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HEAP-LEACH GOLD MINES: WHERE DOES THE CYANIDE GO?

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Abstract

Modern gold and silver mines often use the cyanide heap leach process to separate precious metals from adjoining ores: Cyanide (CN) in an alkaline solution complexes with Au^+ or Ag^+ cations. Citing the short half-life of CN in the environment, mining companies often do not include attenuation of the highly toxic cyanide in their decommissioning processes for closing the mine. To examine this problem, we determined the ability of soil to bind both cyanide and hydroxide anions. Unbuffered alkaline solutions (pH 10.5) infused onto soil columns bound hydroxide avidly, yielding initial effluent at pH 5.5. The soil saturated (effluent pH = 10.5) after 33 pore volumes of added influent. Alkaline cyanide solutions (3.8 mM KCN, pH 10.5) produced initial effluent of 1.4 mM CN, and the soil reached saturation after 28-30 pore volumes of added influent. The amount of CN recoverable from the soil column decreased with first order kinetics ($k = 0.50 \pm 0.07$ day^{-1}) that were unaffected by deaeration or room light. Sunlight, however, increased the attenuation rate more than 2-fold ($k = 1.198 \pm 0.005$ day^{-1}). Loss of cyanide from open solution (as HCN gas) was also a first order process whose rate decreased with alkalinity: $k = 1.09 \pm 0.08$ day^{-1} at pH 9.5 fell to 0.39 ± 0.06 day^{-1} at pH 12 in sunlight-exposed solutions. Given pK_a = 9.2 for HCN, this decrease of only < 3-fold from pH 9.5 to 12 is much less than expected based on the equilibrium concentration of protonated HCN. Cyanide loss from open solution was faster in a fume hood (dim light) than on the building rooftop (sunlight), due to enhanced turbulence. We conclude that under laboratory conditions, soil has a large capacity to attenuate alkaline cyanide spills; however in a natural setting, parameters such as soil composition and consistency must be taken into account as well.

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Introduction

Almost all large-scale modern gold and silver mines use the cyanide heap-leach process to win the noble metals from their ore.[1] In this process, a cyanide solution (250 – 500 mg/L, pH 10.5) is sprayed over a mound of crushed ore for a period of weeks to months.[2],[3] The reduced metallic gold (or silver) in the ore is oxidized and complexed with cyanide to give the soluble anionic complex, $Au(CN)_2^-$, in a "pregnant" solution (Equation *1*, known as the Elsner equation):[4],[5]

$$\text{Equation 1: } 4\,Au(s) + 8\,CN^-(aq) + O_2(aq) + 2\,H_2O(l) \rightarrow 4\,Au(CN)_2^-(aq) + 4\,OH^-(aq)$$

The "pregnant" solution is subsequently pumped onto activated carbon columns, which adsorb the $Au(CN)_2^-$. Finally, a "stripping solution" is added to the column to reduce the Au(I) in the bound $Au(CN)_2^-$ to Au(s) and elute it from the column.[2] Thus, the key features of a heap-leach mine are: (i) a large pit; (ii) piles of several million tons of rock; (iii) roughly a million tons of ore tailings; (iv) an ore heap pad for cyanide leaching; and three different types of cyanide ponds: (v) a "barren" cyanide pond (alkaline cyanide solution); (vi) a "pregnant" cyanide pond (containing $Au(CN)_2^-$), and (vii) a tailings pond containing cyanide and other ionic metal waste. (For further details on CN heap-leach mines, see Appendix, section I.)

The large open pit and tons of waste rock and ore cause obvious landscape problems, and can often produce toxic acid mine drainage. Additionally, four types of problems can stem from the cyanide ponds:[2],[5],[3] (i) poisoning of wildlife that mistake CN-laden ponds for potable/fishable water; (ii) accidental spills of CN waste water from ponds/dams; (iii) leakage/seepage of CN from ponds or pipes into groundwater (from tailings slurry); (iv) drainage of tailings slurry CN from legacy sites. (For more information on mining accidents, see Appendix, section V.).

Cyanide is a potent, rapidly acting poison with a human lethal dose of 50 – 90 mg (1 tsp of a 1% solution)[1],[6],[7],[8] that can be delivered by ingestion or by inhalation of HCN(g).[8] Cyanide exerts its primary acute toxic effects on cytochrome c oxidase, the terminal electron transfer complex in mitochondria, by complexing tightly with oxidized metal cations in the oxygen-binding center: cytochrome a_3 (Fe_{a3}^{3+}), and possibly also copper (Cu_B^{2+}).[9],[8],[10] This keeps these metals from becoming reduced, and thus inhibits oxygen binding, which in turn inhibits the mitochondrial electron transfer pathway, shutting down oxidative phosphorylation. The lack of ATP damages tissues with the highest metabolic demand, e.g., brain, central nervous system, and heart muscle. In addition, cyanide inhibits several other key metabolic enzymes (see Appendix, section II).

The two major biological detoxification pathways for cyanide are: (i) oxidation to cyanate (Equation *2*), followed by hydrolysis to carbon dioxide and ammonia (Equation *3*); and (ii) oxidation and sulfidation to thiocyanate (Equation *4*).

$$\text{Equation 2: } \quad \textit{oxidation: } CN^- + \tfrac{1}{2}\,O_2 \rightarrow OCN^-$$

$$\text{Equation 3: } \quad \textit{hydrolysis: } OCN^- + H_2O + H^+ \rightarrow CO_2 + NH_3$$

$$\text{Equation 4: } \quad \textit{oxidation: } CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$$

Cyanide can also be converted to thiocyanate under geochemical conditions in the presence of persulfide (e.g., pyrite, FeS_2, Equation *5*):

$$\text{Equation 5: } \quad CN^-(aq) + FeS_2(s) \rightarrow SCN^-(aq) + FeS(s)$$

Finally, cyanide can be complexed with various metals: Weak-acid dissociable (WAD) complexes form with Zn, Cd, Cu, and Ni cations[6]; WAD-CN is not itself toxic, but in the acidic environment of the stomach it dissociates to release toxic free cyanide.[6] Strong cyanide complexes (e.g. those with Fe, Co, and Au cations) are non-toxic even at acidic pH, but they slowly photolyze to release free cyanide when exposed to UV light (e.g., sunlight); this decomposition is accelerated by high temperature, low pH, O_2, dissolved solids, and soil adsorption.[6]

Documents produced by mining companies, regulatory agencies, and their supporters often claim that cyanide is not a major environmental concern because it decays quickly, especially in the presence of sunlight, into "harmless" CO_2 and either NH_3 or NO_3^-.[1],[2],[6],[12] Regulatory agencies generally require mines to monitor only three forms of cyanide: (i) free (i.e., CN^- + HCN); (ii) weak-acid dissociable (WAD-CN); and (iii) total cyanide. The implication is that only free CN and WAD-CN are of concern; strong metal complexes ($= [CN]_{total} - [CN]_{free} - [WAD\text{-}CN]$) are deemed non-toxic. There are two problems with this approach. First, as noted above, strong metal-CN complexes photolyze, releasing toxic free CN. Secondly, cyanide breakdown products (e.g., cyanate, thiocyanate, cyanogen, ammonia), while less toxic than free cyanide, are nevertheless still toxic (see Appendix, sections II and III). Because these compounds (aside from ammonia) are not monitored at mining sites, the level of toxicity presented by mines is not fully appreciated.

