

U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

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by

Robert O. Rye¹ and Craig A. Johnson²

Open-File Report 97-82

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¹Denver, CO

²Pacific Western Technologies, Ltd., Lakewood, CO 80228

The use of stable carbon- and nitrogen-isotope data in quantifying cyanide loss from mine wastewaters*

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ABSTRACT

Measurements of the stable isotope ratios $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ in cyanide in mine wastewaters can potentially be used to identify the mechanisms responsible for cyanide loss and to quantify the amount of cyanide that has been lost via a specific mechanism. Cyanide typically has large negative $\delta^{13}\text{C}$ values (VPDB scale) and near-zero $\delta^{15}\text{N}$ values (air scale) as it is initially applied to ores. Two cyanide loss mechanisms that occur naturally in mine wastewaters, evaporation as HCN gas and complexation with ferrous iron, have been found to fractionate the stable isotopes in laboratory experiments. Short-duration evaporation increased $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in the residual cyanide as would be predicted for a kinetically-controlled evaporation process. Longer-duration evaporation increased $\delta^{15}\text{N}$ but decreased $\delta^{13}\text{C}$ reflecting either liquid-vapor isotopic exchange or some degree of cyanide hydrolysis in the experiments. Complexation increased $\delta^{15}\text{N}$ slightly and decreased $\delta^{13}\text{C}$ slightly. The experimental results suggest that cyanide loss in industrial settings will also cause isotopic fractionation and thereby leave an isotopic signature in the residual dissolved cyanide. To fully evaluate the potential of isotopic tools, it will be important to carry out case studies at active and abandoned mines.

INTRODUCTION

Solutions of cyanide (CN^-) are used at a large number of mines throughout the world to leach gold and silver from ores. The cyanide levels in these solutions decline during leaching and also during solution storage in surface ponds or tailings impoundments. A number of mechanisms are known to lead to cyanide loss, including evaporation, complexation with metals, oxidation, sulfidation, hydrolysis, precipitation as cyanometallic compounds, and bacterial processing (Smith and Mudder, 1991), but in case studies it can be difficult to identify the operative mechanisms or to determine their relative importance. The reason that the mechanisms are difficult to identify is that some of the important products are dispersed as gases or precipitated as solids. They are therefore difficult to detect and almost impossible to quantify.

Cyanide loss from mine process waters and wastewaters is an important process to understand for two reasons. The first reason results from the fact that cyanide can be toxic (eg., Heming and Thurston, 1985). Natural degradation must be understood to realistically evaluate the environmental risks that would be associated with accidental release of process waters or with cyanide mobilization from tailings after mine abandonment. The second reason is that an understanding of cyanide loss can be used to minimize cyanide consumption thereby reducing mine operating costs (eg., Botz et al., 1995).

A prerequisite for understanding cyanide loss is site-specific, quantitative information on the loss mechanisms. In this report we show how stable isotope tools may

* This report contains the text of a talk, slightly modified, that was delivered October 31, 1996 at the Geological Society of America meeting in Denver, CO. An abstract of the talk was published previously (Rye and Johnson, 1996).

provide this information by (1) allowing the mechanisms to be identified, and (2) allowing the cyanide loss via a particular mechanism to be quantified.

ISOTOPE THEORY

Carbon and nitrogen, the constituent elements of cyanide, each has more than one naturally-occurring stable isotope. The behavior of the isotopes during cyanide loss can be illustrated by examining as an example one of the important mechanisms, evaporation as HCN gas. Figure 1 is a schematic diagram of the process.

In aqueous solutions equilibrium is reached between the cyanide anion, CN^- , and molecular HCN (figure 1). The position of the equilibrium is pH dependent. In active leach circuits where pH is about 10.5, CN^- is dominant, and in abandoned operations where pH drops over time, HCN becomes increasingly important. The sum of CN^- and HCN_{aq} is typically referred to as free cyanide.

