Modeling Cyanide Degradation in Heap Leach Systems: From Laboratory to Reality

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Abstract

Heap leaching is a common technique used to extract gold and other metals from generally low grade ore. Gold is typically mobilized by leaching with cyanide; the success of this technique is driven by its reasonable cost. However cyanide toxicity requires that management strategies be put in place during operation and after closure to prevent any impact to the environment and potential receptors.

This case study presents a gold cyanide leach operation where the aim was to quantify and predict the life expectancy of cyanide species after closure in order to assess closure options and design appropriate mitigation strategies. This duration was predicted by modeling the flux of cyanide through the heap leach, determining the speciation of cyanide between the different reservoirs of the system and assessing the effects of natural degradation mechanisms.

The predictions were run for 20 years and the results indicate that the majority of the cyanide mass at any given time is within the core mass of the heap, while the lowest concentration occurs on the upper heap leach pad. From an initial Total cyanide concentration in excess of 900 mg CN/L at closure, the simulations predict cyanide concentration to remain above local comparable regulatory values for up to 10 years.

Based on the approach here, closure of this heap will require significant inventory reduction through evaporation or water usage or active treatment prior to environmental release.

Key words: case study, cyanide degradation, heap leach, modeling

Introduction

Heap leach mining is a technique used to extract gold and other metals from generally low grade ore where the target material is placed on an impermeable liner and sprinkled with a leaching solution. Gold is generally mobilized using cyanide; the success of this technique is driven by its reasonable cost. However cyanide toxicity requires that management strategies be put in place during operation and after closure of the mining operation (Botz and Mudder 2000) to prevent any impact to the environment and potential receptors.

The ore, deposited on the heap leach pad ore is leached using cyanide solution. Where leachable copper is present in the ore then the rate of cyanide usage is comparatively high, and the resultant cyanide concentrations in the barren and pregnant leach solutions are high; typically in excess of 300 mg/L cyanide.

At closure the active irrigation of the heap leach pad will cease, however, draindown of cyanide bearing fluids will continue for an extended period. Completion of the closure phase of the mine may be dependent upon the cyanide concentrations decreasing to within acceptable limits. Cyanide removal from the system occurs through three main processes, the volatilization of the cyanide into the atmosphere, degradation into breakdown products through biodegradation and cyanide photodissociation by ultraviolet light (Mudder et al., 2000; Parshley et al 2012).

This case study aims to quantify and predict the life expectancy of cyanide species after closure in order to assess closure options and design appropriate mitigation strategies. This duration was predicted by modeling the flux of cyanide through the heap leach pad, determining the speciation of cyanide between the different reservoirs of the system and assessing the effects of natural degradation mechanisms.

Method

Case study

This paper considers a heap leach gold mine using cyanide to mobilize gold. In order to anticipate closure and the different closure strategies SRK modeled the heap leach system once operations have stopped. After mine closure the solution circuit will be shut down and the solution will no longer be processed. Due to a large copper load in the system the cyanide concentrations are anticipated to be high (in excess of 900 mg/L) and the seepage volume from the heap will exceed the volume of the Storage Pond. The solutions will therefore be managed by continuing to irrigate the heap with solution from the Storage Pond.

