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The fate of cyanide in leach wastes at gold mines: An environmental perspective

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ABSTRACT

This paper reviews the basic chemistry of cyanide, methods by which cyanide can be analyzed, and aspects of cyanide behavior that are most relevant to environmental considerations at mineral processing operations associated with gold mines. The emphasis is on research results reported since 1999 and on data gathered for a series of U.S. Geological Survey studies that began in the late 1990s. Cyanide is added to process solutions as the CN^- anion, but ore leaching produces numerous other cyanide-containing and cyanide-related species in addition to the desired cyanocomplex of gold. These can include hydrogen cyanide (HCN); cyanometallic complexes of iron, copper, zinc, nickel, and many other metals; cyanate (CNO^-); and thiocyanate (SCN^-). The fate of these species in solid wastes and residual process solutions that remain once gold recovery activities are terminated and in any water that moves beyond the ore processing facility dictates the degree to which cyanide poses a risk to aquatic organisms and aquatic-dependent organisms in the local environment.

Cyanide-containing and cyanide-related species are subject to attenuation mechanisms that lead to dispersal to the atmosphere, chemical transformation to other carbon and nitrogen species, or sequestration as cyanometallic precipitates or adsorbed species on mineral surfaces. Dispersal to the atmosphere and chemical transformation amount to permanent elimination of cyanide, whereas sequestration amounts to storage of cyanide in locations from which it can potentially be remobilized by infiltrating waters if conditions change. From an environmental perspective, the most significant cyanide releases from gold leach operations involve catastrophic spills of process solutions or leakage of effluent to the unsaturated or saturated zones. These release pathways are unfavorable for two important cyanide attenuation mechanisms that tend to occur naturally: dispersal of free cyanide to the atmosphere and sunlight-catalyzed dissociation of strong cyanometallic complexes, which produces free cyanide that can then disperse to the atmosphere. The widest margins of environmental safety will be achieved where mineral processing operations are designed so that time for offgassing, aeration, and sunlight exposure are maximized in the event that cyanide-bearing solutions are released inadvertently.

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1. Introduction

The first recorded use of cyanide to extract gold from ores was in 1889 at the Crown Mine in New Zealand (Dorr, 1936). The procedure, in which the gold was dissolved by a dilute cyanide solution, was one of the first applications of hydrometallurgy. The implementation of cyanide techniques represented a major advance for the gold mining industry because it allowed for higher recoveries than the prevailing gravity concentration and mercury amalgamation methods (Rose, 1898; Marsden and House, 2006).

Elsner (1846) studied gold solubility in cyanide solutions and proposed that the dissolution could be described by the following reaction:

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH. \quad (1)$$

In writing this reaction, Elsner recognized two key elements of the process. The first is that an oxidant is required to ionize the gold, and the second is that each gold ion combines with two cyanide anions (CN^-) to form a soluble complex. The same key elements underlie the modern understanding of gold dissolution, although it has been demonstrated that hydrogen peroxide is important as both reactant and product in the overall process:

$$2Au + 4CN^- + O_2 + 2H_2O = 2Au(CN)_2^- + H_2O_2 + 2OH^- \quad (2)$$

$$2Au + 4CN^- + H_2O_2 = 2Au(CN)_2^- + 2OH^- \quad (3)$$

Marsden and House (2006).

The cyanide leach method has been greatly improved since it was first implemented, and now several variations differ in the way that the ore is prepared or in process details. Major advances have included the development of pretreatments for sulfidic or carbonaceous ores that are otherwise not amenable to leaching, the development of carbon-in-pulp and carbon-in-leach methods, and the development of heap leach technology, which involves dripping cyanide solutions through ore heaps constructed on impermeable pads. By the late 1990s, cyanide leach methods had become widespread, supporting some 90% of global gold production (Yarar, 2001). As a consequence, cyanide management is now a consideration nearly everywhere that gold ores are mined and processed.

Much research has been carried out on the chemistry and behavior of cyanide, and there is a large literature on these topics. Fortunately, extensive summaries have also been published giving the interested reader easy access to the detailed literature (Flynn and Haslem, 1995; Smith and Mudder, 1999; Mudder et al., 2001; Young et al., 2001; Dzombak et al., 2006; Marsden and House, 2006). The purpose of this paper is to give a brief review of cyanide chemistry and analysis methods, and then to review aspects of cyanide behavior that are most relevant to environmental considerations at mineral processing operations. These aspects are principally (1) the fate of cyanide in spent ore heaps, tailings, and residual process waters once gold recovery activities are terminated, and (2) the fate of cyanide in any water that moves beyond the ore processing facility into the broader environment. The emphasis here is on research results that have been reported since the cyanide environmental review of Smith and Mudder (1999) and on data from ore processing operations that were gathered by the U.S. Geological Survey over a 10 year period starting in the late 1990s. For an overview of cyanide from a metallurgical perspective, the reader is referred to Marsden and House (2006).

At most modern gold leach operations, cyanide is managed according to recommended practices for transport, use, and disposal (see International Cyanide Management Code for the Gold Mining Industry at http://www.cyanidecode.org/). Typically, solid wastes are stored in ore heaps or tailings impoundments and cyanide-bearing process waters are recovered for reuse, sent to a tailings storage facility, or treated to detoxify or recover the cyanide. Common detoxification treatments, which result in oxidation of cyanide, employ chemical additives (sulfite, Caro's acid (H_2SO_5), or hydrogen peroxide) or bacteria (Marsden and House, 2006; Hewitt et al., 2012). The interest in the fate of cyanide in leach wastes stems from the need to manage environmental consequences of releases that are unintentional, examples of which are accidental spills of cyanide-containing waters (Posey et al., 1995; Beebe, 2001; DeVries, 2001), seepage of cyanide to the unsaturated or saturated zones (Filipek, 1999; Woody et al., 2010), and drainage from legacy sites where cyanide detoxification was not practiced or did not lower cyanide concentrations sufficiently to protect aquatic or aquatic-dependent fauna (Johnson et al., 2008).

2. Chemistry of cyanide in leach solutions

Leach solutions are normally prepared by dissolving reagent salts (NaCN, KCN, $Ca(CN)_2$) in water or by diluting concentrated solutions. The cyanide anion undergoes hydrolysis,

$$CN^- + H_2O = HCN + OH^-, \quad (4)$$

and the resulting hydrogen cyanide undergoes dissociation as follows:

$$HCN = H^+ + CN^- \quad (5)$$

The sum of CN^- and HCN is referred to as free cyanide.

As a consequence of reaction (5), the relative abundances of CN^- and HCN depend on pH (Fig. 1). For 25 °C solutions prepared from pure water, CN^- and HCN are equally abundant at pH 9.2 (the pK_a). CN^- dominates at higher pH and HCN dominates at lower pH. The pK_a changes with temperature, increasing to 9.6 as temperature is lowered to 10 °C and decreasing to 8.9 as temperature is raised to 40 °C. Ionic strength (I) also affects the abundances of CN^- and HCN, but the magnitude of the effect is relatively small. For ionic strengths like those encountered in actual leach solutions ($I \sim 0.1$, Johnson et al., 2000), pK_a for 25 °C decreases from 9.2 to 9.0.

Molecular HCN has a high vapor pressure—81.7 kPa (613 Torr) at 25 °C (Schlessinger, 1973). As a consequence, it will volatilize from aqueous solutions. To minimize cyanide loss to the atmosphere, leach solutions are kept alkaline—typically pH 10 or above—so that nonvolatile CN^- is favored over volatile HCN.