Aside from the cyanide reactions discussed above (e.g., oxidation, hydrolysis, sulfidation, metal complexation), two other processes are important in the natural attenuation of CN in the environment: volatilization of HCN(g), and adsorption to soil and suspended solid particles. Volatilization of HCN(g) from solution is a fairly well-studied process (see Appendix, section IV), but less is known about soil-cyanide interactions. Because of the possibility of leaks and seepage causing groundwater contamination[2],[5],[13], it is important to understand better how cyanide solutions interact with soil. Accordingly, we set out to study the attenuation of cyanide, both in aqueous alkaline solution and on columns of soil, under various conditions of light and oxygenation.

Materials and Methods

Materials:

Soil was collected from sites within a mile of Newmont Mining Company's proposed Grassy Mountain heap leach gold mine in Malheur County, Eastern Oregon. Alkaline cyanide stock solutions (pH 12.0, 1000. mg/L) were prepared from reagent grade KCN and NaOH. Soil columns were assembled using Becton-Dickinson disposable 60 cc syringes with glass wool at the bottom to prevent soil loss. Free cyanide concentration [CN-] was measured with an Orion model 710A pH/ISE meter, an Orion cyanide electrode (model 94-06), and a double-junction reference electrode from Microelectrode, Inc. To measure pH we used a Corning model 130 digital pH meter.

Analytical Procedures:

The cyanide electrode was standardized each day using at least five standard solutions ranging from 10 to 1000 mg CN/L, and plotting mV readings vs. log[CN]. Linear regression fits were excellent, with R^2 values ranging from 0.980 to 0.995. Relative mV readings were strongly influenced by pH and ionic strength, so all samples were adjusted to pH 12.0 before reading.

Soil Columns:

All soil was air-dried and screened to 40 mesh to exclude organic matter and stones. Soil density varied from 1.2 to 1.4 g/mL, and soil porosity was 0.40, that is, 20 mL of elutant had to be added to the top of a soil column containing 50 mL of soil before any liquid eluted from the bottom of the column. Thus, the pore volume of a 50 mL soil column was 20 mL of aqueous solution.

Roughly 50 mL of soil was gently packed into a 60-mL syringe while vibrating the column. Each data point was measured in triplicate on three different columns. Effluent flow rate was adjusted to approximately 5 mL/hr, and fractions were collected automatically. Fractions were assayed for volume, pH, and [CN]. Fraction collection was terminated when the elution rate dropped to zero due to column blockage. For cyanide effluents, one mL of 6 M NaOH was added to the collecting test tubes in order to trap the solute in its deprotonated, non-volatile form (CN-).

To test cyanide degradation/attenuation on soil columns, a 15 mL aliquot of cyanide solution was added to each of eight columns. The first column was immediately eluted with 60 mL of 0.5 M HCl[1*], while a stream of nitrogen gas blown through the top of the sealed syringe carried all volatilized HCN into a 6 M NaOH trap. This measurement represents the amount of bound cyanide that is acid-elutable at time zero. Columns were acid-eluted at various times over the ensuing week, and the amount of recoverable cyanide was found to decrease exponentially with time (first order kinetics). Soil columns were exposed to various laboratory conditions, including control (room light, aerated), dark/aerated, dark/deaerated (by flusing with N_2 gas), and sun-exposed/aerated.

Cyanide volatilization from solution:

Cyanide solutions were prepared by diluting the stock solution (pH 12., 1000. mg/L) to 1.0 L of 450 mg/L (7.3 mM), then adjusting the pH with 6 M HCl. Though the initial amount of cyanide was thus 7.3 mmol in each beaker, the initial measured amount varied due to volatilization of HCN upon HCl addition. The amount of this initial loss of cyanide varied from around 8% at pH 12 to around 40% at pH 9.5. After pH adjustment and measurement of initial [CN], the beakers were placed either in a fume hood or on the building rooftop (sun-exposed). The pH, [CN], and volume of each solution were assayed daily for 7 days. From these data we characterized the fluctuations in solution pH, and the first order decay of [CN] with time.

Results and Discussion

pH and cyanide decline in open alkaline solutions

Cyanide solutions at heap-leach gold mines are alkaline (typically unbuffered OH^-), pH ≈ 10.5. We studied the behavior of such open solutions exposed to sunlight on the roof of our building (Figure *1*). Because the solutions were unbuffered (similar to those at heap-leach mines), pH was unstable: It increased due to water evaporation (which increased the concentration of hydroxide), and decreased due to the dissolution of atmospheric carbon

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[*] Acidifying the column with HCl protonates the CN^- anion, neutralizing it and causing its release from positive soil binding sites. Tests showed that 60 mL of 0.5 M HCl was sufficient to elute > 95% of the releasable cyanide from a soil column.

dioxide (which reacts with hydroxide to give bicarbonate).

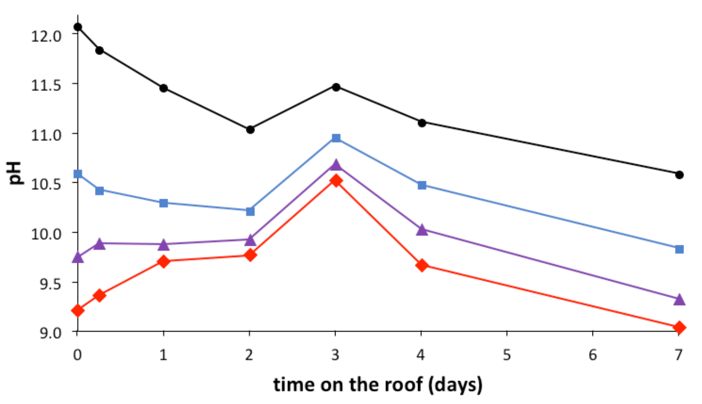

Figure 1. pH change of open unbuffered alkaline CN solution (1.0 L of 7.3 mM KCN (190 mg CN/L) with various initial pH values: pH_0 = 12.1 (black circles); pH_0 = 10.6 (blue squares); pH_0 = 9.75 (purple triangles); and pH_0 = 9.2 (red diamonds). Solutions were in unstirred open 2 L beakers exposed to sunlight on the building roof. Afternoon temperatures during the 7-day period were 32 – 34 °C, but on day 3 it reached 41 °C.

From the results plotted in Figure *1* it seems likely that the latter process, CO_2 dissolution, was both time-dependent and pH-dependent. Over the first two days, pH fell fastest when starting at pH 12, was roughly constant when starting at pH 9.75 – 10.6, and rose when starting at pH 9.2. Assuming that water evaporation was roughly constant over this initial 2-day period (T = 32 – 34 °C), we can conclude that CO_2 dissolution increased with pH. (pH rose in all solutions on day 3 due to enhanced evaporation at the elevated T = 41 °C. Water loss averaged 102 ± 9 mL on day 3, compared to only 66 ± 7 per day on the other 6 days.). Interestingly, from days 4 – 7, pH fell at the same rate for all four solutions; presumably, CO_2 dissolution exceeded evaporation by roughly the same amount over this period. The overall trend over the 7-day period for all solutions starting at pH > 9.5 was a decline in pH due to CO_2 dissolution. Thus NaOH (or KOH) must be added periodically to these open unbuffered solutions in order to counter the effect of CO_2 acidification.