Conceptual model

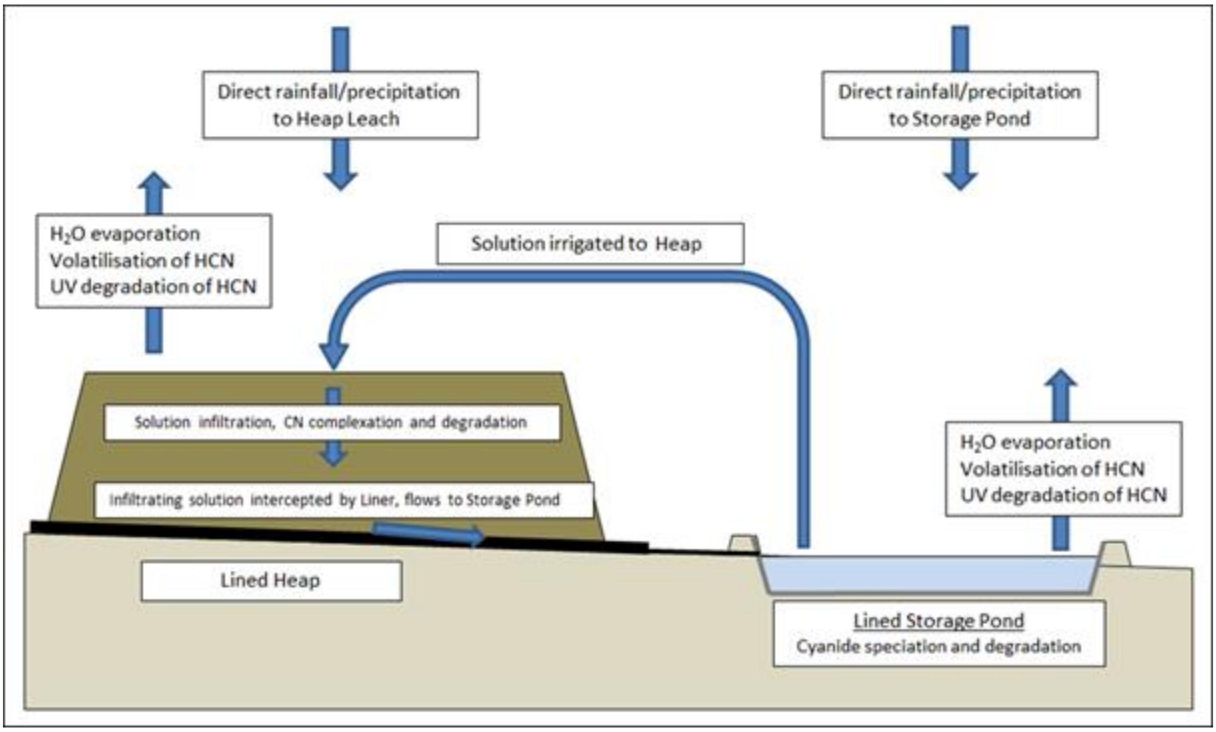

***Figure 1** : Conceptual model of the system*

The conceptualization of the post-closure fluid handling is shown schematically in Figure 1. Solution draining from the heap will flow to the Storage Pond, which will be spray-irrigated back to the Heap Leach. The only additional water inflows to the system are from direct rainfall/snow, it will percolate through the heap to the liner, where it will drain to the Storage Pond. Whilst the cyanide concentrations are elevated there will be no discharge of the waters. Therefore, the only solution losses from the circuit will be evaporation from the Storage Pond and from the heap. Evaporation is determined to significantly exceed rainfall/snow, such that the circuit will lose water over time. As the solution inventory decreases the rate of drainage will decrease, as will the degree of saturation of the Heap Leach.

Cyanide bearing solution will drain from the heap to the Storage Pond. Cyanide concentrations in the Storage Pond will decrease primarily as a result of the breakdown of cyanide by ultraviolet light and the volatilization of HCN gas into the atmosphere. The rates of cyanide degradation will be dependent upon cyanide speciation e.g. iron cyanide and copper cyanide complexes must first degrade to free cyanide species (CN^-) before the cyanide can be lost by breakdown or volatilization. Spray irrigation of the Storage Pond solution to the surface of the heap will permit further losses of cyanide by volatilization to the atmosphere and degradation by UV breakdown. Solution at the near surface of the heap will be subject to further volatilization, but not to UV breakdown.

As solution migrates through the heap mass there will be further attenuation/breakdown of cyanide by bacteria and/or oxidation processes, however, these processes are much slower than losses to the atmosphere and via UV breakdown and were therefore neglected in this study.

Numerical model

The numerical model for the draindown/water balance calculations of solution from the heap leach pad is based upon the HLDE model Version 1.2 (JBR Environmental Inc. and Newmont Mining Corporation 2011). However, a bespoke model was developed in order to incorporate the calculation of cyanide degradation/losses at different stages in the model.

As illustrated in Figure 1 the model has two main reservoirs – the heap leach pad and the storage ponds, from which water is transferred by pumping and irrigation, moved by seepage and lost by evaporation, each resulting in a change in storage for the different reservoirs on a daily timesteps. In order to allow for different cyanide attenuation mechanisms the water balance split the Heap Leach Pad into two 'reservoirs', an Upper Heap Leach Zone, and a Lower Heap Leach Zone, with the seepage from the Lower Heap Leach then draining to the Storage pond.

