A discussion on the dissolution rate of gold in alkaline cyanide solutions or - "Why worry about oxygen?"

J. O. Marsden
April 27th, 1987

Primary conclusion: The dissolution rate of gold in alkaline cyanide solutions under atmospheric conditions, and at practical cyanide levels, is directly proportional to the dissolved oxygen concentration.

Following some interesting discussions with Larry Todd and Bill Pennstrom at Mesquite last year, and as a result of recent corporate interest in oxygen 'purging' and the Kamyr Oxygen Process, I have been inspired (?) to look into some solution chemistry theory.

The rate of dissolution of gold in alkaline cyanide solution is dependent on a number of factors, principally the solution composition (pH, complexant concentration), the redox potential (oxidant concentration), the surface area of the gold, temperature and mass transport rates (mixing).

In a practical situation, several of these factors can be ignored since they are either constants or we have no direct control over them:

1) Temperature

Under atmospheric leaching conditions there is little that can be done to control the temperature - we will assume that it is a constant for the purposes of these calculations.

2) Surface area of gold

This is a function of the mineralogy in the case of heap/dump ores. For milled ores the surface area will be a function of the mineralogy but may also be affected by the grinding process (actual grinding of gold particles). This effect is approximately constant for grinding to a particular liberation size and can be ignored.

3) pH

There is a narrow operational pH 'band' within which we need to operate. The pH conditions for gold dissolution to occur are illustrated in figure 1, the Eh-pH diagram for the

gold-cyanide aqueous system. The area above the O_2/H_2O line represents the Eh-pH range under which oxygen reduction can occur (and corresponding oxidation of gold). Below pH 9.5 cyanide is lost by hydrolysis. At high pH cyanide consumption is unnecessarily increased. (See J. Arnold note, Golden Opportunities, Feb 87.) And in the extreme case, the gold becomes passivated.

We will assume that the pH is 'fixed' at an optimum safe value of 10.5.

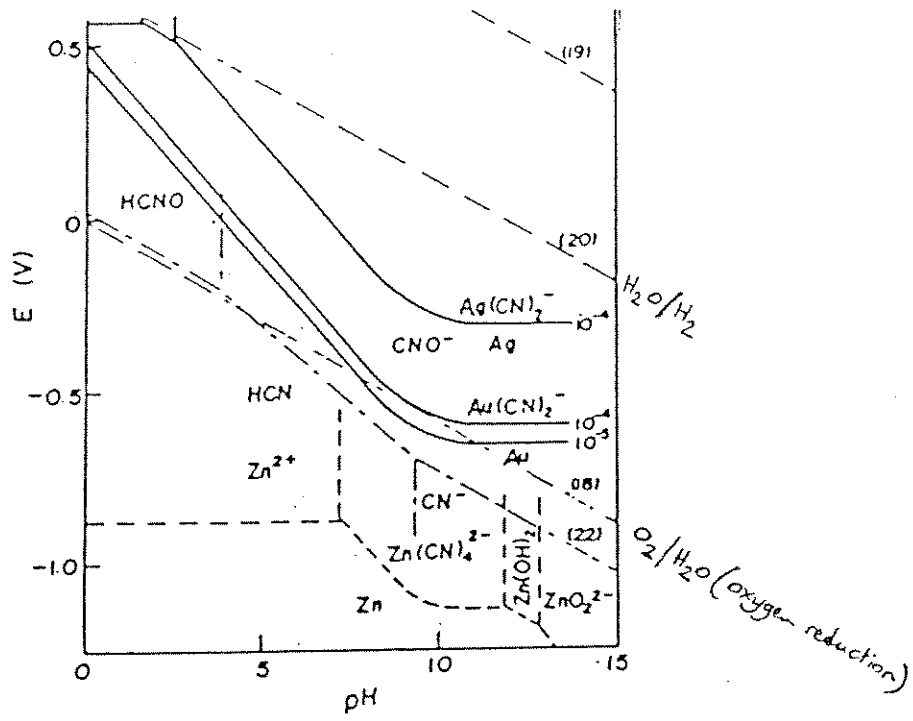

Figure 1: Eh-pH diagram for cyanidation processes.