Approximately 98.5% of the free cyanide in solution will contain the common stable isotopes, carbon-12 and nitrogen-14. The remaining 1.5% will contain one or both of the minor isotopes, carbon-13 and nitrogen-15. Each of the different isotopic species shown in figure 1 has a slightly different equilibrium vapor pressure and evaporates at a slightly different rate. As a consequence, whether evaporation is a reversible equilibrium process or whether it is non-reversible and is governed by kinetics, the abundances of the isotopic species will differ in the gas and liquid phases (cf., Dansgaard, 1964). The differences will be on the order of parts per thousand or perhaps a few parts per hundred. The isotopic differences between the free cyanide and the evaporated gaseous cyanide can be expressed as fractionation factors (α) defined by the following equations for nitrogen and carbon, respectively,

$$\alpha_N = \frac{(^{15}\text{N}/^{14}\text{N}) \text{ in HCN gas}}{(^{15}\text{N}/^{14}\text{N}) \text{ in free cyanide}} \quad (1)$$

$$\alpha_C = \frac{(^{13}\text{C}/^{12}\text{C}) \text{ in HCN gas}}{(^{13}\text{C}/^{12}\text{C}) \text{ in free cyanide}} \quad (2)$$

The effect of evaporation on the isotopic composition of the residual free cyanide can be predicted using the Rayleigh distillation model. The governing equation is

$$\delta_{\text{free cyanide}} = (\delta_{\text{free cyanide-initial}} + 1000) F^{(\alpha-1)} - 1000 \quad (3)$$

where F is the fraction of cyanide remaining in the solution, δ is the isotopic composition expressed as the deviation of $^{15}\text{N}/^{14}\text{N}$ or $^{13}\text{C}/^{12}\text{C}$ from the same ratio in a standard material in parts per thousand (‰), and α is defined as in equations (1) and (2) above.

The Rayleigh model is shown graphically in figure 2 for a hypothetical case where $\alpha=0.995$ and $\delta_{\text{free cyanide-initial}}=0\text{‰}$. It is apparent from the figure that the δ -value for the residual free cyanide is driven upward with progressive evaporation. There is an equation parallel to equation (3) for the gaseous HCN that is produced. The result for gaseous HCN, which is also shown in figure 2, shows that the δ -value for the evaporation product is also driven upward. At any point in time (in other words, at any value of F), the gaseous HCN has a lower δ -value than the free cyanide by 5‰.

The plot in figure 2 is the basis for quantifying cyanide loss. If the loss mechanism is known and if there is a fractionation factor characteristic of the mechanism, then the isotopic shift in either the reactant or the product can be used to determine the fraction of cyanide that has been processed. If the total quantity of cyanide in the system is known, then the quantity of cyanide lost and the quantity of products generated can also be calculated. Where more than one loss mechanism is operative, the overall effect on the isotopes will be a linear combination of the effects of the individual mechanisms.

With respect to identifying loss mechanisms, our expectation is that the fractionation factors will differ from one mechanism to another. If this proves to be the case then one could, for example, analyze a solution repeatedly over a period of time and derive fractionation factors that would earmark the mechanism. There will be independent factors for nitrogen and for carbon, so the isotopic signature would not be a unique number but a unique combination of two numbers.

EXPERIMENTAL RESULTS

We have taken three steps in developing isotopic tools for use in cyanide studies. The first step was to work out analytical techniques because prior to our work the isotopic compositions of cyanides had never been measured. For solids we developed a combustion technique to form CO_2 gas and N_2 gas for mass spectrometry (Johnson, 1996). For dissolved free cyanide we developed a method of precipitating the cyanide as a solid which can then be filtered, dried, and combusted.