The Upper Heap Leach Zone is a thin zone (0.5 m) at the surface of the heap where evaporation and cyanide volatilization losses can occur. Solution in the Upper Heap layer is allowed to infiltrate through to the Lower Heap layer at a rate equal to the irrigation rate.

The Lower Heap comprises the bulk of the heap and contains the majority of solution and cyanide mass. Degradation of cyanide in the Lower Heap is limited to conversion/equilibration of cyanide species and a slower rate of degradation; there are no losses of HCN by volatilization, and no degradation of HCN by UV light.

Solution draining from the Heap Leach enters the Storage Pond. Within the Storage Pond the cyanide is subject to volatilization as HCN and degradation by UV light, including the photolysis of complexed metal-cyanide species to HCN and CN^-.

The HLDE model is based on the Corey and Brooks (1964) equation to represent how the hydraulic conductivity varies with saturation. Because water flows more easily through saturated media, as the degree of saturation decreases the hydraulic conductivity will decrease proportionally. This model also applies the Brooks and Corey (1964) equation to correct the drainage rate as the moisture content decreases.

$$K(\theta) = K_S \left(\frac{\theta - \theta_r}{\theta_{sat} - \theta_r} \right)^{\gamma}$$

Where: Θ is the volumetric moisture content

K_s is the saturated hydraulic conductivity

Θ_r is the residual moisture content

Θ_{sat} is the porosity or saturated moisture content

γ is an empirical parameter related to grain size distribution

Gamma is an empirical factor, and data are not available for it. The gamma value is dependent upon the pore size distribution, with crushed ore the value is typically less than10. Gamma values greater than one indicate that the K_{sat} decreases rapidly relative to moisture content, whilst gamma values less than one mean that K_{sat} decreases rapidly reducing moisture content. The hydraulic conductivity of the heap is assumed to remain moderately high with reducing moisture content, and as such a gamma value of 0.5 has been applied to the model.

Cyanide speciation and breakdown rates

Cyanide speciation in water is complex, with cyanide partitioning between various soluble and gaseous phases depending upon the solution pH, temperature and other solute chemistry. Each cyanide species behaves differently with respect to dissociation and breakdown. Cyanide interactions in natural systems are complex, and cyanide species can undergo volatilization, chemical oxidation, biological oxidation, hydrolysis, precipitation, complexation and sorption.

Studies report that the volatilization of hydrogen cyanide accounts for 90% of the cyanide removed from tailings impoundments (Botz and Mudder, 2000), with the other 10% losses occurring through other mechanisms. The main natural attenuation mechanisms of cyanide destruction occur through degradation under Ultraviolet (UV) light, and through biodegradation, with those processes occurring once the cyanide occurs as free cyanide (HCN and/or CN^-).

Therefore, the key mechanisms for cyanide loss and destruction, as depicted schematically in Figure 2, are dependent upon the conversion of complexed cyanide species to the free cyanide forms. This free cyanide will be subsequently volatilized and/or destroyed. It is understood that the loss of HCN by volatilization occurs according to a first-order rate equation which is directly proportional to the hydrogen cyanide concentration (Botz and Mudder 2000, Simonvic, 1984).