Cyanide forms stable complexes with many metals besides gold. Multiple transition metals are present in most gold ores, so a variety of cyanometallic complexes form during leaching. The most probable complexes contain ferric iron ($Fe(CN)_6^{3-}$), ferrous iron ($Fe(CN)_6^{4-}$), or copper (predominantly $Cu(CN)_3^{2-}$). Other

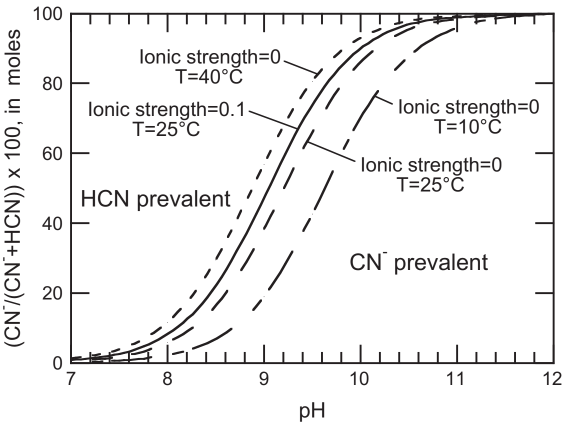

Fig. 1. Plot showing the relative abundance of dissolved CN$^-$ and HCN in cyanide solutions as a function of pH. Curves are shown for ionic strengths of 0 (pure water) and 0.1 (equivalent to process solutions in active leach circuits) and for temperatures ranging from 10 to 40 °C. CN$^-$ is prevalent (relative to HCN) in solutions with pH > 8.9–9.6, the exact threshold value depending on the specific conditions. Dissociation constants from Flynn and Haslem (1995).

cyanometallic complexes that can form are listed in Table 1. Platinum-group metals (Pt, Pd, Rh, Ir, Ru, Os), molybdenum, tungsten, and rhenium are also known to form stable cyanocomplexes (Sharpe, 1976; Beck, 1987; Flynn and Haslem, 1995), but their chemistry has not been thoroughly studied, nor are these metals generally analyzed in process solutions or effluents. The exceedingly low concentrations of platinum-group metals and rhenium in most gold ores (for example, Dean and Pratt, 1988; Emsbo et al., 2003) suggest that cyanocomplexes of these metals are probably insignificant relative to other cyanocomplexes in most cases. In contrast, molybdenum and tungsten can exceed 100 μg/L in remediation stage effluents (Johnson et al., 2008), which is sufficient to suspect the presence of Mo(CN)$_8^{3-}$ and W(CN)$_8^{3-}$.

Cyanometallic complexes are usually classified as weak or strong according to criteria that can differ from one context to another: tendency to decompose under acidic conditions, formation constant smaller or larger than ~10^{30}, and tendency to decompose when exposed to hypochlorite. Most cyanometallic complexes fall into the same category irrespective of the choice of criterion, but some—confusingly—do not, or else show transitional behavior (for example, Ag(CN)$_2^-$ and Hg(CN)$_2$; Milosavljevic and Solujic, 2001). Also, the strong cyanocomplexes of iron and cobalt undergo photodissociation, so the decomposition of these species can be catalyzed where solutions are exposed to sunlight (Flynn and Haslem, 1995). The weak cyanocomplex of chromium also undergoes photodissociation (Flynn and Haslem, 1995).

Table 1
Cyanide species and cyanide-related species that can be found in leach solutions and effluents from leach wastes, and their relative toxicity (acute toxicity to aquatic organisms.) [a]

Group	Species	Intrinsic toxicity
Free cyanide	CN$^-$	High
	HCN$_{aq}$	
Weak complexes	Zn(CN)$_4^{2-}$	Intermediate
	Ag(CN)$_2^-$	
	Cd(CN)$_4^{2-}$	
	Ni(CN)$_4^{2-}$	
	Cu(CN)$_3^{2-}$	
	Cr(CN)$_6^{3-}$[b]	
	Mn(CN)$_6^{3-}$	
Strong complexes	Fe(CN)$_6^{3-}$[b]	Low
	Fe(CN)$_6^{4-}$[b]	
	Co(CN)$_6^{4-}$[b]	
	Au(CN)$_2^-$	
	Pt group metal complexes[c]	
Cyanide-related species		
	CNO$^-$	Low
	SCN$^-$	Low
	C$_2$N$_2$[c]	High
	CNCl[c]	High

[a] From Boening and Chew (1999), Bhunia et al. (2000), and Gensemer et al. (2006).
[b] Subject to photodissociation.
[c] Presence/significance in leach solutions is uncertain.

Cyanide-related anions can also form during ore leaching (Table 1). Cyanate (CNO$^-$) forms by oxidation of cyanide, and thiocyanate (SCN$^-$) forms by reaction of cyanide and intermediate valence sulfur species that can be produced where ores are sulfidic. Two other species, cyanogen (C$_2$N$_2$) and cyanogen chloride (CNCl), are highlighted in Table 1. These species may form where cyanide solutions have been detoxified by alkaline chlorination (cyanogen chloride) or where solution pH has declined in the presence of copper minerals (cyanogen) (Moran, 1998). However, whether either species persists in actual leach solutions is difficult to assess in the absence of published analytical data.

Free cyanide is the most toxic of the cyanide species to aquatic and aquatic-dependent species (Gensemer et al., 2006). (Cyanogen and cyanogen chloride, if present, would also be highly toxic (Boening and Chew, 1999)). The toxicity results from inhibition of the cytochrome oxidase enzyme, which mediates oxygen transfer from blood to tissues. Some cyanometallic complexes have intrinsic toxicity (for example, Ag(CN)$_2^-$) but, for most complexes, the environmental significance stems from their tendency to release free cyanide by dissociation (Gensemer et al., 2006). Accordingly, strong cyanometallic complexes are generally considered to have less environmental significance than weak complexes because they do not dissociate as readily. However, experiments on the strong cyanocomplex of cobalt have shown orders of magnitude greater toxicity in simulated sunlight than in darkness as a consequence of photodissociation (Little et al., 2007). Thus, photocatalysis may merit consideration in environmental risk analyses (see also Broderius and Smith, 1980).

3. Analysis methods and regulatory standards

The traditional analysis methods for cyanide detect groups of cyanide species rather than individual species. The most commonly analyzed groups are referred to as free cyanide, weak acid dissociable (WAD) cyanide, and total cyanide. The WAD cyanide methods are generally considered to report free cyanide and cyanide contained in weak cyanometallic complexes, and the total cyanide methods are generally considered to report free cyanide and cyanide contained in all cyanometallic complexes. These viewpoints are generally correct, but they will be incorrect in certain situations, as explained below.

For most leach operations, regulatory compliance is demonstrated by chemical analysis using methods that have been developed or certified by government agencies such as the U.S. Environmental Protection Agency or the U.S. Geological Survey, or professional organizations such as the International Organization for Standardization, ASTM International, or the American Public Health Association (Ghosh et al., 2006). Commonly employed methods (along with designation numbers of published examples) are reviewed briefly here, as are other methods that can be useful in mineral processing applications. Detailed descriptions can be found in print manuals (Fishman and Friedman, 1989; Eaton et al., 2005) or can be obtained via the internet from the U.S. Environmental Protection Agency (http://www.epa.gov/osw/hazard/testmethods/sw846/index.htm), ASTM International (http://www.

astm.org/BOOKSTORE/BOS/index.html), or the International Organization for Standardization (http://www.iso.org/iso/iso_catalogue.htm).

Free cyanide can be measured by silver nitrate titration (USEPA 9014, APHA 4500-CN-D), colorimetry (USEPA 9014, APHA 4500-CN-E), or ion selective electrode (ASTM 4500-CN-F), but these methods are more useful as finishes for distillations because they can be inaccurate when applied directly to chemically complex waters (Ghosh et al., 2006). A free cyanide microdiffusion technique has also been developed (USEPA 9016, ASTM D4282) in which HCN migrates from a sample previously adjusted to pH 6 into a sodium hydroxide absorber solution. The absorber solution is then analyzed by colorimetry. This technique represents an important advance in analytical methodology, but it can liberate HCN from weaker cyanometallic complexes and, as a consequence, will overreport free cyanide in some types of samples (Ghosh et al., 2006).

