



Residual cyanide distribution in a neutralized gold leach heap
by James Gregory Poell

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation

Montana State University

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Abstract:

Kendall Mine Heap Leach Pad No. 1 is located in Fergus County northwest of Lewistown, Montana. The heap, constructed in the early 1980s, was most recently leached with sodium cyanide for gold in 1988. After leaching, Pad No. 1 was neutralized in spring, 1989 with fresh water rinsing followed by alkaline chlorination using calcium hypochlorite. Thirty months later, samples were taken from 15 boreholes across the heap at incremental depths in order to determine the speciation, concentration, and vertical and areal distribution of cyanide and associated metals. Two pore water samplers were used to monitor cyanide and metals levels near the heap base during the spring and summer of 1992.

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Across the heap, significant differences were found between boreholes for total cyanide, weak acid dissociable cyanide, pH, cadmium, and copper. However, only cadmium levels, declining significantly from west boreholes to east boreholes, exhibited any areal pattern. These results indicate that areal patterns are not likely to be found across leach heaps.

Pore water cyanide data indicate that total and weak acid dissociable cyanide degradation may have occurred as pore water drained the heap through spring and summer 1992. Pore water data suggest that soluble copper and nickel levels decreased over the same period. These changes may be due to the relative stability of metallo-cyanide complexes and competing degradation processes in the heap. Cadmium, iron, zinc and pH in pore water did not change significantly over time and distance.

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A thesis submitted in partial fulfillment
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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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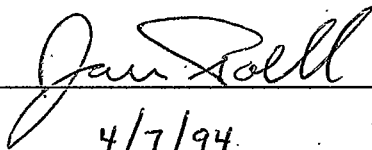
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ABSTRACT

Kendall Mine Heap Leach Pad No. 1 is located in Fergus County northwest of Lewistown, Montana. The heap, constructed in the early 1980s, was most recently leached with sodium cyanide for gold in 1988. After leaching, Pad No. 1 was neutralized in spring, 1989 with fresh water rinsing followed by alkaline chlorination using calcium hypochlorite. Thirty months later, samples were taken from 15 boreholes across the heap at incremental depths in order to determine the speciation, concentration, and vertical and areal distribution of cyanide and associated metals. Two pore water samplers were used to monitor cyanide and metals levels near the heap base during the spring and summer of 1992.

Analysis of solid ore samples showed significant increases in weak acid dissociable cyanide levels from the surface to middle of the heap. This may correspond to the interface of two lifts or benches of ore in the heap. Deeper in the heap, weak acid dissociable cyanide levels significantly decrease. Soluble copper and nickel levels had a similar vertical distribution pattern. No significant differences with depth were found for total cyanide, pH, cadmium, iron, or zinc.

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INTRODUCTION

In the past 25 years there has been a wide expansion of the use of cyanide heap leaching by the mining industry. This process allows profitable recovery of gold and silver from low-grade ore. Heap leach pads are constructed on slight drainage grades and lined with an impervious clay and/or geotextile. Mined ore is stacked and leached in successive ten to thirty foot lifts or benches on the pad. Sprinkler systems set on the surface of the lift to be leached deliver a high pH sodium cyanide solution that, in its percolation through the ore, forms stable complexes with gold, silver, cobalt, iron, copper, nickel, zinc, and cadmium. This "pregnant" solution is then collected as it drains off the pad for precious metal recovery and refinement.

After leaching, the heap still contains interstitial and adsorbed cyanide species, including free cyanide and metal-complexed cyanides. The metal-complexed cyanides are present as weak acid dissociable (WAD) complexes of cadmium, copper, nickel, and zinc, and extremely stable iron and cobalt cyanide complexes (Smith and Mudder 1991). These cyanides, in sufficient concentration, have the potential to degrade surface and ground water resources.

The Montana Water Quality Act directs the Montana Department of Health and Environmental Sciences (MDHES) to maintain standards for pollutants threatening its nondegradation policy. The standards are referenced by the Montana Department of State Lands in mine operation and reclamation regulation. Standards of interest to cyanide heap leach mining are listed in Table 1.

