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Review

Potential Technologies for Removing Thallium from Mine and Process Wastewater: An Abbreviated Annotation of the Literature

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ABSTRACT

Thallium is more toxic to humans than mercury, cadmium, lead, copper or zinc. Its chemical behavior resembles the heavy metal lead and the alkali metals (K, Rb, Cs). It occurs almost exclusively in natural waters as monovalent thallium (Tl^{+1}). The solubility of thallous compounds (e.g., thallous hydroxide) is relatively high so that Tl^{+1} is readily transported through aqueous routes into the environment. The major sources of thallium are the base metal sulfides and precious metal bearing sulfides. Therefore, it has been shown to be a contaminant constituent in waters emanating from heavy metal sulfide bearing deposits.

A comprehensive survey of the thallium literature was conducted to answer two questions:

- Is thallium contamination in mine and effluent wastewater a significant problem and, if so,
- What technologies are available for removing thallium from the waters to achieve current U.S. effluent discharge regulations?

An annotation of the available literature, descriptions of potentially appropriate technologies, and recommendations for future study are presented in this paper.

Keywords: Thallium; Extraction; Precipitation; Adsorption

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1. INTRODUCTION

1.1. Technology literature search

An extensive survey of the literature has been conducted related to technologies that have been developed for thallium removal from wastewater. Only the publications concerned with the removal of thallium from aqueous solutions have been reviewed and summarized in this presentation, i.e., publications concerned with health effects, general chemistry, geochemistry, and toxicity have not been reviewed.

The information summarized in this presentation emphasizes possible mine wastewater treatment technologies. However, some of the unit operations described in the literature for cleanup of municipal wastewater, stream waters, metallurgical and chemical wastewater and process waste solutions have been surveyed. Therefore, much of the additional information is presented here with the idea that technology transfer may be possible. Because of the extensiveness (on a world-wide basis) of the thallium literature a portion of the annotation comments are based on a review of abstracts rather than a review of complete publications.

All of the following thallium bearing water sources have been included in the literature survey: groundwater pumped to conduct mining operations, waters emitted from abandoned mines, process waters used in mining and mineral processing operations (including milling,

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concentrating, smelting and refining), and waters produced during mine closure (such as effluents from heap leach rinsing).

The literature databases searched for thallium publications included: Applied Science Abstracts, Chemical Abstracts, Chemical Engineering and Biotechnology, Enviroline, GeoRef, and Metadex. Each database was searched for the entire dates available. However, because of space limitations only those studies published during the last ten years will be included, except for several critical publications. For complete coverage of the literature the authors recommend that the reader refer to the publication by the US EPA Mine Waste Treatment Program (MWTP, 1999).

1.2. Thallium in the environment

A recent review of the occurrence of thallium in the environment has been edited by Nriagu (1998). A summary of the review is presented in Table 1. Other extensive reviews for thallium occurrence in the environment, the production and uses of thallium, the biological effects of thallium in humans, animals, and thallium uptake in plants are included in bibliography (Bagat *et al.*, 1997; Kemper *et al.*, 1991; Micke *et al.*, 1983; Sabbioni *et al.*, 1984; Sager, 1994; Schoer, 1984; Smith *et al.*, 1978; Zitko, 1975).

Table 1
Thallium in the environment

Source	g/L (ppb)	g/kg (ppb)
Drinking water	7.2	
Groundwater, river water, groundwater	20-24	
Marine sediment		200-5,700
Deep sea sediments		10-5,700
Deep sea manganese nodules		to 100,000
Coal power plants (worldwide), kg/y		599,000
Lanmuchang thallium ores, Hg-Tl	0.4-27	720,000-3,800,000
Water (well, spring, stream, minewater)		
Nanhua thallium ores, As-Tl	0.1-16.5	960-1,900
Water (spring, minewater, slag water)		
Sulfide minerals: Chalcopyrite		to 5%
Galena		1,400-20,000
Sphalerite		8,000-45,000
Pyrite		5,000-23,000
Production from sulfides (Worldwide), kg/y		15,500 in 1988
Entering Pb, Zn, Cu smelting (Worldwide), kg/y		>160,000
Production from iron smelting (U.S.), kg/y		>140,000
Total world mobilization, kg/y		>2,000,000