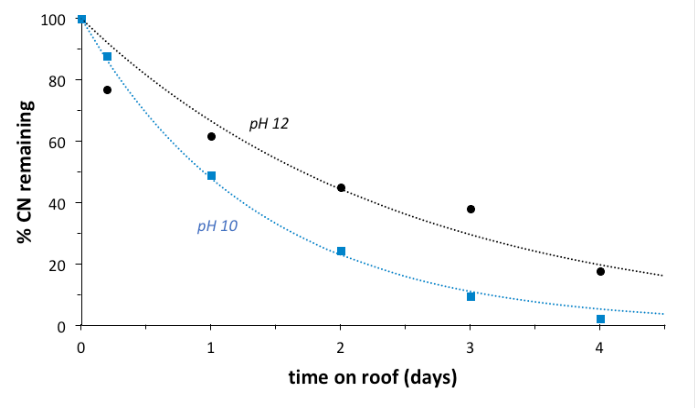

Figure 2. Decline in cyanide concentration of open unbuffered alkaline CN solution (same as in Figure 1) at initial pH_0 = 10 (blue squares) and 12 (black circles). Dotted lines are first order decline curves fitted to the data by nonlinear regression: At pH 10, k_{obs} = 0.735 ± 0.024 dy^{-1}, R^2 = 0.998; at pH 12, k_{obs} = 0.40(6) ± 0.05 dy^{-1}, R^2 = 0.922.

Next, we examined the decline in cyanide from the same solutions exposed to sunlight on the building roof (Figure *2*). As expected, the CN decline was first order, and was faster at lower pH: Only neutral, protonated HCN (pK_a = 9.21 at I = 0 M; 9.04 at I = 0.1 M)[5] can escape from solution, while deprotonated CN^- anion must remain behind, and the fraction of cyanide that is protonated (HCN) increases as pH declines. This is in fact why cyanide solutions at heap-leach mines are maintained at pH > 10. Daily decline in cyanide concentration is substantial: 52% per day at pH 10, and 33% per day at pH 12; 95% decline was attained after 4 days at pH 10, and after 7 days at pH 12.

Although cyanide decline was 81% faster at pH 10 compared to pH 12 (k(obs) ratio = 0.735/0.406 = 1.81), if the difference had been solely due to the proportion of cyanide in solution present as HCN, one would have expected a much bigger effect. Given pK_a(HCN) = 9.2 at pH 10 and 9.1 at pH 12, one can calculate from the Henderson-Hasselbalch equation that cyanide should be 11.1% protonated at pH 10, and only 0.16% at pH 12. Thus, the rate of volatilization of HCN should be 70-fold higher (= 11.1/0.16) at pH 10. On the other hand, we can estimate from Figure *1* that the pH of the pH_0 = 10 solution remained roughly constant over the 7-day period, whereas the pH_0 = 12 solution may have maintained an average pH of roughly 11. At pH 11, cyanide should be 1.4% protonated, which would give an 8-fold higher HCN volatilization rate at pH 10 (= 11.1/1.4). The fact that the rate of CN decline is only 1.8-fold higher at pH 10 cf. 12 suggests that CN loss at pH 10 is inhibited (relative to what one would expect based solely on the concentration of protonated HCN), and/or CN loss at pH 12 is enhanced.

In order to examine this effect in more detail, we determined the first-order k_{obs} for CN decline from pH 9.5 to 12 (Figure *3*).

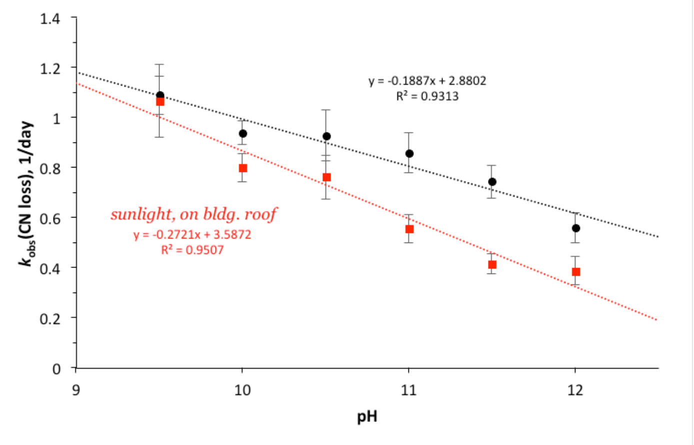

Figure 3. pH dependence of observed first-order rate constants for cyanide decline in open solutions: in the dark (in a laboratory fume hood, black circles); and exposed to sunlight (on the building roof, red squares). [CN] vs. time data sets were analyzed and fitted as in Figure 2.

The first point of interest regarding the pH-dependence of k_{obs} for CN decline plotted in Figure *3* is that k_{obs} declines linearly with increasing pH, with slope of -0.189 ± 0.026 per day per pH unit in the dark, and -0.272 ± 0.031 per day per pH unit in sunlight. Although we expect to see a lower rate at higher pH due to the decrease in the concentration of protonated HCN, the decline is not sigmoidal, as expected in a typical pH titration. For example, for an acid with $pK_a \approx 9$, the decline of k_{obs} should be steepest from pH 9 to 10, and should level off above pH 10. This is clearly not what we see in Figure *3*, which supports our conclusion above that CN loss at pH < 10 is inhibited (relative to what one would expect based solely on the concentration of protonated HCN), and/or CN loss at pH > 10 is enhanced.

Secondly, it is clear from Figure *3* that at pH ≥ 10, k_{obs} for CN loss is greater in the dark fume hood than it is on the sunlight-exposed roof. Clearly, UV-light exposure does not enhance CN loss. The reason for this is most likely the strong, constant air turbulence maintained in the fume hood, because k_{obs} has been shown to increase with wind and surface turbulence.[14] This differs from the results that Zhang et al reported for TiO_2 photocatalysis of cyanide oxidation to cyanate.[15] They reported k_{obs} values of 0.03 – 0.06 dy^{-1} in the dark (and in the absence of TiO_2 catalyst), vs. 1 – 3 dy^{-1} in the presence of TiO_2 + light. Thus, the k_{obs} values that we observed, ≈ 0.5 – 1 dy^{-1} at pH 9.5 – 10.5, are similar to the photocatalyzed oxidation rates observed by Zhang et al. Presumably, this means that enhanced turbulence is just as effective as photocatalysis in increasing CN decline in solution.

Thirdly, we observed that pH-dependence is somewhat stronger in sunlight than in the dark, with slopes of -0.27 ± 0.03 vs. -0.189 ± 0.026 per day per pH unit, respectively (Figure *3*). Finally, it is also of interest that at pH ≈ 9, when cyanide is ≈ 50% protonated HCN, k_{obs} for CN loss is identical in the dark and in the light, ≈ 1.2 dy^{-1}.

pH and cyanide decline in soil columns

We collected soil samples from sites within a mile of Newmont Mining Company's proposed Grassy Mountain cyanide heap-leach gold mine in Malheur County, Eastern Oregon. We studied the ability of soil to bind hydroxide anion, and to bind and break down cyanide.