Weak acid dissociable (WAD) cyanide is traditionally measured by a distillation procedure in which sample pH is lowered to 4.5–6, the weak cyanometallic complexes are dissociated during boiling, and the resulting free cyanide and any indigenous free cyanide are offgassed to an alkaline trap for quantification (ASTM D2036-C, APHA 4500-CN-I). Automated methods have been developed through the use of thin film distillation (ASTM D4374), ligand-exchange reactions to release weakly complexed cyanide (ASTM D6888), and membrane diffusion of free cyanide followed by amperometric detection (ASTM D6888, ASTM D7237). For most samples, similar results will be obtained by measuring cyanide amenable to chlorination, which involves determining total cyanide before and after free cyanide and weakly complexed cyanide have been destroyed by hypochlorite (for example, USEPA 9010C). However, erroneous results may be obtained for waters that contain cyanocomplexes of mercury, silver, or nickel, which give complete yields in the WAD ligand exchange method, but incomplete yields in the cyanide amenable to chlorination method (Milosavljevic et al., 1995; Milosavljevic and Solujic, 2001). Incomplete yields for cyanocomplexes of mercury are also obtained in the WAD distillation method (Milosavljevic et al., 1995; Milosavljevic and Solujic, 2001).

Total cyanide is traditionally measured by a distillation procedure in which pH is lowered to less than two, cyanometallic complexes are dissociated during boiling, and the resulting free cyanide and any indigenous free cyanide are offgassed to an alkaline trap for quantification (for example, USEPA 9010C, USGS I-3300-85, ASTM D2036-A, APHA 4500-CN-C, ISO 6703-1). Automated variations have been developed that employ thin film distillation (ASTM D4374), ligand-exchange reactions to release complexed cyanide (ASTM D7511), automated colorimetric quantification (USEPA 9012B, USGS I-4302-85), and(or) membrane diffusion of free cyanide followed by amperometric detection (USEPA 9012B, ASTM D7284). In some methods, the sample is irradiated by ultraviolet (UV) light to catalyze dissociation of strong cyanometallic complexes (USGS I-4302-85, ASTM D4374, ASTM D7511). The complexes of gold, cobalt, palladium, platinum, and ruthenium are known to resist dissociation or to dissociate incompletely, even in the methods that employ UV irradiation (Goulden et al., 1972; Grimes et al., 1999; Milosavljevic and Solujic, 2001; Johnson et al., 2008). Thus, cyanide contents will be underreported for samples containing these complexes, no matter which variation of the method is used. Also, the methods do not generally report cyanide contained in organocyanides (nitrile compounds, for example), cyanogen chloride, cyanate, or thiocyanate (Ghosh et al., 2006), although thiocyanate can release HCN in methods that employ irradiation (Goulden et al., 1972; Johnson et al., 2008).

Cyanate and thiocyanate are analyzed by colorimetry (APHA 4500-CN-L and -M). However, these species are rarely analyzed because they are not generally regulated.

Other techniques that can be useful include the picric acid method for WAD cyanide (Fisher and Brown, 1952; Drochioiu et al., 2003), ion chromatographic methods for analysis of specific cyanometallic complexes (ASTM D6994), capillary zone electrophoresis methods for analysis of specific cyanometallic complexes (Aguilar et al., 1993; Petre et al., 2008; Safizadeh et al., 2013), and an attenuated total reflectance-Fourier transform infrared method for analysis of free cyanide (Strauss et al., 2002). These methods are less commonly used, or have yet to be used, in mineral processing applications, so it is important that they be verified for accuracy and precision. A key consideration for the chromatographic and capillary zone electrophoresis methods is that free cyanide is used in eluent solutions to stabilize the target cyanometallic complexes. For remediation-stage effluents and environmental samples—many of which lack free cyanide—the addition of free cyanide could change the species being measured by creating cyanometallic complexes from free metal ions or metals weakly bound to other ligands. Thus, caution is warranted.

Two additional considerations are important for obtaining accurate analytical results. First, most cyanide analytical methods are vulnerable to interferences that can lead to erroneous results if corrective steps are not taken. Interfering species that are common to several methods include oxidizing agents, sulfide, carbonate, and thiocyanate. The ligand exchange methods are susceptible to fewer interferences than distillation methods (Milosavljevic and Solujic, 2001). Second, it is generally recommended that samples be preserved with NaOH to minimize HCN offgassing and that sample bottles be stored chilled to suppress bacterial activity and in darkness to suppress photolytic reactions. The degree to which cyanide results are vulnerable to interferences or preservation protocols can be site specific and, depending on the problem, measured concentrations can be either erroneously high or erroneously low. During the design of site monitoring programs, some amount of experimentation in the details of sampling and sample holding procedures can improve analytical accuracy and lead to a better understanding of cyanide speciation and persistence (for example, Grimes et al., 1999; Johnson et al., 2008).

A common regulatory threshold for cyanide in discharge from mineral processing operations is 0.2 mg/L, the same as the maximum contaminant level promulgated by the U.S. Environmental Protection Agency (Nakles et al., 2006). The governing regulations normally specify the cyanide species that are subject to the threshold (WAD or total), but in some cases they do not (Smith and Struhsacker, 1988; Nakles et al., 2006). In the United States, the state of Nevada typically regulates effluent cyanide on the basis of WAD cyanide measurements, whereas the state of New Mexico typically regulates effluent cyanide on the basis of total cyanide measurements (for example, U.S. Environmental Protection Agency, 1997). The European Union regulates discharge to tailings ponds on the basis of WAD cyanide (Laitos, 2012).

4. Fate of cyanide in wastes and effluents

In the following sections, the fate of cyanide in leach wastes and released effluents is reviewed from two different perspectives. The first perspective is empirical; chemical comparisons are made between process solutions at active leach operations, effluents from remediated operations, and effluent-impacted groundwaters. If this spectrum of samples is taken to represent aging of cyanide solutions or progressive interaction with the environment, then the data reveal general trends in the fate of cyanide in wastes or in solutions released to the environment. For the second perspective, the most important cyanide attenuation mechanisms are described, drawing on experimental and theoretical studies as well as empirical studies. Where information is available, comments are also made on two parameters that are important for environmental risk assessment: (1) the reversibility of cyanide attenuation, and (2) factors that control the rate of attenuation.

4.1. Chemical comparison of active process solutions, effluents from remediated operations, and effluent-impacted groundwaters

Complete chemical analyses of these types of solutions are available, although sparse, in the published literature (for example, Filipek, 1999). For the purpose of this discussion, examples are taken from U.S. Geological Survey studies of several leach operations in the southwestern United States: three active operations (comprising three heap leach circuits and two milling circuits), two heap leach operations undergoing remediation, and three operations where process waters had seeped into the subsurface (Johnson et al., 2008). The study sites span three states and a variety of gold host lithologies, including carbonaceous sedimentary rocks, silicified limestone, felsic volcanics, and volcanic/hydrothermal breccias. These sites are not representative of all leach operations. However, they serve to illustrate general aspects of cyanide behavior and are well suited for a comparative overview because the chemical analyses (124 samples in total) were obtained using the same methods, some of which were optimized to eliminate specific sources of inaccuracy.

Process waters collected from various points in the active leach circuits ranged from 0.1 to 1.2 wt.% total dissolved solids. Sodium and calcium were the dominant cations, and sulfate, chloride, and nitrate were the dominant anions. pH ranged from 2.6 to 11.4. The higher pH values reflect the addition of base to minimize cyanide offgassing, whereas the lower values reflect oxidation of acid-producing sulfidic material in some heap leach cells. Cyanate and thiocyanate were 15–27 mg/L (relatively few measurements) and 0–53 mg/L, respectively.