1.3. Thallium sources

Thallium is normally associated with sulfide minerals and is often found in mineralized areas interspersed with sulfide deposits (Zitko, 1975). Thallium bearing sulfide minerals exist but they exist in low concentrations, e.g., the following sulfide minerals have been identified: carlinite ($\mathrm{Tl_2S}$), lorandite ($\mathrm{TlAsS_2}$), christite ($\mathrm{TlHgAsS_3}$), ellisite ($\mathrm{Tl_3AsS_3}$), weissbergite ($\mathrm{TlSbS_2}$), galkhaite ($\mathrm{Tl(Hg,Cu,Zn)_6(As,Sb)_4S_{12}}$) (Percival *et al.*, 1993), $\mathrm{Tl_2(As,Sb)_8S_{13}}$ (Wilson *et al.*, 1991), lorandite ($\mathrm{Tl_2As_2S_3}$), Crookesite ($\mathrm{Cu_{15}Tl_2AgSe_9}$), Vrbaite ($\mathrm{Tl_5S.2As_2S_3.Sb_2S_3}$), Hutchinsonite ($\mathrm{(Ag,Tl)_2S.As_2S_3}$) (Shaw, 1952, 1957).

The ionic radii of $\mathrm{Tl^{+1}}$ is similar to $\mathrm{K^{+1}}$, i.e., ($\mathrm{Tl^{+1}}$=1.40A°; $\mathrm{K^{+1}}$=1.33A°). Therefore, $\mathrm{Tl^{+1}}$, isomorphically substitutes into potassium mineral structures. These isomorphic mineral phases are sometimes present near or in oxidized regions near sulfide deposits. It is not unusual for thallium to be present in mined sulfide materials processed for recovery of gold, copper, lead, zinc and uranium (Percival and Radtke, 1993). The geochemistry of thallium is well established and a number of reviews have been published (Shaw, 1952, 1957; Sahl, 1978; Sager, 1992; Moh, 1993; Percival and Radtke, 1993).

Ores are presently only mined for thallium in China (Zhang *et al.*, 1998); i.e., Nanhua, Yunnan and Lanmuchang, Guizhou. The Nanhua property is an As-Tl containing thallium up to 0.19%. The Lanmuchang property is a Hg-Tl deposit containing up to 0.38%. Elevated thallium concentrations in the areas surrounding the mining operations and in associated waters are a major health problem, e.g., thallium in soils surrounding the Lanmuchang mining operation range from 4-55mg/kg, waste residues contain 86-240mg/kg; waters contain from 0.4-27mg/L.

1.4. Environmental standards

The USEPA specifies that the Best Demonstrated Available Technology (BDAT) for the thallium wastewater is oxidation of Tl^{+1} species followed by precipitation (Rosengrant and Craig, 1990). The BDAT for treating wastewater must lower the thallium to $<140\mu g/L$. Other environmental standards are presented in Table 2.

Table 2
Environmental standards

Source	Standard, µg/L
USEPA Primary Drinking Water Regulations, (MCL)	2
Human Health Effects in Seawater	4
Wastewater (for USEPA RCRA categories: P113, P115, U214, U215, U216, and U217) BDAT	140
Soils, Federal Republic Germany	1 mg/kg
Environmental Threshold Exposure to Thallium Compounds in U.S., Federal Republic Germany, Switzerland	0.1 mg Tl/m^3

2. DESCRIPTION OF THALLIUM REMOVAL TECHNOLOGIES

2.1. Adsorption processes

A large number of investigations have focused on surface adsorption as a means of removing metals, arsenic, and selenium from aqueous phase solutions, e.g., adsorption on ferric hydroxides, aluminum hydroxides, alumina, activated carbon, clays, etc. However, much less has been published concerning thallium removal by adsorption. Adsorption phenomena on ferric surfaces has been the emphasis of most of the investigations for metals, arsenic, and selenium but most of the thallium adsorption literature is based on manganese dioxide adsorption.

