## CONSIDERATIONS IN THE RECLAMATION OF CYANIDE HEAP LEACH DUMPS

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#### ABSTRACT

Planning for the reclamation of spent ore dumps produced by cyanide heap leach processing should begin at an early stage during project feasibility studies and metallurgical testing. The key issues influencing the reclamation of cyanide heap leach dumps are site characteristics, the design of the heap leach facility, and the cyanide neutralization behavior of the ore. Water quality permit conditions and bonding provisions for heap leach facilities in most western states in the U. S. now specify residual cyanide levels for spent heaps. One way to address regulatory concerns regarding cyanide detoxification is to provide data from column cyanide neutralization tests performed on leached columns used for metallurgical testing.

Heap leach project reclamation planning and closure requirements should consider the evidence that natural degradation of cyanide and cyanide attenuation by hydrogeochemical processes are capable of minimizing or eliminating short— and long—term potential water quality impacts from heap leach systems. As an overview of this topic, this paper will integrate the theoretical chemical data on cyanide with the observed geochemical behavior of cyanide in the decommissioned heap leach environment. The cyanide species that are likely to exist within an abandoned heap leach system will be identified, and the relative toxicity and potential environmental effect of these cyanide species will be discussed. These data will then be used to evaluate reclamation requirements for spent cyanided ores with respect to cyanide detoxification regulations, and recommendations will be made for obtaining cyanide neutralization data during initial project planning.

## CYANIDE IN THE ENVIRONMENT

Cyanide is a generic term indicating the presence of the cyanide ion  $(CN^-)$ . Cyanide is a very common, naturally occurring

compound produced by many biochemical reactions. Many plant species synthesize organic compounds which contain cyanide in the form of cyanogenic glycosides (Knowles, 1976). For example, trace amounts of cyanide are present in the seeds and leaves of many members of the Rosaceae (rose) family (Kingsbury, 1964).

Many common items such as lettuce, maize, sweet potatoes, kidney beans (Oke, 1969) almonds, and cigarette smoke contain cyanide. As an example, a recent chemical analysis of chocolate-covered almonds revealed a total cyanide content of about 2 ppm (Steffen Robertson and Kirsten, 1987). The US Surgeon General (US Department of Health, 1964) has shown that cigarette smoke contains up to 1600 ppm total cyanide.

The chemistry of cyanide solutions is complicated because the cyanide ion forms compounds and complexes with many elements. Some cyanide species are highly toxic whereas others are relatively inert and harmless. Molecular hydrogen cyanide (HCN) is the most toxic form of cyanide. Under most conditions, HCN exists as a gas which readily dissipates or reacts with the environment to form less toxic or non-toxic forms of cyanide. Thus HCN is an ephemeral toxin, and many naturally occurring geochemical processes reduce the HCN concentration of a heap system with time.

As discussed below, free-cyanide includes the two species, ionic cyanide (CN) and molecular hydrogen cyanide. Free-cyanide toxicity in man, mammals, and aquatic species is well documented (Doudoroff, 1976; Ecological Analysts, 1979; Towill et al., 1978). The lethal doses reported for human adults vary with the type of exposure as follows:

- 1) 1 to 3 mg/kg body weight if ingested;
- 2) 100 to 300 ppm if inhaled; and
- 3) 100 mg/kg of body weight if absorbed.

Acute toxicity of free cyanide to freshwater invertebrates ranges from 0.028 to 2.295 mg/l, depending on species and test conditions. Generally, free-cyanide concentrations greater than 0.1 mg/l are expected to kill sensitive species in freshwater or marine environments (Doudoroff, 1976; Cardwell et al., 1976). Concentrations of HCN as low as 0.05 mg/l can be lethal to fish (Scott and Ingles, 1981). Several site specific variables including the solution pH and temperature, oxygen content of the water, ionic strength, species acclimation, and body size can affect the degree of free-cyanide toxicity.

