

MERCURY CYANIDE CONTAMINATION OF GROUNDWATER FROM GOLD MINING AND PROSPECTS FOR REMOVAL

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ABSTRACT

Ore bodies from which gold is mined are often composed of minerals containing sulfur, selenium and tellurium. Mercury is also associated with these three elements and is simultaneously dissolved during gold extraction. When cyanide salts are used to extract gold, mercury cyanide complexes that form enhance mercury mobility and increase mercury concentrations in groundwater. In one instance this resulted in mercury contamination of drinking water supplies where removal to an acceptable level could only be achieved at an exorbitant cost. A combination of precipitation and adsorption are most often used to achieve metal removal from waste streams. However, mercury removal is problematic because in addition to being acutely toxic, mercury tends to be soluble in the presence of many common anions and soil materials, and compared to other metals it is highly volatile. Further research into treating mercury contaminated waste streams and into the gold mining process is needed.

RÉSUMÉ

Les minerais desquels l'or est extrait contiennent du soufre, du sélénium et du tellure. Le mercure est aussi présent dans ces minerais et se dissout durant le processus d'extraction de l'or. Quand les sels du cyanure sont utilisés pour extraire l'or, les complexes de cyanure de mercure qui se forment augmentent le facteur de mobilité du mercure et haussent la concentration de celui-ci dans la nappe phréatique. Dans un cas particulier, ceci a mené à la contamination de la réserve d'eau potable, où la décontamination aura été seulement possible à un coût exorbitant. Le précipitation et adsorption sont le plus souvent utilisées pour décontaminer les eaux usées. Toutefois, l'enlèvement du mercure est problématique car le mercure a tendance à être soluble en présence de plusieurs anions et minéraux communs et il est très volatil. Plus de recherche sur le traitement des eaux contaminées et le processus d'extraction de l'or est nécessaire.

1. INTRODUCTION

In the late 1980's Canada was the third largest producer of gold and most of the mills in Canada were using the cyanidation process to extract, on average, about 7.1 g of gold from each tonne of ore (Scott, 1989). Sodium and potassium salts of cyanide are commonly employed in mining operations to extract gold but these salts are not selective and they also dissolve other elements in the ore bodies (Scott, 1989). Sodium cyanide has been the single most widely used solvent for extracting gold in recent times (Matlock et al., 2002).

During gold (and silver) mining operations other elements that are often present and also dissolved include copper, lead, zinc, nickel, iron, cobalt and mercury (Boyle and Smith, 1994). Cyanide forms complexes with all the above elements, but the soluble mercury-cyano complexes are some of the most stable and are especially difficult to remove from mine waste effluents (Boyle and Smith, 1994; Tassel et al., 1997; Gillis and Al, 1998; Matlock et al., 2002).

Gold is associated with minerals containing sulfur, tellurium and selenium (Müezzinoğlu, 2003). Mercury occurs in compounds with gold, silver and the platinum metals, it forms sulphides, selenides and a telluride and it complexes with antimony and arsenic. The most common mineral

deposits of mercury are cinnabar (HgS), metacinnabar (HgS) and livingstonite (HgSb₄S₇) (Jonasson and Boyle, 1971). Other chalcocite minerals containing mercury include tiemannite (HgSe) and coloradoite (HgTe) as HgTe(II) and HgTe(III) (Yu et al, 1981). In soils, mercury bonds with clays, organic matter and sesquioxides (Mitra, 1986), the highest mercury concentrations are observed in clays and organic matter (Anderson, 1979), and the mercury taken up by these soil fractions is not leached under natural conditions (Steinnes, 1990).