The concentrations of WAD cyanide and total cyanide in the active circuits are shown in Fig. 2A. Solutions that had been freshly amended with reagent (free) cyanide had the highest total cyanide concentrations, 37–70 mg/L. Pregnant solutions had variable cyanide, but were as low as 1–2 mg/L total cyanide. Clearly, cyanide consumption during leaching can be considerable. In all three circuits, barren solutions contained predominantly free cyanide or weakly complexed cyanide (total cyanide ≈ WAD cyanide) whereas pregnant solutions contained a more significant component of strongly complexed cyanide (total cyanide > WAD cyanide). This is consistent with a general pattern in which free cyanide and weakly complexed cyanide decline during leaching to a greater extent than strongly complexed cyanide.

Effluent from process water-rinsed ore heaps, seepage-impacted groundwaters, and waters from holding ponds were lower in total dissolved solids, ranging from 0.02 to 0.5 wt.%, with the same major cations (sodium, calcium) and anions (sulfate, chloride, nitrate) as the active leach solutions. pH ranged from 9.4 to 6.3. Cyanate and thiocyanate were <0.7 mg/L and <1.5 mg/L, respectively, and were undetectable in most samples.

The concentrations of WAD cyanide and total cyanide in the remediation-stage solutions and groundwaters are shown in Fig. 2B. The concentrations were mostly much lower than in the active circuits. In fact, WAD cyanide was undetectable (below 0.01 mg/L) in several samples. For more than half the samples plotted in Fig. 2B, no special remediation measures were taken or else remediation was limited to rinsing of spent ore heaps with recycled process water. For the remaining samples, remediation consisted of water circulation through sprayers or water acidification to promote cyanide offgassing. (Subsequent sections describe the attenuation mechanisms that these measures were intended to promote.) The lowest cyanide concentrations in Fig. 2B correspond to effluent-impacted groundwaters, some of which were diluted in the flow of ambient groundwater.

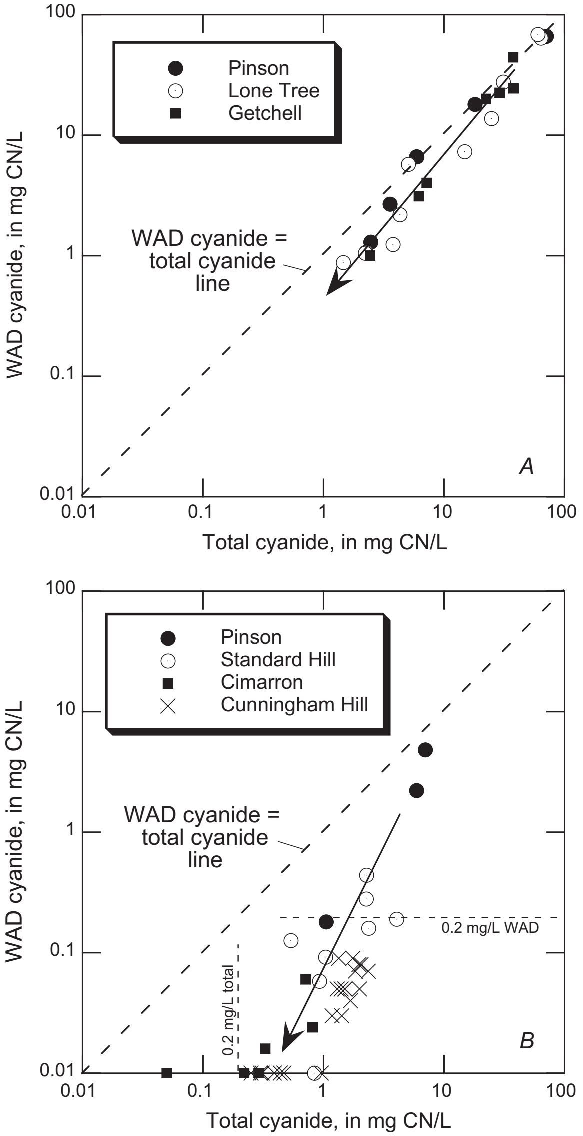

Fig. 2. Plots of weak acid dissociable (WAD) cyanide versus total cyanide for (A) barren, pregnant, and holding pond solutions at active leach operations, and (B) remediation-stage heap effluent, effluent-impacted groundwaters, and remediation-stage ponds. Study sites are located in the southwestern United States. The steep decreases in WAD cyanide are evidence that, in active circuits and residual leach wastes, free cyanide and weakly complexed cyanide attenuate faster than strongly complexed cyanide. Data from Johnson et al. (2000, 2002, 2008).

In Fig. 2B, the data diverge from the total cyanide = WAD cyanide line more than the active solutions. This suggests that inactive ore heaps and groundwater are characterized by a greater disparity between the attenuation rates of WAD and strongly complexed cyanide than active circuits. It is noteworthy that, whereas most sites represented in Fig. 2B would be eligible for decommissioning if regulatory compliance were based on a standard of 0.2 mg/L WAD cyanide, the same sites would not be eligible if compliance were based on a standard of 0.2 mg/L total cyanide. Total cyanide is high in some Cimarron and Cunningham Hill samples in spite of remediation for more than a decade at these sites.

Overall, to the extent that the progression from active solutions to remediation-stage solutions to effluent-impacted groundwaters and ponds represents a time continuum for cyanide attenuation, three generalizations can be made. First, total and WAD cyanide decline as a consequence of natural attenuation mechanisms as well as remediation measures. Second, free cyanide and weakly complexed cyanide decline faster than strongly complexed cyanide. And third, the cyanide-related species cyanate and thiocyanate decline to levels that are, for the most part, below the detection limit of conventional analytical methods. These generalizations are consistent with patterns that have been observed by other workers at a number of other sites (Zagury et al., 2004; studies summarized by Smith and Mudder, 1999).

4.2. Cyanide attenuation mechanisms

In leach wastes or solution discharges to the environment, cyanide can attenuate by a variety of different mechanisms—volatilization, complexation, precipitation of cyanides, adsorption, biological transformation, and sulfidation—that collectively account for the declines in dissolved concentrations shown in Fig. 2. The mechanisms that are most important from an environmental standpoint are reviewed briefly in the following sections. For the most part, these mechanisms proceed naturally, although steps can be taken to accelerate them in order to minimize environmental risk or expedite site decommissioning. For details of the chemical and biological cyanide detoxification technologies that are used at gold leach operations, the reader is referred to Marsden and House (2006) and Wong-Chong et al. (2006).

4.2.1. Volatilization

The high vapor pressure of HCN causes free cyanide to volatilize where conditions favor a significant concentration of this species (pH below ~10, see Fig. 1). Volatilization occurs naturally when leach operations become inactive or where effluents are released to the environment. The reason is that solution pH tends to decline as a consequence of carbon dioxide uptake from the atmosphere, dilution by precipitation, or mixing with receiving waters, most of which are circumneutral.

The rate of cyanide volatilization increases with decreasing pH, increasing temperature, and increasing agitation or surface area-to-volume of the solution. Remediation steps that can be taken to promote volatilization include acidification, aeration, and circulation of water through sprayers.

In settings that approach closed systems, such as pore spaces in the saturated zone or deep interiors of tailings piles, volatilized cyanide can be redissolved by changes in pH or temperature. However, from a broader perspective, volatilization from leach wastes is effectively irreversible because the released hydrogen cyanide is eventually dispersed to the atmosphere where it is oxidized by reaction with OH or O radicals (Cicerone and Zellner, 1983) or is taken up by the oceans (Li et al., 2003). On a global scale, industrial and urban emissions of all types are only a minor source of atmospheric HCN (<10%); biomass burning and biogenic emissions are the main sources (Li et al., 2003; Shim et al., 2007). The dominant sink for atmospheric HCN is ocean uptake; oxidation by free radicals is minor in comparison (Li et al., 2003). The mean lifetime of HCN in the troposphere is 5–6 months (Li et al., 2003, 2009).

4.2.2. Complexation

In a strict sense, complexation of cyanide does not qualify as an attenuation mechanism because the cyanide anion is neither destroyed nor necessarily removed from solution. However, most cyanometallic complexes are less toxic than free cyanide, so the process does attenuate cyanide-related toxicity (Gensemer et al., 2006). In addition, complexation is an intermediate step in other processes that do remove cyanide from solution (see below).