Remarkably, when soil columns were infused with 0.32 mM NaOH (pH 10.5), the pH of the initial effluent was only 5.5 ± 0.2 (Figure *4*), identical to the pH of distilled water. The soil thus retained all of the "excess" hydroxide anion in the initial pH 10.5 eluant solution. This initial hydroxide binding by the soil column amounted to a 100,000-fold reduction in concentration (pH 10.5 → 5.5 → 10^5-fold reduction). Hydroxide retention gradually saturated, with the effluent pH increasing by 0.0076 units per mL (slope of line in Figure *4*); this corresponds to a rise of 1 pH unit over ≈ 130 mL effluent. The ability of soil to bind hydroxide was extrapolated to saturate at 660 mL of effluent (33 pore volumes), the point at which the effluent pH would be identical to the pH of the infused solution, 10.5. This is the point at which the horizontal dashed line intersects with the dotted linear fit line in Figure *4*.

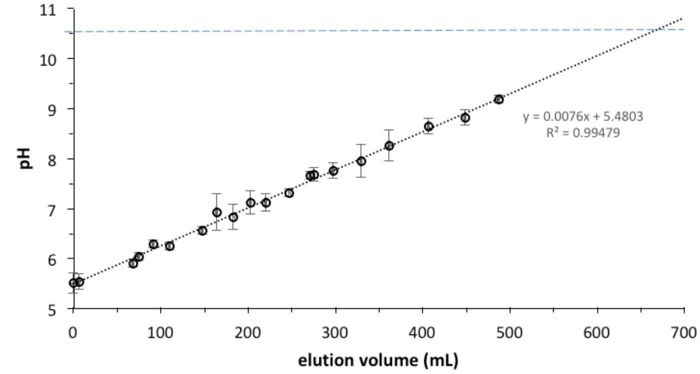

Figure 4. pH of the eluant from 50 mL soil columns infused with 0.32 mM NaOH, pH 10.5.

We were unable to run more than ≈ 500 mLs of eluant through soil columns because elution rates decreased with time, from an initial rate of 5 mL/hr down to 1 mL/hr after one week. After 10 days, elution stopped completely (alkaline solutions are known to have this effect on soil), hence the effluent reached a maximum pH of only 9.2. Tests carried out using a pH 12 influent solution gave very similar results.

This prodigious ability of soil to consume added hydroxide anion was due to: (i) buffers in the soil; (ii) CO_2 bound to the soil reacting with hydroxide to give HCO_3^-; and (iii) positively charged surfaces on the soil particles adsorbing anions such as OH^- (and also CN^-). Because reactions (i) and (ii) are specific for OH^-, we expect soil to lower $[OH^-]$ more effectively than $[CN^-]$. The following experiments showed this to be the case.

Soil columns infused with alkaline cyanide solution (3.84 mM KCN = 100 mg CN/L, pH 10.5) yielded an initial effluent of 1.4 mM CN (Figure *5*), and pH 7.55. Thus, soil retention lowered $[OH^-]$ by 890-fold (pH 10.5 → 7.55 → $10^{2.95}$), while lowering $[CN^-]$ by only 2.7-fold. Clearly, the hydroxide binding affinity of soil greatly exceeds its cyanide binding capacity. As with hydroxide biding, cyanide binding saturated, with [KCN] increasing by 0.0043 mM per mL of effluent (slope of line in Figure *5*); this corresponds to a rise of 1 mM over ≈ 230 mL effluent. The ability of soil to bind cyanide was extrapolated to saturate at 600 mL of effluent (30 pore volumes), where the horizontal dashed line intersects with the dotted linear fit line in Figure *5*. Interestingly, this attenuation capacity of 30 pore volumes is slightly less than that found above for hydroxide (33 pore volumes (660 mL), Figure *4*).

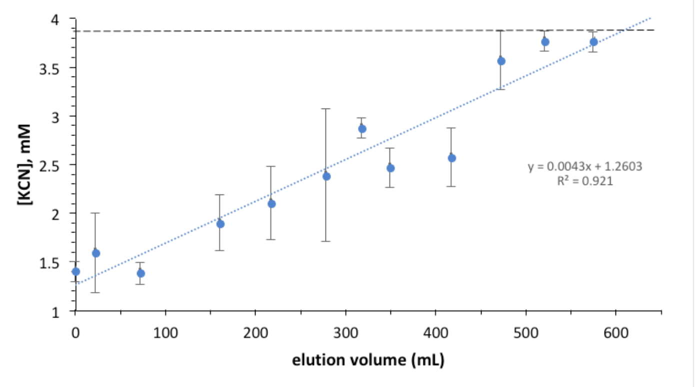

Figure 5. Soil columns (triplicate) eluted with alkaline cyanide solution – 3.84 mM KCN, pH 10.5. The pH of the initial effluent was 7.55.

Finally, we note that cyanide seems to compete with hydroxide for some binding sites: For pure NaOH solutions infused onto soil columns (Figure *4*), the attenuation of $[OH^-]$ in the initial effluent was 100,000-fold, but for KCN + NaOH solutions the initial hydroxide attenuation was only 890-fold. Thus, cyanide seems to occupy some of the hydroxide binding sites, decreasing the ability of soil to bind hydroxide. At the same time, we reiterate our conclusion above that soil's hydroxide binding affinity and capacity exceed that for cyanide binding.

Cyanide degradation kinetics

To assess the fate of cyanide bound to soil we loaded a 15 mL aliquot of CN solution (3.84 mM KCN, pH 10.5) onto a series of soil columns. We then immediately added 60 mL of 0.5 M HCl to the first column to elute the bound cyanide. From this first column (time zero), only 50 – 70% of the loaded CN was eluted. Hence, soil seems to irreversibly bind or attenuate 30 – 50% of bound CN, immediately upon contact.

The amounted of acid-releasable CN declined exponentially with time, hence the CN attenuation process demonstrates first-order kinetics (Figure *6*). To examine the influence of light and oxygen on the rate of CN attenuation, we tested soil columns under four different ambient conditions: (i) control (room light); (ii) dark; (iii) dark, deaerated; and (iv) sunlight-exposed. From the fitted first order rate constants (Table *1*) we see that the rate of CN decline is identical for conditions i – iii, hence room light and aeration by atmospheric oxygen have no effect on CN attenuation. On the other hand, sunlight enhanced the rate of CN attenuation by more than two-fold. Presumably, a UV-photooxidation reaction converts some of the cyanide to cyanate (or possibly SCN^-).