Table 1. Selected Montana water quality standards applicable to cyanide heap leach effluents (MDHES 1993).

Pollutant	Acute Aquatic Life Standards ($\mu\text{g l}^{-1}$)	Chronic Aquatic Life Standards ($\mu\text{g l}^{-1}$)	Human Health Standards for Surface Waters ($\mu\text{g l}^{-1}$)
WAD Cyanide	22.0	5.2	200.0
Cadmium	3.9*	1.1*	5.0
Copper	18.0*	12.0*	1000.0
Iron	---	1000.0*	300.0
Nickel	1400.0*	160.0*	100.0
Zinc	120.0*	110.0*	5000.0

* Water hardness dependent criteria (100 mg l⁻¹ used).

--- No standard has been adopted.

Cyanide in the heap will degrade naturally, if the heap is not disturbed. Natural degradation of cyanide can occur through volatilization, biodegradation, photodecomposition, and oxidation (Rolfes 1989). Other degradation mechanisms associated with cyanide chemistry include complexation with transition metals, precipitation of complex cyanide compounds, formation of thiocyanate, and the hydrolysis of free cyanide (Smith and Mudder 1991). How degradation will proceed, though, is site specific, depending on the interaction between geochemical conditions in the heap and site conditions such as precipitation, ore mineralogy, and ore permeability (Struhsacker and Smith 1990, van Zyl et al. 1988). To speed this degradation process, most mines use fresh or chemically-treated water rinses. Rinsing is continued until effluent draining from the pad falls and remains below regulatory standard for a specified period of time. Currently, the Montana

Department of State Lands considers a spent heap to be neutralized for reclamation when effluent WAD cyanide concentrations remain below 0.220 mg l^{-1} through one full spring after rinsing. This WAD cyanide standard, commonly used by western state mine regulators, is $20 \mu\text{g l}^{-1}$ above the MDHES human health standard (Table 1).

Despite acceptable effluent levels from abandoned leach heaps, later "spikes" or "slugs" of cyanide have been measured in effluent following large precipitation events or rinsing (Haight 1991, Struhsacker and Smith 1990). It is believed that residual cyanide in spent ore, pore spaces, and/or blind-off zones diffuses out into the heap over time. Subsequent wetting fronts generated by precipitation events may pick up this cyanide as they pass through the heap, degrading effluent water quality. Spent ore sampling that does not examine the full depth and breadth of a heap may not give a representative measure of neutralization success.

The concentration of cyanide throughout a decommissioned leach heap has not been thoroughly investigated. With funding supplied by the Montana Department of Natural Resources and Conservation and the cooperation of the Montana Department of State Lands Hardrock Bureau and Canyon Resources Corporation, the Reclamation Research Unit of Montana State University sampled a decommissioned leach heap from October, 1991 through summer 1992. The objective of this study was to measure the concentration of residual cyanide species and associated metals throughout the heap, comparing the results for evidence of

vertical or areal distribution patterns. A second objective was to monitor cyanide and metals levels in pore water at the base of the heap through spring and summer 1992.

This study was limited to one relatively small leach heap with limited construction and operation documentation. No control data were available for ore leached in the heap. Rather than being a definitive work explaining the behavior of residual cyanide in neutralized leach heaps, this study will provide basic data to decision makers regarding the concentrations and distributions of cyanide species that may develop under similar conditions.

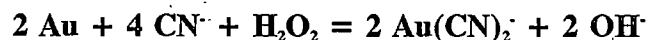
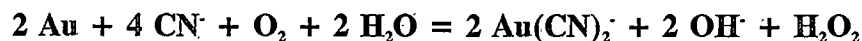
LITERATURE REVIEW

History Of The Cyanide Leach Process

The evolution of cyanidation technology in the pursuit of precious metals dates back 200 years in the historical record. In 1793, potassium cyanide was recognized as a gold solvent (Hiskey 1985). In 1844, Elsner investigated the reactions of various metals in a potassium cyanide solution, discovering that gold dissolution took place only in the presence of dissolved oxygen (Bosqui 1899). This dissolution reaction, known as Elsner's Equation, is written as:



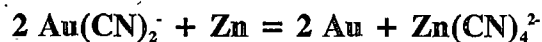
In 1896, Bodlaender found that the dissolution of gold was a two-step reaction with intermediate production of hydrogen peroxide (Hiskey 1985). This reaction proceeds as follows:



The sum of this reaction sequence is equivalent to the dissolution reaction developed by Elsner. It is written as:



The extraction of gold from gold ore using cyanidation was developed into a commercial process in Scotland by John MacArthur and Drs. Robert and William Forrest (von Michaelis 1985). They were issued patents for their process in 1887 (Britain) and in 1889 (United States). The extraction is based on the agitation of finely ground gold ore in aerated potassium cyanide solution. Metals in the ore, including gold, complex with cyanide during the agitation. The gold cyanide complex is precipitated with zinc shavings (Eisele 1988). This precipitation proceeds as follows:



The Merrill-Crowe process, as it is known in use today, improved gold recovery by removing oxygen from gold-bearing cyanide solutions before the addition of zinc (Hiskey 1985). After treatment with zinc, the solution is filtered under pressure to remove the gold precipitate for smelting.

Carbon adsorption technology to recover dissolved gold from cyanide solutions was developed by Chapman in 1939 (Hiskey 1985). This technology did not require the filtration and deaeration of gold-bearing solutions as did the Merrill-Crowe process (Heinen et al. 1978). Activated charcoal, introduced to a cyanide-ore pulp (slurry), adsorbed the dissolved gold and floated away for collection (Hiskey 1985). As burning the enriched charcoal was the only known method to recover gold, carbon adsorption was not widely used (Eisele et al. 1984).

The Merrill-Crowe process was the predominant method of solution gold recovery when Zadra and his associates (1952) developed a method to desorb gold from carbon. This process sent hot caustic cyanide solution through enriched carbon, stripping the gold for electrowinning onto stainless steel wool. Despite lower costs, the low price of gold in the 1950s and 1960s precluded an expansion in the use of carbon adsorption and solution gold mining in general.

Leach Heap Cyanidation

Heap leaching may be defined as the percolation leaching of piles of low-grade ores or mine waste that have been stacked or piled on specially prepared watertight drainage pads for the collection of precious metal-enriched "pregnant" solution (Heinen et al. 1978). Heap leaching of minerals dates back to sixteenth century Hungarian copper mines, with large-scale practice developed by the eighteenth century in Spanish copper mines (Hiskey 1985). Uranium producers have utilized heap leaching as an extraction technology for low-grade ores since the late 1950s (Dorey et al. 1988). Heap leach cyanidation of porous, low-grade, gold-bearing ores was first proposed in 1967 by U.S. Bureau of Mines metallurgists (Heinen et al. 1978). This treatment chemistry is the same as that of Bodlaender's two-step dissolution reaction. Gold is recovered from the pregnant solution draining from the heap leach using either Merrill-Crowe or carbon adsorption processes.

In order to widen the applicability of cyanide heap leaching to include

impermeable high-clay ores, the U.S. Bureau of Mines developed an ore agglomeration treatment. After crushing, ore is mixed with 2 to 7 kg/metric ton (5 to 15 lbs/short ton) of portland cement (to act as a binding and pH control agent), wetted with 8 to 16% (by weight) water, and subjected to mechanical tumbling to ensure adhesion of fines to coarser particles (Heinen et al. 1978, Heinen et al. 1979, McClelland and Eisele 1982). By 1983, it was estimated that agglomeration pretreatment allowed half of cyanide heap leach projects to operate (McClelland et al. 1983).