## CYANIDE TERMINOLOGY AND ANALYTICAL METHODS

One of the difficulties in discussing cyanide and the environment and establishing cyanide regulatory standards is that the terminology used to describe cyanide species is confusing. To add to the confusion, there are a variety of analytical methods used to test for the various cyanide species. Thus comparing analytical data from one laboratory to another may not be valid (Conn, 1981). The following discussion will attempt to clarify cyanide terminology and review the most commonly used analytical methods.

# Free Cyanide

The term "free cyanide" means the two species, ionic cyanide (CN") and molecular hydrogen cyanide or hydrocyanic acid (HCN). In acidic and weakly-alkaline solutions, the dominant free cyanide species is molecular hydrogen cyanide.

Most analytical techniques for measuring free cyanide involve solvent extraction or sparging the HCN from solution and collection of it for measurement (Conn, 1981). Even though HCN is the species that is measured and *is* the dominant toxic species of concern, free cyanide is generally expressed in the literature as "CN". To add to the confusion, free cyanide is sometimes written as "CN" (Environmental Protection Agency, 1980).

It should also be noted that there is a significant body of data indicating problems with free cyanide analyses. There are many examples where the apparent free cyanide level are higher than the total cyanide determined in the same sample, due to interference, often by thiocyanates. Free cyanide analyses are, therefore, highly questionable.

## Total Cyanide

Total cyanide refers to the sum, in terms of cyanide ion  $(CN^-)$ , of molecular hydrogen cyanide (HCN), cyanide ion  $(CN^-)$ , and most cyanide bound as metallic complexes and compounds. Acid reflux/distillation using a catalyst to break down most metallic cyanide species is the analytical technique commonly used to measure total cyanide. This method cannot measure completely the cyanide content of gold-, cobalt-, platinum-, and some iron-cyanide species. The accuracy and precision of the method are also compromised by interference from thiocyanates  $(CNS^-)$ . The thiocyanate interference problem, coupled with variations in analytical procedures, has led to great difficulties in comparing total cyanide data produced by the mining industry (Conn, 1981).

Because total cyanide is expressed in terms of  $(CN^-)$ , total cyanide data can be difficult to distinguish from free cyanide data, also labeled  $(CN^-)$ . The use of the words "free" and "total" can prevent this confusion.

Some cyanide regulations are expressed in terms of total cyanide rather than free cyanide. Most biologists and environmental scientists would prefer regulations expressed as free cyanide, because total cyanide is toxicologically meaningless (Conn, 1981). However, as mentioned above there are significant analytical problems with the analysis of free cyanide.

# Other Methods for Determining Cyanide

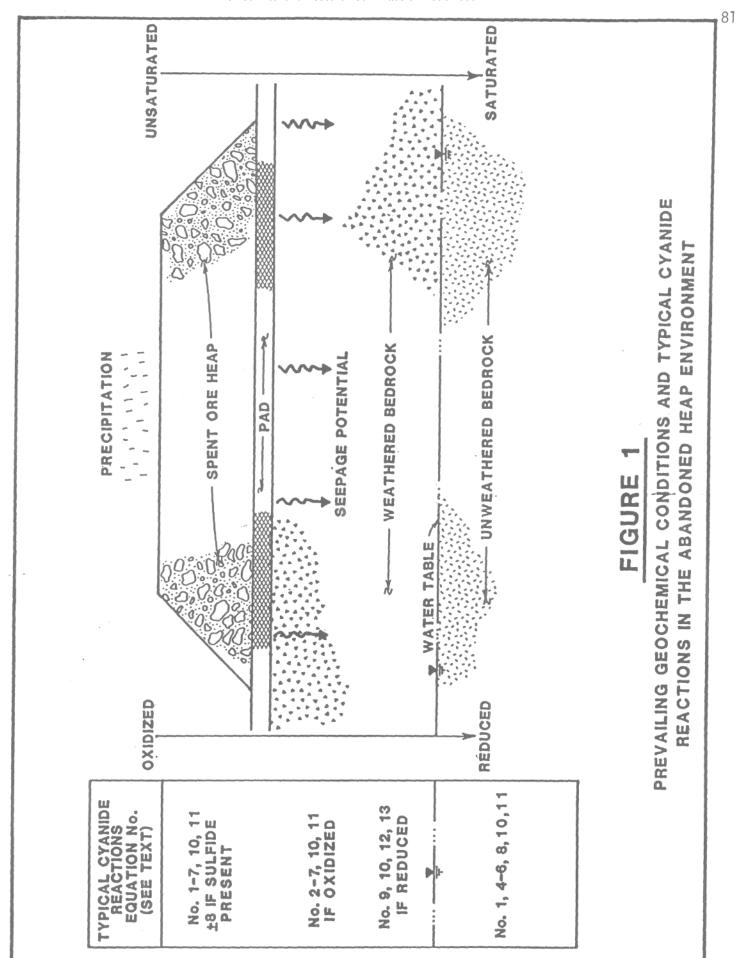
There are various methods for measuring free cyanide plus the cyanide evolved from certain metal cyanide complexes under specified conditions. Some cyanide regulations are based upon these determinations which measure less than total cyanide. The cyanide amenable to chlorination method is based upon the difference between total cyanide determinations on a sample before and after alkaline chlorination. The alkaline chlorination process oxidizes all cyanides except the iron complexes and thiocyanate. The difference between the two total cyanide values is reported as cyanide amenable to chlorination. This method is subject to the same drawbacks and thiocyanate interference problems as the total cyanide method (Gannon, 1981).