2.2. Manganese dioxide adsorption

A number of studies have been directed toward evaluating the adsorptive power of a variety of types of manganese dioxide for thallium and heavy metals: natural and chemically precipitated manganese dioxide, e.g., Bidoglio *et al.*, 1993; Grossl *et al.*, 1994; Flegal *et al.*, 1989; electrolytic manganese dioxide, e.g., Dahal *et al.*, 1996, 1998; and manganese dioxide sludge, e.g., Jibiki, 1995.

Chemically precipitated manganese dioxide-Bidoglio *et al.* (1993) have reviewed adsorption of thallium on chemically precipitated manganese dioxide (δ-MnO_2). These authors also conducted experimental work comparing the adsorption of thallium on δ-MnO_2 ($190m^2/g$), SiO_2 ($200m^2/g$), and γ- Al_2O_3 ($130m^2/g$). They found complete thallium adsorption (from solutions containing 24 μg/L to 41mg/L thallium) on δ-MnO_2 at pH levels of 4.7-8.5. The mechanism for removal was surface adsorption of Tl^{+1} with subsequent oxidation to Tl_2O_3. Comparative tests using γ-Al_2O_3 and SiO_2 showed essentially no thallium adsorption over the same pH range.

Means *et al.* (1978) conducted a literature review of manganese dioxide adsorption that provides a number of reasons why it is a good adsorbent for cations. Their points include: Manganese dioxides are much better heavy metal scavengers than other surfaces, e.g., the degree of adsorption is manganese oxide>organic matter>iron oxides>clay minerals. Surface areas of manganese minerals, like birnessite δ-MnO_2, range up to 350m^2/g. The pzc (point of zero charge) is unusually low, i.e., pH=1.5-2. Therefore, the surface is negatively charged for pH conditions of many waters which provides electrostatic attraction for cations. The cation exchange capacity is relatively large, e.g., 1.5 equivalents/100g (compares to 0.1 equivalents/100g of montmorillonite clays) at a pH of 8.5.

Electrolytic manganese dioxide (EMD)-EMD is commercially formed by electrolytic oxidation of manganese sulfate solution under acidic conditions at temperatures near the boiling point (Dahal, 1996, 1998). Its major use is in disposable and rechargeable batteries. Conditions for complete removal of thallium were not specified, i.e., manganese loading, pH, time, temperature, influence of other solution species.

Adsorption on EMD is normally a function of initial ion concentration, presence of other ions, and solution pH. Dahal, *et al.* (1996, 98) demonstrated that adsorption of metal ions follows the simple Langmuir adsorption equation. The order of specie adsorption from solutions (10-2000 mg/L) was shown to be (pH<2): $Bi^{+3}\sim Pb^{+2}>Tl^{+1}>Cr^{+3}>Cu^{+2}$ and (pH 4), $Pb^{+2}>Cu^{+2}>Tl^{+1}>>Cr^{+3}$.

Manganese dioxide sludge-Manganese dioxide sludge produced during zinc electrowinning has been shown to be very effective in removing thallous ions from zinc process waters and from lead smelting effluent wastewater (Jibiki, 1995) has demonstrated thallium removal from lead smelting effluent waters to less than 100μg/L (12.5mg/L thallium initial). His recipe includes the following, i.e., electrolytically formed manganese dioxide is required (manganese ores, mineral forms of MnO_2 and chemically precipitated manganese dioxide were not as effective as the electrolytically produced manganese sludge); -38µm particles are recommended; a dose of one gpl; a pH of <4 is desirable; and a residence time in a stirred reactor of one half to one hour. The loaded manganese dioxide can be treated to recover the thallium, e.g., the manganese dioxide can be leached in a weak acidic solution in the presence of a reducing agent such as sulfur dioxide, sulfite chemicals, ferrous chemicals. The thallium can then be recovered from solution by precipitating elemental thallium using zinc dust.

