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**Kyle, J.H., Breuer, P.L., Bunney, K.G. and Pleysier, R. (2012)
*Review of trace toxic elements (Pb, Cd, Hg, As, Sb, Bi, Se, Te)
and their deportment in gold processing: Part II: Deportment in
gold ore processing by cyanidation. Hydrometallurgy,*
111-112 . pp. 10-21.**

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Accepted Manuscript

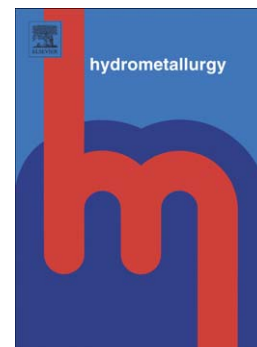
Review of trace toxic elements (Pb, Cd, Hg, As, Sb, Bi, Se, Te) and their deportment in gold processing. Part II: Deportment in gold ore processing by cyanidation

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PII: S0304-386X(11)00199-X
DOI: doi: [10.1016/j.hydromet.2011.09.005](https://doi.org/10.1016/j.hydromet.2011.09.005)
Reference: HYDROM 3433

To appear in: *Hydrometallurgy*

Received date: 8 March 2011
Revised date: 30 August 2011
Accepted date: 7 September 2011



Please cite this article as: Kyle, J.H., Breuer, P.L., Bunney, K.G., Pleysier, R., May, P.M., Review of trace toxic elements (Pb, Cd, Hg, As, Sb, Bi, Se, Te) and their deportment in gold processing. Part II: Deportment in gold ore processing by cyanidation, *Hydrometallurgy* (2011), doi: [10.1016/j.hydromet.2011.09.005](https://doi.org/10.1016/j.hydromet.2011.09.005)

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Review of trace toxic elements (Pb, Cd, Hg, As, Sb, Bi, Se, Te) and their department in gold processing.

Part II: Department in gold ore processing by cyanidation.

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ABSTRACT

The second part of a literature review on the deportment of trace toxic elements in gold processing by cyanidation is presented. Part 1 of this review collated the relevant information on trace element mineralogy, aqueous solution chemistry and toxicity for lead, cadmium, mercury, arsenic, antimony, bismuth, selenium, and tellurium. This paper reviews the deportment of these elements during gold ore cyanidation (including carbon adsorption and elution) and tailings disposal. It also captures related information from the treatment of industrial wastes and wastewaters, including fixation and encapsulation processes that may be applicable to tailings generated from gold ore processing.

The main findings were that only lead, cadmium and mercury form cyano complexes ranging from very weak (Pb) through moderate (Cd) to the strong mercurio complexes. The neutral cyano-complexes of cadmium and mercury strongly adsorb onto activated carbon and thus potentially deport to the gold recovery circuit and carbon regeneration kiln. The strong mercury cyano complexes will persist in tailings storage environments. Arsenic, antimony and bismuth do not form cyanide complexes. The less metallic of these (As and Sb) may form oxyanions and/or thioanions that consume oxygen and retard or prevent gold dissolution. They can be present in solution, including tailings solutions, at relatively high concentrations. Bismuth, being more metallic, remains in the solid phase as a sulfide or oxide during cyanidation. Depending on the redox potential in solution, selenium and tellurium form the oxyanions selenite and tellurite or selenate and tellurate in cyanide solutions. Selenium may form selenocyanate (SeCN^-) cyanide solutions, which is thermodynamically more stable than the oxyanions selenite and selenate. Tellurocyanate is unstable and does not form. The potential for adsorption of

selenium or tellurium onto activated carbon is unknown, as is their persistence in tailings storage facilities.

Lead, cadmium and mercury are best removed from wastewaters by precipitation as sulfides or adsorption onto activated carbon or iron or aluminium oxides. Arsenic and antimony in acidic tailings and mine drainage waters are also attenuated by precipitation onto iron oxides, or by precipitation as scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) or senarmontite (Sb_2O_3). Selenite in wastewater efficiently adsorbs on to both iron and manganese oxides but, selenate does not. Tellurium is less soluble in the aqueous phase than selenium and adsorbs more strongly onto iron oxides.

1. Introduction

The deportment of trace toxic elements during mineral processing is an area of increasing concern to the mining industry as processing can concentrate these elements presenting hazards to both personal health and the environment. Part 1 of this review (Kyle et al., 2011) collated the relevant information on trace toxic element mineralogy, aqueous solution chemistry and toxicity for lead, cadmium, mercury, arsenic, antimony, bismuth, selenium, and tellurium. This paper reviews their deportment during gold ore cyanidation (including carbon adsorption and elution) and tailings disposal, and also captures related information from the treatment of industrial wastes and wastewaters, including fixation and encapsulation processes that may be applicable to tailings generated from gold ore processing.

The chemistry and deportment of copper and zinc during cyanidation of gold ores are well known and have been the subject of numerous studies (Muir et al., 1989; Tran et al., 1997; Rees and Van Deventer, 1999; Lu et al., 2002; Marsden and House, 2006). However, there is currently only limited understanding of the behaviour and deportment during cyanidation of other trace toxic elements. A symposium on minor elements in 2000 focused on arsenic, antimony, selenium, tellurium and bismuth, and it was clear from a number of papers presented at this symposium (Chen and Dutrizac, 2000; Nishimura et al., 2000; Nordstrom, 2000) that the understanding of the behaviour and deportment of trace toxic elements during mineral processing, other than arsenic and to a lesser extent mercury, is very limited.

Lead has been used as an additive to catalyse the gold leaching reaction and assist in the control of soluble sulfides during gold processing (Sandenburgh and Miller, 2001; Marsden and House, 2006; Sandenburgh and Mahlangu, 2007). Mercury has in

recent years become a trace element of concern in ore roasting, pressure oxidative leaching, and gold cyanidation. Arsenic has been widely studied in gold processing, particularly the precipitation and disposal of solubilised arsenical wastes, and several commercial processes now exist for the fixation and encapsulation of arsenical wastes from the roasting, pressure oxidative leaching or bacterial leaching of gold ores and concentrates. Research into the long term stability of these treated wastes continues, as do investigations into the behaviour and deportment of arsenic aimed at further reducing health and environmental risks, especially in tailings discharges. Much less is known about antimony, bismuth, selenium or tellurium due to their generally lower concentrations in gold ores.

This is becoming an area of increasing concern with regards to potential health and environment risks not just within a mine site, but also within the immediate vicinity and surrounding area of the mining and minerals processing operations. In addition, this concern extends to the transport of concentrates and other products from site to other facilities for further processing. In many cases the hazards associated with trace toxic elements in the ore are exacerbated through their concentration in the processing plant. A major future challenge for the mining industry will be to stay profitable whilst satisfying the progressively more stringent environmental laws and regulations.

2. Deportment in gold processing

It is known that pure gold dissolves more slowly in cyanide solutions than gold containing small quantities of other metals (Jeffrey and Ritchie, 2001). Trace amounts of lead, mercury, thallium or bismuth reduce the passivation effect on gold surfaces thereby accelerating gold leaching rates (Marsden and House, 2006).

However, these metals can also have a detrimental effect on the adsorption of gold

onto activated carbon and its subsequent elution by competing for adsorption sites and by consuming elution reagents. They also may report to the final product (and need to be removed during refining) or to the tailings from where they may be discharged to the environment.

In this section, the deportment of trace elements during gold processing is reviewed, including dissolution during leaching, carbon adsorption and elution, cyanide detoxification and tailings storage.

2.1 Lead, cadmium and mercury

These metals may enter the atmosphere from gold cyanidation operations during the roasting of ores or concentrates, and during reactivation of carbon. They can also be mobilised within the tailings storage facilities. Mercury has been and still is used by many artisanal and small scale gold miners in developing countries to recover gold by amalgamation which has over time released thousands of tons of mercury into the atmosphere during separation of the gold from the mercury (Lacerda, 1997).