The second step was to analyze commercial compounds to determine the isotopic compositions of cyanide as it is initially applied to ores (Johnson, 1996). For six different compounds, $\delta^{13}\text{C}$ was found to range from -35 to -23‰ on the Vienna Pee Dee Belemnite scale. The large negative values are in the range characteristic of sedimentary organic materials (figure 3). The cyanide isotopic compositions appear to reflect the carbon source that is used in the manufacturing process, normally natural gas or coal-derived coke (Kroschwitz, 1993). The $\delta^{15}\text{N}$ values are very close to zero on the air scale (figure 4). The nitrogen isotopic compositions appear to reflect the nitrogen source that is used in the manufacturing process, air (Kroschwitz, 1993).

The third step was to carry out experiments to determine whether cyanide loss does in fact fractionate the isotopes. In one series of experiments HCN was allowed to evaporate into closed head spaces from solutions of sodium cyanide. The initial and final δ -values and the initial and final cyanide concentrations were measured, and the results were used to solve for the fractionation factors using equation (3).

In a separate series of experiments we reproduced another important cyanide loss mechanism, complexation with ferrous iron. Solutions of sodium cyanide were prepared and different amounts of ferrous chloride were added to complex different proportions of the free cyanide as ferrocyanide. The initial and final free cyanide concentrations were measured as were the isotopic compositions of the starting free cyanide and the complexed cyanide. Equation (3) was then used to solve for the fractionation factors.

The results of the calculations are given in table 1. The fractionation factors for evaporation differed between the 7-day and 50-day experiments. The 7-day results indicate preferential loss of the light isotopes which is consistent with the kinetic control expected of an evaporation process. The 50-day results reflect preferential loss of light nitrogen and heavy carbon. The non-kinetic behavior of carbon may be explained by an approach to isotopic equilibrium between the dissolved and gaseous cyanide. The implication would be

that carbon is more tightly bonded in the HCN gas molecule than in the CN^- anion, whereas nitrogen is more tightly bonded in the CN^- anion. An alternative explanation is that the 50-day results reflect in part cyanide loss by a mechanism other than evaporation. Cyanide can slowly hydrolyze in aqueous solutions according to the reaction



cyanide + water = ammonia + formate.

Some degree of cyanide hydrolysis in the 50-day experiments may explain the observed difference in behavior of the carbon isotopes compared with the 7-day experiments. The isotopic compositions of the residual free cyanide would under these circumstances have been controlled by isotopic partitioning among CN^- , HCN_{aq} , HCN_g , NH_3 , and HCOO^- .

Using the fractionation factors in table 1 one can predict the isotopic signatures that short-duration evaporation, complexation, and longer-duration evaporation (+hydrolysis?) would leave in the residual free cyanide. Figure 5 illustrates the trajectories of the residual cyanide on a $\delta^{15}\text{N}$ - $\delta^{13}\text{C}$ plot starting at a typical initial isotopic composition. The trajectories would represent samples collected over a period of time at one location or samples collected simultaneously at different locations along a process water or wastewater flow path.

Figure 5 demonstrates that cyanide loss can indeed fractionate the stable carbon- and nitrogen-isotopes. For the conditions of the experiments, short-duration evaporation, complexation with ferrous iron, and longer-duration evaporation (+hydrolysis?) produce different slopes on a $\delta^{15}\text{N}$ - $\delta^{13}\text{C}$ plot and are therefore distinguishable from one another using isotopic analysis. A further distinction among the mechanisms is that the isotopic shifts for complexation are smaller than for an equivalent amount of evaporation (or evaporation+hydrolysis).

FUTURE DIRECTIONS

Overall, we are encouraged that isotope techniques will be useful in monitoring cyanide loss. It is important to point out though that there is a wide variation in cyanide behavior in real leach circuits because of the complex and variable nature of these systems. Isotope measurements will be of little value in the absence of other chemical data. To fully understand isotope behavior in mine process waters and wastewaters, it will be important to determine fractionation factors for other cyanide loss mechanisms and to know the sensitivity of those factors to temperature, pH and other possible rate-controlling parameters. The most important developmental step, however, will be to make empirical observations at active and abandoned mines.