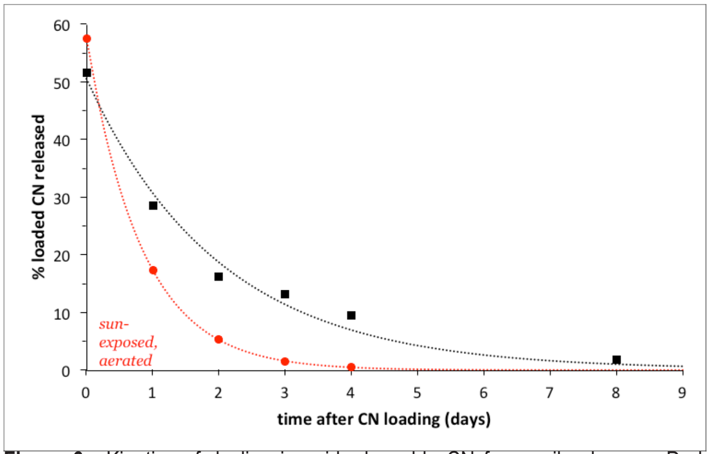

Figure 6. Kinetics of decline in acid-releasable CN from soil columns. Dark columns were wrapped with aluminum foil. Deaerated columns were flushed with N_2(g). Data fit by non-linear regression to exponential decline: Black squares: dark, aerated columns, initial % = 50.5 ± 2.3 %, $k = 0.50 \pm 0.04$ dy^{-1}; $R^2 = 0.985$; red circles: sunlight-exposed, aerated columns, initial % = 57.60 ± 0.10 %, $k = 1.198 \pm 0.005$ dy^{-1}; $R^2 = 0.999$.

treatment	k (day^{-1})	R^2
(i) control	0.49 ± 0.05	0.96
(ii) dark, aerated	0.50 ± 0.04	0.985
(iii) dark, deaerated	0.49 ± 0.07	0.91
(iv) sunlight	1.198 ± 0.005	0.999

Table 1. Best fit rate first-order constants for the exponential decline of acid-releasable CN from soil columns; (i) control = aerated, room light; (ii) dark = aerated, foil-covered; (iii) dark, deaerated by flushing with N_2(g); (iv) sunlight = aerated, exposed to sunlight on roof

Our data (Figure *6*) show that under conditions i – iii, less than 2% of the bound CN was acid-releasable after one week; for the sunlight-exposed columns, only 1% of the bound CN was recovered after 3 days. We may conclude that upon contact with soil, cyanide is attenuated within a week, by a combination of three processes: irreversible binding, chemical degradation, and volatilization to the atmosphere (as HCN).

Conclusions

Cyanide loss from open alkaline solutions was a first order process, with half-times ranging from 16 hr at pH 9.5 (65% loss per day, $k = 1$ dy^{-1}), to 44 hr at pH 12.0 (32% loss per day, $k = 0.4$ dy^{-1}). This process is due primarily to HCN volatilization.[3,14] Hydroxide concentrations in these unbuffered open solutions fluctuated from day to day, but pH generally trended downward, due most likely to OH^- reaction with aqueous CO_2 to give HCO_3^-. Open CN holding ponds thus require constant recharging with both CN and OH^-.

The soil we tested in this study had a large capacity and affinity for binding hydroxide, and a somewhat lower but still notable capacity and affinity for cyanide: 28 – 30 pore volumes for CN^- vs. 33 for OH^-. About one-third to one-half of the CN attenuation by soil was due to immediate and irreversible binding/complexation. The remaining acid-releasable bound CN degraded exponentially within a week (first-order $k = 0.5$ day^{-1}; half-time = 42 hr) in a process that was independent of room light and aeration; the process was photocatalyzed by sunlight ($k = 1.2$ day^{-1}; half-time = 14 hr). These rates correspond to a decline in acid-releasable CN of 75% per day in sunlight, and 33% per day in its absence. This CN loss is likely due to UV-enhanced oxidation to OCN^-.

From our results, we may conclude that a CN spill or leak at a heap leach mine that is short-term is not likely to pose a serious long-term hazard. The CN will be readily attenuated by binding, complexation, degradation, or volatilization. However, two provisos must be noted: First, the toxicity of volatilized HCN(g) and the OCN^- oxidation product must be kept in mind.[1,6] Second, laboratory conditions cannot always be accurately extrapolated to field conditions. Natural soil parameters such as uneven packing and consistency, percolation fissures, and soil composition must be considered in a site-specific fashion in order to draw firm conclusions hazards at individual mining sites.

Finally, long-term CN leaks, such as those that can occur through cracks in the plastic lining underneath holding ponds, could saturate the CN binding capacity of the underlying soil. This could lead to CN contamination of ground water, as has occurred in the past.[2,5,13,16] It therefore seems prudent to require redundant layers of both plastic lining and CN detection sensors beneath these CN holding ponds.

Addendum

This project was undertaken in response to a 1992 proposal by the Newmont Mining Company to reopen the Grassy Mountain mine as a CN heap-leach gold mine. When Initiative Measure 14, a set of rules strictly regulating the operation and clean-up of these mines, qualified for the November 1994 ballot, Newmont Mining Company saturated the TV airwaves with advertisements touting the safety of CN heap-leach mines. Finding these advertisements to be misleading and even irresponsible, in order to ascertain the facts we initiated this CN research project; most of the data in this paper were collected by undergraduate chemistry major Jonathan (Yi) Zhang in the early 1990s. As concerned citizens and scientists, Yi and I set out to determine whether the soil-cyanide interaction was as benign as claimed by Newmont and some literature reports. A preliminary version of this paper was published in a Willamette University in-house publication, the *Willamette Journal of the Liberal Arts* (1997): issue 11 (summer), pp. 1 – 23.

In the end, Oregon Measure 14 was defeated in November 1994 by 56% to 44%, proving the influence of saturation advertising: Newmont spent nearly $4 million on the election, compared to the $50,000 available to the measure's proponents. In a final irony, in January 1996 Newmont withdrew their Grassy Mountain heap-leach proposal. After three years and $33 million spent on development, their studies showed that the site did not "hold sufficient deposits of gold to allow the company to continue with plans to open a heap leach mine in Malheur County." Newmont had hoped to extract one million ounces of gold at Grassy Mountain, but their studies suggested a 40% lower yield; that plus the decline in the price of gold led them to abandon their proposal. It is worth noting that in 1991, in anticipation of Newmont's proposal, the Oregon state legislature passed a rigorous set of regulations controlling the operation and closure of cyanide heap-leach mines (ORS 517.952 to 517.992).

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Appendix: Cyanide Heap-Leach Gold Mining: Mineralogy, Chemistry, Toxicology, and Mining Accidents

I. Gold and gold mining

Gold, being a noble metal, is generally found in nature in its reduced elemental form, Au(s), as nugget or grain pure phase inclusions within rocks, veins, or alluvial deposits that are mostly quartz (SiO_2), mica ($M_{\approx 6}Si_8O_{20}(OH,F)_4$), or pyrite ($FeS_2$, iron(II) persulfide). In order to separate and purify the gold, it must be "won" from the ore. Nowadays this is almost always done by cyanide leaching, which was first employed in New Zealand in the early 1900s,[1] but was introduced in the United States by the U.S. Bureau of Mines in 1969. By 1970-1980, all easily accessible high concentration Au deposits had been discovered and removed worldwide, leaving only low-grade ore deposits that were uneconomical to mine. Cyanide-leaching, which is relatively fast, efficient (> 97 % Au recovered), and inexpensive, made the mining of low-grade deposits profitable. By 1998, > 90% of Au was mined by CN-leaching;[2] as of the year 2000, over 30% of the annual global usage of NaCN (360,000 tons) was for gold and silver mining and recovery.[2]

On the other hand, CN-leaching creates huge quantities of waste: To get 1 oz. of gold, one must remove 100 – 200 tons of rock! In the average low-grade ore mine, 3 – 6 million tons of rock are removed and crushed to get ≈ 1 million tons of ore, from which 1 ton of Au(s) is extracted.[3],[4],[5] In addition to piles of several million tons of rock and a million tons of ore tailings, mines contain a "barren" cyanide pond (alkaline cyanide solution), an ore heap pad for cyanide leaching, a "pregnant" cyanide pond (containing $Au(CN)_2^-$), and a tailings pond containing cyanide and other ionic metal waste.