2.3. Ferrihydrite adsorption

Ferric precipitation as ferrihydrite has been extensively covered in the literature. In fact, there is a recipe book (Schwertmann and Fechter, 1995) on how to prepare hydrated iron oxides. All of the iron oxides are crystalline except Ferrihydrite. Ferrihydrite is normally of low crystallinity and is actually a range of compounds that exhibit different degrees of structural order. In general, ferrihydrites are characterized according to the number of broad X-ray peaks, e.g., 2-line (completely amorphous) and 6-line (semi-crystalline). The generally accepted formula for ferrihydrite is $5Fe_2O_3.9H_2O$ (Schwertmann and Cornell, 1991).

There has not been a through experimental investigation of the adsorption of thallium on ferrihydrite. What little data exists is based on phenomenalogical observations that thallium concentrations (mostly as thallic ions) in sediments appear to higher in ferrihydrite and manganese dioxide bearing sediments. Other evidence for believing that ferrihydrite is effective for adsorbing thallium is provided by surface adsorption modeling work by Lin and Nriagu (1998). They have modeled the adsorption of Tl^{+1} and Tl^{+3} on ferrihydrite by using the MINEQL calculational two-layer adsorption model. Their results predict that the order of adsorption effectiveness for thallium on ferrihydrite at pH 6 is $Tl^{+1}>Tl^{+3}>Pb^{+2}>Cu^{+2}>>Zn^{+2}>Cd^{+2}$.

Kikuchi *et al.* (1990) demonstrated the removal of thallium from synthetic and process solutions. They demonstrated that thallium could be effectively removed by doping the solution with iron powder, then oxidizing with hydrogen peroxide, then raising the pH. The proposed removal mechanism was a combination of thallic hydroxide precipitation and thallium aqueous specie adsorption on freshly formed ferrihydrite. The authors treated thallium solutions containing 100-500mg/L with an iron dosage 12.5g/L and a peroxide dosage of 100cm^3 of 30% H_2O_2/L for 15 minutes and achieved removal to 1-20mg/L.

Brewster and Passmore (1994) developed a similar process called the Andco Process. Their process utilizes an iron sacrificial anode to produce ferrous ions in the wastewater which are then oxidized to form ferrihydrite for adsorption of aqueous ionic species. This process has not been applied industrially for thallium removal but it has been applied industrially for the removal of arsenic (Twidwell *et al.*, 1999a, b). They demonstrated complete (<5µg/L) thallium removal in a pilot plant study (107.26L) for a superfund landfill site water containing 32µg/L thallium.

Loux *et al.* (1989) modeled the results of previous experimental test work on Wisconsin aquifer materials containing ferrihydrite. The order of predicted adsorption was found to be the same as the observed, i.e., Pb>Cu, Be>Zn>Cd>Tl>Ni, Ba.

Dutrizac (1997) and Zinck and Dutrizac (1998) have demonstrated that thallium (10-3000mg/L) is not effectively removed from high zinc (75g/L zinc, pH 2.5-4.5, 40°-75°C) bearing solutions by ferrihydrite adsorption. The thallium removal that did result (even though only a small fraction was removed at the lower temperatures) was identified to be removed via thallium jarosite precipitation ($TlFe_3(SO_4)_2(OH)_6$). However, this work does not negate the possible effectiveness of ferrihydrite adsorption of thallium under other conditions, i.e., this study was conducted in the presence of high concentrations of zinc cations which likely saturate the available adsorption sites thus precluding the adsorption of thallium aqueous species.

2.4. Zeolite adsorption

Eyde *et al.* (1993, 1998) have applied zeolite (CABSORB ZS500RW) to the removal of thallium from actual minewater. The authors treated a western gold mining company's mine closure drainage and process waters containing 50-1000µg/L thallium in bench scale and pilot scale studies by their zeolite adsorption technology. The treatment lowered the thallium to <1.7µg/L. The pilot scale treatment was conducted in upflow fluidized bed packed columns using a single pass exposure system at flowrates of 56.78-94.64 liter/minute. The closure technology chosen by the mining company consisted of reverse osmosis followed by zeolite adsorption polishing. In 1998 over 41.6 million L of RO permeate were polished by the zeolite system to a thallium of <2µg/L. The <2µg/L was achieved in the first column utilizing a five minute retention time. Over 22,000 bed-volumes passed through the original bed without need for replacement of the zeolite. A pilot scale demonstration (fluid bed adsorber) at the ASARCO lead smelter using their water treatment thickener overflow water successfully reduced the thallium to less than their effluent standard, i.e., <56µg/L. However, the process was not selected for use because manganese was not successfully lowered to the desired limit.