2.1.1 Behaviour during cyanidation

In Part I of this review (Kyle et al., 2011) it was indicated that lead is sparingly soluble as lead hydroxo-complexes in cyanidation solutions, the extent of which increases with increasing pH. The solubility of lead is low at typical cyanidation pH's (9 to 10.5) and thus lead minerals that undergo dissolution will mostly re-precipitate as insoluble lead compounds and deport with the solids to the tailings storage facility. Both cadmium and mercury on the other hand form stable cyanide complexes and, depending on the solubility of the minerals containing these elements, may at least partially deport to the solution phase during cyanidation.

Lead is sometimes used as an additive during gold cyanidation, usually in the form of lead nitrate, to assist in the gold dissolution process, by reducing passivation of the gold surface (Marsden and House, 2006). The role of lead in assisting in the treatment of complex gold ores has been the subject of much investigation (Nicol, 1980; Jeffrey and Ritchie, 2000; Sandenburgh and Miller, 2001). The lead is thought to reduce the passivation of the gold by deposition of a metallic monolayer on the gold surface thereby disrupting the AuCN monolayer causing the passivation (Sandenburgh and Mahlangu, 2007).

Sulfide ions are known to hinder gold dissolution (Jeffrey and Breuer, 2000). Insoluble lead sulfide is formed which catalyses the oxidation of the sulfide ions (Hedley and Tabachnick, 1968; Sandenburgh and Mahlangu, 2007; Breuer et al., 2008). Galena has been observed to change colour from black to a milky white in a cyanide solution (Dai and Jeffrey, 2006), which suggests the galena is oxidised to a lead hydroxide or basic lead carbonate.

In a manner analogous to lead, the presence of small amounts of soluble mercury during cyanidation can enhance gold leaching rates, possibly due to the deposition of small amounts of elemental mercury on the gold surface. However, if amalgams are formed, the presence of mercury may actually retard cyanidation (Nicol, 1980).

During the cyanidation process, generally only 10-40 % of mercury in the ore is extracted along with the gold and silver, although the extent of mercury extraction is highly dependent on the concentration of cyanide in solution and the mineralogy of the mercury (Menne, 1991). The leaching rate of mercury minerals appear to be slower than for copper and gold (Zaraté, 1985). Work conducted by Oraby et al. (2010) showed that mercuric chloride dissolved within 24 hours in a 2.5 g/L NaCN

solution open to the air, where as cinnabar (HgS) and elemental mercury only partially dissolved (around 10 and 1 % respectively). Dissolution of these minerals has not been investigated under the more aggressive conditions used in the treatment of sulfide containing gold ores (e.g. in the presence of oxygen, peroxide and/or lead ions).

2.1.2 Adsorption onto activated carbon

Although the use of activated carbon to remove heavy metals from natural waters and wastewaters is well known and documented (Reed, 2002), the behaviour of trace elements during gold adsorption from cyanide solutions is less well known. The adsorption of lead (II) from wastewater solutions onto activated carbon is poor unless the carbon surface is chemically modified by soaking in acid (Nadeem et al., 2006). The adsorption of lead from alkaline cyanide solutions has not to our knowledge been studied, probably because the lead has only a low solubility under typical cyanidation conditions.

The adsorption of cadmium from alkaline cyanide solutions onto activated carbon has not been well documented. Huang and Smith (1981) reported good cadmium adsorption from electroplating waste solutions containing cyanide onto powdered activated carbons. However, the results from this study are difficult to relate to gold process solutions. Ibrado and Fuerstenau (1989) studied the adsorption of the cyano-complexes of cadmium onto activated carbon as a function of pH and compared the extent of adsorption to the metal-complex species distribution diagrams. They deduced that the neutral and singly negatively-charged complexes of cadmium (Cd(CN)_2^0 and Cd(CN)_3^-) do adsorb onto activated carbon, but the positively charged

species (CdCN^+) and doubly negatively-charged complex ($\text{Cd}(\text{CN})_4^{2-}$) do not.

Similar adsorption behaviour was shown for the cyano complexes of mercury.

McDougall (1980) has also shown that mercury, in the form of $\text{Hg}(\text{CN})_2$, strongly adsorbs onto activated carbon and competes with gold for adsorption sites, whereas the negatively charged species $\text{Hg}(\text{CN})_4^{2-}$ does not (Adams, 1991; Ibrado and Fuerstenau, 1989). As the more highly charged complexes of mercury are formed at higher pH (>9) and higher cyanide concentration, the adsorption of mercury onto activated carbon can be minimised in plant practice by keeping the pH and cyanide concentration sufficiently high (Fleming, 1982). However, this may also encourage further leaching of mercury from the ore. This decreasing adsorption with increasing negative charge of the metal cyanide complex observed for cadmium and mercury is consistent with the investigations of copper cyanide adsorption by Dai et al. (2010).

2.1.3 Elution from activated carbon

A number of processes are used for gold elution from activated carbon. The most common are (1) Zadra: elution with $\sim 1\%$ sodium cyanide in $\sim 2\%$ caustic soda solution at about $95\text{ }^\circ\text{C}$, or (2) Pressure Zadra: as for 1 but at an elevated temperature ($\sim 140\text{ }^\circ\text{C}$) and pressure (400-500 kpa), and (3) AARL (Anglo American Research Laboratories process): deionised water elution at $110\text{-}120\text{ }^\circ\text{C}$ and 100 kPa pressure following a pre-soak in $\sim 3\%$ sodium cyanide and 1-2 % caustic soda.

No published reports were found on the elution of lead and cadmium from activated carbon.

Mercury, unlike gold and copper, is poorly eluted from activated carbon in the atmospheric Zadra process (Zaraté, 1985; Menne, 1991) but is eluted with gold in the

AARL process. Contrary to this, it has been shown that mercury is preferentially desorbed (along with other base metals) before the gold with an ambient temperature alkaline cyanide solution prior to gold and silver elution using a conventional pressure Zadra process (Smith, 1986). Bunney et al. (2010) have recently investigated the elution behaviour of gold and mercury from activated carbon using a laboratory-scale elution circuit. They showed that mutually exclusive conditions were required for separate mercury and gold elution, with mercury being eluted most effectively at temperatures below 100 °C in strong caustic cyanide solutions and gold in low ionic strength solutions at temperatures above 100 °C following a soak in concentrated cyanide solution. Although most of the mercury could be eluted separately from the gold in a split elution system, a complete separation of the metals could not be achieved.

2.1.4 Carbon regeneration, gold electrowinning and smelting

Lead, cadmium and mercury can all be emitted to the atmosphere during carbon regeneration and gold smelting. Lead and its inorganic compounds are not volatile but are emitted to the atmosphere as fine particulate matter in industrial processes (Corrin and Natusch, 1979). Cadmium and mercury are more volatile and are readily volatilised and emitted to the atmosphere as gases during a range of industrial processes including zinc smelting, alumina refining, the manufacture and re-processing of cadmium-containing metals, and as a minor contaminant in the burning of fossil fuels, cadmium-weighted plastics and sewage sludge (Fleischer et al., 1974). Therefore, emissions of all these metals, if remaining on the carbon following elution, might be expected during carbon regeneration.

In processing plants using zinc precipitation to recover the gold, mercury will co-precipitate with the precious metals, whereas in gold electrowinning, the mercury in solution, being more electropositive, will be reduced to elemental mercury in preference to gold. In both cases, retorting at 600-700 °C is effective in removing the elemental mercury from the gold (Zaraté, 1985). The mercury can be captured as liquid mercury metal and sold for recycling. Work done by the US Bureau of Mines (Sheya et al., 1988) indicated that mercury could potentially be selectively electrowon from cyanide solutions also containing gold.