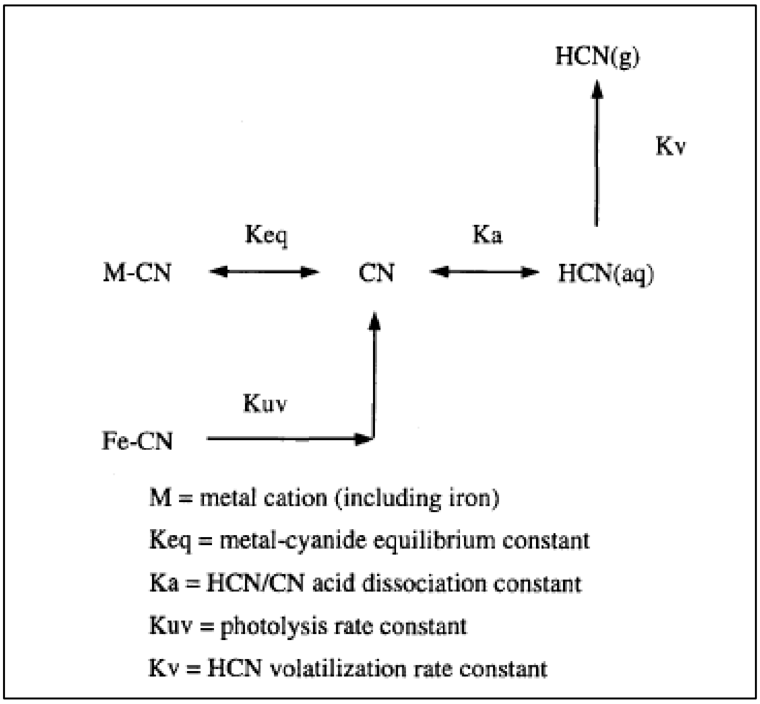

Figure 2: *Routes to Hydrogen Cyanide volatilization (from Botz and Mudder, 2000)*

The relationships shown in Figure 2 can be summarized as follows:

- HCN is lost by volatilization,
- CN^- is at equilibrium with HCN based on the equilibrium constant,
- Photolysis converts Fe-CN to Fe(dissolved) and CN^-,
- Me-CN complexes convert to metal ions (dissolved) and CN^- based on equilibrium constants.

The slowest steps in the process are the dissociation of Fe-CN and Me-CN to release cyanide. These processes are therefore the rate determining steps for the release and loss/destruction of cyanide.

Measurement of specific individual elemental-cyanide complexes is rarely undertaken. However, the cyanide speciation was calculated using the site aqueous metal concentration and the cyanide concentration. This speciation was used to define the initial cyanide distribution between the different cyanide species/complexes. The solute chemistry model includes speciation for different cyanide species, primarily to assess the partitioning of cyanide into HCN which can then be lost by volatilization. The majority of the cyanide in solution is retained as copper complexes, which then are assumed to rebalance the distribution as HCN is lost. This approach avoids the assumption that all cyanide can be lost as HCN.

It was assumed that the cyanide speciation can be calculated using the same proportional distribution of cyanide species as per the initial cyanide source term, with most of the cyanide occurring as copper complexes, with some partitioning into HCN which can then be lost to degradation/volatilization. These proportional distributions may not hold true at low cyanide concentrations where more exact speciation calculations may be warranted. However, given the elevated cyanide concentrations within the heap, this is considered an acceptable simplification for the initial models.

Cyanide speciation is also sensitive to pH, where a greater proportion of the cyanide exists as HCN at pH values below pH 9. This model does not couple the pH and cyanide complexation, instead relying on the assumption that the pH will remain around pH 9. This may be a fair assumption, as the seepage pH will be equilibrated with carbonate species, given the extensive liming of the leach pad that will have been conducted to maintain the operational process solutions around pH 11.