At inactive leach operations or in effluents released to the environment, the most important complexation reactions are probably those involving iron to produce ferricyanide ($Fe(CN)_6^{3-}$) or ferrocyanide ($Fe(CN)_6^{4-}$). This stems from the fact that iron is the most abundant transition element in the ores, rocks, soils, and sediments that most cyanide-bearing solutions encounter. For waters that are alkaline and in contact with spent ores or tailings, the most reactive iron minerals are normally sulfides. Pyrrhotite reacts fastest among the iron sulfides, followed by marcasite, and then pyrite. Depending on the availability of O_2 or other oxidants, the resulting ferrocyanide can be oxidized to ferricyanide; the reaction proceeds by electron transfer rather than ion replacement (Sharpe, 1976). For waters that are neutral to acidic, and(or) in contact with sulfide-free rocks, soils, or sediments, the most reactive iron minerals are normally goethite or other ferric oxyhydroxides. The reaction of cyanide with ferric oxides forms both $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ because some ferric iron is reduced in the process (Flynn and Haslem, 1995). Complexation is known to be slower and less complete when iron is supplied as ferric oxides rather than dissolved Fe^{2+} (Flynn and Haslem, 1995; Marsden and House, 2006).

The formation constants for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ are large, $10^{42.3}$ and $10^{35.4}$, respectively (Flynn and Haslem, 1995), but the complexes can become unstable below pH 5–8, the specific value depending on physicochemical conditions (Meeussen et al., 1992a; Ghosh et al., 1999; Hummel, 2003; Sidenko et al., 2009). Thus, complexation with iron is an attenuation mechanism that is potentially reversible, although the dissociation kinetics can be slow (Meeussen et al., 1992a). Possible scenarios under which free cyanide might reappear by decline of pH are the aging of leach wastes; mixing of alkaline process solutions with rain, snowmelt, or circumneutral receiving waters; and interaction of alkaline process solutions with sulfide minerals in spent ores or waste rocks.

In addition to dissociating in response to physicochemical changes, iron cyanocomplexes can also dissociate photochemically. The mechanism and kinetics of photodissociation have been examined in both experimental studies (Broderius and Smith, 1980; Rader et al., 1993; Kuhn and Young, 2005) and studies of actual effluents (Johnson et al., 2002). Questions have been raised as to whether photodissociation can be sufficient, or rapid enough, to yield environmentally significant free cyanide (Doudoroff, 1980; Smith and Mudder, 1999). In an empirical study designed to address this question, Johnson et al. (2002) documented diurnal cycles in $Fe(CN)_6^{3-,4-}$ and WAD cyanide in an open channel downstream of a draining remediated ore heap (Fig. 3). The cycles are consistent with photodissociation of iron cyanocomplexes during daylight hours to produce free cyanide. Starting at sunrise, iron cyanocomplexes declined by 0.9 mg CN/L while WAD cyanide increased by 0.5 mg CN/L. Evidently, photodissociation of cyanocomplexes of iron gave rise to WAD cyanide concentrations that could be significant from the standpoint of both environmental risk assessment and regulatory compliance.

The strong cyanocomplexes of cobalt can also photodissociate. These species have been recognized only recently in leach wastes (Johnson et al., 2008). Cobalt is not especially abundant in common gold ores, but during remediation the cobalt complexes can persist longer than other cyanide species and consequently can become the dominant cyanide species over time. A survey of four remediation-stage leach operations in the southwestern United States has shown that cobalt cyanocomplexes can carry as much as 1.9 mg CN/L (Johnson et al., 2008). Rainbow trout exposure tests have shown that $Co(CN)_6^{3-}$ has low intrinsic toxicity, but considerably higher toxicity in simulated sunlight as a consequence of photodissociation (Little et al., 2007).

4.2.3. Precipitation of cyanides

Metal cyanide compounds might be expected to precipitate in leach wastes or in locations where leach solutions are released to the environment (Dzombak et al., 2006). Numerous metal cyanide compounds have sparing solubility in water, including compounds

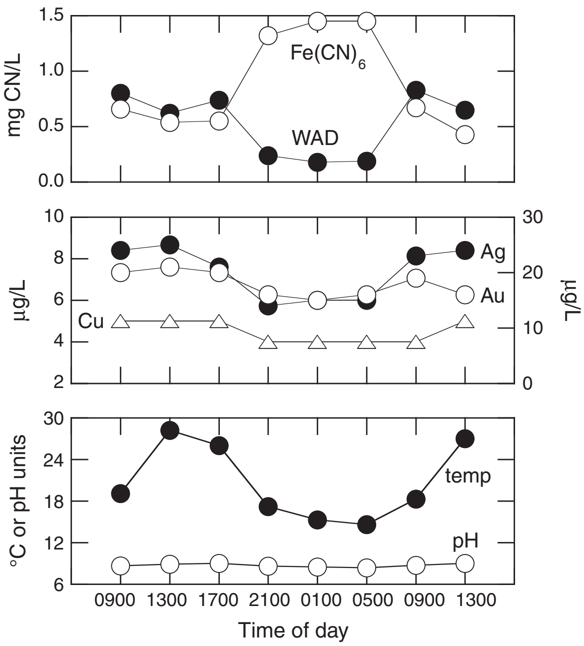

Fig. 3. WAD cyanide, iron-complexed cyanide, trace metals, and other parameters in water samples collected every 4 h from an open channel downstream of a remediated ore heap. The lower concentrations of $Fe(CN)_6$ during daylight hours reflects photodissociation to produce free cyanide, which appeared as increased WAD cyanide concentrations. The released free cyanide caused increases in dissolved silver, gold, and copper by remobilizing the metals as cyanocomplexes from bottom sediment or suspended particles. Temperature measurements show sunlight heating and nighttime cooling of the water. Data from Johnson et al. (2002).

with transition metals (for example, $Cu_2Fe(CN)_6$) and compounds with alkali or alkaline earth elements as well as transition metals (for example, $Na_4Fe(CN)_6{\cdot}10H_2O$). Because iron is abundant in common ores, soils, and sediments, the most likely compound to precipitate is probably Prussian blue ($Fe_4(Fe(CN)_6)_3$, also referred to as Berlin blue). This compound has long been used as a pigment; the first published report of its synthesis dates to the early 18th century (Ludi, 1981). Turnbull’s blue is an isostructural compound with lower Fe^{3+}/Fe^{2+} ratio (Ghosh et al., 1999). Prussian blue has been documented in tailings-contaminated sediments in Balmer Lake, western Ontario (Jambor et al., 2009).

Prussian blue can form rapidly when solutions of $FeCl_3$ and $K_4Fe(CN)_6$ are mixed (Ludi, 1981). However, its rate of formation in leach wastes or released effluents, where ferric iron is contained mainly in oxyhydroxide solids, has not been studied in a systematic way.

The solubility of Prussian blue increases with pH (Meeussen et al., 1992b; Theis et al., 1994; Ghosh et al., 1999). Thus, its precipitation represents a cyanide attenuation mechanism that is potentially reversible. The direct products of dissolution, however, are ferricyanide and ferrocyanide ions, which pose less toxicity risk than free cyanide and may not be regulated depending on the jurisdiction. For the redox conditions characterizing mildly reduced to oxidized soils, the dissolution of Prussian blue produces hydrogen ions, and thus acidity, as in the following reactions:

$$Fe_4(Fe(CN)_6)_3 + 12H_2O = 4Fe(OH)_3 + 3Fe(CN)_6^{3-} + 3e^- + 12H^+ \tag{6}$$

$$Fe_4(Fe(CN)_6)_3 + 3Ca^{2+} + 12H_2O = 4Fe(OH)_3 + 3CaFe(CN)_6^{2-} + 12H^+ \tag{7}$$

$$3Fe_4(Fe(CN)_6)_3 + 32H_2O = 4Fe_3(OH)_8 + 5Fe(CN)_6^{4-} + 4Fe(CN)_6^{3-} + 32H^+ \tag{8}$$

(Meeussen et al., 1994, 1995). The remobilization of $Fe(CN)_6^{3-,4-}$ by infiltrating waters depends on the capacity of the local environment to neutralize this acidity. High acid neutralizing capacity would tend to buffer solution pH and favor continued dissolution of Prussian blue, whereas low acid-neutralizing capacity would allow hydrogen ions to persist, lowering pH and stabilizing the remaining Prussian blue.