The weak acid dissociable method (WAD), otherwise known as Method "C" from the ASTM designation, involves a procedure similar to the total cyanide technique except that it uses difference reagents. This method recovers all the cyanide from zinc- and nickel-cyanide complexes, but only recovers about 70 percent from copper- and 30 percent from cadmium-cyanide complexes. It does not recover any cyanide from ferro- ferri-, and cobalt-cyanide complexes. There is no thiocyanate interference problem with this method (Gannon, 1981). This method is currently favored by some engineers and geochemists because it obviates the problems associated with free cyanide analyses and it is not subject to thiocyanate interference.

# THE GEOCHEMISTRY OF CYANIDE IN AN ABANDONED HEAP

One approach to understanding cyanide behavior in a decommissioned heap leach operation is to identify the cyanide reactions likely to take place, and the cyanide species likely to be present in the various geochemical environments within the heap, the pad, and the underlying sediments and bedrock. Figure 1 is a schematic diagram of an abandoned heap system showing the major components of the system and the prevailing geochemical conditions within the heap environment. These conditions vary for different parts of the system. The upper portions of the system, including the heap itself, the pad, and the underlying weathered bedrock are likely to be oxidized, and relatively dry or at least unsaturated. The underlying unweathered bedrock is more likely to be a reduced and saturated environment.

Obviously the specific geochemical conditions within a heap leach system will be strongly influence by site conditions such as the position of the water table, amount of precipitation falling on the heap, the mineralogy of the spent ore and of the underlying bedrock, and the fracture density and permeability of the bedrock. For purposes of this discussion, however, the geochemical conditions shown in Figure 1 are assumed to be a common scenario.



The following discussion identifies the cyanide species most likely to be present within various components of the abandoned heap environment.

# Hydrolysis and Volatization

Reaction between water and the cyanide ion (hydrolysis) results in the formation of molecular hydrogen cyanide (HCN) as shown in Equation (1).

$$CN^{-} + H_{2}O \rightarrow HCN + OH^{-}$$
 (1)

This reaction is strongly dependent on pH. At a pH of 9.36, the pKa of the hydrolysis reaction, the concentrations of CN" and HCN are equal. At all lower pH values, hydrogen cyanide is the dominant species at pH 7, 99 percent of the cyanide exists as HCN (Huiatt and others, 1982). Most heaps have an operational pH of about 10.5. Following decommissioning and abandonment, there will be a gradual decrease in pH with time due to neutralization of the alkaline environment during rinsing procedures and due to infiltration of rainwater and carbon dioxide uptake. Thus, HCN will be produced by most newly abandoned heaps.

Molecular hydrogen cyanide (HCN) has a high vapor pressure and rapidly volatilizes into a gas. This volatilization process is moderately temperature sensitive. The HCN produced by hydrolysis of CN" is thus readily volatilized into a gas and is continuously evolved from the heap environment through dissipation or destroyed by oxidation as discussed below. The net result is thus a loss of cyanide from the system.