In order to keep cyanide from becoming protonated and escaping from solution as HCN(g), solutions are maintained at pH above 9.5, usually 10.3 – 10.5.[1],[26] (The pK_a of HCN is 9.21, but at the typical ionic strength of 0.1 M, it is 9.04.[7]) The cyanide source is usually[4] NaCN or KCN, less commonly, $Ca(CN)_2$; optimal cyanide concentration in the leachate solution in the barren pond is 500 mg/L (0.05%).[6] The leachate ("barren" cyanide) solution is sprayed over the heap of crushed ore on the leach pad for weeks to months.[1] Spraying helps to aerate the leaching solution, supplying the required oxygen. The leaching reaction is given by the Elsner Equation[8]:

Equation A1:
$$4\,Au(s) + 8\,CN^-(aq) + O_2(aq) + 2\,H_2O(l) \rightarrow 4\,Au(CN)_2^-(aq) + 4\,OH^-(aq)$$

It has been shown that this is actually a 2-step redox reaction with H_2O_2 intermediate:[7]

Equation A2:
$$2\,Au(s) + 4\,CN^- + O_2 + 2\,H_2O \rightarrow 2\,Au(CN)_2^- + H_2O_2 + 2\,OH^-$$

Equation A3:
$$2\,Au(s) + 4\,CN^- + H_2O_2 \rightarrow 2\,Au(CN)_2^- + 2\,OH^-$$

The resulting "pregnant" solution (containing $Au(CN)_2^-$) is collected in a pond (or tanks), then pumped onto activated carbon columns, which adsorb the $Au(CN)_2^-$. Finally, the Au(I) in

$Au(CN)_2^-$ bound to the column is reduced to Au(s) and eluted from the carbon column by a stripping solution.[1]

The large open pit and tons of waste rock and ore cause obvious landscape problems, and can often produce toxic acid mine drainage. Additionally, four types of problems can stem from the cyanide ponds: (i) poisoning of wildlife that mistake CN-laden ponds for potable/fishable water; (ii) accidental spills of CN waste water from ponds, dams; (iii) leakage/seepage of CN from ponds/pipes into groundwater (from tailings slurry); (iv) drainage of tailings slurry CN from legacy sites. Although several other less toxic Au leaching processes have been studied and tested, they are either more expensive, less efficient, slower, or not well-studied.[1,9] Hence even with its problems, CN-heap leaching remains the method of choice.

II. Cyanide toxicity

Cyanide is a potent, rapidly acting poison with a human lethal dose of 50 – 90 mg (1 tsp of a 1% solution; Table A*1*).[3,4,10,11] It can be delivered by ingestion or by inhalation of HCN(g).[11] Toxicity data for animals and aquatic wildlife can be found in Table A*1*. Cyanide exerts its primary acute toxic effects on cytochrome c oxidase, the terminal electron transfer complex in mitochondria. CN^- complexes tightly with oxidized metal cations in the oxygen-binding center: cytochrome a_3 (Fe_{a3}^{3+}), and possibly also copper (Cu_B^{2+}).[12,11,13] This keeps these metals from becoming reduced, and thus inhibits oxygen binding. This in turn inhibits the mitochondrial electron transfer pathway, shutting down oxidative phosphorylation. The lack of ATP affects tissues with the highest metabolic demand, e.g., brain, central nervous system, and heart muscle; neurons in the central nervous system are also damaged by lipid peroxidation.[14] In addition, cyanide inhibits the following enzymes, most of which are iron- and/or copper-containing metalloenzymes: glutamate decarboxylase, xanthine oxidase, superoxide dismutase, NO synthase, and nitrite reductase.[14]

Table A1: Toxicity of cyanide and its breakdown products; all concentrations in mg/L (ppm).

	CN^-	OCN^-	SCN^-	NH_3
Human LD*	50 – 90 mg (Refs. [3,4,10,11])			
Rat oral LD50*	2 – 4 mg/kg (ref. [15])	440 mg/kg (ref. [15])	510 mg/kg (ref. [15])	350 mg/kg (ref. [15])
Animal acute LC*	40 – 200 mg/L (Ref. [4])			
Animal chronic HC*	0.1 mg/L (Ref. [10])			
aquatic acute LC	0.02 – 0.64 (Refs. [3,16])		90 – 200 (Refs. [4,16])	0.08 – 4.6
Trout acute LC	0.02 – 0.08 (Ref. [4])	13 – 82 (Ref. [4])	24 – 70 (ref. [17])	
Trout chronic HC	0.005 – 0.020 (Ref. [4])			
EPA freshwater AC*	0.0052 mg/L			
EPA marine AC*	0.0010 mg/L (Ref. [4])			
EPA potable water AC	0.2 mg/L			

*LD = lethal dose; LD50 = dose that kills 50% of cohort; LC = lethal concentration; HC = harmful concentration; AC = maximum allowed concentration

Cyanide is detoxified by three different metabolic pathways: 15% is incorporated into 2-aminothiazoline-4-COOH[14]; 5 – 20% is oxidized/hydrolyzed to CO_2 (which is exhaled) and NH_3 (excreted in urine; see Equation A*4* and Equation A*5*)[12,14]; but most (60 – 80 %) is converted to thiocyanate (SCN^-)[14], in reactions catalyzed by rhodanese (a.k.a. thiosulfate transferase) in liver and kidney mitochondria[11,12], and by 3-mercaptopyruvate transferase (see Equation A*6*).[14] The halftime for the thiocyanate conversion process in blood plasma is 20 – 60 minutes, and [SCN-] peaks at 1.5 mg/L after 6 hours.[14]

Equation A4: *oxidation:* $CN^- + \frac{1}{2} O_2 \rightarrow OCN^-$

Equation A5: *hydrolysis:* $OCN^- + H_2O + H^+ \rightarrow CO_2 + NH_3$

Equation A6: *oxidation/sulfidation:* $CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$

Although thiocyanate is about 200 – 1000x less toxic than cyanide (Table A*1* and ref. [12]), it is still toxic, decreasing the synthesis and secretion of levothyroxine from the thyroid gland.[14] SCN^- is the same charge and roughly the same size as I^-, thus it competitively inhibits the cellular uptake of iodide, inhibiting its incorporation into thyroxine; at higher concentrations, SCN^- competitively inhibits the binding of I^- to thyroid peroxidase.[18] Thus, the thyroid gland is a prominent secondary target of cyanide poisoning.