Beyond their potential for environmental monitoring of cyanide, isotopic tools may also be of use in mine planning. Tools that improve the understanding of cyanide behavior in bench-scale or pilot plant tests may lead to improved designs for leach circuits, for cyanide recovery processes, or for wastewater treatment processes.

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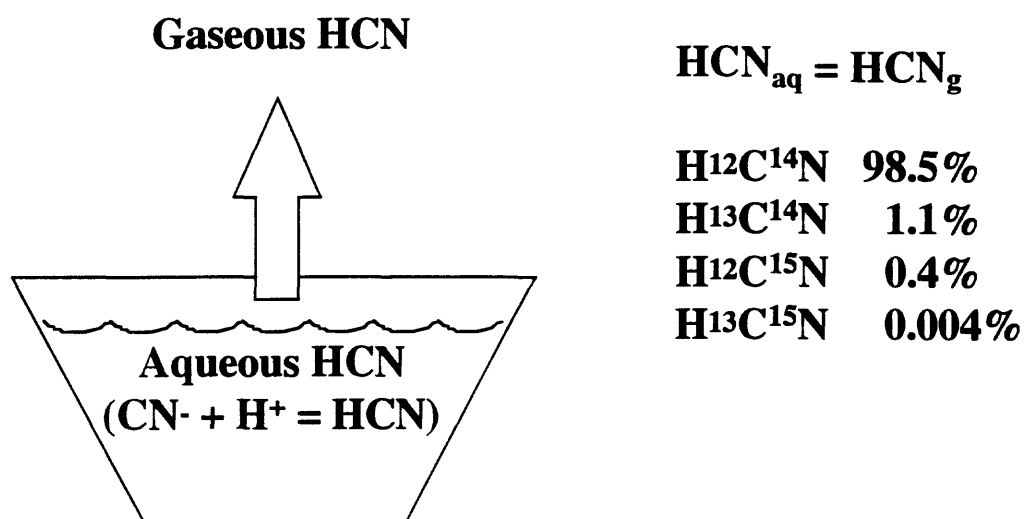


Figure 1. Schematic illustration of HCN evaporation from a standing solution. Dissolved CN^- and dissolved HCN maintain chemical equilibrium. The approximate natural abundances of the different isotopic species are given for the HCN molecule.