As shown in Figure 1, hydrolysis of ionic cyanide is most likely to occur within the upper portions of the heap, under oxidized and unsaturated conditions. However, this reaction is not Eh dependent and can also occur in the reduced and saturated portions of the heap environment.

It should be noted that if the heap contains agglomerated ore, the lime agglomerating medium may buffer the hydrolysis reaction by keeping the pH above 9.36. This will temporarily prevent hydrolysis and the production of HCN. With time, infiltration of water and carbon oxidize into the heap will neutralize the cement agglomerating agents. The heap is then no longer buffered at an elevated pH, and the hydrolysis of CN to HCN will take place.

## Oxidation of HCN and CN-

The oxidation of either HCN or CN is generally restricted to the upper, oxidized portions of the heap environment as shown in Figure 1. The oxidation of HCN produces hydrogen cyanate (HCNO) as shown in Equation 2 (Owenback, 1978).

$$2HCN + O_2 \rightarrow 2HCNO$$
 (2)

The direct oxidation of  $CN^-$  (Equation 3) requires a mineralogical, bacteriological, or photochemical (sunlight) catalyst, and produces cyanate ions ( $CNO^-$ ).

$$2CN^- + O_2 + catalyst \rightarrow 2CNO^-$$
 (3)

Hydrogen cyanate and cyanate ions are much less toxic than HCN. Within the heap environment, HCNO and CNO readily hydrolyse to form ammonia and carbon dioxide which are evolved from the system as gases as illustrated by Equation 4.

$$HCNO + H_2O \rightarrow NH_3(g) + CO_2(g)$$
 (4)

The ammonia generated in Equation 4 can either form ammonia compounds or be oxidized to form nitrates depending upon the pH (Hendrickson, 1973). In this manner, oxidation of HCN or CN lowers the overall cyanide content of the system.

# Hydrolysis/Saponification of HCN

As the system pH falls, HCN can be hydrolyzed by a different route to form formate, either formic acid or ammonium formate by:

$$HCN + 2H_2O \rightarrow NH_4 \cdot COOH$$
 (ammonium formate) (5)

or

$$HCN + 2H_2O \rightarrow NH_3 + H \cdot COOH$$
 (formic acid) (6)

The system pH will determine the extent of formation of each compound, a lower pH favoring formic acid formation. This form of hydrolysis has been referred to as "saponification" by some workers, although this term normally refers to the formation of soapy compounds or fatty soaps (stéarates, etc.).

# Aerobic Biodegradation of HCN

Under aerobic conditions within the upper, oxidized portions of the heap, biological processes may consume hydrogen cyanide and generate hydrogen cyanate as shown in Equation 7 (Towill and others, 1978). The hydrogen cyanate is in turn hydrolyzed into ammonia and carbon dioxide (Equation 4).

$$2HCN + O_2 + enzyme \rightarrow 2HCNO$$
 (7)

$$HCNO + H2O \rightarrow NH3 + CO2$$
 (4)

As indicated in Equation 7, this process requires an enzyme but is otherwise identical to the oxidation reaction shown in Equation 3.

# Formation of Thiocyanate

Thiocyanate ions (CNS<sup>-</sup>) can be formed by the reaction between cyanide and any sulfur species such as sulfide, hydrogen sulfide, or thiosulfate. Thiocyanate will be a common cyanide species in a heap containing sulfidic ore, or in heaps placed upon sulfide-rich bedrock. As such, thiocyanate formation depends more upon mineralogic conditions than on pH and Eh, and can occur anywhere in a heap environment with available sulfur species. Examples of thiocyanate forming reactions include the following equations:

$$s_x + s^2 + cn^- \rightarrow s_{x-1} + cns^-$$
 (8)

$$s_2 o_3 + c n^- \rightarrow s o_3^2 + c n s^-$$
 (9)

In oxidized portions of the heap environment, the  $SO_3^{2-}$  formed in Equation 9 will react with oxygen to form sulfate  $(SO_4^{2-})$ .