The formation of Prussian blue can be environmentally advantageous if its solubility in infiltrating waters is low. This will ensure that the concentration of $Fe(CN)_6^{3-,4-}$ in effluent from the waste or soil is also low, and that free cyanide production—if the effluent becomes sunlight-exposed—will be minimal. However, investigations of contaminated soils in the Netherlands suggest that the solubility of Prussian blue can be sufficiently high in some settings that its formation is environmentally detrimental. At these sites (Meeussen et al., 1994), cyanide was leached from contaminated surface soils and transported downward by infiltrating precipitation. Prussian blue precipitated again within a depth interval in the soil profile that corresponded to the seasonal variation in the water table. At the present time, the precipitates are dissolving slowly and giving rise to sustained, elevated concentrations of $Fe(CN)_6$ (>0.2 mg/L total cyanide) in downgradient groundwater several decades after the contamination occurred. Similar $Fe(CN)_6^{3-,4-}$ “bleed” from gold leach wastes would impede regulatory compliance in jurisdictions where regulations are based on total cyanide analyses. In jurisdictions that rely on WAD cyanide, elevated $Fe(CN)_6^{3-,4-}$ would have regulatory significance only if free cyanide were produced as a consequence of sunlight exposure (Grimes et al., 1999; Johnson et al., 2002) or changes in physicochemical conditions (for example, mixing with acidic waters, Plumlee and Edelmann, 1995).

At heap leach operations, a common remediation strategy is to rinse spent ore heaps with recycled process water. The amount of rinsing that will be required to lower effluent cyanide concentrations to a particular threshold is typically estimated using models in which cyanide is assumed to behave conservatively (for example, Decker and Tyler, 1999). If Prussian blue or other metal cyanide compounds are present in the spent heaps, and if these compounds slowly release cyanide as they do in the soil profiles studied by Meeussen et al. (1992a, 1992b, 1995), then a simple rinsing strategy might fail to provide for timely elution of the residual cyanide. At sites where the pads beneath ore heaps have been compromised and seepage has occurred to the subsurface (examples include the Cimarron and Cunningham Hill sites), Prussian blue or other metal cyanide compounds could form in the subsurface. Slow dissolution of these compounds may then cause slow release of iron cyanocomplexes to flowing groundwater.

Other cyanide compounds have been identified in leach wastes. A zeolitic compound ($NaKZn_3(Fe_{1.9}Cu_{0.1})(CN)_{12}{\cdot}3.7H_2O$) has been reported in an ore heap at the Landusky mine in Montana (Sidenko et al., 2009). Nickel-, Cu-, and Zn-bearing cyanide compounds coexist with Prussian blue in the tailings-contaminated sediments in Balmer Lake (Jambor et al., 2009). Johnson et al. (2001) reported Zn-, Fe-, Cu-bearing cyanide compounds, with low but detectable Co, in calcite-rich scale at the Pinson heap leach operation in northern Nevada (Fig. 4). In another scale sample, cyanide was present as a sodium or calcium salt intergrown with calcite, sodium sulfate, gypsum, and halite. These compounds almost certainly formed by evaporation in the arid Nevada climate. Their constituents, including cyanide, would be easily remobilized by the next rain event.

4.2.4. Adsorption

Cyanide species can adsorb onto common constituents of soils and sediments. Hydrogen cyanide does not interact with mineral surfaces (iron oxides, aluminum oxides, clays), but adsorbs strongly onto organic matter (Theis and West, 1986; Chatwin and Trepanowski, 1987; Higgins and Dzombak, 2006). Weak cyanometallic complexes adsorb onto both minerals and organic matter. Several weak complexes have been examined in experimental studies using a variety of different substrates, including goethite, manganese oxides, aluminum oxides, silica, and clays (Theis and Richter, 1980; Theis and West, 1986). Overall, the experiments show that the cyanometallic complexes do exhibit adsorption behavior, although complexation with cyanide can cause adsorption of the metal to be suppressed relative to adsorption in the absence of cyanide.

The behavior of zinc in the presence of goethite can be taken as an example (Fig. 5). In solutions containing cyanide, zinc adsorption increases with pH to a maximum of 60% near pH 6, and then decreases. Below pH 6, the adsorption behavior is the same as for zinc in the absence of cyanide, whereas above pH 6 adsorption of zinc is suppressed. The suppression reflects the formation of zinc cyanocomplexes. Below pH 5 zinc was present mainly as the free ion, whereas at higher pH the metal was increasingly complexed, forming mainly $Zn(CN)_2$, $Zn(CN)_3^-$, and $Zn(CN)_4^{2-}$ and approaching complete complexation by pH 7. The suppression of zinc adsorption at high pH reflects electrostatic repulsion between $Zn(CN)_3^-$ or $Zn(CN)_4^{2-}$ and the goethite surface, which is negatively charged under alkaline conditions (Theis and West, 1986). Despite the suppression of zinc adsorption, the analyses of experimental solutions and the constant capacitance adsorption model both reveal finite adsorption of zinc at pH values greater than 7, which implies that zinc cyanocomplexes adsorb, at least weakly, across a wide range of pH values.

Experiments on the weak cyanocomplexes of nickel, copper, and cadmium have shown adsorption behavior similar to the weak cyanocomplexes of zinc. For nickel, adsorption was found to be enhanced at low pH reflecting either electrostatic attraction between $Ni(CN)_4^{2-}$ and the goethite surface, which is positively charged under acidic conditions, or the formation of surface complexes (Theis and Richter, 1980).

The strong cyanocomplexes of iron have been shown to adsorb onto a variety of minerals (goethite, aluminum oxides, manganese oxides, clays) and onto soil organic matter. For goethite and aluminum oxide (Fig. 6), adsorption is strongest at low pH consistent with electrostatic attraction between the negatively charged complexes and positively charged surfaces of the solids (Theis and West, 1986; Rennert and Mansfeldt, 2001; Bushey and Dzombak, 2004). Ferrocyanide ($Fe(CN)_6^{4-}$) is less sensitive to pH in its adsorption behavior than ferricyanide ($Fe(CN)_6^{3-}$), as displayed in Fig. 6 (Rennert and Mansfeldt, 2001). Ferrocyanide also adsorbs more strongly than ferricyanide (Rennert and Mansfeldt, 2001). (The reverse relationship is indicated in Fig. 6, but this is a consequence of different experimental conditions for the Theis and West (1986) and U.S. Geological Survey studies.) For ferrocyanide, the interaction with goethite may be complicated by the formation of a new phase on the mineral surface (Rennert and Mansfeldt, 2001).

Experimental results for the strong $Co(CN)_6^{3-}$ complex are also shown in Fig. 6. $Co(CN)_6^{3-}$ adsorbs onto goethite at low pH, although the extent of adsorption is less than for $Fe(CN)_6^{3-}$ or $Fe(CN)_6^{4-}$.

Ferricyanide adsorption onto goethite is rapid. Theis et al. (1988) reported that ferricyanide removal from solution was essentially complete after 5 min of contact time at concentrations of 1–5 µM. Desorption was similarly rapid, being essentially complete 15 s after the transition from acidic to alkaline conditions (pH 8.5). The rapidity of the process is consistent with a simple electrostatic model for the interaction between $Fe(CN)_6^{3-}$ and the goethite surface. The overall kinetics of adsorption and desorption in actual leach wastes is likely to be controlled by the rate of transport of ferricyanide to active mineral surfaces rather than by the rate of surface reactions.