Gold and mercury are two of the least abundant elements in the earth crust (Schacklette and Boerngen, 1984) and mercury is acutely toxic (Mercone et al., 1999). Bioaccumulation of organo-mercury is significant as mercury concentrations in fish may be 10⁶ to 10⁷ times greater than mercury concentrations in ambient waters (Riddle et al., 2002) enabling mercury to move up the food chain. Mercury has a high vapour pressure and most compounds of mercury are volatile and are readily volatilized. For example, air in equilibrium with liquid mercury and cinnabar will contain 14 and 10 mg Hg/m³ respectively, while the maximum safe level of atmospheric mercury is considered to be 0.05 mg Hg/m³ (O'Neill, 1993). It is evident that rapid and efficient removal of mercury from waste streams needs to be a high priority (Monteagudo and Ortiz, 2000), as does reducing the extent to which mercury is being released into the environment. It is estimated that

current gold mining techniques may be responsible for extracting more mercury than they do gold (Korte and Coulston, 1997). This is possible given that mercury appears to be somewhat more abundant than gold (Schacklette and Boerngen, 1984).

The first step in metal removal operations is commonly metal precipitation (Brown et al., 2000) and metals may be precipitated with the addition of sulphide, hydroxide or carbonate species, removing the bulk of the metal from the liquid phase. Mercury is usually soluble when it combines with carbonate (Jonasson and Boyle, 1971) and both mercury hydroxides, $\text{Hg}(\text{OH})^+$ and $\text{Hg}(\text{OH})_2$ are quite soluble in water (Cotton and Wilkinson, 1999). Of the sulphide, hydroxide and carbonate minerals, the sulphides are the most insoluble and for this reason metal sulphide precipitation is most often used (Beszedits, 1979). The sulphides normally form stable compounds with mercury under anoxic conditions, (Hutchison and Atwood, 2003) however in the presence of mercury cyanide complexes stable mercury precipitates cannot be obtained (Tassel et al., 1997).

The soluble mercury-cyano complexes, such as $\text{Hg}(\text{CN})_2$ and $\text{Hg}(\text{CN})_4$, increase mercury mobilization (Miller et al., 1996; Gilliss and Al, 1998) and mercury concentrations in groundwater, usually as Hg^{2+} (Andren and Nriagu, 1979). Mercury is also soluble when it combines with chloride, nitrate, sulphate and some organic compounds (Jonasson and Boyle, 1971).

The second step in metal removal operations is usually adsorption, since water quality and drinking water quality guidelines may not be achievable with precipitation alone (Brown et al., 2000). Adsorption techniques are able to achieve acceptable levels of metal removal and adsorption is considered to be a promising technique. However, adsorption has not become widely used because activated carbon and ion exchange resins are expensive. This has led to the search for more economical adsorbent materials (Ho et al., 2002).

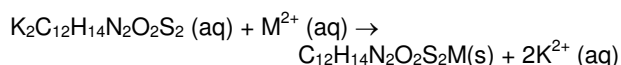
With the use of precipitation, followed by a polishing step such as adsorption, it is ideal when the greatest possible amount of metal removal can occur at the precipitation stage. One problem encountered with the use of adsorbents for final removal of excess mercury is that mercury may be volatilized during regeneration of the adsorbent (Matlock et al., 2002). However, if inexpensive adsorbents are developed so that they can be safely disposed of along with the mercury, then this might be an alternative.

Two treatments for the removal of mercury released during gold mining activities are reviewed and commented upon in this paper. However, at present, there may not be a method for removal of mercury after cyanide leaching of gold that is economical and adequately protects the environment, and the presence of mercury cyanide complexes is a factor in this.

2. TREATMENTS FOR MERCURY

One of the recent treatments proposed by Matlock et al. (2002) for the removal of mercury from gold leachate solutions, prior to removal of the gold, is the use of a dipotassium salt of 1,3-benzendiamidoethanethiol (BDET^{2-}). BDET^{2-} is a soft base that reacts with soft acids such as Hg^{2+} and Cd^{2+} as predicted by the hard soft acid base theory, but does not react with gold or silver. It is also reported to be effective in removal of Pb^{2+} (Hutchison and Atwood, 2003).