Results

Base Case Model results: Heap Leach draindown

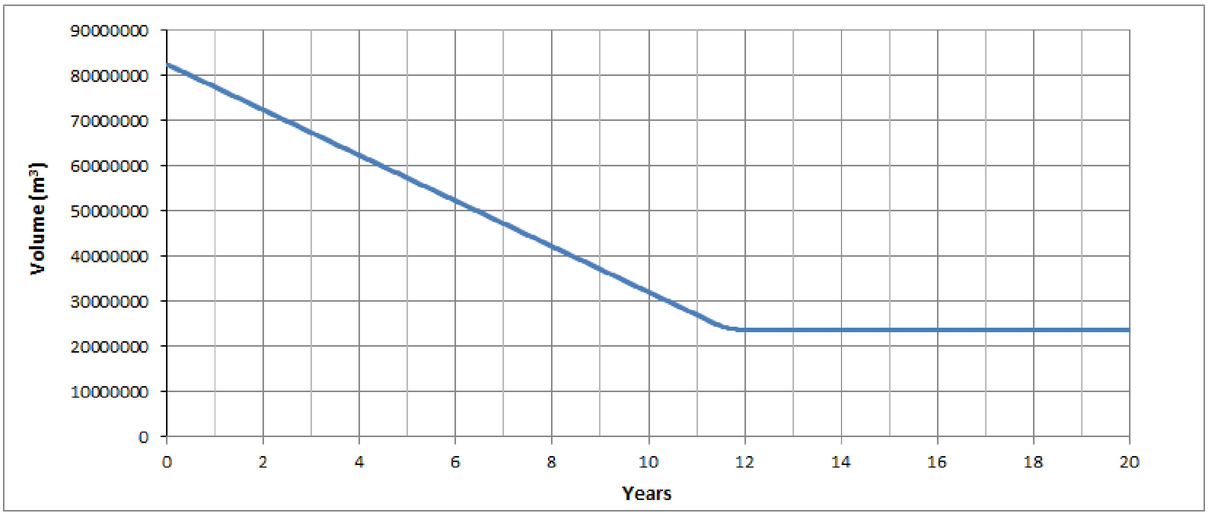

Figure **3** shows the modeled change in water volume within the heap as the draindown period progresses. The change in rate of the heap draindown and the moisture content are plotted in

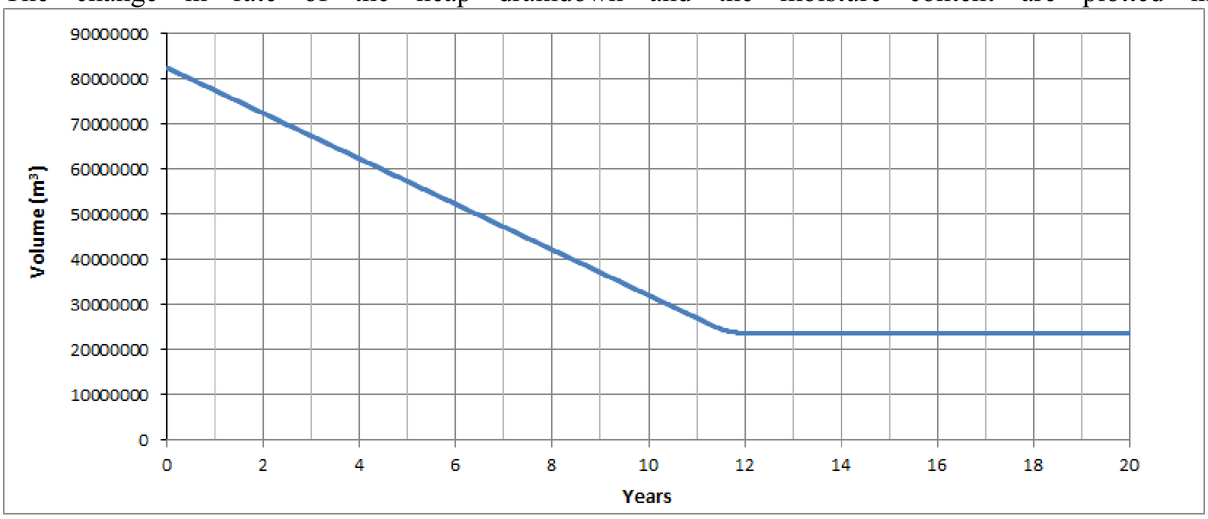

Figure **3**. As the degree of saturation the heap decreases, the rate of seepage also decreases, due to the reduction in the effective hydraulic conductivity. The moisture content within the heap steadily decreases to a point at which the moisture content reaches the specific retention value (assumed to be 10%) such that the net moisture entering the system as recharge is effectively equivalent to the rate of seepage discharging from the base of the heap.

Once the rate of pond evaporation exceeds the seepage rate it is assumed that pumping and irrigation of the water is stopped, and the pond then acts as a net sink of water: water enters from the heap and by rain/snow, and water is lost by evaporation. No pumping or discharge of water occurs. The model predicts that after around 11 years the seepage rate from the heap is less than the pond evaporation rate and that pumping ceases. At that stage the moisture content in the heap remains constant and there is a net loss of water from the storage ponds.

The decreasing volume/moisture content of the heap is linear through time as the simplified water balance assumes that the pumping rate from the heap decreases steadily through time, maximizing the volume stored in the pond and irrigated, thereby optimizing the rate of evaporation and cyanide destruction. Therefore, the average rate of water pumped from the pond and irrigated to the heap is equal to the rate of water draining from the heap to the pond, after accounting for direct rainfall and evaporation.