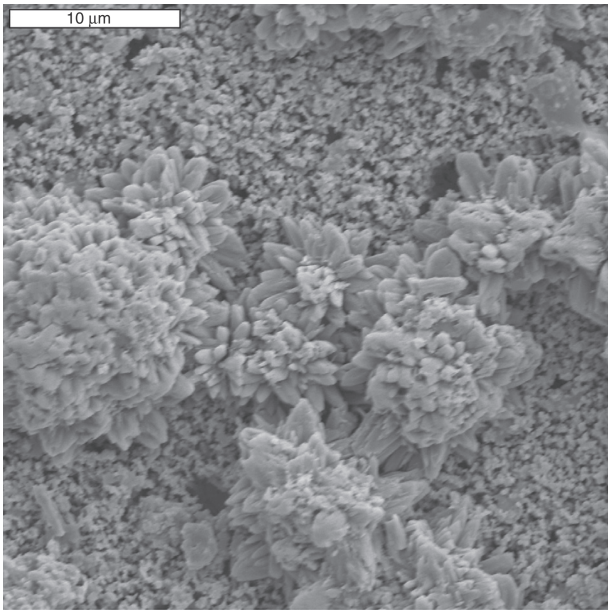

Fig. 4. Scanning electron microscope image of pond scale from a heap leach operation in Nevada. The flower-shaped crystal aggregates are a cyanide compound that contains zinc, copper, and iron. Fine-grained matrix is calcite with minor iron oxide and clay. An alkaline leach of this material yielded 0.69 mg $Fe(CN)_6$/g (analysis by ion chromatography).

Ferrocyanide also adsorbs quickly onto goethite. However, desorption of ferrocyanide is both slower than ferricyanide and incomplete (71% in the first 15 min after the transition to alkaline conditions, Rennert and Mansfeldt, 2001). The contrast with ferricyanide is thought to reflect precipitation of a distinct phase on the goethite surface (Rennert and Mansfeldt, 2001).

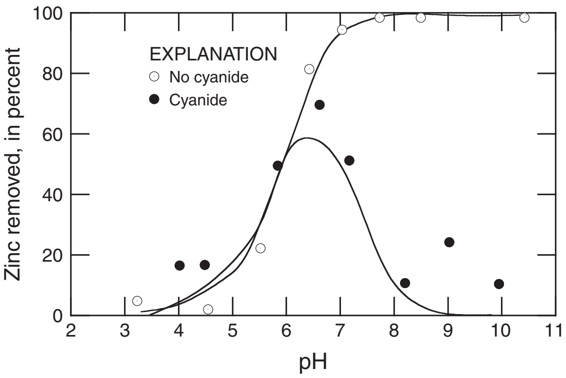

Fig. 5. Adsorption of zinc onto goethite as a function of pH in the presence of cyanide (filled circles) and in the absence of cyanide (open circles). Zinc forms negatively-charged complexes with cyanide above pH 6 ($Zn(CN)_3^-$, $Zn(CN)_4^{2-}$) that are repelled by negatively charged goethite surfaces that form above pH~6–7. Consequently, zinc adsorption is suppressed relative to the cyanide-free experiments. Curves represent constant capacitance models. Modified from Theis and West (1986). Experimental conditions: 23 °C, 0.1 M KNO_3, 0.6 g/L FeOOH, and either 1.73×10^{-5} M total Zn and 2×10^{-3} M total cyanide (filled circles) or 2.41×10^{-5} M total Zn (open circles).

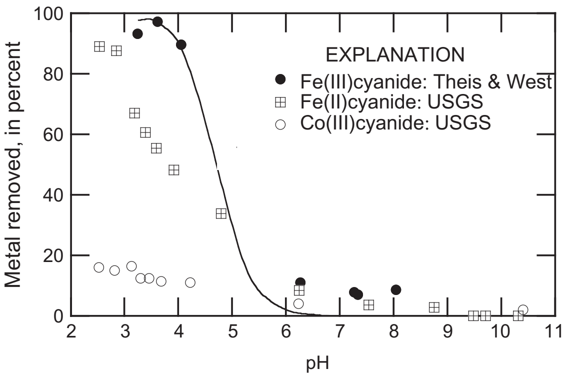

Fig. 6. Adsorption of the strong cyanocomplexes of iron ($Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$) and cobalt ($Co(CN)_6^{3-}$) onto goethite. The pH dependence reflects electrostatic repulsion at high pH, where the goethite surface is negatively charged, and electrostatic attraction at low pH, where the goethite surface is positively charged. $Fe(CN)_6^{4-}$ may also have formed a distinct phase on the goethite surface. Data are from Theis and West (1986) (filled circles) and this report (other symbols). Experimental conditions: 23 °C, 0.1 M KNO_3, 0.6 g/L FeOOH, 2×10^{-5} M $Fe(CN)_6^{3-}$ (filled circles); 0.1 M KCl, 2.3 g/L FeOOH, 9.4×10^{-5} M $Fe(CN)_6^{4-}$ (open circles); 0.1 M KCl, 2.3 g/L FeOOH, 9.3×10^{-5} M $Co(CN)_6^{3-}$ (squares).

It is evident from Figs. 5 and 6 that adsorbed cyanometallic complexes can be released to solution by increases or decreases in pH. Thus, cyanide attenuation by adsorption is potentially reversible. In leach wastes, increases in pH are probably rare because pore waters in tailings and spent ore heaps are initially alkaline, and residual liquids tend to decrease in pH over time for reasons that were enumerated in Section 4. Thus, desorption of strong cyanometallic complexes—which is favored by increasing pH—would not be expected, but desorption of the weak cyanocomplexes of zinc, copper, cadmium, and nickel—which can be favored by decreasing pH—may be expected. Decreasing pH would also favor dissociation of released cyanometallic complexes. Overall, the environmental significance of cyanide desorption would be dictated by the kinetics of the process, which would depend on site-specific factors.

4.2.5. Biological transformation

There are a number of biological pathways by which cyanide can attenuate in leach wastes or discharged waters, either naturally or as a result of treatment (Akcil and Mudder, 2003; Ebbs et al., 2006; Wong-Chong and VanBriesen, 2006). The pathways are directly linked to free cyanide, although thiocyanate may also be utilized, as described in the following section. Biological transformations can be mediated by a number of different bacteria, fungi, or plant species that either convert cyanide to carbon and nitrogen species that can be used for cell growth or assimilate CN^- directly into organic compounds. Some plants employ a direct mechanism by which cyanide is converted to a volatile form that is released from the plant as a gas.

Metal-complexed cyanide has also been reported to attenuate biologically, but in most studies it is difficult to determine whether the attenuation was by direct utilization of the complex or by utilization of free cyanide released by complex dissociation. Whether or not utilization is direct, weakly complexed cyanide is typically found to decline where biological cyanide attenuation is operating. In contrast, strongly complexed cyanide is typically resistant to biological attenuation (Oudjehani et al., 2002).

Bacteria that are capable of metabolizing free cyanide include members of the *Arthrobacter*, *Bacillus*, *Pseudomonas*, and *Thiobacillus* genera, among others. Cyanide metabolizers are common constituents of the microbial consortia that naturally populate leach wastes (for example, Garcia et al., 1995; Oudjehani et al., 2002). Depending on the prevailing physicochemical conditions and the availability of carbon and nitrogen sources other than cyanide, the bacteria can break down cyanide by (1) oxidative pathways in which cyanide reacts with O_2 to produce ammonia and carbon dioxide, (2) reductive pathways in which cyanide reacts with H^+ to produce ammonia and methane, (3) hydrolytic pathways in which cyanide reacts with H_2O to produce formate or formamide and ammonia, or (4) assimilatory pathways (Ebbs et al., 2006; Dash et al., 2009).