This leaves the complexant concentration [CN-], oxidant concentration $[O_2]$ and mass transport rate considerations which will be discussed in more detail.

There are five steps in any dissolution reaction. One, or any combination, of these will determine the overall reaction rate:

(1) Bulk transport of species to the boundary layer surface

(2) Diffusion of species through the boundary layer at the mineral surface

(3) Chemical reaction between species

(4) Diffusion of reacted species through the boundary layer at the mineral surface

(5) Bulk transport of reacted species away from the boundary layer

We will assume that (1) and (5) are fast, or at least that they are much faster steps than (2) or (4) and that they do not affect the overall rate. In the case of vat or tank leaching the extent of mixing will determine the bulk transport rates. For heap/dump leaching the solution percolation rate, size distribution of ore, uniformity of heap construction, even-ness of solution spray application and many other factors will affect the bulk transport rate.

We will also assume that the chemical reaction (3) is fast (in comparison to the chemical diffusion processes) and that cyanide and dissolved oxygen are consumed as soon as they reach the gold surface. According to the literature this <u>is</u> a reasonable assumption to make - the rate of gold dissolution is not electrochemically controlled but rather "mass transport" controlled. (Note: "mass transport" includes both "bulk transport" and "diffusion" of species)

This leaves us with the diffusion of ionic species (CN^-, O_2 $An(CN)_2^-$, etc.) to and from the gold surface through the boundary layer as the rate determining factors. It has been shown experimentally that the diffusion rates of species away from the mineral surface are not rate detemining i.e. the overall diffusion rate away from the mineral surface is > the diffusion rate of species to the mineral surface. This means that the diffusion rates of CN^- and O_2 to the mineral surface determine the rate of gold dissolution.

Starting from first principles: Fick's law, which is used to describe linear diffusion rates, states that;

$$j = -D \frac{dc}{dx} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where: j = diffusion rate of a particular species
D = diffusion coefficient for that species
$\frac{dc}{dx}$ = concentration gradient in the solution

In a real system, where we have a boundary layer at the mineral-solution interface, dc/dx is obviously non-linear. (see figure 2) Nernst suggested that Fick's equation could be simplified by assuming a linear gradient over a distance, δ, from the mineral surface. (δ - the Nerst diffusion layer thickness)

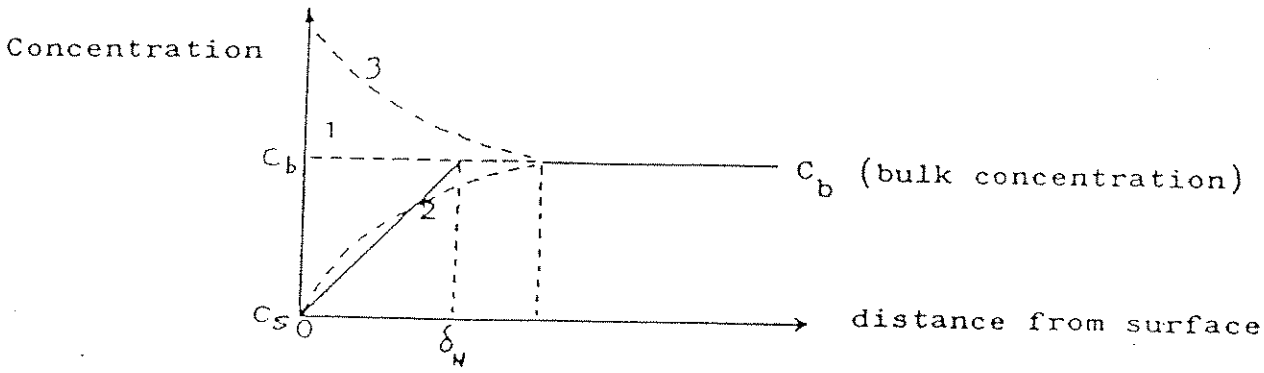

Figure 2: Concentration profiles in the steady state boundary layer (Nernst)

