ability of the sludge to dewater may limit the choice of options available. A sludge that can dewater without mechanical assistance will not only reduce the area required for disposal, it also makes it more attractive for reuse options. The ability of sludge to dewater depends on its particle size, morphology and surface charge. As a particle deviates from a spherical shape, the surface area per unit volume increases, resulting in reduced settleability and decreased dewatering rate (Vachon et al., 1987). These characteristics are linked directly to the treatment process selected and the raw water chemistry.

Sludges often require further dewatering post treatment to remove excess moisture. This improves sludge handling as well as reduces the volume of sludge that needs to be disposed of. The ability of sludge to dewater will ultimately impact on sludge management (disposal and reuse) options and costs. Settled sludge may need to be pumped to disposal areas or placed in tankers for haulage to the disposal site. In either case, handling large volumes of water as is the case with low density sludge, increases sludge management costs. Percent solid, sludge viscosity, pump flow rate have to be taken into account for transportation requirements. The cost to transport sludge short distances by truck ranges from $15 to $60/t. Transportation costs via pipes depends on the length and diameter of the pipe. Periodically these pipes need to be cleaned at a cost of $2-$15/m. Pumping operations are important and must avoid plugging or freezing during wintertime operation (Murdoch et al.,1995).

Dewatering options range from settling ponds to sand lined ponds, to sophisticated filter presses and dryer applications. While ponds and sand filtration can usually double sludge densities, there is a limit to the degree of dewatering that can be achieved. Filter presses can achieve a minimum of 50% solids for most sludge. Dryers can be used to dewater sludge to greater than 90% solids. There are several different types of mechanical and thermal dewatering devices commercially available. The cost of more sophisticated dewatering techniques can be offset if sludge reuse options are available.

Physical dewatering processes such as pressure filters, centrifuges and vacuum filters are not a common practice, but Vachon et al. (1987) cite some references for AMD sludge mechanical dewatering (Crocker, 1982; Campbell and Le Clair, 1975; Akers and Moss, 1973).

The rate of sludge production, its volume and solids content are very important factors in sludge management. For example, high density sludges are much easier to handle and are less voluminous compared to low density sludges. In addition, HDS sludges often discharge to dewatering type impoundments while LDS sludges deposit in the bottom of settling ponds where they have to be either left in place or dredged. However, LDS tends to be more chemically stable at least in the short term compared to HDS, due to their excess alkalinity. These factors must be evaluated on a site-specific basis along with the chemical stability of the sludge, disposal costs, regulatory requirements and social factors in the design of an effective sludge management strategy.

Sludge Disposal

The storage and disposal of sludge from wastewater treatment is not a problem unique to acidic drainage or lime treatment sludge. Pulp and paper, tannery, municipal and acidic drainage sludges all face similar issues. Economics and land availability usually determine the sludge disposal strategy adopted (Vachon et al., 1987). Sludge disposal constitutes a significant proportion of the overall treatment costs. In the following sections a review of the various disposal options available will be presented and discussed.

Pond disposal

Sludge management involves three principle steps; solid-liquid separation, sludge dewatering and disposal. Many sites utilize settling ponds as an efficient sludge management option. The sludge generated is pumped to a settling pond where solid-liquid separation, dewatering and in many cases disposal occurs. While settling and disposal in the same pond requires large land areas, this approach is simplistic requiring minimal design and construction (Lovell, 1973). Pond disposal refers to long-term disposal of the sludge in an impoundment or pond. Examples of pond disposal are presented in Figure 7.

There are several types of sludge ponds that are used for settling and disposal. The characteristics of the sludge frequently dictate the type of sludge pond required. Types of sludge ponds include excavation, earthen dam, concrete, lined, and beached. Open pits can be used in the same way as ponds and are discussed later in the report.

The issues with respect to pond disposal are minimal. Wind resuspension and dusting can be a problem at some sites particularly in arid or northern regions. Due to the large requirement for space, land use can be a challenge for some sites although this, at present, is not a concern at most Canadian sites. However, with perpetual chemical treatment this may become an issue. Due to the thixiotropic nature of sludges (viscosity decreases as shear strength increases), pond failure could present some concern although not to the same extent as with tailings impoundments. However, in a pond environment either with or without a water cover, the degree of metal leaching is expected to be minimal as the excess alkalinity available in the sludge is enough to sustain a moderate pH for decades, even centuries (Zinck et al., 1997).

Sludge disposal in a pond environment can be either subaerial or subaqueous. In a subaerial environment, the sludge is exposed to weathering conditions. Sludge cracking due to moisture loss at the surface is prevalent causing an increase in surface water infiltration. Under these conditions, sludge dewatering occurs at the surface while the majority of the sludge at depth is still very moist. The desiccated surface may be reclaimed. Sludge pond reclamation is discussed later in the report.

The cost of pond sludge disposal depends on the sludge production rate and the stability of the sludge. However, this method of disposal is relatively inexpensive. Ponds are seldom designed to meet realistic requirements and frequently fill-up prematurely. Mechanical sludge removal can be an added cost at approximately $5 per tonne for removal with a truck and backhoe to as much $30 per tonne sludge.

For example, Kidd Creek Metallurgical Site (Timmins, Ontario) spends upwards of $1 million per year on dredging costs (Scott, 2004). Ackman (1982) evaluates sludge removal techniques in terms of storage capacity, economics, maintenance and versatility. Due to the high long-term maintenance costs of this option, it is best if the sludge can be disposed of long term in the pond in order to avoid frequent and costly sludge removal from the pond. If long-term pond disposal is not an option, the sludge must be removed and disposed of in a more suitable, site-specific location (e.g. in underground workings).

In general, sludge disposal in ponds exhibits minimal metal leaching. Where sludge leaching is a concern, the application of a water cover proves to be effective in reducing metal mobility. In a laboratory study (CANMET, 2004), sludge was found to be more chemically stable when a water cover was applied to a pond disposal scenario. In this case, the amount of Cd, Cu, Mg and Zn mobilized was significantly lower with a water cover compared to without. The presence of a water cover over the sludge provided for better distribution of the alkalinity and buffering capacity resulting in better pH control and lower metal mobility. The application of a water cover may reduce metal mobility (e.g. zinc) by as much as 10%. Zn and Cd are frequently the metals that mobilize readily and as such are problematic. Liners may also be required if sludge leaching is a problem. The cost for liners can range from $4-$12/m^2 for a synthetic liner and more than double that amount for a clay liner.

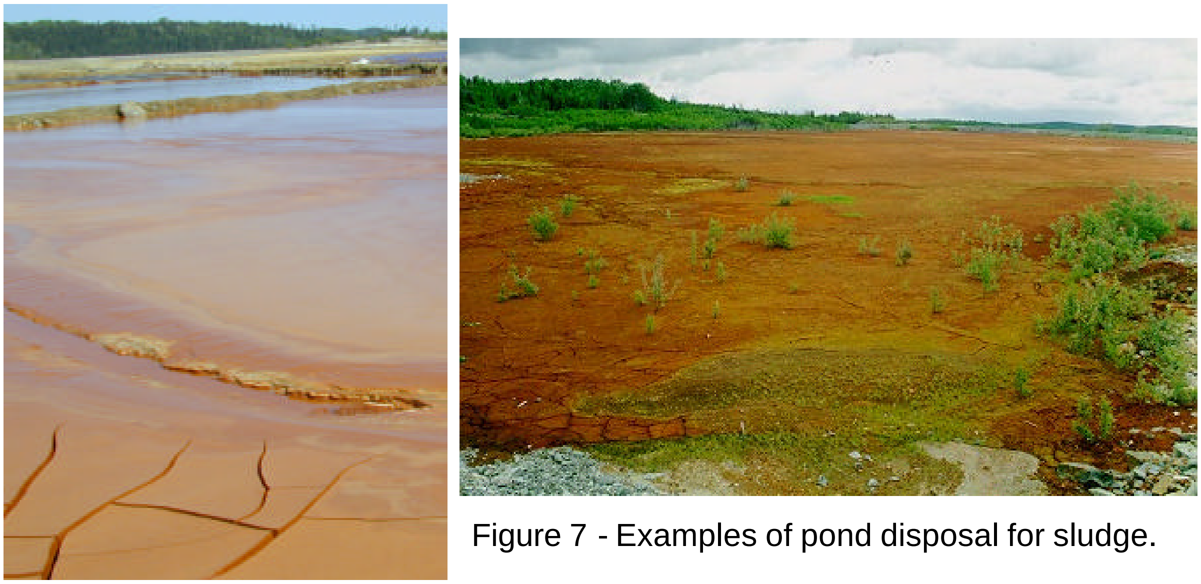


Figure 7 - Examples of pond disposal for sludge.