Thiocyanate is a relatively stable and less toxic form of cyanide, and thiocyanate formation is an effective way of removing cyanide from the heap environment. However, in heaps with elevated sulfide concentrations, acidic conditions can form which in turn can influence the cyanide geochemistry. As described above, acidic conditions will favor the hydrolysis of CN to HCN. Acidic conditions may also cause the dissociation of heavy metal-cyanide complexes and compounds, resulting in the increased mobility of some heavy metals and creating potential heavy metal contamination problems.

## Simple Cyanide Compounds

Cyanide forms simple compounds (i.e., simple salts) with single ions of certain metals. In solution, these simple cyanide compounds oxidize and produce free metal cations and cyanide. An example of this type of reaction is shown in Equation 10.

$$NaCN \rightarrow Na^+ + CN^-$$

Some of the metal cyanide compounds commonly found in a heap environment are listed in Table 1. Obviously the presence and relative abundance of any of these compounds depends upon the composition and mineralogy of the ore in the heap and the underlying bedrock.

As indicated in Table 1, the solubility of simple cyanide compounds ranges from readily soluble to fairly insoluble. Generally speaking, all simple cyanide compounds are relatively non-toxic, and the formation of simple cyanide compounds is another naturally occurring geochemical process that removes toxic cyanide species from the heap environment. However, the soluble simple cyanide compounds such as NaCN, KCN, Ca(CN) $_2$  and Hg(CN) $_2$  dissociate readily in solution and produce cyanide ions (Equation 10). At pH values lower than 9.36, this ionic cyanide will hydrolyze and produce hydrogen cyanide (Equation 1).

# Metal-Cyanide Complex Ions

Cyanide can also react with metals to form metal-cyanide complexes. Metal-cyanide complex ions form as the products of the reaction between the insoluble cyanide compounds and excess cyanide ions. Equation 11 is an example of this type of reaction.

$$Zn(CN)_2 + 2CN^- + Zn(CN)_4^2$$
 (11)

As shown in Table 1, some of these metal-cyanide complexes are relatively to exceptionally stable (i.e., insoluble), whereas others ionize readily, and form  $CN^{\sim}$  which in turn hydrolyzes to form HCN (Equation 1).

As with the simple cyanide compounds, the toxicity of metal cyanide complexes is due to production of HCN as a dissociation and hydrolysis product. However, copper- and silver-cyanide complexes appear to be toxic in their undissociated forms to fish (Gannon, 1981). Although the iron-cyanide complexes are quite insoluble, they may be destroyed through photolysis (reaction with ultraviolet radiation) thereby releasing ionic cyanide (CN).

## Anaerobic Biodegradation

Anaerobic biodegradation of cyanide and hydrogen cyanide is restricted to the moderately to strongly reduced portions of the heap environment (Figure 1), and can only occur if HS or  $H_2S_{(aq)}$  are present. (The sulfur species present will depend on pH. At a pH value greater than 7, HS is the dominant species. At a lower pH,  $H_2S_{(aq)}$  will be present). Equations 12 and 13 illustrate the anaerobic biodégradation of cyanide.

Table 1. Relative Stability of Meteil Cyanide Compounds and Complexes in Water (Listed in Approximate Order of Increasing Stability)

# CYANIDE SPECIES EXAMPLES PRESENT IN THE HEAP ENVIRONMENT

1.	Free Cyanide	CN-, HCN
2.	Simple Cyanide Compounds	
	a) readily soluble	NaCN, KCN, $Ca(CN)_2$ , $Hg(CN)_2$
	b) relatively insoluble	Zn(CN) <sub>2</sub> , CuCN, Ni(CN) <sub>2</sub> , AgCN
3.	Weak Metal-Cyanide	$Zn(CN)_4^{2-}$ , $Cd(CN)_3^{-}$ , $Cd(CN)_4^{2-}$
4.	Moderately Strong Metal- Cyanide Complexes	$Cu(CN)_2^-$ , $Cu(CN)_3^-$ , $Ni(CN)_4^2^-$ , $Ag(CN)_2^-$
5.	Strong Metal-Cyanide Complexes,	$Fe(CN)_6^{3-}$ , $Fe(CN)_6^{4-}$ , $Co(CN)_6^{4-}$ , $Au(CN)_2^{-}$ , $Hg(CN)_4^{2-}$