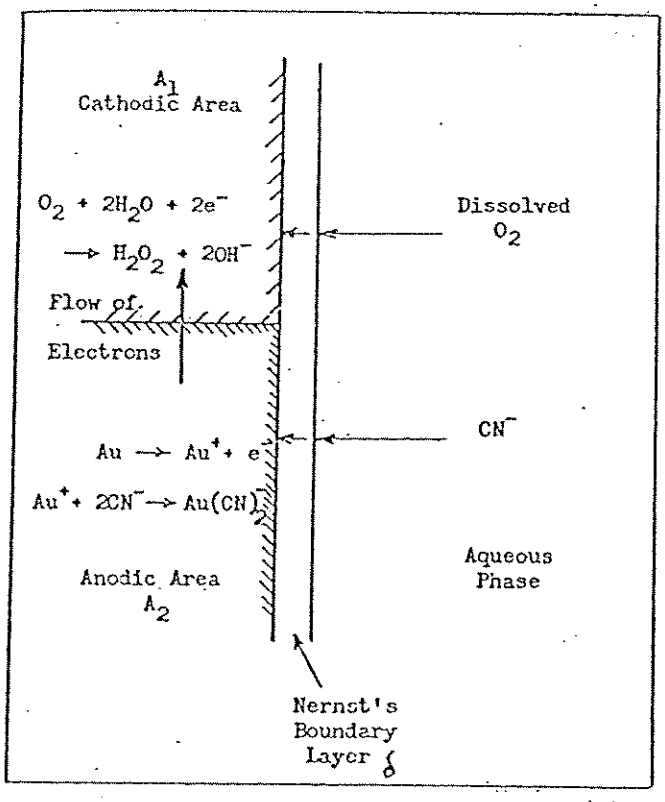

Figure 3: Schematic representation of the dissolution of gold in alkaline cyanide solution

The expression then simplifies (?) to:

$$j = \frac{-D(c_b - c_s)}{\delta} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

where: c_b = concentration of species in bulk solution
C_s = concentration of species at mineral surface

From this boundary layer theory we know that $c_s = 0$, so....

$$j = \frac{-Dc_b}{\delta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

If we now consider the generally accepted gold dissolution reaction;

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

(see figure 3)

Then, from its stoichiometry (the number of moles of each species involved) we can deduce that, for the dissolution of one mole of gold, half a mole of oxygen and two moles of cyanide must diffuse to the gold surface.

The 'critical' (or optimum) condition for gold dissolution is that the diffusion rates of the two species (cyanide and oxygen) be the same and be maximized ie. if the diffusion rate of one species is lower than the other, the overall rate is limited by the lower value.

At this critical condition: $j_{CN} = j_{O_2}$

$$\text{ie.} \quad \frac{1}{2} \times \frac{D_{CN}[CN^-]}{\delta} = 2 \times \frac{D_{O_2}[O_2]}{\delta} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

which simplifies to $D_{CN}[CN^-] = 4\ D_{O_2}[O_2]$ .....(5)

Since D_{CN} and D_{O_2} are known constants (1.83×10^{-9} and $2.76 \times 10^{-9} m^2 sec^{-1}$ respectively) we get that;

$$\frac{[CN^-]}{[O_2]} = 6 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

This we will call the "critical cyanide - oxygen ratio".

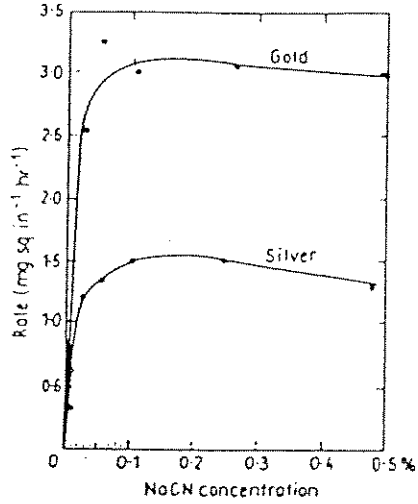

Figure 4: Effect of cyanide concentration on dissolution rate of gold and silver

Figure 4 shows the variation in gold dissolution rate with cyanide concentration. The dissolution rate increases linearly up to a cyanide concentration of about 0.03% NaCN. The maximum dissolution is obtained at approximately 0.15% NaCN after which the curve flattens out and the dissolution rate actually starts to decrease.

This data compares well with results obtained from many other sources and cyanide strengths agree with those used in practice!