Stability of sludge in reducing conditions

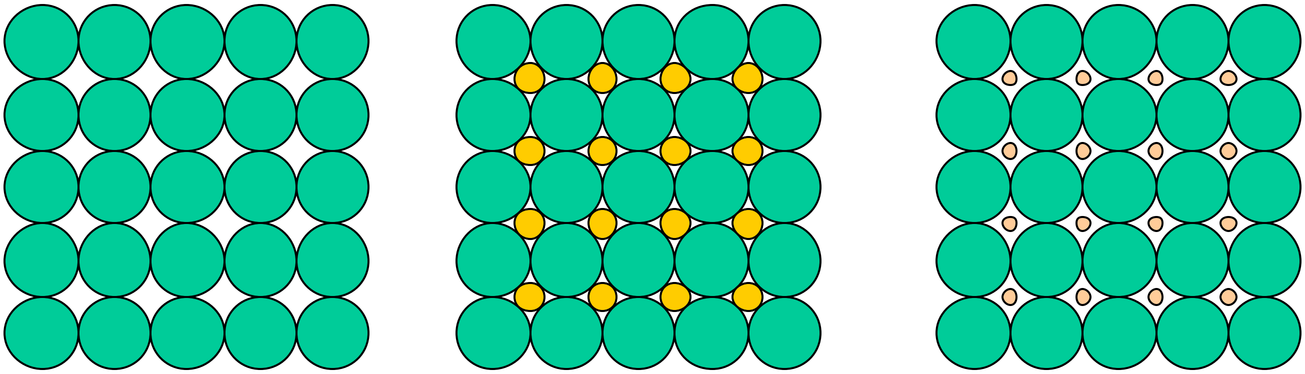
Researchers at CANMET (Beauchemin et al., 2004), recently conducted a study evaluating the stability of sludge in reducing conditions. The objective of the study was to determine the impact of reducing conditions on the dissolution of arsenic in a neutralization sludge stored under a water cover. Reducing conditions which may develop in the sludge under a water cover could favour the reduction and solubilization of Fe(III) to Fe(II), leading to the mobilization of any contaminant associated with the Fe-phase. For arsenic, the reduction of As(V) to As(III) would further result in the conversion of this contaminant into a more toxic and mobile form than the oxidized As(V) species (Inskeep et al., 2002). Despite the reduction treatments applied in the study, As remained as As(V) species and Mn was the redox-active element in the sludge. CANMET's results suggest that the As(V) species would remain kinetically stable against reduction during long-term exposure to anoxic conditions, as long as a significant amount of Mn(IV) is present. In sludge disposal sites, where no mixing occurs, O_2 diffusion into the sludge should be limited, but a lack of metabolizable organic carbon should limit microbial reduction.

Codisposal with tailings

Many mine sites choose to dispose of treatment sludge with mill tailings to reduce the waste disposal resources required to dispose tailings and sludge separately. While there is some perception that the addition of lime treatment sludge to a tailings impoundment area may provide buffering capacity, this has yet to be validated. Moreover, the long-term stability of acidic drainage treatment sludge disposed with tailings is generally unknown and requires considerable, further investigation.

The practice of co-mixing tailings with treatment sludge for disposal involves injecting the treatment sludge into the tailings slurry prior to discharge to the impoundment. Typically, the sludge to tailings ratio is less than 1:20. Here the sludge serves to fill void spaces (Figure 8) within the tailings, in theory reducing the potential for water or air infiltration and the hydraulic conductivity of the mixture. This method of disposal could be an effective option provided that the tailings are either non-acid generating or that tailings oxidation is prevented. However, if the tailings undergo oxidation and commence acid generation, the likelihood for sludge dissolution and metal mobilization is very high. In addition, an alternative sludge disposal strategy would be required post closure as sludge continues to be generated while tailings production ceases.

When fresh tailings were mixed with treatment sludge and leached over time in the laboratory with synthetic rainwater, the long-term stability of the sludge was compromised (CANMET, 2004). Results showed that the net alkalinity only offset acid generation and metal mobility in the short term. Once oxidation was established, the available alkalinity in the sludge was quickly depleted. Under acidic conditions sludge dissolution occurs, opening void spaces (Figure 8) and increasing infiltration and metal leaching. If under these same conditions a water cover was applied to the waste, then it is expected that limited metal leaching would occur as oxidation would be discouraged.



Tailings

Tailings codisposed with sludge

Partial sludge dissolution

Figure 8 - Schematic of sludge-tailings codisposal.

Sludge as cover over tailings

The application of wet and dry covers to prevent acidic drainage is a widely accepted and adopted practice. These covers serve as a barrier to prevent oxygen from reaching the potentially acid generating material. Laboratory results (CANMET, 2004) suggest that using sludge as a cover material was not effective to impede oxidation when placed over tailings. Contrary to what was expected, the sludge layer did not act as a barrier to oxygen and did not significantly reduce the rate of sulphide oxidation. However, these results were obtained from laboratory trials and several limitations were encountered. Some of the issues related to the application of a sludge cover on tailings are cracking and preferential channeling. Sludge needs to be disposed in a manner in which the particles will not segregate and consequently remain saturated. Maintaining water in the sludge pore space will prevent sludge cracking and minimize exposure of tailings to oxygen. The application of a water or vegetative cover would be beneficial in keeping the sludge saturated thereby limiting cracking and channeling. Figure 9 presents some examples of sludge disposed of over tailings.

Figure 9 - Field example of sludge layered over tailings. Inset shows a core of sludge over tailings disposal scenario.

Mian and Yanful (2004) investigated the effect of wind-driven resuspension of sludge placed over tailings in a pond at the Heath Steele site in New Brunswick. They concluded that wind resuspension of fine sludge particles caused the total suspended solids (TSS) in the discharge to exceed the Canadian effluent limits during periods of high winds. Peacey et al., (2002) studied the same site and found that, in the long-term, sludge formation and resuspension should not be an environmental problem with this disposal option.

Sludge disposal with waste rock

Disposing sludge with waste rock has several of the same potential benefits as disposal with tailings, including utilization of excess alkalinity to offset acid generation and filling of void spaces. This practice of disposing treatment sludge in waste rock piles is being adopted at some sites. NB Coal's Fire Road mine (Minto, New Brunswick) started looking at the option of codisposal of sludge with waste rock in 1993 after it was determined that there was 160-770 years of sludge storage capacity within the waste rock.

Coleman et al. (1997) conducted an investigation into the placement of sludge on acid generating waste rock. While their results showed that sludge was not effective as a capping material as originally hoped, this method was found to be a low-cost final disposal option as the sludge filled pore spaces and voids within the waste rock pile. The mine water chemistry has been monitored since 1993 and there appears to be no adverse identifiable chemical effects (Coleman and Butler, 2004).

Figure 10 - Sludge management practices at Wheal Jane (UK).

<u>Disposal in mine workings</u>

Disposal of treatment sludge into underground mine workings has several benefits that make it an attractive sludge management option. The deposition of sludge into underground mines reduces the footprint required for disposal sites (landfills and impoundments), eliminates the potential for surface water pollution, reduces the potential for subsidence, and improves the aesthetics of the local area. Also, in acidic mine workings, the disposal of sludge underground could have the additional benefit of reducing the acidity of the mine water (Gray et al., 1997).