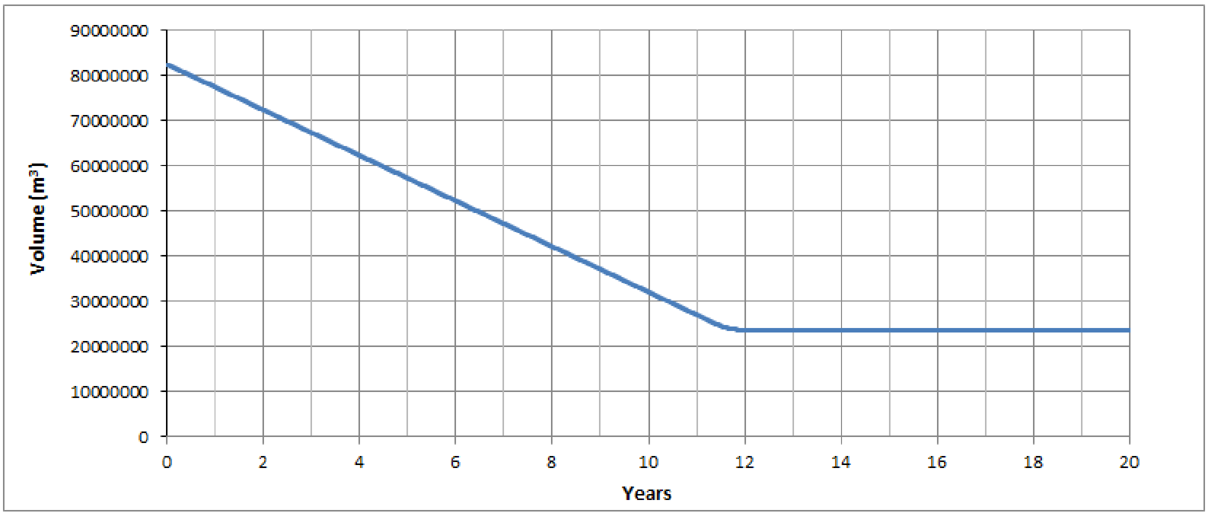

Figure 3: *Reduction in water stored within the Heap Leach Pad for Base Case model*

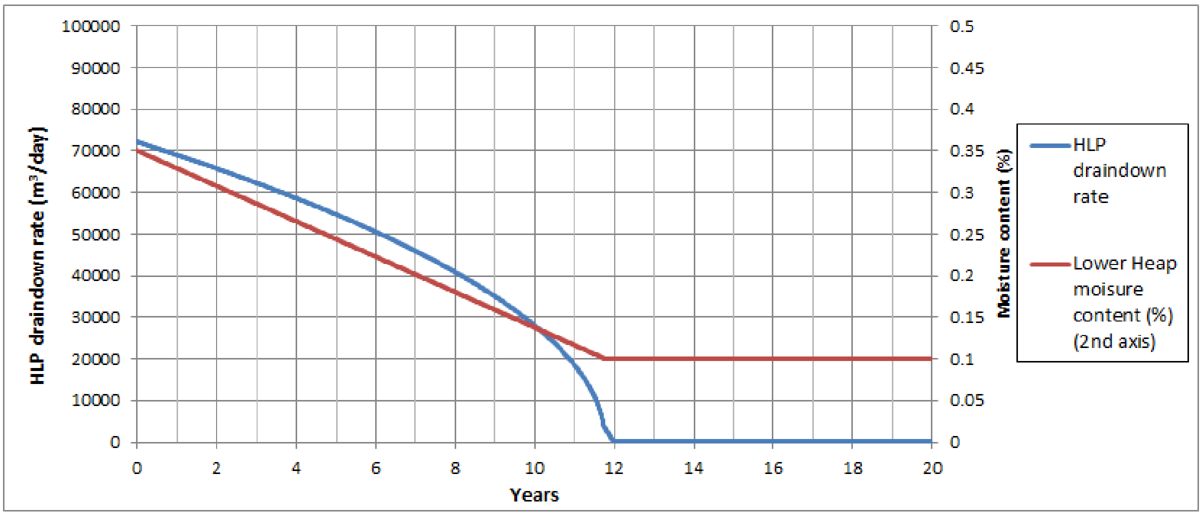

Figure 4 : *Draindown rate and change in heap moisture content*

Cyanide concentrations

The model results are presented as Total Cyanide concentrations to account for all cyanide species present. The modeled cyanide concentrations are presented in