If we substitute a value of [CN-] = 0.05% (corresponding to 0.1% NaCN) back into equation 6 above, we get a required dissolved oxygen concentration of 83 ppm to give maximum dissolution rate. At oxygen concentrations below this critical value the dissolution rate is proportional to the dissolved oxygen concentration.

Unfortunately the maximum dissolved oxygen concentration attainable at sea level under atmospheric conditions of temperature, pressure and oxygen content of the air (21%) is 8.2 ppm, and this value drops with height above sea level as the partial oxygen pressure drops.

Location	Approx. Elevation (ft)	Approx. Dissolved Oxygen Conc. (ppm)
Mesquite	700	8.0
Chimney Creek	5,200	6.7

We have no way of achieving 83 ppm dissolved oxygen under atmospheric conditions. Consequently the dissolution rate of gold for atmospheric leaching is directly proportional to the dissolved oxygen content of the solution under the conditions described.

In fact, by re-substitution of a realistically attainable dissolved oxygen value (ie. 8 ppm) back into the critical-ratio formula (equation 6), it can be seen that the rate is dependant on dissolved oxygen concentration down to a cyanide concentration of approximately 0.01% NaCN. Below this value, the rate is dependent on cyanide concentration.

Conclusions

(1) Under atmospheric leaching conditions, the dissolved oxygen content of a leach solution must be maximized to maximize dissolution rate of gold.

(2) No kinetic advantage is gained by operating at cyanide concentrations above 0.01% NaCN under atmospheric conditions. In practice, the cyanide measurement should be made for solutions coming out of heaps/dumps or grinding circuit pregnant solutions (after leaching) to ensure that 'safe' operating levels of cyanide are maintained during leaching. Realistic operating levels are 0.02% - 0.025% NaCN but some ores (high cyanide consumers) may require operation at higher values.

This argument provides good motivation for on-line cyanide monitoring and control of cyanide strengths close to the minimum value for maximum dissolution rate: - Operation at strengths higher than the minimum requirement represents a direct waste of cyanide (cyanide broken down by sunlight, lost in side reactions, etc.).

(3) In many cases the rate of gold dissolution may not be an important factor since it has little or no effect on the overall recovery of gold in a system. For example, In the case of heap/dump leach operations, using a "permanent" liner, increasing the dissolution rate will

give a quicker return on an investment but does not necessarily improve the overall recovery. In the Chimney Creek grinding circuit the dissolution rate is an important factor. We are trying to maximize the recovery of gold to a CIC circuit - this relies on fast dissolution of gold during milling and in the subsequent CCD thickener - leach circuit. Maximization of the dissolved oxygen concentration, and consequently the dissolution rate, may be an important factor at Chimney Creek, particularly in view of the relatively low dissolved oxygen concentration attainable at the Chimney altitude. (The relative importance of this will depend on the actual dissolution rates achieved in the plant based on gold particle size, etc.)

(4) Oxygen "purging" during leaching (heap, dump or vat) is a realistic and attractive possibility in applications where accelerated leach kinetics would have a significant effect on the economics of the operation. Increased revenue from either a quicker rate of return or from extra gold recovery must offset the cost of any oxygen "purging" process.

(Oxygen "purging" produces non-atmospheric conditions by increasing the oxygen content in the air (above 21%), thereby increasing the partial oxygen pressure (PO_2) and consequently the dissolved oxygen concentration.)

(5) Increasing mass transport rates in real, operating, systems will serve to reduce the boundary layer at the mineral surface and consequently reduce the "diffusion" distance that ionic species have to travel.(ie. better mixing/agitation in vats, increased percolation in heaps, better stacking in heaps, even application of solution, etc.)