This practice involves pumping or trucking sludge to boreholes, which are drilled into underground inactive mines. Some of the factors that need to be considered in this disposal option include:

- site availability and access
- mine capacity, void space, configuration
- sludge properties (e.g. viscosity).

Meiers et al. (1995) looked at the technical feasibility of placing fixated scrubber sludge into underground coal mines. The sludge was injected through boreholes at a rate of 215 to 500 m^3/day. Short-term results indicated no discernable chemical effects on the mine water or groundwater quality. Gray et al. (1997) identified several sites in the United States that are using the practice of underground mine disposal for other wastes such as coal ash and kiln dust.

Since 1987, Mettiki Coal has been injecting alkaline metal hydroxide sludge from its mine drainage treatment facility along with thickener underflow from its coal preparation plant into inactive portions of its underground mine in Garrett County, Maryland under an Underground Injection Control (UIC) permit (Ashby, 2001). Based on available data, it is felt that alkaline solids addition will assist Mettiki in maintaining an alkaline environment in its underground mine pool at closure and minimize acid generation. From 1996 to 2000 the pH of the mine water increased from 5.98 to 6.1.

Aubé et al. (2003) observed a similar trend. A laboratory study simulating the disposal of HDS and ferrous sludge into underground coal mine workings containing high strength acidic drainage was completed. Figure 11 shows the pH effects of sludge addition.

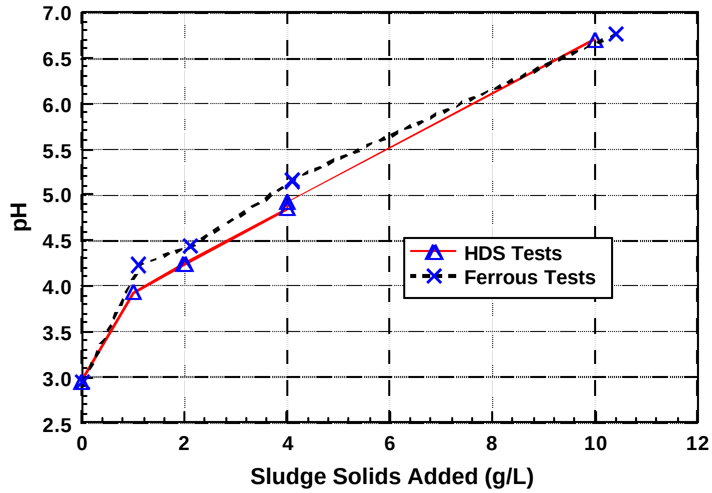


Figure 11 - Change in pH as sludge is added to mine water (Aubé et al., 2003).

In all cases where sludge was added, the concentrations of both Al and Fe decreased in the mine water. Figure 12 shows that some metal concentrations increased prior to decreasing at higher sludge addition rates. These metals (Cd, Ni, and Zn) are typically mobile at neutral or acid pH. The results also show that there is a greater increase in concentration when the ferrous sludge is added. The ferrous sludge is not in equilibrium with the mine water. Since ferrous iron is soluble below ~pH 7, sludge dissolution will occur and the metals entrained or adsorbed on to the sludge will be mobilized.

It appears that the sludge is stable in this environment as the iron is in equilibrium, as presented by the Pourbaix diagram in Figure 13 (Aubé, 2004). When the sludge is in equilibrium with the surrounding mine water, little or no dissolution of the iron sludge will occur. Any addition of either hydroxide ions or ferric ions would result in precipitation.

These results suggest that sludge returned to the underground workings would actually reduce the lime required to treat the acidic mine water.

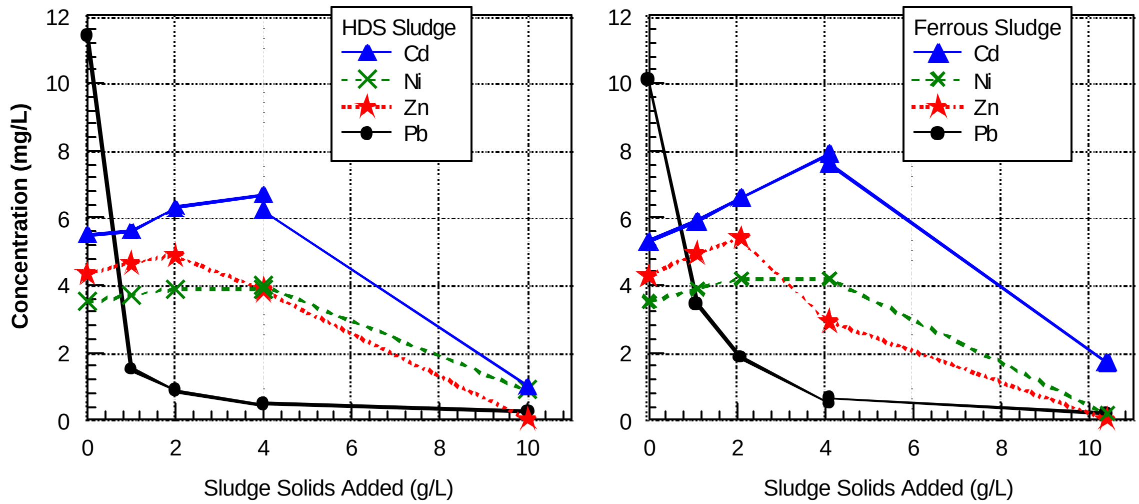


Figure 12 - Sludge dissolution in simulated underground disposal environment (adapted from Aubé et al., 2003).

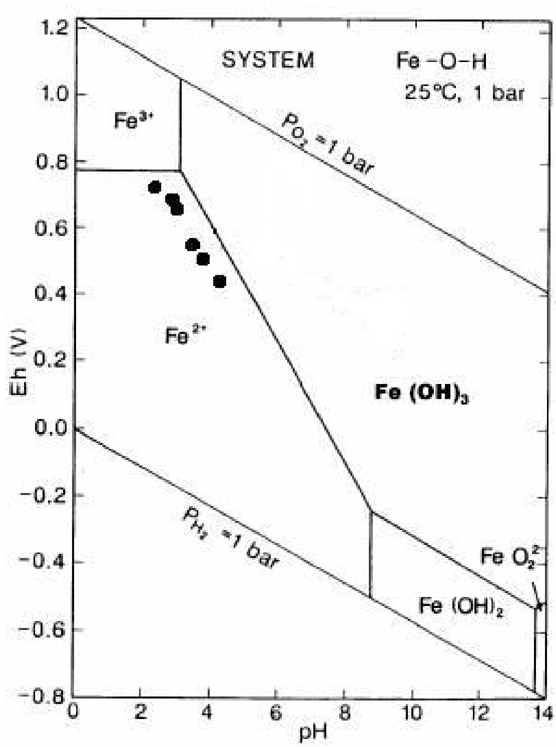


Figure 13 – Fe-O-OH system. ? – water chemistry at various mine sites (Aubé, 2004). The sites plot in the stability field for ferric iron, which implies that the ferric sludge would remain stable in these mine water environments; ferrous sludge however, would not.

This method is very attractive from an economic and environmental standpoint. However, like most disposal options presented this is clearly site specific. Sludge with high iron content can probably be disposed of this way economically. Disposal of sludge with high Cd, Zn, or Ni content in this manner may or may not be economic or environmentally acceptable depending on contact means (solids/AMD (S/L) ratio), alkalinity of sludge, and acidity of the acidic drainage (Aubé, 2004).