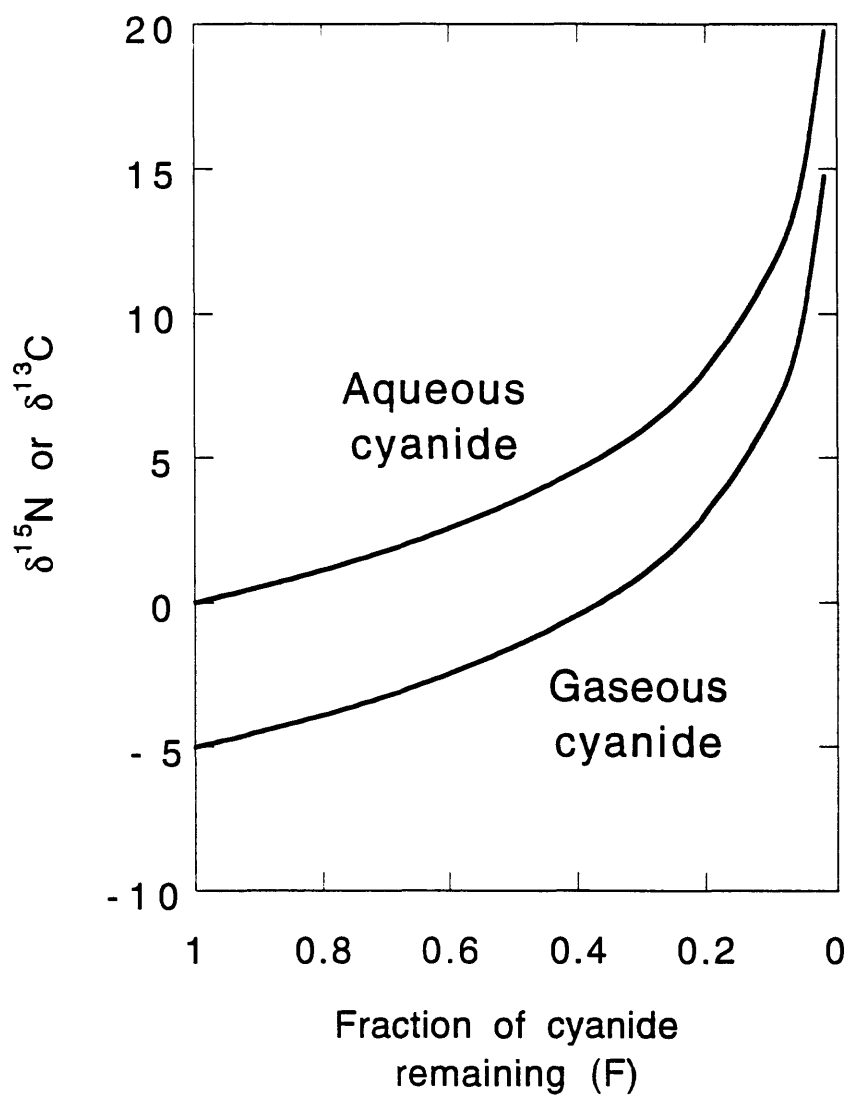


Figure 2. Behavior of the isotopes during progressive HCN evaporation for the hypothetical case where $\alpha=0.995$ and $\delta_{\text{free cyanide-initial}}=0\text{‰}$. The isotopic compositions of the gaseous HCN and the residual aqueous cyanide are shown.

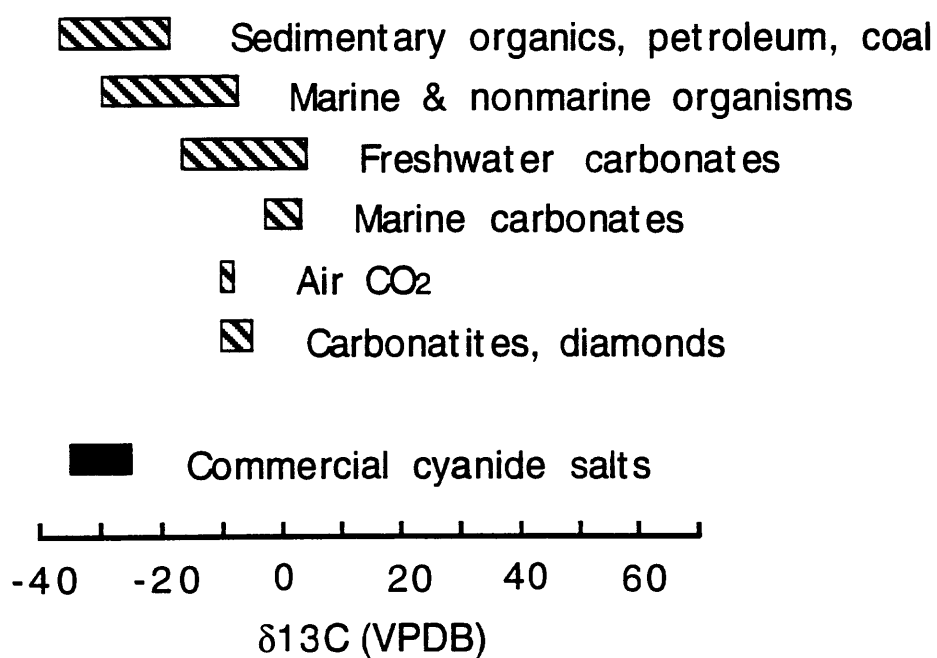


Figure 3. The $\delta^{13}\text{C}$ values for commercial cyanide compounds compared with the values characteristic of several natural materials.