Cyanide chemistry

Documents produced by mining companies, regulatory agencies, and their supporters often claim that cyanide is not a major environmental concern because it decays quickly, especially in the presence of sunlight, into "harmless" CO_2 and either NH_3 or NO_3^-.[1,3,4,5] Regulatory agencies generally require mines to monitor for only three forms of cyanide: (i) free (i.e., CN^- + HCN); (ii) weak-acid dissociable (WAD), e.g. cyanide complexes with Zn, Cd, Cu, and Ni cations[4]; and (iii) total cyanide. We have discussed the toxicity of free cyanide above. WAD CN is not itself toxic, but in the acidic environment of the stomach it dissociates to release toxic free cyanide.[4] Strong cyanide complexes (e.g. those with Fe, Co, and Au cations) are non-toxic even at acidic pH, but they do slowly photolyze to release free cyanide when exposed to UV light (e.g., sunlight). This decomposition is accelerated by high temperature, low pH, O_2, dissolved solids, and soil adsorption.[4] The concentration of strong complexes can be calculated from:

$$[CN]_{total} = [CN]_{free} + [WAD\text{-}CN] + [\text{strong CN complexes}].$$

There are serious problems with the current regulatory requirements to only monitor free cyanide, total cyanide, and WAD-CN, and the notion that cyanide breakdown products are harmless. First of all, NO_3^- and NH_3 are NOT harmless: For example, from Table A*1* we can calculate that for aquatic wildlife, NH_3 is only about 4 to 7-fold less toxic than CN^-; for rats, it is ≈ 100-fold less toxic. Other breakdown products of cyanide, e.g., cyanate (OCN^-), thiocyanate (SCN^-, see above), cyanogen (NC-CN), ferri-/ferrocyanide, cyanogen chloride (Cl-CN), and monochloroamine ($Cl\text{-}NH_2$) are also somewhat toxic.[3,4,5]

Cyanate, the most common breakdown product, comes from the partial oxidation of cyanide (see for example Equation A*4*) by oxidizing agents such as O_2, O_3, H_2O_2, and ClO^-.[4] In the presence of heterogenous catalysts like TiO_2, ≥ 90% of cyanide is photooxidized to cyanate (first order rate constant $k = 0.3 - 0.9$ day^{-1}).[19] From Table A*1* we can calculate that for trout, cyanate is 700 to 1000x less toxic than cyanide.

Thiocyanate is also commonly found in tailings waste water at concentrations of ≈ 10 mg/L.[4] It forms from oxidation of cyanide by thiosulfate (as in Equation A*6*), or by persulfides (commonly found in pyrite, FeS_2):

Equation A7: $CN^-(aq) + FeS_2(s) \rightarrow SCN^-(aq) + FeS(s)$

The toxicity of thiocyanate is similar to that of cyanate (Table A*1*), roughly 1000x less than that of cyanide. Both cyanate and thiocyanate have been found to persist in the environment and to bioaccumulate in some plants[20] and fish.[21]

Cyanogen, **cyanogen chloride,** and **monochloroamine** are formed when cyanide is oxidized by metal cations (e.g., Cu^{2+}) or chlorine, respectively:[7]

Equation A8: $2\ CN^- + Cu^{2+} \rightarrow NC\text{-}CN + Cu^0(s)$

Equation A9: $CN^- + Cl_2 \rightarrow Cl\text{-}CN + Cl^-$

Equation A10: $CN^- + 2\ Cl_2 + 3\ OH^- \rightarrow Cl\text{-}NH_2 + HCO_3^- + 3\ Cl^-$

Unfortunately, no regulatory standards exist for any of these toxic cyanide breakdown products, with the exception of nitrate and ammonia.[3]

III. Natural attenuation of cyanide in the environment

The common claim that cyanide is not a major environmental concern because it decays quickly into harmless products is not chemically defensible: The breakdown processes are often slow, and many of the products are not harmless. For example, 25 years after processing ceased at a Co/Ni mine, total cyanide in sediment exceeded 5 mg/L, mostly in the form of iron and cobalt complexes.[4] Mining waste water with < 0.05 mg/L of total cyanide or WAD-CN can have concentrations of OCN^- and/or SCN^- ranging from 10 – 50 mg/L;[4] as noted in Table A1, such concentrations are lethal to trout.

Natural attenuation of cyanide in the environment occurs by five main processes:[7],[22]

1. **Adsorption** onto soil (CN^-), organic matter (HCN), or suspended solid particles.
2. **Precipitation** in the presence of Fe^{2+}, Fe^{3+}, Cu^{2+}, Na^+ cations, e.g., Prussian Blue, $Fe(III)_4[Fe(II)(CN)_6]_3(s)$; $Cu(II)_2Fe(II)(CN)_6$; $Na_4Fe(II)(CN)_6$
3. **Metal complexation** in solution: forms WAD-CN or strong complexes, as noted above; e.g., ferro- and ferricyanide adsorb rapidly to soil organic matter, especially at low pH when acidic groups are protonated to give a positive surface charge.
4. **Chemical reactions,** especially redox and hydrolysis:

Oxidation to give OCN^- (Equation A4), followed by **hydrolysis** to give ammonia + bicarbonate:

Equation A11: $OCN^- + 2\ H_2O \rightarrow HCO_3^- + NH_3$

Bioreduction to give ammonia + hydrocarbon:

Equation A12: $CN^- + 3\ NADH + 4\ H^+ \rightarrow CH_4 + NH_3 + 3\ NAD^+$

Hydration to give formamide, followed by **hydrolysis** to give ammonia + formate:

Equation A13: $CN^- + 2\ H_2O \rightarrow HCONH_2 + OH^-$

Equation A14: $HCONH_2 + OH^- \rightarrow HCOO^- + NH_3$

Volatilization of HCN(g): Shown to account for more than 90% of CN loss from tailings ponds,[23] but this was most likely due to low pH (≈ 7). Alkaline solutions in the natural environment are progressively acidified by $CO_2(g)$ incursion from the air to give carbonic acid, and by the metabolic activity of bacteria and microorganisms.[7]

The rates of these attenuation processes depend on pH, temperature, redox poise, UV light, the surface/volume ratio of the pond, and the degree of mixing. The most common attenuation processes in tailings ponds, ore heaps, and contaminated soil are: volatilization, bacterial oxidation, and hydration/hydrolysis reactions. In fresh tailings (≤ 3 months old), 85% of newly added CN is consumed within three months; in old tailings (≥ 6 years), 85% of newly added CN is consumed within one month.