Disposal in pit lakes

Disposal in an abandoned open pit is typically one of the most economical solutions for sludge storage if a pit is within a reasonable pumping distance from the treatment plant. Many companies frequently take advantage of open pits available on site as an appropriate short or long term sludge disposal option. McNee et al. (2003) conducted a three year research program studying two pit lakes at the Equity Silver Mine near Houston, British Columbia (2004). The Main Zone pit (Figure 14) is of interest as neutralization sludge was added to this pit at a rate of ~5 L/s. The discharge of sludge into the Main Zone pit had a pronounced effect on its physical limnology. Their research found that the addition of sludge to the pit lake introduced oxygen into the lake through entrainment. Specifically, the input of dense oxygen-rich slurries and their rapid sinking, were found to cause lake mixing and produced oxygenated bottom waters. In addition, they found sludge disposal in the pit lake resulted in a plume of metal-rich particulate matter at depth (70-120 m). This did not however have an increase in the dissolved metal content or total suspended solids levels at discharge. The pit experienced increased production of the lake observed by the reduced light transmission and increased plankton biomass in the surface waters. It was postulated that the increased production was due to the delivery of phosphate into the lake with the sludge. Overall, the dynamics of the lake changed considerably and whole-lake mixing occurred with the introduction of the sludge (McNee, 2004). Longer term studies are required on sludge disposal in pit lake. However, as it appears, sludge disposal does not seem to negatively impact dissolved metal and TSS concentrations in the discharge waters.

Figure 14 - Main Zone Pit at Equity Silver Mine. Arrow points to sludge addition location.

<u>Sludge disposal in the North</u>

A two-year project was initiated to study the physical behaviour and environmental impact of treatment sludge in northern climates (Fiset et al., 2003a). The objectives of the project were to evaluate and assess metal mobility and chemical stability of lime treatment sludge under northern environmental conditions through both field trials and laboratory testing. The study assessed treatment sludge from two mine sites located in the Yukon: United Keno Hill (Elsa) and the Faro mine site (Faro). Parallel field and laboratory studies were conducted to examine both the freeze-thaw effects and the chemical stability of the sludge. In terms of chemical stability, column leaching studies revealed minimal metal release due to the high neutralization potential of the sludge. As discussed earlier, for these sludges, the freeze-thaw process was found to be extremely beneficial for sludge densification (discussed further in the next section).

Freeze-thaw

The capacity of freeze-thaw processes for sludge dewatering is well known. The dewatering effect is attributable to separation and segregation of ice crystals within the sludge structure. As a result the sludge is compressed by the ice front. When the ice melts, the sludge solids content remains in the compressed state, which promotes water drainage and sludge dewatering (Vesilind and Martel, 1990; Vesilind et al., 1991). Freeze-thaw processes have been extensively studied by various researchers (Hung et al., 1996) for municipal sludge treatment, however limited research has been conducted for acidic drainage treatment sludge. Noranda conducted an analysis of the effect of freeze-thaw on the Waite Amulet mine sludge ponds (Vachon et al., 1987). Subject to a single freeze-thaw cycle, the percent solid in the sludge increased from 6-11% to 21-23%. Fiset et al. (2003a) found sludge densification by freeze-thaw in the field increased the percent solids of the fresh sludge from 23 to 60% for the United Keno Hill sludge and from 28 to 58% for the fresh Faro sludge after only one winter. Both sites are located in the Yukon and are subjected to harsh winters. Freeze-thaw studies conducted in the laboratory gave similar final percent solids values. In these examples, the capability of the sludge to dewater to higher levels was explained by the low concentration of iron hydroxide in the sludge and consequently the sludge did not behave as a colloidal precipitate.

Sludge in backfill

The use of paste backfill is a common practice in the mining industry. Paste backfill integrates tailings, sludge and slag along with other wastes into backfill material to reduce the amount of waste to dispose on the mine surface. Paste backfill is defined as an engineered mixture of fine solid particles (with or without binder) and water, containing between 72% and 85% solids by weight. Unlike a slurry, particles in a paste mixture will not settle out of the mixture if allowed to remain stationary. It can be placed in stopes with or without binder addition depending on the strength requirements for the backfill. Improved pumping technology, environmental concerns, and the need for a low cost/high strength fill in mines, are driving mine operators to consider paste backfill as a tailings management and mine backfill alternative. Incorporating sludge into paste serves to both cementiously stabilize the sludge and allow for codisposal of wastes underground. The URSTM (Université du Québec en Abitibi-Témiscamingue) and CANMET are investigating the option of incorporating sludge in paste backfill (CANMET, 2004). The objective of their study is to develop and to evaluate the performance of a novel cemented paste backfill technique consisting of incorporating various treatment sludges within the conventional paste mixture. They found that while the performance of the Portland cement based binders appeared to be negatively impacted by sludge addition, slag based cement seemed to benefit from sludge addition.

Recently Teck-Cominco's Pogo Mine in Alaska examined options to have sludge from water treatment facilities backfilled underground during operation (Zuzulock, 2003). Unfortunately, the long-term strength of the material was not adequate for backfill. At present the sludge at Pogo is dewatered in a plate and frame press and then placed in drifts underground (Higgs, 2004). During life of mine, an estimated 11 million tonnes of tailings will be produced, with approximately half returned underground as paste backfill.

Landfill

Landfills are a common method used to dispose of hazardous waste. A landfill is defined as a disposal facility or part of a facility where hazardous waste in bulk or containerized form is placed in or on land, typically in excavated trenches, cells, or engineered depression in the ground (Figure 15). The aim is to avoid any hydraulic [water-related] connection between the wastes and the surrounding environment, particularly groundwater. Disposal by landfilling involves placement of wastes in a secure containment system that consists of double liners, a leak-detection system, a leachate-collection system, and a final cover (US Army Corps. of Engineers, 1994).

The EPA defines two types of landfills, sanitary and secure or hazardous. Sanitary landfills are disposal sites for non-hazardous solid wastes spread in layers, compacted to the smallest practical volume, and covered by material applied at the end of each operating day. Secure chemical landfills are disposal sites for hazardous waste, selected and designed to minimize the chance of release of hazardous substances into the environment. Sludge is disposed of in a secure landfill.

Landfilling is becoming less of a viable option, as environmental problems and restrictive legislation are making landfills a buried liability (Pickell and Wunderlich, 1995). One of the specific issues regarding the practice of landfilling treatment sludge is solid-liquid separation. Due to the low solids content of the treatment sludge it requires significant dewatering and drying before it can be transported. There may be additional public concern with the transportation of sludge off the mine site to a landfill facility. Depending on the sludge, stabilization may be an added requirement. The cost of disposing sludge in a landfill is estimated at $50-90 US/t. If the sludge requires stabilization the cost rises to $120 US/t. Although sludge is not considered a hazardous waste it can fail the TCLP (Toxicity Characteristic Leaching Procedure) test for some metals such as cadmium. The cost for disposal in a hazardous waste landfill is on the order of $160 US/t not including additional costs that may be required for stabilization (Mosher, 1994).

Figure 15 - Lined landfill. (Courtesy Solid Waste Online).

Reprocessing of Sludges

Many of the sludges produced have potential economic value as they contain high concentrations of recoverable metals such as zinc and copper. For instance, copper ore normally contains less than 1% copper, where copper precipitate sludges from the printed wire board industry average 10 to 15% copper (IPC, 2000). Acidic drainage treatment sludge can contain upwards of 22% zinc (Aubé and Zinck, 1999). Wastewater treatment sludges from electroplating operations, predominantly from the metal finishing and printed wire board industries, represent one of the largest sources in the United States of untapped metal-bearing secondary material amenable to metals recovery.

Metal recovery from sludges has been discussed for decades. The cost of sludge reprocessing is often considered to be prohibitive and the process problematic. As a result, technologies for metal recovery from sludges are rarely adopted. However with increasing environmental pressures and mining costs the option for metal recovery from treatments sludges becomes more attractive, especially when coupled with the revenue from the recovered metals. With this in mind, we may see a move towards technologies that recover metals from mine wastes such as sludge.

There are two principal approaches used for metal recovery: hydrometallurgical and pyrometallurgical. Many of the hydrometallurgical approaches involve leaching of the sludge followed by solvent extraction or ion exchange while the pyrometallurgical processes tend to involve metal recovery using smelting. The following sections present examples of metal recovery options.