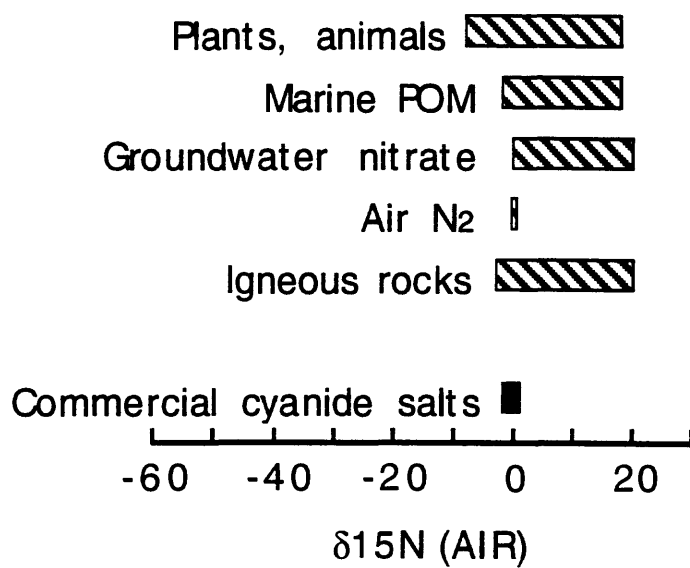


Figure 4. The $\delta^{15}\text{N}$ values for commercial cyanide compounds compared with the values characteristic of several natural materials.

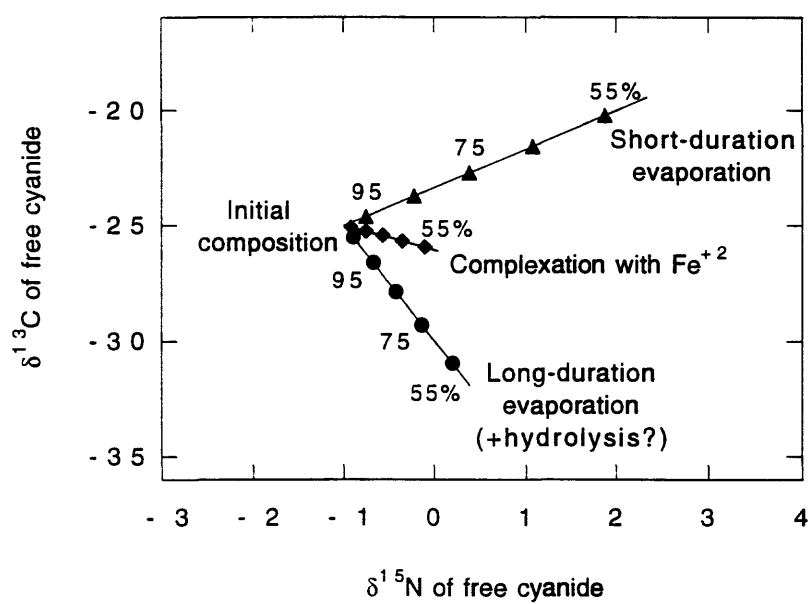


Figure 5. The isotopic shifts in dissolved cyanide that are predicted to accompany progressive evaporation and progressive complexation with ferrous iron. Percentages refer to the amount of cyanide remaining in solution.

Table 1. Isotopic fractionation factors (α) for two cyanide loss mechanisms, evaporation as HCN and complexation with ferrous iron, determined from laboratory experiments. The 50-day evaporation results may reflect some degree of cyanide hydrolysis (see text).

Reaction	α_C	α_N
free cyanide -> HCN_g (7 days)	0.9920	0.9952
free cyanide -> HCN_g (50 days)	1.0101	0.9980
free cyanide -> Fe(CN)₆⁴⁻	1.0016	0.9985