Notes: Atmospheric conditions: Temperature = 298 K
Pressure = 1 Atm
Oxygen content = 21%

[CN-] = Free cyanide concentration (%)

[O_2] = dissolved oxygen concentration (%)

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A few comments on least month's excellent article by John Marsden concerning gold dissolution rates:

Original testwork by Mountain States on Mesquite ore resulted in the conclusion that 2.0 lb/ton sodium cyanide concentrations in leach solutions were needed for optimum gold dissolution rates and maximum overall recovery. As a result, this became the target setpoint during all pilot plant leach tests and continued when leaching commenced at Mesquite in January, 1986. Average NaCN concentration averaged slightly below the setpoint, in the 1.65 to 1.85 lb/ton range, throughout most of 1986. In late December the setpoint was lowered to a 1.25 lb/ton maximum, which has to date resulted in an apparently significant decrease in cyanide consumption. Leach rates have remained constant or improved since the drop in leach solution cyanide concentration. The lowered setpoint was prompted by 1) experience at other heap leach operations with low cyanide solution concentrations, 2) lab and plant observations that tended to support the idea that the original cyanide concentration was unnecessarily high, 3) cyanide consumption in excess of 1.0 lb/ton even during cooler months, and 4) a review of early metallurgical testwork which indicated that the recommendation for a 2.0 lb/ton concentration was based on limited and somewhat sketchy data.

The maximum NaCN concentration target was lowered in late May to 1.0 lb/ton and based on information in John's article has the potential to be lowered again pending additional evaluation. Mesquite ore has few cyanicides and readings taken in the field indicate that dissolved oxygen is typically at or near saturation levels; potentially an ideal situation for low cyanide residuals.

One caveat that John pointed out in his article that I'd like to stress is that in practice some ores do require an unusually high cyanide residual to maintain acceptable recoveries. The ores invariably are high cyanide consumers and not surprisingly they usually are excessive consumers of oxygen. Undoubtedly some leach problems have been tackled by adding excessive amounts of cyanide when the underlying problem was a lack of dissolved oxygen in the leach solutions.

An extreme case of ore requiring high cyanide residuals are the gravity or flotation concentrates that are processing by intensive cyanidation. Based on literature I've read the process usually involves intense agitation/aeration and cyanide concentration of 10 lbs/ton or more. If anyone is familair with this type of process I'd be interested the hearing comments concerning 1) Are high cyanide residuals maintained throughout this type of intensive leach and if so, 2) Why? What solution chemistry is involved that alters the leach kinetics in systems with cyanide consumers that apparently supercedes predicted kinetics in a "clean" leach solution?

Larry Todd 6/1/87

Footnote to: "A discussion on the dissolution rate of gold in alkaline cyanide solutions"

John O. Marsden
May 29, 1987

In a well-agitated slurry system (where the bulk transport is not the rate controlling factor) the gold dissolution rate actually drops as dissolved oxygen concentration increases above about 20 ppm (mg/l). This is apparently due to "passivation" of the gold at the surface (oxide layer formation). This really blows my theoretical observation that the optimum dissolved oxygen concentration for gold dissolution is 83 ppm! Actually it would be true if this "passivation" effect did not occur. Realistically we can only hope to achieve somewhere in the order of 15 ppm dissolved oxygen in solution by purging with pure oxygen in an agitated tank under atmospheric conditions.

In a poorly agitated system (where the rate is at least partially controlled by bulk transport of ion species), such as a heap or dump leach, this passivation effect is not as prominent since even at high oxygen concentrations only a small amount of the oxygen reaches the gold surface. I have no idea what sort of dissolved oxygen concentrations we could hope to achieve in heap leach solutions using some kind of oxygen purging system but it is extremely unlikely that we would ever observe oxygen passivation effects.

Is anyone measuring dissolved oxygen concentrations in agitated slurry leach systems, heap/dump leach feed and run-off solutions, etc.? If so it would be interesting to hear some figures.

Incidentally, there's only one dissolved oxygen meter out there that works so far as I know: the Leed and Northrup Model 7931 Dissolved-Oxygen Analyzer. It has a protective membrane covering the probe to protect against abrasion/corrosion. This does affect the response time slightly. The instrument is robust, reliable and fairly cheap.

I was very interested by Larry Todd's comments in last month's "GO" which provide real encouragement for reducing cyanide strengths, and consequently consumptions, in our plants.

As further follow-up, I have some responses to some of the other points that he raised in his discussion: I am not directly familiar with intensive cyanidation procedures but my understanding in this area is as follows:

Intensive cyanidation falls into two categories;

(1) Intensive cyanidation of ores/gravity concentrates containing coarse or coated gold

(2) Intensive cyanidation of ores/flotation concentrates with high sulphide content or gold locked in sulphides

(Intensive cyanidation refers to anything from running an atmospheric leach at elevated cyanide concentrations to operating a high temperature, high pressure leach at high cyanide strengths.)