Modified after Huiatt and others, 1982; and Brickell, 1981.

$$CN^{-} + H_2S_{(ac)} -> HCNS + H^{+}$$
 (12)

$$HCN + HS^{-} \rightarrow HCNS + H^{+}$$
 (13)

The HCNS will then hydrolyze to form  $NH_3$ ,  $H_2S$  and  $CO_2$  (Schmidt and others, 1981).

# Formation of HCN Polymers

There is a growing body of data indicating that, under natural conditions in or below heap leach operations or tailing facilities, HCN can form polymers. Though its may be based on theoretical considerations of the behavior of liquid HCN, it is known that HCN in the presence of trace amounts of ammonia can form adenine  $(C_5H_5N_5)$ , a biochemically important molecule that occurs in DNA and RNA. This reaction is not shown in Figure 1. However, the environmental effect of cyanide polymerization would be to remove cyanide from solution by forming insoluble polymers.

# SUMMARY OF THE ENVIRONMENTAL EFFECTS OF CYANIDE IN AN ABANDONED HEAP

As discussed in the preceding sections and as shown in Figure 1, numerous cyanide species exist within an abandoned heap environment. Many of the cyanide species present are not highly toxic and are relatively stable complexes or compounds under most conditions. Some cyanide species, however, are not stable and react with the environment to produce HCN, the toxic form of cyanide.

As described above, there are a number of potential naturally occurring geochemical reactions within the heap environment which degrade HCN into less toxic or non-toxic compounds. Thus with time, the heap environment tends to be self-neutralizing, and the HCN concentration will decrease.

Englehardt (1984) documented that in an inactive heap containing silver-lead ore tailings, the molecular hydrogen cyanide (HCN) content in the solutions entrained in the heap decreases rapidly due to natural degradation. Based upon data collected at regular intervals for one and one-half years, roughly 85 percent of the original cyanide content dissipated or degraded by natural processes within 18 months. Cyanide destruction in this heap occurred as a result of first order chemical reactions proportional to the concentration of the residual cyanide in the heap. Extrapolation of these data suggest that the cyanide in this heap would be totally destroyed in less than four years following closure.

More recently, RRCC (1987) on behalf of Dupont, have produced a phase 1 report of a study on the attenuation of cyanide. Their

interim conclusions suggest the major mechanisms for cyanide reduction in the vadoze (unsaturated) zone will be volatization, chemical reaction or adsorption with soils/rocks in this zone and, possibly, biodegradation. In addition, those materials which attenuated cyanide in their tests continued to be effective at the 50 pore volume stage when the tests were halted.

# CYANIDE NEUTRALIZATION AND RECLAMATION REQUIREMENTS FOR SPENT HEAPS

Smith and Struhsacker (1988) present the results of a survey of regulatory officials from 14 states concerning maximum allowable residual cyanide concentrations in spent heaps. A wide diversity of responses was received in this survey, and no two states have identical regulations. However, some generalizations about the survey data can be made. Most states took one of the following approaches:

- 1) Strict adherence to a universally applicable cyanide detoxification standard (generally the EPA drinking water guideline of 0.2 mg/l total cyanide); or
- 2) Establish permit conditions on a case-by-case basis depending on site-specific conditions.

In most states, cyanide neutralization criteria are specified in the "zero-discharge" water quality permit required to build and operate a heap leach facility. In addition to neutralization requirements, these permits also specify design, construction, operational and monitoring criteria. Acquiring a permit to construct and operate a heap leach facility in several states includes a bonding provision to cover the cost of rinsing and detoxifying the heaps, and release of this bond is tied to neutralizing the spent heaps to a specified standard.

Oregon, for example, has recently drafted legislation which defines cyanide neutralization as a reclamation issue, and establishes the State's authority to require a bond for all cyanide ore processing operations. This bond is in addition to the bond posted for reclamation of surface disturbance.