Hydrometallurgical metal recovery

Hydrometallurgical recycling methods use wet chemistry to extract usable metals from sludges. While these methods have been in use for many years, they are currently receiving more attention due to their ability to extract and reuse metals from sludges.

Park (2001) evaluated the technical and economic feasibility of applying ammoniacal leaching and solvent extraction, followed by standard metallurgical recovery steps, to recycle nickel, copper, cobalt, zinc, and cadmium from hydroxide sludges. The project demonstrated that the technology was a viable option for recycling certain metals from hydroxide sludges. However, economics show that the technology was only potentially attractive if considered as an alternative to an expensive sludge disposal option, such as hazardous waste landfill disposal. Further work in the area of zinc and nickel recovery may improve the economic feasibility of the process.

Copper recovery from waste galvanic sludge from metal plating industry, containing about 3% copper, was investigated by Jandova et al. (2000). In this study, the sludges were first leached with sulphuric acid, the copper was then precipitated as a hydroxide then calcined. The sludge was again leached to recover copper with a purity sufficient for utilization in the metallurgical industry. In another study, the researchers tested a multi-step selective precipitation method processing zinc waste galvanic sludge (Jandova et al., 2002). This method involved acid leaching of sludge in sulphuric acid, purification of sulphate leach liquors using a sequence of hydroxide, sulphide, and fluoride precipitation to remove trivalent metals, Cu, Cd, Ca, Mg, and Si, oxidative precipitation to remove Mn, and finally precipitation of Zn as zinc carbonate. Due to incomplete leaching of the sludge, the overall recovery efficiency was only 63-65%. Bacterial leaching of metal-bearing sludges has also been investigated with some success (Shen et al., 2003).

Smelting

Recovering metals present in treatment sludge is an attractive sludge management option. Depending on distance to the nearest smelter, transportation costs, quantities generated, and contaminants present, the mining industry may be able to use this process as an alternative to current disposal methods. Unlike hydrometallurgical options, metal recovery using pyrometallurgy requires sludge drying (via rotary dryer to less than 20% moisture). In addition, certain impurities in the sludge can have a negative impact on smelter performance. However, process upsets may be offset by such advantages such as additional metal revenue and minimal costs (including liability) associated with surface sludge disposal.

Asai et al., (1997) presented a new pyrometallurgical process using a reverberatory-type recycling furnace to treat industrial wastes such as galvanizing and wastewater treatment sludges. Initially the sludges are transformed into matte by sulphidization with pyrite followed by metal recovery in a smelter.

In an industrial example, HDS sludge from the Yak Tunnel treatment plant is shipped by rail to Asarco's East Helena smelter in Montana (Mosher, 1994; Ramachandran, 1994). The smelter uses sintering, a blast furnace, dross furnace, and a reverberatory furnace. A key raw material in the process is lime which serves as a flux. In the process sludge is substituted kilogram for kilogram of dry lime equivalent. Remarkably, the sludge is not dried prior to sintering. In 1993, the smelter used 26,100 tonnes lime (as $CaCO_3$) and 1,425 tonnes sludge. After accounting for water and metal content, sludge replaces about 1.5 % of lime used (as $CaCO_3$). Other metals in the sludge are normally encountered in the smelting process and as such do not pose a problem. The Pb reports to the bullion, the Cu to the matte and speiss, Cd to the bag-house dust, and Zn, Fe, Al, and other trace metals to the slag. While the primary benefit of sludge addition is the lime content, incidental Pb and Cu units recovered have value as well.

In another example, the Process Effluent Treatment System (PETS) treats effluent streams from the Port Pirie Smelter in Australia to remove heavy metal contaminants (Ausenco, 2002). The treatment process involves lime neutralization of the incoming effluent followed by treatment with sodium sulphide and ferric chloride to precipitate the contained metals, including cadmium, lead and zinc. The slurry is thickened and filtered with the solids being returned to the smelter for re-processing. This process eliminates the need for landfills and the potential risk of heavy metals leaching into the water table.

In the majority of these metal recovery processes, the heavy metals are recovered for revenue and environmental reasons. Typically, a sludge still remains but it is free of many of the metals of concern and is thus easier to effectively dispose.

Stabilization/Solidification

Solidification/stabilization technology as applied to wastes uses physical and chemical processes to produce chemically stable solids with improved contaminant containment and handling characteristics. There are six main types of stabilization methods: sorption, lime-based, cement-based, thermoplastic techniques, polymeric and encapsulation.

Several studies have been conducted to investigate stabilization/solidification (S/S) techniques for metal hydroxide sludges (Tseng, 1998; Chang et al., 1999; Conner and Hoeffner, 1998). Treatment sludge typically consists of metal hydroxides, gypsum, unreacted lime and calcite. The solubility of metal hydroxides is pH dependent; each metal has its own metal precipitation domain. The majority of the metals are soluble at pH below 6 and some anionic complexes (As, Cr) exist in the range of 10-12. The S/S process is an interesting technology for sludge treatment because it can convert the waste into an inert material independent of the metal solubility of each metal. Also, it is possible to control some physical and chemical parameters such as permeability, compressive strength and metal mobility by proper selection of chemical additive types and ratios. The strength development could be improved by increasing the curing temperatures, lowering the water to cement ratio, or using early strength Portland cement or calcium chloride additives. Various waste solidification methods have been developed using Portland cement (Cohen and Petry, 1997; Fisher and Lannert, 1990; Taub, 1986; Bowlin and Seyman, 1989), fly ash (Gabr et al., 1995), fluidized-bed-combustion ash (Knoll and Behr-Andres, 1998), silicate (Bowlin and Seyman, 1989; Reimers et al., 1989) and phosphate (Rao et al., 2000).

Portland cement (PC) is used to convert the waste into a high strength and durable material. Five different types of Portland cement are manufactured. Each of them has specific uses, setting times and costs. The four major constituents in Portland cement are tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminiferrite. In contact with water, Portland cement triggers a series of reactions leading to the formation of hydration products, which, through several types of bonding interactions, yield a dense stable matrix. The main pure phase hydration reaction has been described by Mindess and Young (1981).

Utilization of fly ash (FA) can provide an economic alternative to Portland cement, and already often replaces 25 to 55% of the Portland cement normally used for industrial purposes. Gabr and Bowders (2000) studied acidic drainage sludge stabilized with cementitious material. The stabilized sludge could be used for a cover application because the properties of the mixture satisfied the excavability and workability in the same way that shotcrete has been tested as a cover for waste rock (MEND, 1996). A mixture of 10% acidic drainage treatment sludge, 2.5% PC and 87.5% FA provided the requirement for hardening time and physical stability.

Sludge characteristics have a great influence on the compressive strength of a solidified sample (Tseng, 1998). Concentrations of zinc, copper, lead and cadmium may cause a large variation in setting time and significant reduction in physical strength (Tseng, 1998). Also, organic materials tend to interfere in the hydration of cement.

Limitations of the Portland cement / sludge mixture are related to the effect of the sludge on the setting and stability of the silicates and aluminates that form when Portland cement hydrates (Culliane and Jones, 1989). Also, transportation, operational and cement costs are important limiting factors. The availability of cements and of the pozzolanic material near the mining site is very important for economic reasons. Mixture designs must be optimized for each site because of sludge characteristic variation from site to site.

A recent CANMET study (Fiset et al., 2003b) revealed that Portland cement could be used as a binder to chemically and physically stabilize treated sludge. Other binding systems such as combinations of Portland cement and fly ash, Portland cement and slag, lime and fly ash and a phosphate binder were also evaluated. For two different stabilized sludges, compressive strength values typically ranging between 0.3 MPa and 3.0 MPa were obtained using 5 to 20% of binder. Fiset et al. (2003b) estimated the cost to stabilize acidic drainage sludge with Portland cement and fly ash to be in the range of \$5/tonne (Figure 16).