Studies of cyanide attenuation by microbes isolated from tailings, ore heaps, and soils have found that both oxidative and hydrolytic pathways can be utilized by the indigenous organisms (Aronstein et al., 1994; Garcia et al., 1995; Oudjehani et al., 2002). Oudjehani et al. (2002) found that the residual cyanide in 6–9 year old tailings was not undergoing biological degradation, but that newly added free cyanide was readily degraded by bacteria with 85–100% of the new cyanide consumed after 65 days. The rate of biological degradation decreased with increasing cyanide concentration reflecting toxicity to the microorganisms. In contrast, fresh tailings (3 months old) showed signs of ongoing biological degradation of the residual cyanide. Newly added free cyanide was also degraded, with 85% consumption by biological pathways after 170 days. In the fresh tailings, the degradation rate was invariant over a range of cyanide concentrations, which suggests that the microorganisms were acclimated to cyanide. Active biological cyanide degradation in fresh tailings but not in old tailings was hypothesized by Oudjehani et al. (2002) to reflect differences in cyanide speciation: the fresh tailings contained weakly complexed and(or) free cyanide, whereas the older tailings contained mainly strongly complexed cyanide, which resists biodegradation.

Biological activity can also affect cyanide indirectly by impacting other attenuation mechanisms. For example, metabolic activity can result in a lowering of pH, which favors cyanide volatilization (Oudjehani et al., 2002). Metabolic activity can also catalyze the oxidation of ferrocyanide to ferricyanide, which can impact the adsorption behavior of the cyanide (Zimmerman et al., 2008). In addition, enzymes can bind to mineral surfaces and affect cyanide adsorption by altering surface charge characteristics (Zimmerman et al., 2008).

4.2.6. Sulfidation

Where sulfide minerals are present, cyanide can react with sulfide oxidation products to form thiocyanate (SCN^-), a species that is less toxic to aquatic organisms than free cyanide and most cyanometallic complexes (Bhunia et al., 2000). The reaction pathways involve polysulfide (S_xS^{2-}) or thiosulfate ($S_2O_3^{2-}$):

$$CN^- + S_xS^{2-} = SCN^- + S_{x-1}S^{2-} \tag{9}$$

$$CN^- + S_2O_3^{2-} = +SCN^- + SO_3^{2-} \tag{10}$$

(Luthy and Bruce, 1979).

The rate of reaction (9) increases as pH increases from 8.2 to 12.0 (Luthy and Bruce, 1979). At a pH value of 8.2, the rate of the polysulfide reaction is three orders of magnitude greater than the rate of the thiosulfate reaction (Luthy and Bruce, 1979). Thus, attenuation of cyanide can be rapid where sulfide oxidation is by pathways that produce polysulfide, but substantially slower where sulfide oxidation is by pathways that produce thiosulfate. Experimental results obtained using a variety of different sulfide minerals have shown that thiocyanate production is enhanced by increasing temperature (McGill et al., 1985), but can be inhibited by metals, which compete for cyanide as they form cyanometallic complexes. Thiocyanate can also be inhibited by ammonia (Luthy and Bruce, 1979).

Under certain conditions, thiocyanate can revert to free cyanide. This can occur on exposure to hydrogen peroxide, ozone, or other strong oxidants of the type that are used for cyanide detoxification (Flynn and Haslem, 1995). However, the free cyanide is transient; it is normally destroyed by excess oxidant. In most environmental settings, thiocyanate is degraded via pathways that produce species such as cyanate (CNO^-), ammonia, carbonate, and sulfate. A number of bacteria have been identified in soils and sediments that can mediate thiocyanate degradation (Brown and Morra, 1993), including alkaliphilic bacteria that utilize thiocyanate as either as a source of nitrogen or a source of energy (Sorokin et al., 2001). Bacterial utilization of thiocyanate accelerates with increasing temperature to 30 °C, beyond which non-biological degradation becomes important (Brown and Morra, 1993). Bacterial utilization is inhibited by high concentrations of ammonia, which can ultimately be toxic to the organisms. Some strains circumvent the toxicity problem by converting thiocyanate to cyanate instead of ammonia. Cyanate is unlikely to revert to free cyanide (Resnick et al., 1958).

4.2.7. Other attenuation mechanisms

Cyanide can also attenuate by abiotic oxidation or hydrolysis. Abiotic oxidation is the basis for chemical detoxification procedures that utilize hydrogen peroxide, hypochlorite, $SO_2 + O_2$, or other strong oxidants (Marsden and House, 2006). However, in the settings of concern in this review—residual wastes at leach operations and solutions released to the environment—abiotic oxidation and hydrolysis are less important than other attenuation mechanisms. In the absence of strong oxidants, catalysts (for example, activated carbon, UV, copper, TiO_2), or high temperature (Frank and Bard, 1977; Smith and Mudder, 1999; Sarla et al., 2004), these mechanisms are likely to be slow and to account for only a minor portion of the overall cyanide attenuation (Flynn and Haslem, 1995; Smith and Mudder, 1999).

5. Summary

Cyanide residues in leach wastes are subject to attenuation mechanisms that lead to their dispersal to the atmosphere, chemical transformation to other carbon and nitrogen species, and(or) sequestration in solid form as cyanometallic precipitates or adsorbed species on mineral surfaces. Cyanide in solutions that are discharged to surface waters or that seep into the subsurface are subject to the same general mechanisms. Of these fates, dispersal to the atmosphere and chemical transformation amount to permanent elimination of the cyanide, whereas sequestration amounts to storage of cyanide. If physicochemical conditions change, stored cyanide can potentially be released to infiltrating waters by means of dissolution or desorption reactions (see Table 2). Released cyanide would be mostly in the form of cyanometallic complexes, which have lower intrinsic toxicity than free cyanide. Although complexed cyanide can revert to free cyanide, the extent to which this occurs—and the environmental significance—will depend on site-specific factors, the most important of which may be the degree of sunlight exposure.

Table 2
Factors that can favor release of free cyanide by reversal of cyanide attenuation mechanisms.

Attenuation mechanism	Factors favoring release of free cyanide	
	Strongly complexed cyanide	Weakly complexed cyanide
Adsorption	Increase in pH	Increase or decrease in pH
Precipitation	Increase in pH	–
Complexation	Decrease in pH Sunlight exposure	Decrease in pH Decrease in free cyanide

Empirical observations at a variety of active and inactive leach operations confirm a general pattern in which free cyanide and weakly complexed cyanide decline in concentration naturally as leach wastes age. Strongly complexed cyanide also declines, but more slowly. The rate of cyanide attenuation in mine wastes or released solutions depends on a variety of parameters that will vary from one site to another. These parameters include speciation of the cyanide, pH, temperature, redox conditions, degree of agitation of solutions, surface area-to-volume ratio of ponds, degree of sunlight exposure, and microbial activity. Thus, the time required to achieve particular water quality standards will also vary from one site to another. The environmental importance of cyanide remobilization from solids—and the potential for long-term cyanide "bleed" from leach wastes—will depend on (1) the existence and abundance of cyanide-bearing compounds or adsorbed cyanide in the wastes, soils, or sediments, (2) the extent to which this cyanide is soluble in infiltrating waters, and (3) the extent to which the released cyanometallic complexes are subject to dissociation to produce free cyanide.

From an environmental perspective, the most significant cyanide releases from gold leach operations have involved catastrophic spills of process solutions or leakage of effluent from solid wastes to the unsaturated or saturated zones. Key to the environmental significance of spills and leakage is that these release pathways are unfavorable for two important cyanide attenuation mechanisms that can occur naturally: catastrophic spills allow little time for offgassing of free cyanide to the atmosphere, and effluent leakage to the subsurface does not allow for photodissociation of strong cyanometallic complexes to give free cyanide that can offgas. With respect to cyanide dispersal from gold leach operations, the widest margins of environmental safety will be achieved if operations are designed so that time for volatilization, aeration, and sunlight exposure are maximized if cyanide-bearing solutions are released inadvertently.

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