Generally speaking, most of the states adopting a drinking water guideline as their cyanide neutralization criterion do not have many active cyanide heap leach operations and thus do not have much direct experience with heap leach technology. In contrast, the states with several active cyanide heap leach projects have opted for the more site specific approach, giving them some flexibility in determining permit conditions.

Those states which do consider site specificity in setting neutralization requirements and other permit conditions generally try to select reclamation procedures and neutralization and abandonment requirements appropriate for the project site. When

site conditions are taken into consideration, it becomes apparent in many cases that it is impractical and unnecessary to impose drinking water guidelines on the rinsate from a detoxified heap. The environmental sensitivity of the project site may not warrant such stringent requirements. Furthermore, it may be costly, if not impossible, to neutralise to a drinking water guideline.

There is also no consensus of opinion among the states surveyed concerning the cyanide species specified in the regulations. Some of the states express their cyanide requirements in terms of free cyanide, whereas others have standards defined in terms of total cyanide. At least one state (Idaho) includes weak acid dissociable cyanide in its regulations. Some states also express neutralization requirements as a range of pH values in lieu of a specified cyanide level.

## OBTAINING COLUMN CYANIDE NEUTRALIZATION DATA

Because many states include cyanide detoxification requirements in their permits for heap leach projects, it is advisable if not mandatory to determine the cyanide neutralization characteristics of the ore during the early stages of a project. These characteristics may influence project design, economics, and the stringency of closure and bonding requirements.

During the column leach metallurgical testing phase of a project operators should consider rinsing one or more of the leached columns to determine the following parameters:

- Reasonable and practically attainable cyanide neutralization levels;
- 2. The most effective cyanicides or detoxifying reagents;
- 3. The length of time required to rinse and neutralize the ore to a required standard; and
- 4. The costs associated with heap rinsing and cyanide detoxification.

Like leaching characteristics, cyanide detoxification characteristics of leached ores vary considerably depending upon the mineralogy and physical condition of the ore in question. The procedures outlined in this paper are based upon our experience in designing detoxification tests to satisfy regulatory requirements.

## Column Cyanide Neutralization Procedures

The leached column selected for detoxification testing should be representative of the physical and mineralogical conditions of the ore to be leached during operation, and the column leaching procedures employed should be representative of the worst case

field conditions (i.e., the longest probable leach cycle and the maximum cyanide loading). The neutralization tests should also be designed so that the number of variables potentially influencing the detoxification results are limited and the behavior of specific chemical species in the system can thus be properly simulated.

Once a representative, worst-case leaching cycle is completed, (i.e., maximum cyanide loading has been achieved) the detoxification process can commence. The leached columns should be allowed to drain in order to reach the equilibrium saturation of the material. This follows the procedure normally used in heap leach pad decommissioning. Once the excess leach solution has drained from the columns, detoxification can begin.

An operator may wish to use several different cyanide detoxification reagents (cyanicides) on separate leached columns in order to determine the best (i.e., most cost effective and environmentally acceptable) detoxification procedure. The three most common cyanicides include the following:

- 1) "fresh water" either rain water, snowmelt or groundwater collected from the project site, or a suitable analog (i.e., pH-adjusted tap water);
- 2) a sodium or calcium hypochlorite solution consisting of 10 to 20 percent Na(OCl) or Ca(OCl); and
- 3) a hydrogen peroxide solution consisting of 30-50 percent  $H_2O_2$  to which a small volume of a copper catalyst (+ 5 mg/l equivalent) may be added should there be insufficient copper available in the ore.

Each column should be eluted with a separate cyanicide solution. A single effluent pore-volume (volume of the void space in the ore) of the eluate should be collected by allowing the solution to discharge into an opaque bottle containing a known volume of sodium hydroxide (NaOH) to produce a solution with a pH greater than 12.0, in order to stabilize the eluate solution and prevent any decomposition of residual cyanide in the eluate. The design of the collection vessel should be based on a positive discharge principal, preventing any ingress of oxygen. This will eliminate any potential for secondary oxidation of residual cyanide in the eluate. Once each pore volume is collected, the collection vessel should be replaced and the sample of eluate plus sodium hydroxide solution should be analyzed for total and free cyanide as well as any other cyanide species likely to be specified as a permit condition. The final residual cyanide concentrations should be adjusted for the initial volume of sodium hydroxide stabilizing solution in the collection vessel.