BDET^{2-} forms a chelation complex that is able to remove mercury from solution in the pH range of 0 to 14 and the process occurs in a matter of minutes, with a concentration of only 8 ppb of mercury remaining in solution. The precipitate that forms is then removed in a subsequent filtration step. BDET^{2-} also removes copper, and copper is naturally more abundant than mercury. Therefore, when copper is also present the total amount of mercury and copper need to be determined in order to know the stoichiometric dose of BDET^{2-} required. The reaction, in water, is given below where Me^{2+} represents the divalent metals that will react with the BDET^{2-} (Matlock et al., 2002).



Since 2002, studies with BDET^{2-} have shown that it is efficient at removing mercury from gold leachate solutions after cyanidation, and the compound is now being marketed at US\$200 per gram (Atwood, 2003). Hutchison and Atwood (2003) describe this technology as promising and suggest that using ligands to precipitate mercury is one of the most effective treatments. The fact that Matlock et al. (2002) are proposing that the mercury be removed prior to the gold would be protective of the environment. The long term effectiveness of this technology may not yet be fully known.

Hutchison and Atwood (2003) review a number of techniques for the removal of mercury but only provide a strong endorsement for the use of BDET^{2-} . In their review they mention five compounds that complex mercury and all of them contain at least one sulphide ligand. Much of the literature on mercury draws attention to the association and interaction of mercury with sulfur.

Veiga and Meech (1995) suggest that remediation of sediments contaminated with mercury during gold mining activities may be effectively accomplished with liming and the addition of selenium. Their article is with respect to gold mined in developing countries by burning amalgams rather than by employing sodium or potassium cyanide to extract the gold. In the absence of mercury cyanide complexes, mercury may be more easily precipitated, however, this technology raises the question as to whether selenium might have a broader role in treating effluents containing mercury cyanide complexes.

Selenium is in the same group of the periodic table as sulfur and shares some similar properties with sulfur. Insoluble

metal selenides are able to exist across a wide range of pH under strongly reducing conditions and are dissolved under oxidizing conditions (Séby et al., 2001). Species of mercury and selenium are highly insoluble under anoxic conditions and highly unstable in the presence of oxygen, and transformations between the reduced and oxidized states are rapid (Mercone et al. 1999). Selenium is also known to lessen toxicity to mercury in mammals (Mercone et al., 1999).

Sulfur is a major element in the earth's crust and its abundance is in the order of 1,600 mg/kg. Selenium is a trace element that may have an average concentration in soils of about 0.39 mg/kg, compared to a typical background mercury concentration in soils of 0.09 mg/kg (Schacklette and Boerngen, 1984).

Apart from the sulphides, hydroxides and carbonates for precipitating metals, selenides and tellurides may also have an important role (Buketov et al. 1964). While there is less information on these latter two and less abundant groups of compounds, the literature does indicate that they are more insoluble than the sulphides. Table 1 shows the estimated solubility product constants for compounds of mercury with the sulphide, selenide and telluride ligands (Buketov et al., 1964).

Table 1. Estimated solubility product constants of selected compounds.

Compound	Solubility Product Constant, K_{SP}	Reference
HgS	2.0×10^{-53}	Jackson, 1986
HgSe	3.2×10^{-65}	Buketov et al., 1964
HgTe	2.5×10^{-70}	Buketov et al., 1964

The literature does not appear to contain any reference to the ability of selenium to precipitate mercury in the presence of the soluble mercury-cyano complexes. However, this is an area where research could be undertaken. Veiga and Meech (1995) suggest that the removal of mercury with selenium could be inexpensive. Reactions with inorganic compounds also tend to be rapid and result in the formation of stable products.

Alternatively, research into the use of complexes or chelates containing selenium or tellurium ligands might be considered for removal of mercury given the highly insoluble nature of these ligands.