Atmospheric mercury emissions in some operations, particularly during carbon regeneration, have been substantial and have resulted in major gold producing companies in Australia and the United States instigating policies to better manage mercury during gold processing (Newmont Mining Corporation, 2010; Barrick Gold Corporation, 2010). This has resulted in the installation of mercury capture systems to minimise emissions during carbon regeneration and smelting and also on-going research to remove mercury prior to carbon regeneration (Mine Safety and Health Administration, 2007; Kalgoorlie Consolidated Gold Mines, 2006; Bucknam, 2004).

2.1.5 Tailings

Although free cyanide is not persistent in a tailings storage facility (TSF) and will be lost through natural degradation, volatilisation and oxidation, the complexed forms of cyanide, such as the cadmium and mercury cyano complexes, are more resilient and release cyanide ions only slowly as they decompose (Smith and Mudder, 1991). The concentration and speciation of these trace metal complexes will therefore be dependent on the pH and free cyanide concentration in the TSF. Lead speciation, on the other hand, will be virtually independent of free cyanide concentration but will

depend on pH as this will govern the solubility of the lead hydroxo- and carbonato-species.

In a comparative study of fresh (3 months) and aged (6-9 years) tailings, Zagury et al. (2004) found that about 85 % of the total cyanide had been lost as the pH decreased from 10.6 to 7.6. The weakly-complexed cyanide species were detected in the fresh tailings, but only the strongly-complexed metal cyanides remained in the aged tailings. They did not attempt to identify the strongly complexed species but assumed they would be mainly ferro- and ferricyanides.

A study by Shaw et al. (2006) of pore water from a tailings deposit containing mercury mainly as cinnabar reinforced the above findings with regard to the stability of mercury cyanide species. The main process for mobilisation of the mercury was found to be as the cyano-complexes. Equilibrium calculations on the pore water (16 mg/L total cyanide, with 60 % present as free cyanide, and up to 12 mg/L total mercury) indicated that about 60 % of the soluble mercury was present as $\text{Hg}(\text{CN})_2$ and 40 % as $\text{Hg}(\text{CN})_3^-$ with minor $\text{Hg}(\text{CN})_4^{2-}$. The percentage of the dicyano-complex increased as free cyanide decreased. These studies indicated that although the weaker cyano complexes like cadmium are decomposed at low cyanide concentrations, the more stable mercury cyanide complexes persist and can be recycled in the process or be emitted to the environment.

2.2 Arsenic, antimony and bismuth

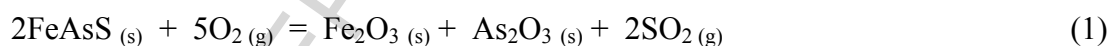
Arsenic, antimony and bismuth are typically present in many gold ores as sulfides. They may enter the atmosphere from gold cyanidation operations during ore or concentrate roasting or during carbon reactivation. They may also undergo oxidation

during cyanidation with discharge into the tailings storage facility as soluble oxyanions and/or as precipitated oxy/hydroxyl solids.

2.2.1 Refractory ores

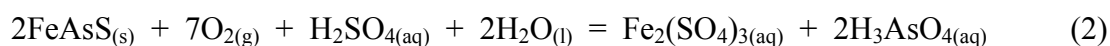
Gold ores and concentrates containing arsenic, antimony and/or bismuth minerals (e.g. arsenopyrite, stibnite, bismuthinite) are often refractory in nature, meaning the minerals need to be destroyed in order to release the associated gold. This is achieved by oxidation of the minerals by roasting, pressure oxidation or bacterial oxidation to form an oxidised ore in which the gold is more amenable to cyanidation.

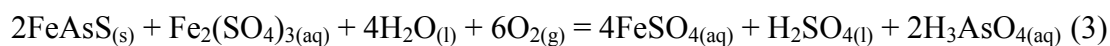
During roasting, the sulfides are converted to sulfur dioxide gas which is released to the atmosphere, scrubbed in lime or converted to sulfuric acid, while the arsenic is converted to a volatile arsenic trioxide which can also be scrubbed in lime or cooled and collected as solid As_2O_3 .



As there is only a limited market for the arsenic trioxide, it is generally disposed in a controlled landfill mostly after stabilisation (see Section 3.2). Antimony and bismuth oxides are less volatile and will remain in the residue.

In pressure and bacterial oxidation, the sulfides are converted to sulfates then precipitated as gypsum during pH modification prior to cyanidation. The arsenic is solubilised as arsenite and/or arsenate species depending on the conditions in the autoclave. Arsenic(V) species will predominate under the highly oxidative conditions produced in pressure oxidation.





During pH modification with lime, and depending on the solution composition and conditions, the arsenite and arsenate can be co-precipitated with the ferric ions to produce a ferrihydrite with adsorbed or co-precipitated arsenic, or precipitated as basic ferric arsenate (Marsden and House, 2006). Antimony and bismuth will generally behave in a similar manner (see Section 3.2). The solid residue from the pre-treatment process is then subjected to cyanidation to recover the gold that has been released from the mineral matrix.

2.2.2 Behaviour during cyanidation

Under alkaline conditions found in gold leaching by cyanidation, arsenic sulfides in the presence of oxygen are oxidised to arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), with the proportion of each dependent on solution composition, oxidation potential and pH. Arsenic sulfide solubility increases with increasing pH. For example, at pH 12 both orpiment (As_2S_3) and realgar (As_4S_4) dissolve appreciably, while at pH 10 only orpiment dissolves to any significant degree. Antimony sulfides behave in a similar manner with dissolution reduced below pH 10 (Hedley and Tabachnick, 1953; Deschênes et al., 2007). Hedley and Tabachnick (1953) identified some of the reaction products and found insoluble calcium arsenates and antimonites are formed. No detailed studies were found on the mechanisms for the dissolution of these sulfide minerals and the sulfur species formed.

The arsenites, antimonites and partially oxidised thioarsenites (AsS_3^{3-}) and thioantimonites (SbS_3^{3-}), formed on the dissolution of their sulfides, affect cyanidation by consuming oxygen and retarding or preventing gold dissolution (Marsden and

House, 2006). Cyanide ions may assist in accelerating the oxidation of these thio-species, forming thiocyanate in the process (Hedley and Tabachnick, 1950):



It is thought that the decomposition products attach to the gold surface, partially preventing the interaction of the cyanide ions and oxygen with the gold. Lead nitrate may be added to improve gold recovery by precipitating arsenites and antimonites from solution (Deschênes et al., 2007). In addition, pre-aeration can assist with any oxygen deficiency caused by the presence of these minerals.

Bismuth, which is commonly present as a sulfide in gold ores, does not dissolve to any appreciable extent during cyanidation but may undergo oxidation consuming oxygen and possibly cyanide, and transforming from a sulfide to an oxide. Like lead, bismuth can also catalyse the leaching of gold (Sandenbergh and Miller, 2001).

2.2.3 Adsorption onto activated carbon

Arsenic adsorbs only very weakly onto activated carbon (maximum of 5 mg/g carbon) and more readily as the arsenate rather than the arsenite ion (Lorenzen et al., 1995).

The maximum adsorption occurs at about pH 5-6 indicating that H_2AsO_4^- is the ion predominantly adsorbed. Adsorption can be improved by using a carbon of high ash content or by pre-treatment of the carbon with metal ions especially copper ions.

Desorption of the arsenate can be achieved in either strongly acidic or strongly basic solutions. Due to their low solubilities in typical cyanidation solutions, no references were found for the adsorption of antimony and bismuth species onto activated carbon.