Following elution by one pore volume of the cyanicide solution, each column should then be washed with site water or a suitable

analog with an equivalent pH, following normal industry operating procedures, and all cyanide values should be determined for each pore volume of eluate. The relationship of all cyanide species versus pore volume should be established, and rinsing should continue until the residual cyanide level curve becomes asymptotic and predictable.

It should be noted that during the detoxification process a secondary spike of elevated cyanide values may occur due to back diffusion of cyanide. Based on our experience, (Smith and Struhsacker, 1988) this appears to be a problem for some ores, particularly fine-grained or agglomerated ores. Therefore the detoxification tests should be run well beyond the point where the cyanide degradation curve has flattened out in order to assess the probability of a secondary diffusion of cyanide out of the system.

The selection of the most cost effective cyanicide should take into consideration any long-term adverse impacts associated with a detoxifying reagent. For example, the alkali chlorination method may introduce into the environment persistent, potentially carcinogenic organic chloride compounds and excess sodium, which unlike cyanide do not readily degrade with time.

In addition to assisting an operator in planning for reclamation, determining neutralization costs, and anticipating bonding and closure requirements, column cyanide neutralization tests can also be critical in the design phase of a project. Depending upon site parameters and the leaching characteristics of the ore, many operators may wish to consider using a reusable pad design in which the ore is loaded onto a permanent asphalt pad, leached, neutralized, removed from the pad and wasted elsewhere, and the pad reloaded with fresh ore, This type of heap leach system design may be particularly desirable for projects with limited space and with ore which leaches and neutralizes relatively quickly and predictably. However, before the reusable pad design can be adopted, the cyanide detoxification characteristics of the ore must be determined by laboratory column detoxification tests.

Of critical importance to the suitability of the ore for a reusable pad design is the length of time (measured as the number of pore volumes of rinse solution) required to achieve an acceptable residual cyanide level. This length of time will greatly influence material scheduling (i.e, heap loading and unloading) and can be a critical factor in choosing between a reusable or dedicated pad heap leach design.

## CONCLUSIONS

An understanding of cyanide geochemistry is a prerequisite to establishing realistic cyanide detoxification standards for abandoned heap leach projects. Environmental regulations should

consider the self-neutralization potential of an inactive heap, the ephemeral nature of molecular hydrogen cyanide, and the environmental sensitivity of a given project. More stringent requirements should be reserved for projects with nearby, downgradient fishable streams or potable surface and groundwater supplies.

Application of a cyanide drinking water guideline on the rinsate from a neutralized heap is neither realistically achievable nor necessary in order to protect surface and groundwater resources in nearly all situations in our experience. Based upon a consideration of site conditions including the attenuating properties of site subsoils and bedrock, the distance to the nearest potential surface and groundwater receptors, and cyanide decay rates, it can be demonstrated that water guidelines are maintained for these receiving waters when higher residual cyanide levels are allowed in the detoxified heaps.

As more heap leach mining permit applications are reviewed and processed by regulatory agencies, more changes in the regulatory environment affecting precious metal heap leach projects can be expected. With increased experience in heap leach operations, and a broadening awareness of the short- and long-term effects of cyanide and the behavior of cyanide in the heap leach environment, more states will hopefully become less dogmatic and will adopt the site-by-site approach to establishing cyanide neutralization requirements.

One of the best ways for an operator to obtain reasonable cyanide neutralization and heap reclamation requirements is to present the regulatory authorities with column-scale laboratory data documenting the cyanide detoxification characteristics of the ore. Demonstrating that the leached ore can be adequately detoxified, and developing the regulator's understanding of the effects of cyanide in the environment may be instrumental in securing reasonable design and closure requirements for a heap leach project.

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