3. CURRENT CONSIDERATIONS

When sodium or potassium cyanides are used to extract gold from ore bodies, the mercury that is released forms stable and soluble complexes with cyanide and the presence of these complexes make the mercury more difficult to precipitate. Modifications to the gold extraction process could minimize the environmental and health risks.

Gold mining goes back as least far as 4000 B.C. when large pieces of gold could be extracted with relatively primitive

methods and tools, and with minimal disturbance to the environment (Müezzinoğlu, 2003). Increasingly however, gold is being mined from ores that are of a lower grade or from ores where the gold is more strongly bonded, because these are the main sources of gold remaining (Miller et al., 1996). In recent times amalgamation and cyanidation have been used to extract this gold but these technologies have adverse environmental effects. Amalgamation results in excessive mercury emissions and is now illegal in many countries (Korte and Coulston, 1997). Cyanidation has been banned in the Czech Republic and in the US State of Montana, while Turkey and Greece have been discouraging its use and other US states are considering restricting its use (Müezzinoğlu, 2003; O'Reilly et al., 2003; Haiduc, 2005). Some industrial accidents including the gold mine tailings pond overflow into a tributary of the Danube River in 2000 has prompted this more critical view of the process (Müezzinoğlu, 2003).

It has been suggested that the cost to benefit ratio for gold mining is currently slightly greater than 1. This, however, does not account for "costs" associated with any environmental impacts (Müezzinoğlu, 2003). One tonne of ore may yield from 2.8 and 21.3 grams of gold (Scott, 1989; Warhurst, 1999; Müezzinoğlu, 2003). The large amounts of waste ore then require land for disposal (Korte and Coulston, 1998). As lands for agriculture, water resources and forests become increasingly scarce a greater need for prioritization of land use will develop and more efficient land use strategies will be necessary (Müezzinoğlu, 2003).

The cyanide salt requirement needs to be greater than that amount consumed by the gold alone, since other metals present in the ore will also react with the cyanide (Müezzinoğlu, 2003) and a large amount of the cyanide used escapes into the atmosphere (Korte and Coulston, 1998). Other metals extracted by cyanide leaching include iron, copper, zinc, cadmium, silver and nickel, and the latter four metals all form highly soluble complexes with cyanide (Müezzinoğlu, 2003).

In the 1970s when there were a number of mercury poisonings due to the consumption of food products contaminated with methyl mercury, this alerted the world to the dangers of mercury pollution and a decline in mercury production and use followed (O'Neill, 1993). However, mercury being emitted into the environment from industrial processes may not have decreased since "despite rigorous controls", between 1987 and 1992 the amount of mercury entering the atmosphere and surface and ground waters increased 114% (Blackman, 1996). Although cyanide leaching is a chemical process, the gold mining industry is not bound by the same controls that apply to processes within the chemical industry (Korte and Coulston, 1998).

4. CONCLUSIONS

From a survey of the literature on the removal of mercury from gold mining wastes, the cyanide leaching method does not appear to be of overall benefit. In addition, the removal of mercury from waste streams following the formation of

the soluble mercury-cyano complexes, is not easily accomplished. Use of the BDET²⁻ ligand to precipitate mercury has received some support, but it would be too costly for widespread use. The price of gold is currently US\$641 per ounce or the equivalent of US\$22.65 per gram. The equation for the reaction of BDET²⁻ with mercury indicates that 1.8 grams of BDET²⁻ will react with one gram of mercury, assuming that no other metals present react with the BDET²⁻. If for every gram of gold that is extracted, one gram of mercury is released into the environment, the cost of removing this mercury becomes US\$360 for each gram of gold obtained.

Sulfur, selenium and tellurium seem to be natural choices for precipitating mercury. Sulfur however, does not work when the soluble mercury cyanide complexes are present and there does not appear to be enough research done on selenium and tellurium to know if they could be used.

If the environmental costs of using cyanide salts for extracting gold are factored into the total costs, then the gold cyanidation process could be, or could soon become, economically unviable.

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