The cyanide heap leach process is an efficient, low cost method of recovering gold and silver from low-grade ore. Average ore grades recovered by heap leaching are 0.9 grams of gold per metric ton of ore (0.03 oz/short ton), with an extreme cutoff grade of 0.2 grams of gold per metric ton (0.006 oz/short ton) at the Round Mountain Mine in central Nevada (Spickelmier 1993). Relative ore grade dictates the choice of two heap leaching methodologies. Higher grade ores are crushed, agglomerated and stacked in short lifts of 1 to 3 m (3 to 10 ft) high on permanent asphalt or concrete leach pads. This method treats 900 to 9,000 metric tons (1,000 to 10,000 short tons) of ore for 7 to 30 days, after which the spent ore is neutralized and removed for disposal (Higgs and Gormley 1992a, Rolfes 1989). Lower grade ores are typically not treated, being stacked as run-of-mine size (including boulders) in lifts of 3 to 9 m (10 to 30 ft) high on compacted clay and/or synthetic-lined pads. On these heaps, leaching of 9,000 to 1.8 million metric tons (10,000 to 2 million short tons) of ore will take months or years, after

which the spent ore heap is neutralized and abandoned (Hiskey 1985, Rolfes 1989).

Pads under all leach heaps are constructed with a 2 to 5% slope to facilitate drainage of pregnant solution (Chamberlin and Pojar 1984). Leach heap pads are also designed to eliminate the loss of pregnant solution to the ground and prevent contamination of local water resources (Heinen et al. 1978).

The objective of heap leach construction is to build a stable, porous heap that allows an even downward percolation of cyanide solution (Herzog 1990). Heaps are commonly built in successive lifts using conveyor stacking, end dumping, or truck and dozer techniques. The criteria in selecting a heap construction technique are to minimize layering, compaction, and ore particle segregation (Dorey et al. 1988).

The completed heap is put under cyanide leaching by a surface network of sprinklers or capillary tubes. Typical application rates, adjusted to result in a partially-saturated flow of leachate through the heap, range from 0.002 to 0.003 l/s/m² (0.003 to 0.005 g/min/ft²) (Dorey et al. 1988). Though it is possible to leach gold with several types of solutions, all current commercial operations use 0.2 to 0.7 kilograms of sodium cyanide (NaCN) per metric ton of water (0.5 to 1.5 lbs of NaCN per short ton of water) (Chamberlin and Pojar 1984, Stanton et al. 1986). This produces a leach solution concentration of 200 to 700 mg l⁻¹ NaCN, or 125 to 350 mg l⁻¹ free cyanide (Stanton et al. 1986). Leach solutions are maintained at pH 9.5 to 11 with lime (CaO) or caustic soda (NaOH) to ensure effective gold

dissolution (Chamberlin and Pojar 1984). Leaching consumes NaCN at a rate of 0.04 to 1.4 kg/metric ton (0.1 to 3.0 lbs/short ton) of ore, depending on ore type, application method, porosity, solution pH, and the concentration of cyanide-consuming metals and sulfides in the ore (U.S. EPA 1986, Stanton et al. 1986).