In soil, CN mobility is limited by the presence of metals (e.g., iron), the clay type (e.g., chlorite, kaolin, gibbsite), and by microorganism metabolism.[24] CN adsorbs to organic and inorganic matter in soil and is normally readily oxidized to OCN^-.[10],[19] In the presence of microorganisms, OCN^- is further hydrolyzed to $CO_2 + NH_3$ (Equation A*11*).[10],[25] The hydrolysis reaction also occurs readily in solution at pH < 6, or at elevated temperatures.[10]

Volatilization of HCN(g) from solution is a fairly well-studied process. Its kinetics are first order ($-d[HCN]/dt) = k_{obs}[HCN]$), where k_{obs} depends linearly on A/V: pond surface area ÷ volume of the mixed supernatant layer.[26] The rate constant also increases with temperature and with degree of mixing (i.e., wind, surface turbulence). In addition, metal cations in mine wastewater bind cyanide and decrease [HCN]. For example, in a copper-containing cyanide solution similar to that found in tailings impoundment ponds (100 mg/L total cyanide + 50 mg/L Cu^+, pH 7 – 9), only 20 – 40% of the cyanide is free ($HCN + CN^-$). In the absence of Cu^+, 60% of cyanide is free at pH 9, and 100% at pH 7.[26]

Simovic[26] developed a model to predict [HCN(aq)] as a function of three cyanide equilibria: acid ionization, pK_a(HCN); metal complexation; and photolysis of ferri-/ferrocyanide. Applying this model to the tailings pond at an inactive mine in 1998 (170 mg/L total cyanide, > 98% as $Fe(CN)_6^{3-}$), they found HCN volatilization to be fast, and ferricyanide photolysis the rate-determining step. Furthermore, photolysis only occurred during April – October, due to winter ice cover. Excluding the winter months, they found the observed first-order rate constant for cyanide decline to be $(5.70 \pm 0.09) \times 10^{-3}\ dy^{-1}$ ($= 2.08 \pm 0.03\ yr^{-1}$).[26] This yields a decline in total cyanide of 16% per month, or 88% per year.

Cyanide decline at the closed Dome Mine in Timmins, Ontario (Canada) was found to be 8-fold faster, with $k_{obs} = 0.048\ dy^{-1}$ (99.92% decline from April to August).[23] This enhanced decline was most likely due to the pH decline from 10.5 to 7.0 over this time period[23], due to the natural incursion of CO_2 which hydrates to give carbonic acid. The lowered pH protonates all CN^- to HCN, which enhances volatilization: Indeed, 96% of the cyanide decrease was attributed to volatilization.[23] (Although Schmidt et al attributed some of the acidification to thiocyanate hydrolysis

[*Equation A15*], that process produces only the weak acid H_2S ($pK_a = 6.98$), which would not significantly lower the pH.

Equation A15: $SCN^- + H_2O \rightarrow OCN^- + H_2S$

In fact, further hydrolysis of the product cyanate [*Equation A16*] produces the weak bases ammonia and bicarbonate:

Equation A16: $OCN^- + 2\,H_2O \rightarrow HCO_3^- + NH_3$

The oxidation of CN^- to OCN^- (Equation A*4*) accounted for 11% of the total cyanide decrease from early April to early June, as [OCN^-] rose from 4.1 to 14.3 mg/L. After June, as the pH dropped dramatically, OCN^- was hydrolyzed to carbon dioxide and ammonium cation (*Equation A17*).

Equation A17: $OCN^- + 2\,H^+ + H_2O \rightarrow CO_2 + NH_4^+$

III. Mining accidents

Although the regulation and safety records of most mines are robust, mining accidents are distressingly common. From 1975 to 2003, Mudder and Botz listed 39 major mining-related environmental incidents (1.3 per year).[2] Most of these were dam failures (72%) and pipe failures (18%), with the remainder transport accidents. About a third of them (30 – 40%) involved cyanide-laden waters (i.e., ≈ one every 2 years).

Two notorious examples are the Aural Mine dam failure in Baia Mare, Romania in 2000, and the Guyana tailings dam collapse in 1995. The former released 25 million gallons of tailings wastewater into the Tisza River, which contaminated over 1200 miles of downstream rivers (including the Danube) in Hungary, Yugoslavia, and Bulgaria, killing over a million fish and eliminating phyto- and zooplankton. It took over four weeks before the contamination plume was finally flushed into the Black Sea. The latter accident released over 600 million gallons of cyanide waste water in a spill that affected ≈ 23,000 Guyanese who used the waterways for fishing, washing, and bathing.

Ghana has also experienced quite a few catastrophic cyanide releases from gold mines.[1],[27] Measurements in the mining town of Bibiani in West Ghana showed[27] increased cyanide in soil (22 mg/kg near mines cf. 6 – 14 mg/kg far away), in well and borehole water (5 – 8 mg/L near mines cf. 2.2 – 3.5 mg/L in control pipewater), and due to acid mine drainage, lower pH in soil (4.5 – 6.0 near mines cf. 7.0 far away) and in well and borehole water (3.1 – 3.4 near mines cf. 7.4 in control pipewater). Note that even in "control" pipewater, the cyanide concentration was over 10-fold higher than the EPA-allowed limit in drinking water in the U.S., 0.2 mg/L.

Legal responses included the outright banning of cyanide heap-leach gold mining in three European countries (Czechia, Hungary, and Germany) and one U.S. state (Montana). The state of Oregon has passed strict environmental protection regulations. Laitos has argued[1] that these legal prohibitions are an unwarranted overreaction that is due to the "enormous gap between the scientific, chemical, ecological, and historical reality of cyanide-dependent mining operations, and the exaggerated, perceived threat of cyanide to environmental quality… Cyanide releases are extremely rare, and when they do occur, their negative effects on natural systems and living organisms are often temporary… [Furthermore] cyanide itself is not inherently toxic, it degrades quickly… to non-toxic forms… usually producing negligible environmental consequences… [and] soils are generally unable to adsorb the negative cyanide anion."

Unfortunately, almost all of these claims are false. Mudder and Botz[2], who are strong supporters of cyanide heap-leach gold mining, showed that significant cyanide releases from mines are NOT rare; they occur about once every other year, as noted above. The claim that "cyanide itself is not inherently toxic" is preposterous, and while it is true that cyanide degrades quickly, its breakdown products (e.g., cyanate, thiocyanate, cyanogen, ammonia), while less toxic than cyanide, are most definitely NOT non-toxic. The claim that "soils are generally unable to adsorb the negative cyanide anion" also runs counter to extensive literature results summarized above.

The argument has been made that the cyanide exposure experienced by the overwhelming majority of people has nothing to do with mining accidents.[12] The most common human CN exposure is from smoke, e.g. cigarette, fire (house, industrial, forest), and vehicle exhaust.[28] Partial combustion in the presence of $O_2 + N_2$ yields HCN; for example, for methane combustion we have:

Equation A18: $2\,CH_4 + 3/2\,O_2 + N_2 \rightarrow 2\,HCN + 3\,H_2O$

About 8 mg of cyanide are produced in vehicle exhaust per km[10], hence the exhaust from 6 km of travel yields the human lethal dose of 50 mg. HCN is also a byproduct of the partial combustion of nitrogen-containing synthetic polymers (e.g., many polyacrylates), and of proteins, including those in natural fibers (e.g., wool, silk).

Equation A19: C_2H_3NO (*amino acid*) $+ O_2 \rightarrow HCN + CO_2 + H_2O$

HCN comprises about 10% of the smoke inhaled from a single cigarette (≈ 5 mg)[10]; this dose of 0.5 mg is about 0.1% of the lethal dose of 50 mg.

Even though most people are not exposed to cyanide from mining accidents, the fact remains that those downstream from cyanide heap-leach gold mines, especially those nearby, are at risk from catastrophic dam, pipe, and transport failure.

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