2.2.4 Tailings

Limited information is available on the changes in speciation and deportment of arsenic, antimony or bismuth in tailings dams. However, a number of studies detailed below confirm the general rule that the arsenic(III) species are more soluble in the environment than the arsenic(V) species (Magalhães, 2002).

The Ketz River mine, Yukon, Canada, contained about 310,000 tonnes of tailings containing about 5 % arsenic that had been treated by a conventional carbon-in-pulp cyanidation process followed by SO₂/Air treatment for cyanide destruction. Paktunc et al., (1998), in a geochemical and mineralogical study of the tailings, found that the arsenic was associated mainly with dominant amorphous or cryptocrystalline ferric hydroxide phases, although at relatively low concentrations. Other major arsenic bearing phases included scorodite, a Fe-Ca arsenate hydrate, a Fe-Bi-As phase, and only minor arsenopyrite remained. The amorphous Fe-Ca arsenate hydrate contained 33-51 % Fe₂O₃ and 28-52 % As₂O₅, and the composition resembled pharmacosiderite (KFe₄(AsO₄)₃(OH)₄•7H₂O) and yukonite (Ca₇Fe₁₁(AsO₄)₉O₁₀•24.3H₂O). No arsenic(III) species were identified.

In a study of historic mine residues in New Zealand, arsenolite (As₂O₃) residues produced from roasting operations were found to have dissolved during rainfall events to produce arsenite ion in solution (Haffert and Craw, 2008). Whether the dissolved arsenic remained as dissolved arsenic(III) or was converted to scorodite depended on the E_H/pH conditions at the site. Where the runoff water was more alkaline (about 250 µmol/L HCO₃⁻ and pH ~7), the arsenic remained as arsenite ions. In more acidic run-off (about 200 µmol/L SO₄²⁻ and pH ~4) the arsenic(III) was oxidised to arsenic(V) by unknown processes and precipitated as scorodite (FeAsO₄•2H₂O). Due to the higher solubility of arsenolite compared to scorodite, total dissolved arsenic

concentrations in the run-off water were much higher in the former case than in the latter, although both greatly exceeded WHO (2001) drinking water guidelines.

A study from the Komsomolsk gold processing plant in Russia has been very informative with respect to changes in arsenic and antimony speciation (Lazareva et al., 1999). The plant treated a mixture of gold-quartz-arsenic-pyrite ores, and some tailings from an antimony smelting plant, for gold extraction by cyanidation and zinc cementation. Total metal concentrations were measured in the process, tailings surface and tailings pore waters. The results, shown in part in Table 1, indicate that as the pH and cyanide concentrations decreased in the tailings over time, the concentrations of copper, zinc and cadmium decreased dramatically, presumably due to decomposition of the cyano complexes and precipitation as hydroxides. The solution concentrations, however, remained high enough to cause the migration and concentration of the metals into the soil below the un-lined tailings dam (not shown). Conversely, the concentrations of iron, arsenic and antimony increased in the pore water compared to the tailings surface water. The increase in iron concentration was presumably due to continuing slow oxidation of sulfide minerals forming iron oxyhydroxide surface layers on the pyrite, and transfer of cyanide from the more labile complexes to form ferro- and ferricyanides. The solubilisation and concentration of the arsenic and antimony in the water over time was due to the solubilisation of their minerals, probably as the more soluble arsenites and antimonites, indicating the high solubility of these species in the neutral to alkaline tailings waters.

McCreadie et al. (1998) studied the composition of residues from a pressure oxidation facility that had been co-disposed with dolomite-rich flotation tailings following

cyanidation for gold recovery. They found that most of the arsenic was present as crystalline ferric sulfarsenate (a ferric sulfate arsenate), with some associated iron oxides and potassium or hydronium jarosites. Pore water analyses indicated that the solution pH was in the range 7-9, with an E_H of approximately +100 mV. The pore water contained significant dissolved arsenic (~5 mg/L mainly as As(III)) and iron (~150 mg/L suggested to be as Fe(II) from speciation calculations) that had increased between sampling periods 12 months apart. The authors suggested that the ferric arsenate, being unstable at the pH of the pore water, was dissolving, probably by a biologically mediated reductive dissolution process, and releasing iron and arsenic into solution as Fe(II) and As(III).

In tailings waters acidified due to sulfide oxidation, however, antimony is much less soluble than arsenic, and although oxidised, will remain in the tailings as senarmontite (Sb_2O_3), or if solubilised be adsorbed onto hydrated iron oxides (Wilson et al., 2004; Craw et al., 2004). Flynn et al. (2003), in a study of five British former mining and smelting sites, also found that although total antimony concentrations at the sites were very high, it remained locked in the surface layers of the soil and did not accumulate in biological systems or leach into groundwater, and therefore did not pose a significant environmental risk. However, it could present a human health risk if contaminated soil dust was inhaled. At an abandoned mine site in Japan, Manaka et al. (2007) reported arsenic and antimony attenuation in drainage waters by adsorption onto hydrated iron oxides, with arsenic concentrations in the water being about 100 times higher than the antimony.

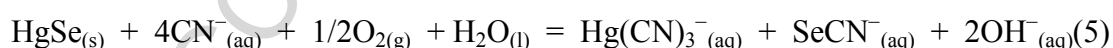
Bismuth tends to remain in the solid phase as a bismuth hydroxide or oxyhydroxide, except at very high pH (>12) where solubilisation as the bismuth tetrahydroxo complex ($\text{Bi}(\text{OH})_4^-$) starts to occur (Kyle et al., 2011).

2.3 Selenium and tellurium

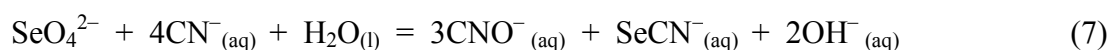
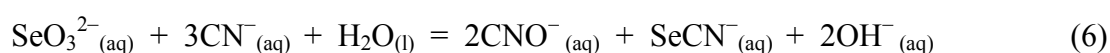
In gold cyanidation solutions, selenium and tellurium containing minerals may oxidise to form selenite (SeO_3^{2-}) and tellurite (TeO_3^{2-}) ions, that may, depending on the E_H , be oxidised to selenate (SeO_4^{2-}) and/or tellurate (TeO_4^{2-}) ions and be discharged into the tailings storage facility. Depending on concentration, the tellurite ions may also partially precipitate into the solid phase as the sparingly soluble calcium or magnesium tellurites (Kyle et al., 2011).

2.3.1 Behaviour during cyanidation

Metal selenide minerals (e.g. HgSe) dissolve in cyanide solutions to form metal cyanide complexes and the selenocyanate ion (SeCN^-):



Elemental selenium also dissolves in cyanide solutions to form selenocyanate, in a manner analogous to elemental sulfur forming thiocyanate (SCN^-). In addition, it can be deduced from equilibrium calculations that any selenite and selenate species that form in solution will oxidise cyanide to cyanate ions, themselves being reduced to form SeCN^- , according to the following equations:



Although thermodynamically favourable (see Table 4 in Kyle et al., 2011), the rates of these reactions, and therefore their importance in selenium deportment, are currently unknown (Flynn and Haslem, 1995). However, a speciation analysis of selenium in gold mine wastewater (Wallschläger and Bloom, 2001) has confirmed that selenocyanate was the main selenium species found, with only minor selenite and selenate present.

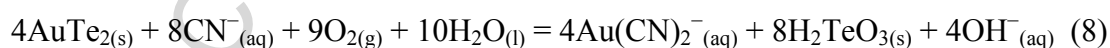
Selenocyanate can form complexes with heavy metals such as cadmium and mercury (OECD, 2005) but they are less stable than the corresponding cyanide complexes (see Table 5 in Kyle et al., 2011). This indicates that these heavy metal complexes will not form in significant amounts in the presence of free cyanide ions, but may be important for selenium speciation in low cyanide environments like tailings storage facilities.