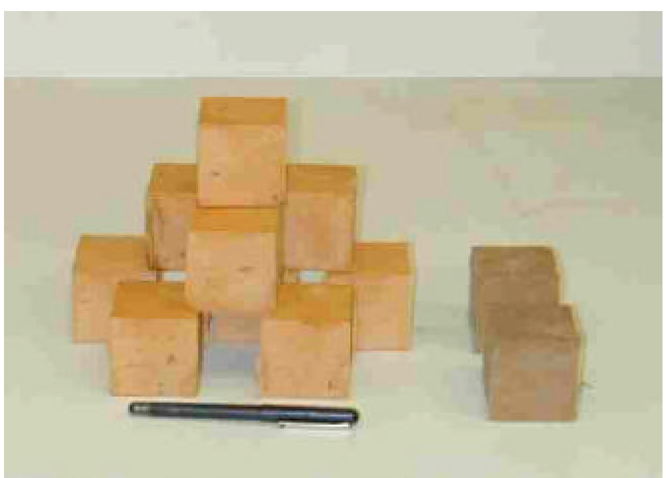


Figure 16 - Sludge stabilized with Portland cement.

Vitrification is another method used to stabilize wastes. Vitrification, or molten glass, processes are solidification methods that employ heat up to 1,200°C to melt and convert waste materials into glass or other glass and crystalline products. Materials, such as heavy metals and radionuclides are incorporated into the glass structure, which is generally a relatively strong, durable material that is resistant to leaching. In addition to solids, the waste materials can be liquids, wet or dry sludges. Borosilicate and soda lime are the principal glass formers and provide the basic matrix of the vitrified product. Vitrification produces a very durable material but because of its very high cost (~$300/t) it is only recommended for extremely hazardous sludges.

Two additional high temperature stabilization/recycling technologies that appear promising are: thermal bonding and sludge slagging (Hazardous and Toxic Materials Project, 1990).

The goal of the thermal bonding process is to detoxify hazardous metal sludges by fixating the metals in a leach-resistant ceramic matrix. A secondary aim is to convert metal waste sludges into a saleable raw material for construction applications. The ceramic pellets or bricks that are produced resist decomposition even when subjected for prolonged periods to low pH environments, and to extreme conditions such as immersion in hot nitric acid. Capital costs for these systems are in the range of $1M and operating costs are approximately $150 per tonne of material processed (Hazardous and Toxic Materials Project, 1990). The exact costs depend on sludge characteristics, and the type of pretreatment required.

Sludge slagging is very similar to thermal bonding except that much of the nickel, iron, copper and other metals contained in the sludge can be recovered and sold. Another advantage of this system is that the volume of waste is reduced by as much as 94%. The process is not able to recover chromium, titanium or aluminum. This process is designed for sludges with high organic carbon contents. However, for sludges with low organic contents, such as acidic drainage sludge, coke can be added. The capital and costs for a small-scale operation are in the order of $100k. Operating costs for a small system are typically $2k per month for fuel, electricity, furnace refractory replacements and additives for the slagging process and during this time the system might process 6 to 8 tonnes of material (Hazardous and Toxic Materials Project, 1990).

Sludge Reuse Options

For the most part, the components that make up sludge, such as gypsum, calcite and ferrihydrite are minerals that are utilized as raw material in the manufacturing of construction materials or other products. It is often the heavy metal components that discourage the reuse of acidic drainage sludge. Further work in the area of sludge reuse is needed. Some studies have looked at the utilization of sludge in construction materials and water treatment. However, the adoption of these technologies is limited.

Utilization of sludge in construction materials

Bricks - The inorganic components in sludge can be used for the production of building materials (Levlin, 1998). Any environmental hazardous contaminants are bound as mineral to the material and utilization of sludge reduces mining of raw material for production of building material. The high aluminum content of sludge produced from treatment of acidic drainage at some coal and gold mines may be useful for production of aluminous cement (Lubarski et al., 1996).

Pulverized sludge ash and dewatered sludge/clay slurries have been used successfully in lightweight concrete applications without influencing the product’s bulk properties (Tay and Show, 1991). Sludge based concrete has been deemed suitable for load-bearing walls, pavements, and sewers (Lisk, 1989). Meeroff and Bloetscher (1999) urge us to imagine sewer pipes made from sludge, the “ultimate in recycling schemes”.

The sludge proportion and firing temperature are key to the compressive strength of the bricks. Weng et al. (2003) found that with up to 20% sludge added to the bricks, they were still able to pass the Chinese National standards for strength. TCLP tests showed metal leaching from the bricks was low. Good quality bricks were manufactured with 10% sludge (24% moisture) and firing temperatures of 880-960°C. Rouf and Hossain (2003) produced bricks from arsenic-iron sludge. They utilized between 15-25% sludge at a firing temperature of 1,000°C. Higher temperatures and longer durations produce larger and more interlocked crystals, resulting in greater compressive strength (Simonyi et al., 1977).

Column testing showed that arsenic leaching was initially high, and then became negligible. However, very limited work has been done to examine the long-term chemical and physical stability of these bricks.

Sludge amended cement - Many of the constituents in sludge are the same as that used in cement manufacturing. Calcite, gypsum, silica, aluminum, iron and magnesium are common raw materials for cement. Simonyi et al. (1977) found that acidic drainage sludge could be added to cement in amounts less than 5% with little or no net effect on compressive strength. All mixtures which contained greater than 25% sludge, disintegrated within one month. Other studies (Hwa et al., 2004) have suggested that sludge can replace up to as much as 30% Portland cement in blended cement. As with most reuse options, the sludge requires drying before it can be utilized. The practice of utilizing treatment sludge in cement manufacturing has been adopted in some specific sites in the United States (EPA, 2000).

Agricultural land applications

For low metal content sludges, such as sludges from coal mining operations, it was found that the excess alkalinity present in the sludge can be utilized to raise soil pH. In an attempt to limit the use of landfills, the Minnesota Pollution Control Agency

(MPCA) (1999) examined the land application of coal ash as a fertilizer. The blend of agricultural lime and coal ash were found to contain useful nutrients such as sulphur and boron. In order to prevent build up of constituents of concern the MPCA place limits for As, Cd, Cu, Pb, Hg, Ni, Se, and Zn on the permit. While this option has very limited application due to public health and other social concerns, it demonstrates that the non-toxic sludge components can be beneficial to other industries.

Metal adsorbent in industrial wastewater treatment

The iron (ferrihydrite) component of sludge is highly adsorbent. Several researchers (Edwards and Benjamin, 1989) have conducted studies on ferrihydrite (ferric hydroxide) and found it to be highly effective for metal removal. Both sludge dosage and pH affect metal removal using sludge from lime treatment plants. Shultz and Xie (2002) found that metal recovery was most effective at pH 7.8. Increasing the sludge dosage increases the metal removal. Copper was found to be the easiest metal to remove. Zinc was also readily removed at pH 7.8 Extreme pH conditions, greater than pH 11, are necessary to remove cadmium (Edwards and Benjamin, 1989).

Similarly, treatment sludge has also been used to remove carcinogenic dyes/colours from wastewater. Researchers from King Mongkut's University of Technology Thonburi in Thailand (Netpradit et al., 2003) investigated the capacity and mechanism of metal hydroxide sludge to remove reactive dyes from aqueous solutions. The study examined dye removal under different conditions, such as, dye loadings, system pH, adsorbent particle size and adsorbent dosage. The dye adsorption was greatest at pH 8-9, close to the zero point charge (pH_{zpc}). The maximum adsorbent capacity of the sludge was determined to be 48-62 mg dye per gram sludge.

Carbon dioxide sequestration

The same mechanism that generates CO_2 in the production of lime can be utilized to sequester carbon dioxide. CO_2 gas can react with treatment sludges and iron-rich metallurgical residues to produce solid Ca, Mg and Fe carbonates while stabilizing the sludge/residue and its impurities. There is evidence that these reactions occur naturally in sludge/residue ponds, but the method requires development and optimization. An estimated 60,000 t CO_2 annually could be sequestered in Canada (not including steel mill sludges) enhancing the stability and compactness of sludges and residues.