In the case of category (1) processes, elevated cyanide concentration alone will not increase the dissolution rate of gold. Elevated pressures and temperatures do increase the rate of dissolution - well documented in the literature. For operations that perform intensive cyanidation on category (1) materials on a batch basis, then elevated cyanide strengths are required to maintain adequate residual cyanide strength in solution throughout the leach. (Cyanide consumption by gold dissolution and side reactions.) It should be noted that at elevated temperatures and pressures (ie. above atmospheric) the rate of cyanide-consuming side reactions is greatly increased.

I have read somewhere (?) that in one particular instance, it was claimed, elevated cyanide strengths helped with the dissolution of coated gold - not very amenable to normal cyanide levels.

The same factors discussed for category (1) processes apply to category (2) processes. In addition, materials treated in category (2) contain high cyanide consumers: Under normal cyanidation conditions free cyanide is used up by "cyanicides" making it unavailable for gold dissolution. In this case intensive cyanidation provides enough cyanide to maintain adequate free cyanide strength for gold dissolution to occur in the presence of cyanicides. Initial cyanide levels required in such a batch process may need to be very high indeed to maintain adequate cyanide strength throughout the leach.

In some cases the gold is completely locked in sulphide material. It has been shown that intensive cyanidation significantly affects the leaching rate of sulphides ie. increasing cyanide strength increases the rate of dissolution of sulphides. This indirectly affects the dissolution rate of gold in that locked gold becomes liberated, or at least exposed, more quickly.

In summary;

(a) Increased cyanide strength* alone does not have any direct effect on gold dissolution rate. Elevated temperatures and pressures, combined with maintaining adequate residual cyanide concentration in solution, do significantly increase gold dissolution rate.

(b) Increased cyanide strength <u>does</u> increase the dissolution rate of sulphides, which may indirectly increase the gold dissolution rate by faster exposure of gold values locked in sulphides.

John Marsden
8/4/87

* ie. above 0.02 - 0.03% NaCN typically

I've got a couple comments on Larry Todd's comments on John Marsden's article. At Ortiz we ran into a some pyrrhotite and marcasite when the ore went from oxide to sulfide in 1983. We went through several machinations to solve the problem and one discovery that we made was that our recovery was almost linearly proportional our cyanide concentration between cyanide concentrations of .7 and 1.0 g/l (as sodium cyanide). We chocked this off to the activity of the pyrrhotite:

1) consuming the oxygen as pyrrhotite causes:
   $2S + 3O_2 \rightarrow 2SO_2$ and later consuming more oxygen in the formation of sulfuric acid,
2) precipitating gold as the ferrous iron oxidizes to ferric iron, reducing the oxidized gold,
3) the reduction in pH with the formation of the acid.

We figured that these rotten guys, pyrrhotite as well as marcasite (except for item 2 above because marcasite is already ferric), were causing us a bunch of problems, so the logical solution was to kick up the cyanide to overcome the cyanicide effects of items 1 and 3 and to releach the gold from item 2. It worked! The increased cyanide helped the recovery proportionally until we got over 1.0 g/l. The ringer was that when we went from the oxide ore to the sulfide our cyanide consumption actually dropped! We went from a consumption of about .7 g/ton to about .4 g/ton, which is low by about anyone's standards.

What happened?

We figure that the oxide material (which used to be sulfides) probably had some residual sulfide salts that were redesolving in the leach cycle and gobbling up our cyanide. The sulfides hadn't oxidized yet, so the only sulfides that were causing problems were the ones that were present as pyrrhotite and marcasite.

At any rate I point this out mainly to show that there are ores that need to have their cyanide concentration in the gram per liter range. It seems the latest rage is to run a circuit at a quarter gram and that's fine, if it works. But I suspect that a lot of the time this is pressure from the manager to keep the solution low enough to keep the migratory bird kill problem to a minimum and not based on sound metallurgical practice.

Jim Arnold
9/6/87