Selenocyanate decomposes at low pH to form elemental selenium and hydrogen cyanide. It can therefore be classified as a “weak acid dissociable” (WAD) cyanide. Oxidation of selenocyanate to selenite can occur in alkaline solutions using oxidants such as hydrogen peroxide, ozone and chlorine dioxide. It can then be removed from solution by co-precipitation with a ferric coagulant. However, the precipitation process is not effective for selenate, meaning the oxidation conditions must be carefully controlled to prevent selenate formation. The removal of selenite and selenate from solution by reductive precipitation to selenium(0) using elemental iron has also been investigated (Meng et al., 2002).

An important process regulating the dissolved concentration and mobility of inorganic selenium is adsorption on to solid surfaces. Selenite efficiently adsorbs onto both iron and manganese oxides. However, sorption tends to decrease with increasing pH and

is further inhibited by the presence of certain dissolved anions such as phosphate, silicate, and molybdate that can compete with the selenite for adsorption sites. On the other hand, selenate adsorbs only weakly onto clays and iron-oxyhydroxides and does not adsorb onto manganese oxides. Its adsorption is further limited by competitive effects with sulfate at neutral pH. Therefore, under appropriate conditions, sorption can reduce concentrations of dissolved selenite but does not significantly influence selenate concentrations, particularly in sulfate rich waters (Frankenberger and Karlson, 1994).

Tellurium exists mainly as gold telluride minerals that are refractory during cyanidation giving low gold dissolution (Henley et al., 1995). The “Superpit” in Western Australia has several tellurium containing minerals, including calaverite, associated with the gold ore. Jayasekera et al. (1991) have studied the dissolution of calaverite (AuTe_2) in both acid and alkaline cyanide media and have attributed the refractoriness to passivation of the mineral surface by insoluble tellurous acid, a reaction product.



The tellurous acid is soluble at low and at high pH (>12) forming the tellurite ion (TeO_3^{2-}). Thus, in acidic solutions at high chloride concentrations, where no passivation occurs, the telluride minerals are oxidised rapidly by ferric ions to produce gold(III) chloride and hexachlorotellurite at rates up to 300 times faster than under normal cyanidation conditions (Jayasekera et al., 1991). Similarly at high pH, the calaverite leach rate during cyanidation increases with increasing pH, but the pH increase is limited by the use of lime as the pH modifier due to its solubility limit (Rumball et al., 2008).

During bacterial leaching of a refractory gold ore concentrate, it was confirmed that the telluride minerals (calaverite and mercury telluride) were also oxidised by the ferric ions in the acidic solution, not the bacteria. The products were elemental gold and hydronium tellurite ions (Climo et al., 2000).



2.3.2 Tailings

Total selenium and tellurium concentrations in dried mine tailings (Moreno et al., 2007) and in downstream waters and sediments (Wray, 1998) have been reported, but no investigation of the speciation of these metals was undertaken. Moreno found that selenium, tellurium and other base metals were mainly associated with the particulate inhalable fraction of the dry tailings, and Wray found elevated levels of these trace elements in waters and sediments downstream from the same tailings deposits.

At low redox potentials, which may occur below the sediment-water interface in tailings storage facilities, Se(IV) and (VI) can be reduced to the elemental selenium or hydrogen selenide (H_2Se). However, if dissolved heavy metals are also present under these conditions, quite insoluble metal selenides can precipitate. Because of this, selenium concentrations are generally less than 0.01 mg/L in water that is in equilibrium with solids which contain heavy metals (Frankenberger and Karlson, 1994).

Harada and Takahashi (2009) have studied the distribution and speciation of selenium and tellurium between the solid and aqueous phases in synthetic soil. They found that under oxic conditions both tellurium and selenium are mainly associated with Fe(III) hydroxides. Selenium(VI) is the most weakly adsorbed as an outer sphere complex,

while selenium(IV), tellurium(IV), and tellurium(VI) are more strongly bound as inner-sphere complexes. Under reducing conditions, tellurium(0) and selenium(0) species were formed and selenites and selenates were more readily reduced to selenium(0) than tellurites and tellurates, as predicted from their E_H -pH diagrams. In terms of the distribution between soil and water, the selenium distribution to water was much higher than that of tellurium under a wide range of redox conditions. The predominant selenium species in water even under reducing conditions was selenium(VI) due to its much higher solubility compared to selenium(IV). The much smaller distribution of tellurium to the aqueous phase was primarily due to the higher affinities of tellurium(IV) and tellurium(VI) for iron(III) hydroxides.

2.4 Summary

A summary of the current knowledge of trace toxic element deportment in CIL/CIP cyanidation processes is graphically presented in Figure 1. The bold outlined arrows indicate the possible discharge points for trace elements from the process (cyanidation tails, gold eluate, carbon regeneration off-gas) from which additional treatment may be required before discharge into the environment (for example, gas scrubbing of the carbon regeneration kiln off-gas or treatment of the tailings before discharge into the tailings storage facility). The solid arrows indicate recycle streams within the process.

The extent to which the trace toxic elements dissolve during cyanidation is largely dependent on their mineralogy within the ore. The subsequent deportment shown for some elements with a question mark indicates the potential for these elements to appear in these streams, or there is no information available.

3. Fixation and encapsulation processes

Given the on-going concern regarding trace toxic elements in mine tailings that may have been mobilised and concentrated during mineral processing operations, consideration has been given to stabilising certain wastes containing significant amounts of these metals to prevent their migration into the environment. Two processes have been considered – fixation and encapsulation.

Fixation means immobilising the trace elements in these wastes by precipitation as insoluble compounds or by adsorption onto suitable adsorbents, while encapsulation (also called solidification) refers to encapsulating them in an insoluble matrix for long term disposal in an environmentally responsible manner. In the past, encapsulation has conventionally been applied to mixing wastes and solidifying them in a monolithic waste form using Portland cement or flyash. This has provided a high pH environment to limit solubility of metals that form insoluble hydroxides (fixation), as well as limiting the ingress of leaching agents by the formation of a low permeability, low surface area monolith (Connor, 1990). Although cement solidification is still widely practised and being further developed (Paria and Yuet, 2006), new technologies are being investigated that may offer advantages over the traditional encapsulation materials by further limiting the ingress of leaching agents into the monolithic waste forms. These include sulfur polymer cements (SPC), chemically bonded phosphate ceramics (CBPCs), carbon-and silicon-based polymers, and calcined dolomite binders (Randall and Chattopadhyay, 2004).

3.1 *Lead, cadmium and mercury*

3.1.1 *Fixation*

Lead is generally precipitated from wastewaters as a basic lead carbonate (e.g. hydrocerussite) or phosphate. However, due to the amphoteric nature of lead, these are both prone to re-solubilisation at high pH as lead hydroxo-complexes, or by re-dissolution as the pH falls below 8. Conversely, cadmium is not amphoteric and can be precipitated as a hydroxide at pH 8-10 or higher. However, if cyanide is present, the soluble cadmium cyano-complexes need to be destroyed by oxidation of the cyanide prior to precipitation.

In the absence of cyanide, lead(II) and cadmium(II) can be adsorbed onto industrial minerals or ferrihydrite as aquo or hydroxo complexes (Parkman et al., 1999; Sauv e et al., 2000; Panuccio et al., 2009). Lead(II) adsorbs more strongly than copper(II), zinc(II) or cadmium(II) onto freshly precipitated iron and aluminium oxyhydroxides (Violante et al., 2003); however, cadmium adsorption onto iron oxyhydroxides is nearly fully reversible, meaning the adsorbed Cd(II) can be released by a relatively moderate lowering of pH (Gunneriusson, 1994; Twidwell and Leonhard, 2008).