Other uses

Spray dried sludge can be utilized as a rock dust substitute for explosion control (Simonyi et al., 1977). In addition, sludge 'gravel' can be produced by drying, pulverizing, pelletizing, and sintering to produce a lightweight, high strength aggregate (Hwa et al., 2004).

Reclamation

Once sufficiently dewatered, natural colonization of vegetation on alkaline acidic drainage treatment sludge is very slow, making it prone to erosion and dusting (Figure 17). These sludges pose many of the same reclamation constraints encountered with fine-grained tailings, such as small particle size, compaction, lack of nutrients, high metal content and, in some cases, salinity. However, the two biggest reclamation challenges are alkaline pH and lack of nutrient availability (Tisch et al., 2004). While acidic tailings can be limed to improve or optimize pH and metal availability, purposely decreasing the pH of treatment sludge is not an option due to the high risk of metal leaching. In addition, metal toxicity can occur as both aluminum and zinc are toxic to roots at relatively low concentrations (Hogan and Rauser, 1979; Rauser and Winterhalder, 1985).

While the high pH is effective for limiting the availability of metals for uptake by plants, it can also severely limit the availability of plant nutrients, especially phosphorus. As discussed earlier, lime treatment sludges are composed primarily of calcite, gypsum and a large amorphous ferrihydrite-like phase. While this ferrihydrite phase is an effective scavenger of metal species such as Al, Cu, Fe, Mg, Na, Ni and Zn (Zinck and Dutrizac, 1998; Zinck et al., 1996), it is also an important sorbent in soil (Guzman et al., 1994). Inorganic fertilizers applied to the sludge will quickly be rendered unavailable to plants both through precipitation with calcium and adsorption to ferrihydrite. As a result, fertilization of alkaline sludges with inorganic fertilizers tends to be very ineffective and expensive. The use of acid generating fertilizers such as those containing ammonium may assist in releasing phosphorus, but any associated decrease in pH is likely to also result in increased metal release (Tisch et al., 2004). The introduction of organic matter or the use of organic fertilizers (including biosolids, papermill sludge etc.) may be a more efficient method of limiting rapid phosphorus fixation. The estimated cost to reclaim sludge ponds through revegetation is expected to be on the order of $1k/ha.

The use of alkaline tolerant and phosphorus efficient species in reclaiming these areas will certainly assist in overcoming some or all of the hurdles associated with treatment sludge. However, the more common reclamation species, at least those that develop extensive root systems that are more efficient in terms of erosion control, tend to be only mildly alkaline tolerant. Species such as Alkali Grass (*Pucinellia distans*) have shown promise as being a key component at some sites (Tisch et al., 2004).

CANMET has initiated a study to develop more efficient methods of establishing a sustainable vegetative cover directly in high-density alkaline treatment sludge (CANMET, 2004). It also aims to examine metal uptake in vegetation, both from a phytotoxicity and phytomining perspective, and to investigate methods of improving phosphate availability. While still in its infancy, the work mainly consists of laboratory studies that will build on information gained from field trials that were undertaken by individual mining companies (Tisch et al., 2004).

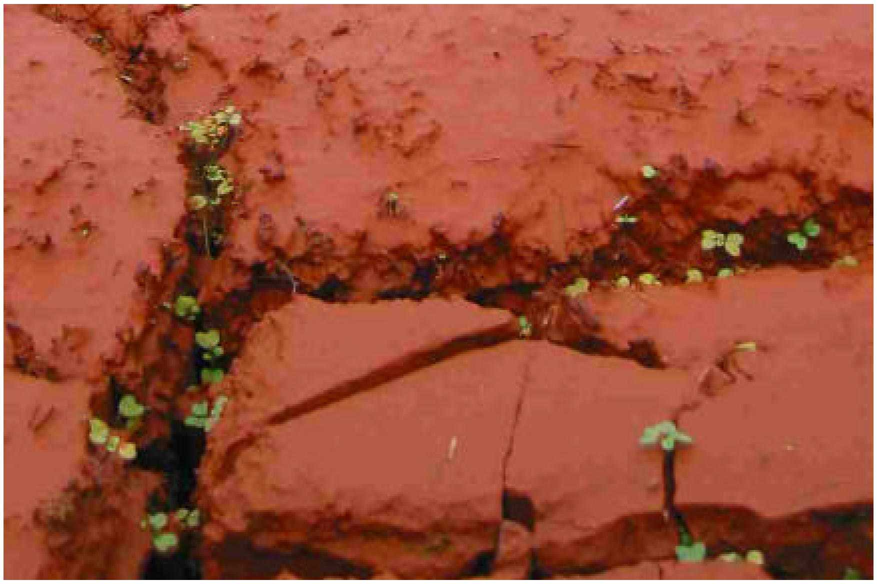


Figure 17 - Vegetation within sludge desiccation cracks (Wheal Jane).

The CANMET study found that in general, root growth was best in distilled water, followed by potting soil and then sludge. In all cases, except Kentucky Bluegrass, root growth was inhibited (by as much as approximately 90%) in the sludge, relative to both distilled water and potting soil (Figure 18). After successful germination, developing seedlings must produce healthy root systems in order to support and provide nutrients for above ground growth. If root development is impaired early on, plant mortality eventually occurs, usually attributed to drought. The roots of many plant species are capable of acidifying their immediate environment in order to increase available nutrients. Thus, while growth rates may be initially impaired, long-term development may still be satisfactory.

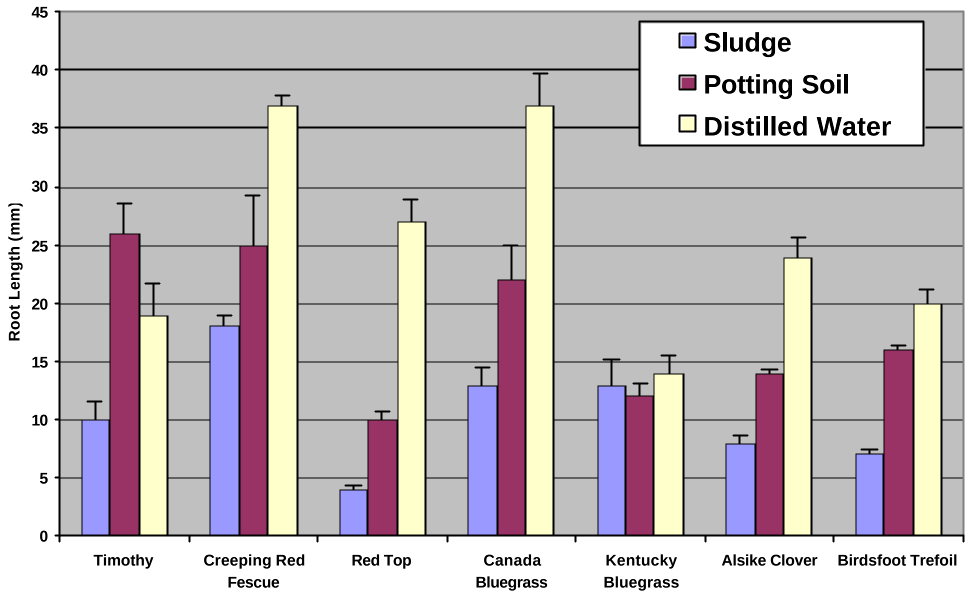


Figure 18 - Root growth for grasses and legumes grown in soil, distilled water, sludge.

KNOWLEDGE GAPS

Sludge management is receiving considerably more attention as operators are getting more concerned with sludge volumes and questions surrounding long-term sludge stability and resulting liability. Unfortunately, the practice of sludge management in Canada is still relatively ad hoc. Sludge is considered by many as a waste generated from another waste.

The data available on sludge management practices is limited and as such, the gaps in the knowledge base are numerous. This section will discuss knowledge gaps and will be classified into three categories; information gaps, research gaps and required changes.