Leach Heap Neutralization

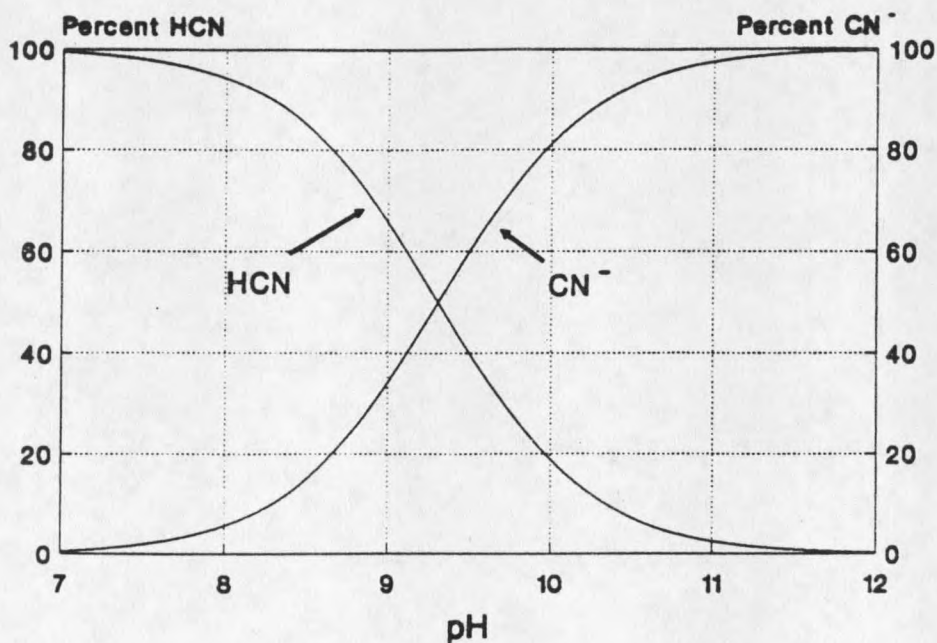
The consumption of NaCN is a major expense in heap leach operations that exploit low-grade ore (Barratt and McElroy 1990). To recover NaCN for use on other leach heaps and maximize precious metal recovery, leached ore is thoroughly rinsed with fresh water at the end of a leaching cycle (Heinen et al. 1978). This recovery action can be regarded as the initiation of heap neutralization in reclaiming a heap leach project. The ultimate purpose of this washing or rinsing is to alter the chemistry of the reclaimed heap so that future drainage from the heap degrades neither surface or groundwater resources (Struhsacker and Smith 1990). Effective neutralization of spent ore heaps involves detoxifying residual cyanides and cyanide complexes found in interstitial solutions, adsorbed on ore particle surfaces, and diffused into the ore (Denton et al. 1992).

Active neutralization methodologies in use today include fresh water rinsing, alkaline chlorination, hydrogen peroxide treatment, sulfur dioxide oxidation, biotreatment and acidification. These methods are well documented by Scott (1984), Rolfes (1989), and Thompson and Gerteis (1990).

Cyanide In The Neutralized Heap

Cyanides comprise a large class of compounds that are characterized by the presence of the cyanide ion (CN^-) in their molecular structures (Higgs and Gormley 1992b). The forms of cyanide of particular interest to the heap leach process are free cyanide, simple cyanide and complex cyanide (U.S. EPA 1986). Free cyanide is the sum of the cyanide ion (CN^-) and hydrocyanic acid (HCN) species released into an aqueous solution by the dissolution and dissociation of cyanide compounds (Mudder 1991). These two species coexist in solution, their relative proportions depending on pH and temperature. The relationship between solution pH and the ratio of CN^- to HCN is illustrated in Figure 1. Below a pH of 7.0, all free cyanide is present as HCN in the toxic gaseous state.

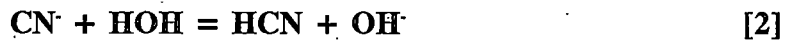
Figure 1. Relationship between HCN and CN^- with pH (Higgs and Gormley 1992b).



Simple cyanides are the salts of hydrocyanic acid that completely and easily dissociate in water (Maynard et al. 1986). These cyanides ionize in water, as sodium does in Reaction [1].



The cyanide ion (CN^-) then hydrolyzes to form HCN in Reaction [2].



Again, the amount of HCN produced depends on solution pH and temperature.

In the heap environment, the formation of gold and silver cyanide complexes is the means of precious metal extraction from ores. Other transition metals present in the ore may also complex with cyanide. Most commonly, these metals are cadmium, copper, cobalt, iron, nickel and zinc (IEC 1979). The stability of these metal-cyanide complexes depends on the stability of the particular metal. Cadmium and zinc are relatively unstable, easily dissociating to release the cyanide ion (CN^-). The dissociation of complex cyanides is inversely related to solution pH and complex ion concentration (Huiatt et al. 1983). The toxicity of complex cyanides is related to their ability to release cyanide ions to solution, producing toxic HCN (Eisler 1991). Metals freed by the dissociation of complex cyanides in a heap are not considered a threat to effluent water quality. Solubility of metals is limited at the high pH levels (7.5 to 9.5) normally observed in leach heaps rinsed of cyanide (Lindsay 1979). Further, once a complex cyanide