Manganese oxides have been found to have more of an affinity for lead than iron oxides (Rickard and Nriagu, 1978) but layered structures such as birnessite ($K_4Mn_{14}O_{27} \cdot 9H_2O$) have the highest capacity for lead adsorption as the lead ions can penetrate between the layers of the adsorbent as inner sphere complexes (O'Reilly and Hochella, 2003).

The primary fixation methods for mercury are sorption on activated carbon and precipitation with sulfide. Mercury cyanide complexes in gold cyanide process solutions have been removed by precipitation of the mercury with sulfide ions (Touro

and Lipps, 1988), sodium dimethyl dithiocarbamate (NaDTC) followed by flocculation and dissolved air flotation (Tessele et al., 1997), sodium polymeric thiocarbonate (Bucknam, 2004), or 1,3-benzenediamidoethanethiol (BDET) (Matlock et al., 2002). It has been claimed that these reagents can remove most heavy metals from solution, including arsenic and selenium, without interfering with the gold leaching or adsorption processes (Touro and Lipps, 1988; Tessele et al., 1997, 1998).

In the absence of cyanide, mercury(II) may also be removed from solution by adsorption onto finely divided minerals such as magnetite, vermiculite or zeolite (Melamed and da Luz, 2006), ion exchange resins (Monteagudo and Ortiz, 2000), synthetic crandallite (Monteagudo et al., 2003) and iron oxyhydroxides for both inorganic and methyl mercury (Rytuba, 2000). In addition, clay minerals, chemically modified by impregnation with mercury-binding compounds such as 2-mercapto-benzothiazole, have been used as adsorbent materials for the removal of mercury and other heavy metals from industrial wastewater (Manohar et al., 2002).

3.1.2 Encapsulation

Having removed the trace toxic elements from the process solutions, the wastes containing the metals still need to be stabilised, often by encapsulation processes. Encapsulation involves the physical stabilisation of a residue by enclosing it in an insoluble and non-porous matrix. Possible matrices include cement, geopolymers, and metallurgical slags that may fix the metals as insoluble compounds as well as encapsulate them, and certain organic thermoplastics that merely encapsulate the metals after fixation.

Cement has proven to be a suitable encapsulating agent for both lead and cadmium, with the dissolution being significantly reduced even after the pH has fallen. This is

thought to be due either to the formation of lead and cadmium silicate species or the encapsulation of the metal ions in a silicate matrix (Connor, 1990).

Cement alone has in general not been used for mercury encapsulation as although the mercury is strongly fixed at short hydration times, it is leached at longer hydration times. No mechanism for this observation has been proposed (Connor, 1990).

Although many systems have been claimed to be effective in fixing mercury wastes, the only processes used commercially appear to be lime/sulfide for metal finishing waste and fly ash for oil and paint sludges. The most effective treatments for mercury fixation have involved sulfide or other sulfur compound additives to fix the mercury prior to encapsulation (Connor, 1990). Sulfur polymer cement (SPC – a thermoplastic material composed of about 95 % sulfur and 5 % cyclopentadiene modifier) has been used to encapsulate mercury wastes. The sulfur initially reacts with the mercury to immobilise it prior to encapsulation. SPC can also effectively immobilise chromium, lead, and selenium wastes. The monolithic waste forms produced on cooling the SPC after mixing with the waste have passed the US EPA Toxicity Characteristic Leaching Procedure (TCLP) (Fuhrmann et al., 2002; Kalb, 2005).

Other alternatives to cement include geopolymers and calcined dolomite-based binders. Both physical encapsulation and chemical fixation are assumed to be responsible for the immobilization of mercury in geopolymers (Qian et al., 2003). The high magnesium calcined dolomite binder system, Dolocrete®, has been used commercially in Australia to encapsulate a range of industrial wastes including mercury and arsenic (Dolomatrix, 2011).

3.2 *Arsenic, antimony and bismuth*

With the market for arsenic and its compounds diminishing and its production and capture from mining operations increasing, mining companies require means for the safe long term disposal of arsenic wastes. There have been a number of excellent reviews and monographs covering arsenic fixation (Reddy et al., 1988; Harris, 2000; Reddy and Ramachandran, 2005). Only a brief summary will be presented here.

3.2.1 *Fixation*

A major area of research has been into the precipitation and fixation of arsenic from acidic solutions emanating from the oxidation of arsenic-containing minerals such as arsenopyrite prior to cyanidation. Early studies looked at the precipitation of arsenate with lime at high pH (Nishimura and Tozawa, 1985). However, as the calcium arsenate transformed to calcium carbonate in the presence of atmospheric carbon dioxide, the utility of this stabilisation method was limited. Calcination above 700 °C was recommended to convert the precipitated $\text{Ca}_3(\text{AsO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ to less-soluble crystalline $\text{Ca}_3(\text{AsO}_4)_2$. Later studies by Bothe and Brown (1999a, 1999b) investigated alternative calcium arsenates that could be formed at lower Ca/As ratios, and lower pH. However, these species had higher arsenic solution solubilities and were not suitable for arsenic immobilisation.

Alternative efforts have focussed on the co-precipitation of arsenic with iron(III) (Krause and Ettel, 1985), or chemical adsorption onto the surface of ferrihydrite (an iron(III) oxyhydroxide), co-precipitation giving a less soluble product than adsorption onto already precipitated ferrihydrite. Ferrihydrite is a nanocrystalline material, possibly having the formula $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$, that may be precipitated by rapid hydrolysis of ferric solutions at ambient or elevated temperature, the latter producing

a lower surface area product with lower arsenate adsorbing capacity. An iron to arsenic ratio of about four has been recommended to minimise arsenic solubility from ferrihydrite (Twidwell et al., 2005).

Other species in the water can have a dramatic effect on arsenic adsorption. In a study using synthetic groundwater, Meng et al. (2000) found that in the presence of 10 mg/L dissolved silica at pH 6.8, the adsorption capacity of ferric hydroxide for As(V) and As(III) was reduced by about 70 % and 75 % respectively, whereas sulfate and carbonate had only a negligible effect on arsenic removal.

Antimony(III) and (V) can also be co-precipitated with ferrihydrite with the minimum concentrations of solution antimony being recorded at about pH 4. However, the precipitation rate for Sb(V) was very slow compared to Sb(III) or As(V) (Nishimura and Umetsu, 2000). Antimony adsorption by iron-bearing ochreous precipitates, especially schwertmannite has also been reported (Manaka et al., 2007) as has bismuth removal from wastewater with ferric coagulants (Hannah et al., 1977).

Although the ferrihydrite precipitation process is now a common practice for iron-rich arsenate solutions, a number of questions remain concerning the long term stability of these systems. The ferrihydrites can convert over time into the thermodynamically more stable goethite, releasing arsenic into solution. (Welham et al., 2000; Twidwell et al., 2005). In addition, the process is not appropriate for arsenic-containing process solutions at high pH, such as found in cyanidation effluents (Tahija and Huang, 2000).

In arsenic-rich and iron deficient process solutions, such as acid plant effluents, copper electro-refining bleed streams, arsenic trioxide flue dusts, and arsenic-contaminated soils, the precipitation of crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) is the preferred technology due to its lower iron requirement (1:1 molar ratio), excellent

settling and dewatering characteristics, and much lower overall precipitate volume. Scorodite can be precipitated hydrothermally at 150-180 °C, as occurs in pressure leaching vessels for the oxidation of sulfide ores and concentrates (Papangelakis and Demopoulos, 1990; Swash and Monhemius, 1994) or at 95 °C and atmospheric pressure in either chloride or sulfate media (Demopoulos et al., 1995; Wang et al., 2000; Demopoulos, 2005). However, in the normal pH range of 5 to 8, scorodite is thermodynamically unstable with respect to goethite (Welham et al., 2000) and may dissolve over time (McCreadie et al., 1998).