2.5. Activated carbon adsorption

There have not been very many studies on the effectiveness of carbon for thallium removal. Rivera-Utrilla *et al.* (1984) studied the adsorption of Cs^{+1}, Tl^{+1}, Sr^{+2}, and Co^{+2} on activated carbons from aqueous solutions. They used three carbon types, e.g., two were produced from almond shells and one purchased from a commercial source. The exposure conditions consisted of adding 0.1 gram of carbon/4 milliliters of 7-10 molar solution of Tl^{+1} at a pH of 6. The results of their work showed greater than 98% of the thallium was removed, regardless of carbon type or content. They also found that thallium was not removed when carbon was not present. The conclusion that the authors presented is that Tl^{+1} was adsorbed but then was oxidized to relatively insoluble thallium hydroxide or oxide.

Sheya and Palmer (1986) investigated the effect of metal impurities (including thallous ions) on adsorption of gold by activated carbon (coconut) in cyanide solutions over the pH range 6.4-12.5. Experiments were conducted in solutions with and without gold and cyanide present.

One gram of activated carbon was added to 250 milliliters of 150mg/L of thallium and 0.5g/L of free cyanide. Thallium showed increased adsorption with an increase in pH, e.g., 14% at a pH of 6.8 and 55% at a pH of 12.5. In the presence of gold (150mg/L) thallium was more strongly adsorbed, e.g., 22% at a pH of 6.8 and 70% at a pH of 12.3.

2.6. Other absorbents

Rauws and Canton (1976) suggest that potassium ferricyano ferrate (prussian blue) absorbs thallium ions almost quantitatively. Prussian blue is an antidote for thallium poisoning in several European countries. The solution conditions, doping concentrations, cost, and final achievable thallium concentrations were not presented.

Srivastava *et al.* (1980) investigated the use of chromium ferrocyanide gel for removal of heavy metals. They found that the gel had a great affinity for heavy metals, including thallium. The order of affinity for metals (pH 2-3) was $Ag^{+1}>Tl^{+1}$, $Cu^{+2}>Co^{+2}>Cd^{+2}>Zn^{+2}>Mn^{+2}>Pb^{+2}>Mg^{+2}$, $Fe^{+3}>Al^{+3}$. The loading capacity for heavy metals was 3.65 milliequivalence/gram of gel.

2.7. Precipitation

Thallium is recovered from process solutions (Minami and Takei, 1990) at the Sumitomo Harima Works (lead/zinc smelter complex) for market. This is one of the few plants that recover thallium for the marketplace. Zinc and lead concentrates are roasted in a sintering operation. The thallium is volatilized along with the cadmium. The thallium and cadmium are scrubbed from the gas phase. The cadmium is removed by ion exchange (thallium follows the cadmium). The concentrated cadmium solution is precipitated as a cadmium carbonate. The solution phase contains the thallium as thallous ions. The thallous ions are oxidized and thallic hydroxide precipitates. The resulting sludge contains from 25-37% thallium. The thallium sludge is releached in hydrochloric acid containing sodium bisulfite and is reduced to thallous chloride. This solution is then treated with zinc dust to reduce the thallous to elemental thallium. The final solution contains approximately 1g/L thallium.

EPA's BDAT is oxidation and chemical precipitation (Rosengrant and Craig, 1990). Th process consists of the steps: lime or caustic is added to a mix tank to raise the pH to 8-10. If thallous ions are present sodium hypochlorite is added as a preliminary step to oxidize the thallous specie to the thallic form. Thallic hydroxide precipitates along with other metal hydroxides. The slurry is then treated by conventional coagulation, settling devises.

2.8. Ion exchange (IX)

IX is widely used in hydrometallurgical applications for treatment of solutions containing uranium, chromium, platinum group metals. However, its application as a treatment technology for removing thallium has not been extensively investigated.