Information Gaps

By far the largest gap in the sludge management toolbox is that of information. This information gap is for the sludge itself, through to site and monitoring data. Acidic drainage treatment sludge as with other wastes is extremely site specific in its composition and behaviour. Unlike tailings or waste rock, treatment sludge is primarily amorphous in nature. The crystalline components of the sludge such as calcium carbonate and gypsum are well characterized. However, it is the amorphous phase of the sludge that is the challenge to manage effectively. It is this phase that dictates the voluminous and gelatinous nature and the chemical stability of the sludge. Case studies on sludge management practice and performance at various mine sites is very limited. Further work is required to effectively characterize the amorphous sludge phase. More advanced characterization techniques such as X-ray Adsorption Near Edge Spectroscopy (XANES) using synchrotron analysis are proving to be very effective in sludge characterization. For example, Beauchemin et al. (2001) were able to identify the zinc speciation in the amorphous sludge phase using XANES. Once these sludges can be effectively characterized, appropriate sludge management strategies can be better developed.

There are no published studies that have evaluated the long-term stability of treatment sludge. Often it is found that studies have been completed but the information is not publicly available. Unfortunately, sludge stability is frequently assessed using TCLP type tests, which poorly simulate sludge disposal environments. These short-term tests cannot determine the degree of metal leaching that might occur over time as the sludge undergoes aging and recrystallization. In addition, batch tests cannot simulate various disposal environments (e.g. codisposal). Laboratory and field test cell data are required to assess sludge stability under various disposal environments. There are several challenges in designing a research program to ascertain this information from the physical nature of the sludge, to site-specific sludge conditions, to kinetic challenges. Unlike sulphidic wastes, sludges are composed of oxidized components and as such accelerating long-term behaviour is very difficult. However, regardless of the challenges, this data is key to understanding the long-term performance of any sludge management strategy.

Laboratory data is very useful in predicting behaviour under controlled conditions; however, case studies are crucial to the knowledge toolbox. Presently, many sites have no regulatory requirement to collect and monitor the leachate from their sludge disposal area, so this field data is limited if not totally absent. Long-term monitoring data from sludges must be collected the same way as other wastes, which are monitored for environmental impact and other characteristics. Monitoring data from codisposal areas would be particularly useful, as the interaction of sludge with other waste is poorly understood.

Presently, there are very few tools available to predict sludge behaviour. Another requirement in the sludge management toolbox are standardized tests to assess sludge stability. This standardized set could include methodologies for short batch tests using a leachant applicable to the disposal environment, methods on how to design and execute long-term column leaching tests, development of accelerated prediction tests, etc. Unlike tailings and other sulphidic wastes, there are just no standardized and accepted prediction tests for sludge. If reliable and consistent data is to be collected the techniques and methods to obtain this data need to be developed, standardized and adopted.

In addition to test methods, it is recommended that a system to classify sludges be developed. For example, if two sludges have the same metal concentrations will they behave in the same manner? Sludge stability depends on several factors as discussed earlier. A classification system could be used as a guide in the selection of appropriate disposal strategies. This classification system could serve as part of the 'Sludge

Management Guidelines' for acidic drainage sludges, another requirement for the sludge toolbox.

As there is still limited data available on sludge management practices and performance, there is an opportunity now to define methodologies and best practices for sludge management. The development of sludge management guidelines is fundamental in ensuring that appropriate sludge management options are implemented.

A nationwide inventory of sludge generation including quantities and general composition is also lacking from the current available data. CANMET (2004) has compiled this information for several sites however many sites have not been surveyed.

This report has presented various disposal options. As discussed above, monitoring data is required to evaluate conventional disposal practices, such as codisposal and pond disposal. However, other sludge management options require further study to either prove the technology, and to address issues that prevent or limit full-scale adoption.

Research Gaps

There are a number of promising technologies with research gaps that need to be addressed before large-scale implementation can occur. Incorporating sludge into paste backfill shows promise both from a land use and sludge stabilization perspective. Further research is required in this area to increase the sludge component of the backfill and to address questions about the long-term stability. At present, the effect that the sludge will have, if any, on the long-term chemical and physical stability of the backfill is generally unknown.

While backfill sludge disposal may be effective for operating mines, sludge disposal continues to be an issue for decommissioned mines. Disposal of sludge in the underground mine workings is a sludge management option that warrants further review. Previous work (Aubé et al., 2003) suggests that this practice may improve mine water quality while addressing sludge disposal requirements. However, again there are limited studies available to properly assess this disposal option. As with paste backfill, this option is attractive since the sludge is disposed underground, reducing the footprint and resulting site liability. Other countries, where land is at a premium, practice underground disposal more frequently. In fact, the Japanese have completed a guidebook on underground sludge disposal (MMAJ, 1997). Underground disposal is practiced in Canada; however, long-term performance data is not readily available. By contrast, the United Kingdom has never practiced disposal of sludge in mining workings due to concerns over the potential for ground water contamination (Jarvis, 2004).

Further study is also required in the area of sludge reprocessing and reuse to make these technologies more feasible. While not economically attractive today, these technologies may become more appealing in the near future with increased environmental pressures. Cost-effective metal recovery technologies require further development. In addition, more work in the area of smelting of metal hydroxide sludges is necessary. This option provides feedstock to the smelters, removes the requirement for sludge disposal, and provides additional revenue through metal recovery. However, issues regarding impurity contamination and moisture contents are some of the many challenges that need to be addressed.

Many of the research requirements deal with the sludge post-production, however there is a need to improve treatment methods to eliminate or reduce sludge production. By reducing sludge volume and increasing solids content reuse/reprocessing options become more feasible and sludge disposal costs are minimized. In addition, modifications should be made to treatment processes to selectively precipitate the heavy metals and segregate them from the gypsum, calcite and iron components of the sludge. By segregating the problematic metals, which represent a small portion of the total sludge volume, from the voluminous iron/gypsum phase, the overall sludge disposal requirement will be reduced and reuse opportunities will improve. Several biosulphide processes such as the Bioteq process (Lawrence et al., 2003) effectively recover the problematic metals (e.g. Zn, Cu) for revenue and produce a relatively inert sludge containing iron oxyhydroxides and gypsum.

Other research areas, which also warrant further study, include: in-situ densification technologies, sludge stabilization and sludge revegetation.

Finally, a shift in thinking is necessary if sludges are to be managed effectively. From the industry, practices need to be introduced so that the approach to sludge management is more systematic and well planned rather than ad hoc. Processes must be selected that reduce sludge volumes and disposal strategies must be appropriate. From regulators, there needs to be increased pressure for information on sludges. Monitoring and sludge volume data needs to be requested from operators. From the consulting and research community there needs to be a creative approach to dealing with sludges and acidic drainage treatment. Alternative options need to be developed and considered rather than only relying on conventional approaches. And finally, there needs to be public patience and open-mindedness.

CONCLUSIONS

Sludge management is an ever-increasing issue as the inventory of sludge continues to grow through *"perpetual pump and treat".* Current sludge management practices are ad hoc and frequently do not address long-term storage, and in some cases, long-term stability issues. While there is a plethora of disposal strategies available for sludges, many have not been fully investigated and monitoring data on the performance of these technologies is limited and not readily available. Further research is required into disposal options that can recover metal, densify existing sludge, or safely dispose of the material in a way that it can either be easily reclaimed or disposed in mine workings. Promising options must be both technologically feasible and also cost effective. In addition, sludge management options must be able to meet increasing environmental standards and pressures. With such limited data available on sludge characteristics, standardized methods, and long-term laboratory and field performance, it is important to focus efforts now to address some of these gaps in the knowledge base. The recommended gaps that require further attention are:

- Advanced sludge characterization
- Long-term laboratory testing to evaluate sludge behaviour under different disposal conditions
- Monitoring data for various disposal strategies at different mine sites, case studies
- Standardized tests – to predict sludge stability, accelerated test methods
- Sludge classification system – sludge management inventory
- Sludge Management Guidelines
- Research Gaps
    - Sludge in paste backfill
    - Disposal in underground workings
    - Sludge reprocessing and reuse

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