In gold process effluents containing cyanide, the above processes are unsuitable due to the high pH, the lower concentrations and speciation of arsenic, and the presence of other species, particularly cyanide. The high pH and presence of arsenite have been shown to interfere with the precipitation of ferrihydrite and the coprecipitation of arsenic species (Tahija and Huang, 2000; Nishimura and Robins, 2000). However, other arsenic-containing solid phases may form under these conditions. Bothe and Brown (1999a) have confirmed the formation of johnbaumite ($\text{Ca}_5(\text{AsO}_4)_3\text{OH}$) at pH 9, and two separate studies (McCreadie et al., 1998; Bluteau et al., 2009) have shown that a Ca-Fe-AsO₄ mineral, possibly yukonite, forms when scorodite is dissolved at pH 9.

At high alkalinity, ferrous sulfate (Weeks and Wan, 2000) and mixtures of ferrous and ferric sulfate have been used to enhance arsenic precipitation. The mixed iron(II) and iron(III) hydroxides that are formed (called “Green rust” or GR) are common in soils and stream sediments and have been the subject of many studies concerning their binding of trace elements. Although GR is generally a reducing agent, it does not reduce arsenic(V) to arsenic(III) (Mitsunobu et al., 2009) and it has been suggested

that GR does in fact oxidise arsenic(III) to arsenic(V) (Su and Puls, 2004). Further studies are required to determine the role and chemistry of GR in metallurgical systems at high pH.

Antimony(V) is also adsorbed strongly onto GR and is not transformed to antimony(III) during the process. The adsorption inhibits the transformation of the metastable GR to magnetite and ferrous hydroxide (Mitsunobu et al., 2009).

To overcome the stability problems of iron oxyhydroxides as fixation agents for arsenic, Misra et al. (2000) have proposed the use of lanthanum chloride, either alone or with ferric sulfate, as a means of precipitating both arsenite and arsenate from gold process solutions. The precipitated arsenic has a much wider region of stability (pH 3 to 10) than precipitates produced by using ferric sulfate alone. Although this process is promising, further research is required to establish its chemistry and the long-term stability of the precipitated species.

Dissolved air flotation (DAF) has also been proposed for the removal of arsenic, selenium and mercury from gold process solutions. The process utilised a precipitant, sodium dithiocarbamate, a coagulant (ferric or lanthanum chloride) and a flocculant prior to flotation. Over 98 % removal of the mercury, arsenic and selenium from solution was achieved. No information however was supplied in regard to the stability or leachability of the flotation concentrate (Tessele et al., 1998).

3.2.2 Encapsulation

Because arsenic forms anions that are soluble at high pH, additives have generally been required to fix the arsenic prior to encapsulation. A number of fixation and encapsulation processes designed specifically for arsenic have been described in the

literature. These include Portland cement for arsenic trioxide (reacts with lime in the cement forming calcium arsenite), calcium arsenate, ferric arsenite and ferric arsenate (Kyle and Lunt, 1991), Portland cement with sodium silicate and other additives, and ferric hydroxide and lime (Connor, 1990). In general, most processes have been able to produce a product with low arsenic leachability, at least in the short term, except for wastes with very high arsenic concentrations.

Alternatives to cement include geopolymers and magnesium oxide binders.

Geopolymers are low-cost and environmentally friendly structural materials made of Si–O–Si polymers. They are readily formed from the addition of alkalis to silicate and aluminate-based materials (Nowak, 2008). Recent research has indicated that geopolymers may be better at fixing heavy metals than Portland cements. Both physical encapsulation and chemical fixation are assumed to be responsible for the immobilization of arsenic in geopolymers (Fernández-Jiménez et al., 2005).

Dolocrete® is a magnesium oxide-based binder prepared from dolomite or magnesite material that is used commercially at the Barrick Kanowna Belle mine in Western Australia for arsenic trioxide encapsulation prior to disposal at a regulated disposal site (Dolomatrix, 2011).

Twidwell and co-workers (Twidwell, 1983; Twidwell et al., 1994) have investigated encapsulation of solid calcium arsenate in glassy copper smelter slag, with an arsenic content up to nearly 20 %. The product had a low leachability of arsenic by the US EPA Toxic Characteristic Leaching Procedure. However, Riveros and Utigard (2000) showed the same process could not be used for solid iron arsenate. The compound decomposed at temperatures above 1000 °C releasing volatile arsenic oxide below the

molten copper slag temperature (1250 °C). The incorporation of iron arsenate into slags did not decrease the leachability of the arsenic.

Antimony and bismuth are generally not regulated metals, and therefore little information is available on their encapsulation by cement or other means. This is because of their low concentrations in most mineral processing or other wastes, and the lack of industrial wastes containing significant quantities of the metals.

3.3 *Selenium and tellurium*

3.3.1 *Fixation*

A recent review by Twidwell et al. (2000) covers a significant portion of the potential technologies for the removal of selenium from process and mine wastewaters. These include reduction, precipitation or adsorption on ferrihydrite, alumina, activated carbon or ion exchange resins. These technologies may be suitable in different applications depending on the specific characteristics of the site and the wastewaters. Selenium does not appear to be well adsorbed onto activated carbon.

In the presence of cyanide in gold process solutions, dissolved air flotation has been used for selenium precipitation and removal (Tessele et al., 1998) without interfering with the gold recovery. In the absence of cyanide, the Best Demonstrated Available Technology (BDAT) for selenium removal from wastewater is by adsorption onto ferrihydrite, although Se(VI) removal is much poorer than for Se(IV) (Twidwell et al., 2000; Nishimura and Umetsu, 2000). The best pH region for maximum selenium adsorption is 4-6, and it rapidly decreases above that with virtually no adsorption above pH 9.5 (Parida et al., 1997). Activated alumina has been used to treat gold

mine effluents for selenium removal, but it has been shown to be ineffective if soluble silica is present (Batista and Young, 1994).

Metal oxides have been investigated for the removal of Se(IV) from aqueous solutions (Sheha and El-Shazly, 2010). High removal efficiency of selenite was observed over a wide range of pH (i.e., 2–8), but the efficiency decreased at pH values higher than 8.

Selenium and tellurium can be removed from mine wastewaters by reduction to elemental selenium or selenides and precipitation with heavy metals. At the INCO Copper Cliff refinery, selenium and tellurium concentrations of <1 mg/L in copper electrolyte were achieved by reduction with metallic copper and precipitation of cuprous selenide and telluride. Other solution impurities (Ni, Co) were also removed (Stewart et al., 1985).

Metallic iron has also been used to remove selenium(VI) from wastewaters. Koyama et al. (2000) found that iron was more effective than ferrous ion, zinc, aluminium, and copper in reducing selenate ions in solution to selenium(0), while McCloskey et al. (2008) used elemental iron in a closed column reactor to reduce selenium concentrations in an industrial waste water from 600 to less than 50 micrograms per litre. Antimony concentrations were also substantially reduced.

Artificial wetlands have been investigated by Gao et al. (2003a, 2003b) as a means of removing selenium from agricultural waste water. The influent selenium, predominantly Se(VI), was removed by reduction to elemental Se and immobilization into the organic phase of the sediments.

3.3.2 Encapsulation

To our knowledge, there has been no requirement to develop technologies for the disposal of selenium and tellurium solid wastes by encapsulation due to their low concentrations in industrial wastes, or the commercial incentive for recycling the high value wastes containing significant amounts of these metals.