Albert and Masson patented (1992) a process utilizing IX. Their patent covers the extraction of thallium from acidic solutions by use of an IX resin containing thiol; stripping of the thallium into a relatively concentrated solution and subsequent recovery of metallic thallium as a marketable product. The treatment can be performed in the presence of arsenic, cadmium and zinc and can be made selective for thallium by controlling the solution pH and potential, e.g., 0.6 volts at pH <1 up to 0.2 volts at pH 6.

2.9. Solvent extraction(SX)

Sato *et al.* (1989, 1992, 1996, 1997) have investigated SX of Tl^{+3} ions from aqueous solutions. They have considered the extraction by common SX reagents, including tributyl phosphate (TBP), trioctyl phosphine oxide (TOPO), trioctylamine (TOA), di 2-ethylhexyl phosphoric acid (DEHPA), 2-ethylhexyl 2-ethylhexyl phosphoric acid (EHEHPA) and 5,8-diethyl-7-hydroxy-6dodecanoneoxime (LIX 63). They found that thallium is effectively extracted by TOPO in benzene (at 25°C) from hydrochloric acid solutions. The thallium can be recovered from the organic phase by stripping in 0.1 M sodium hydroxide. The order of extraction of the Group IIIB elements is Tl>Ga>In. Hasegawa *et al.* (1980) also investigated the use of TOPO for extracting group IIIB elements (including thallium^{+3}, 20.4mg/L) from hydrochloric acid. Their results are in approximate agreement with Sato *et al.* (1992). The order of extraction using TBP was the same as the order for TOPO. Sato *et al.* (1989, 1997) considered the extraction of group IIIB elements from hydrochloric acid solutions by DEHPA and EHEHPA. They found that the order of extraction of the group IIIB elements was In>Ga>Tl>Al (at <0.4 moles HCl/L); In>Tl>Ga>Al (at 0.4-5 moles HCl/L); and Tl>Ga>In>Al (at >5 moles HCl/L); by both DEHPA and EHEHPA, but the extractions were higher in the DEHPA tests. Sato *et al.* (1992) considered the extraction of group IIIB elements from hydrochloric acid solutions by LIX 63. They found that the order of extraction of the group IIIB elements is Tl>In>Ga (at <3M HCl) and Tl>Ga>>In (at >3M HCl). The thallium can be recovered from the organic phase by stripping in 1M sodium carbonate solution.

3. SUMMARY

Very few technologies appear to hold promise for application to minewaters for removing thallium to <2μg/L. A summary of the technologies recommended for further evaluation (either laboratory or pilot scale evaluation) is presented in Table 3.

Table 3
Summary of technologies recommended for further evaluation

Technology	Description	Precautions	Product
MnO_2	MnO_2 adsorption of thallium has been extensively investigated. Conditions for thallium removal can be specified. Other aqueous species will likely influence the removal of thallium, i.e., the order of adsorption (at pH 4) has been shown to be; $Pb^{+2}>Cu^{+2}>Tl^{+1}>>Cr^{+3}$.	Most test work has been directed toward adsorption of thallium from the solution phase; very little information is available as to the extraction of thallium from the adsorbent and the possibility of reuse of the MnO_2. The technology has not advanced to pilot or full scale utilization.	Thallium loaded MnO_2, or if the thallium can be stripped from the MnO_2, elemental thallium.
Ferrihydrite	Surface adsorption modeling suggest that ferrihydrite may be effective at pHs>6. The predicted order of effectiveness is: $Tl^{+1}>Tl^{+3}>Pb^{+2}>Cu^{+2}>Zn^{+2}>Cd^{+2}$.	This technology has not been experimentally demonstrated to be effective for adsorption of thallium. Successful application to a variety of mine waters needs to be demonstrated.	Ferrihydrite sludge. The sludge would have to be handled as a hazardous waste.
Metal Reduction	This process is based on industrial practice for treating process solutions, i.e., zinc reduction of thallium ions. Other cementing metals may be effective, e.g., iron or aluminum scrap.	The product from this treatment cannot be disposed of in tailings ponds. The extent of thallium removal is unknown, i.e., it is unknown whether thallium in solution can be lowered to the μg/L range.	Zinc containing thallium. The thallium content can be built up to several percent.

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