4 Conclusions

A literature review on the deportment of the trace toxic elements lead, cadmium, mercury, arsenic, antimony, bismuth, selenium, and tellurium in gold processing by cyanidation has been completed. This second part of the review covered the deportment during gold ore cyanidation (including carbon adsorption and elution), tailings disposal, and captured related information from the treatment of industrial wastes and wastewaters, including fixation and encapsulation processes that may be applicable in gold processing.

4.1 Lead, cadmium and mercury

Soluble lead(II) and mercury(II) are believed to assist gold cyanidation by precipitating soluble sulfides and reducing passivation of the gold surface layer. Lead(II) has a very low solubility under gold cyanidation conditions forming relatively insoluble sulfide and basic carbonate species, whereas cadmium minerals dissolve to form a range of relatively weak cyano-complexes that are readily dissociated, and report as WAD cyanide. The mercury cyano-complexes are much stronger and persistent in tailings solutions and the environment. The neutral cyano-complexes of cadmium and mercury strongly adsorb onto activated carbon and thus potentially deport to the gold recovery circuit and carbon regeneration kiln.

Lead, cadmium and mercury are best removed from wastewaters by precipitation as sulfides or adsorption onto activated carbon, ferrihydrite or aluminium oxides.

4.2 *Arsenic, antimony and bismuth*

In gold cyanidation, arsenic and antimony minerals can dissolve to form oxyanions and thioanions that consume oxygen and retard or prevent gold dissolution. The use of low pH (~10) and lead nitrate may assist cyanidation by respectively reducing solubility and precipitating arsenites and antimonites from solution. Bismuth does not form oxyanions in aqueous solution, and remains in the solid phase as a sulfide or oxide during cyanidation.

In alkaline waters, both arsenic and antimony can be present in solution at relatively high concentrations whereas bismuth is insoluble except at very high pH. Arsenic and antimony in acidic tailings and mine drainage waters are attenuated by precipitation onto ferrihydrites or precipitation as scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) or senarmontite (Sb_2O_3).

4.3 *Selenium and tellurium*

Selenium may form selenocyanate (SeCN^-) during cyanidation, which is thermodynamically more stable than the oxyanions selenite and selenate. Gold telluride minerals are refractory during cyanidation due to passivation of the mineral surface by tellurous acid, a reaction product. Tellurocyanate is unstable and does not form. In acidic chloride and in bacterial leaching solutions, the telluride minerals are oxidised rapidly by ferric ions to produce chlorotellurite or tellurite ions. The potential for adsorption of selenium or tellurium onto activated carbon is unknown. Selenite in wastewater efficiently adsorbs on to both iron and manganese oxides but,

selenate does not. Tellurium behaves similarly but, in soils, is less soluble in the aqueous phase than selenium and adsorbs more strongly onto iron oxides.

4.4 Summary

Most of the previous studies on trace toxic elements in gold cyanidation have been confined to arsenic and to a lesser extent mercury. However, much is still to be learned about the deportment of these elements during gold processing. In addition, very little research has been undertaken on the other trace elements although most are classified as being very toxic to humans and in the environment. More research is required to elucidate their role and better understand their deportment in the gold cyanidation process.

5 Acknowledgements

The support of the CSIRO Minerals Down Under National Flagship and Parker CRC for Integrated Hydrometallurgy Solutions (established and supported under the Australian Government's Cooperative Research Centres Program) is gratefully acknowledged. Access to information from an internal memorandum prepared by the Gold Technology Group of the Parker Centre on the mineralogy of trace elements in certain gold ores is gratefully acknowledged.

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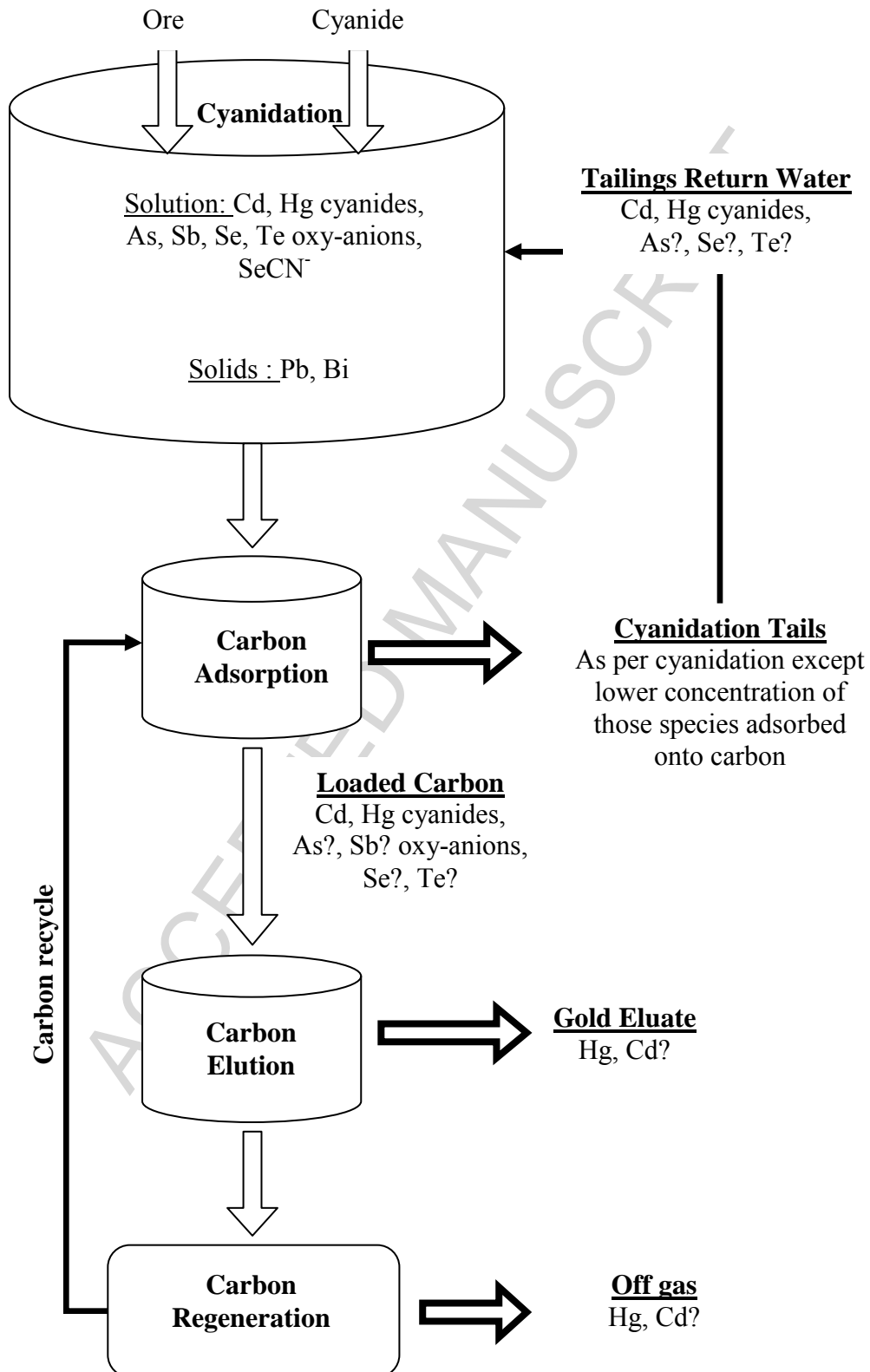


Figure 1. Current knowledge of trace element department in CIL/CIP cyanidation processes.

Research Highlights

- Review of deportment of trace toxic elements during gold processing by cyanidation
- Deportment of the elements Pb, Cd, Hg, As, Sb, Bi, Se, Te are reviewed
- The deportment and chemistry of many trace elements during cyanidation are largely unexplored.
- Relevant information from the treatment of industrial wastes and waste waters is captured.

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