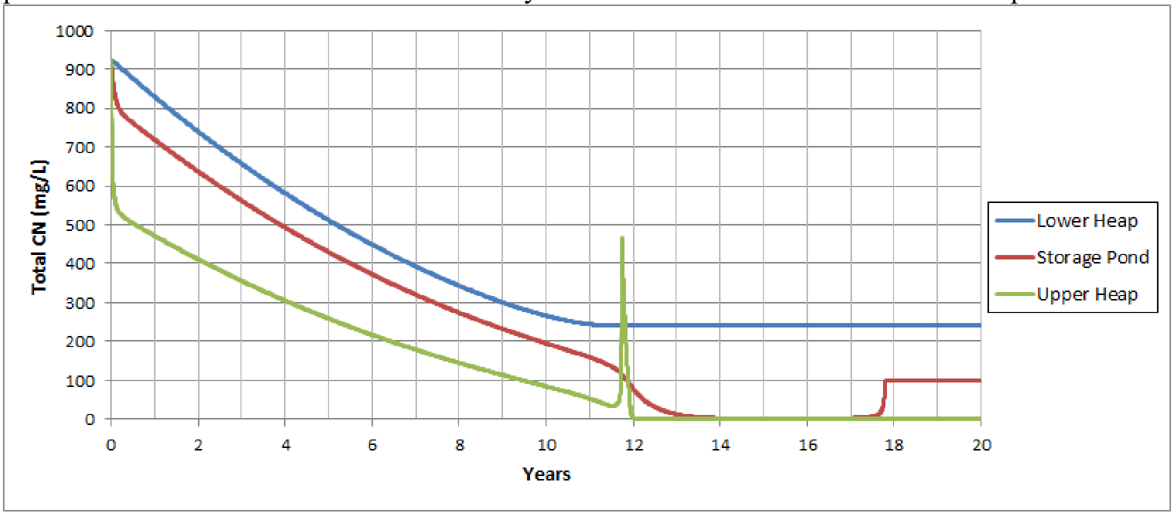

Figure **5**. The model conditions reflect the input conditions and degradation conditions.

The lowest Total Cyanide concentrations occur in the Upper Heap zone; this is because the waters have already experienced cyanide losses in the pond, and are then subjected to further losses due to the enhanced degradation rates applied to the spray irrigated water (with inherent aeration increasing cyanide losses).

The Storage Pond waters also show a more rapid reduction in the Total Cyanide concentration as volatilization losses remove HCN. The removal rates are moderately high, but there is a continual feed of higher cyanide waters entering the pond from the heap seepage.

The highest Total Cyanide concentrations occur in the Lower Heap zone. This comprises the vast majority of the cyanide reservoir at the end of operations. Cyanide is being removed in the seepage waters, and the cyanide added by irrigation is continuously decreasing. However, the overall quantity of water and cyanide retained within the main heap is such that it takes a significant length of time for cyanide levels to decrease, especially as no cyanide degradation is assumed to be active within the Lower Heap zone.

There is a change in behavior at around the 11-12 year stage, at the point when the draindown is less than the evaporation from the storage ponds. The pumping/irrigation to the top of the heap ceases, with the following effects:

- The cyanide concentration in the heap decreases at a much lower rate, as discharge from the heap is at a much lower rate than during the draindown phase and therefore the removal rate of cyanide decreases;
- Cyanide concentrations in the Storage Pond decrease more rapidly, as the residence time in the heap increases and there rate of inflow from the heap decreases. However, the Storage Pond volumes become limited after around 17 years, such that the cyanide concentrations within the reduced pond volume become more elevated (as the pond loses water more quickly than cyanide); and
- Cyanide concentrations in the Upper Heap rise sharply as the moisture content within the thin Upper Layer rapidly reduces once irrigation ceases. The cyanide concentration then reduces rapidly due to volatilization and that no further cyanide is added to the surface.

From an initial Total Cyanide concentration in excess of 900 mg cyanide/L, the modeled seepage concentration from the heap is predicted to be in excess of 800 mg/L after 1 year, over 700 mg/L after 2 years and still be in excess of 200 mg/L after 10 years. When run out for 20 years, the model predicts that seepage from the heap will contain over 200 mg/L Total Cyanide, as it assumes very low further losses over time and no cyanide degradation.

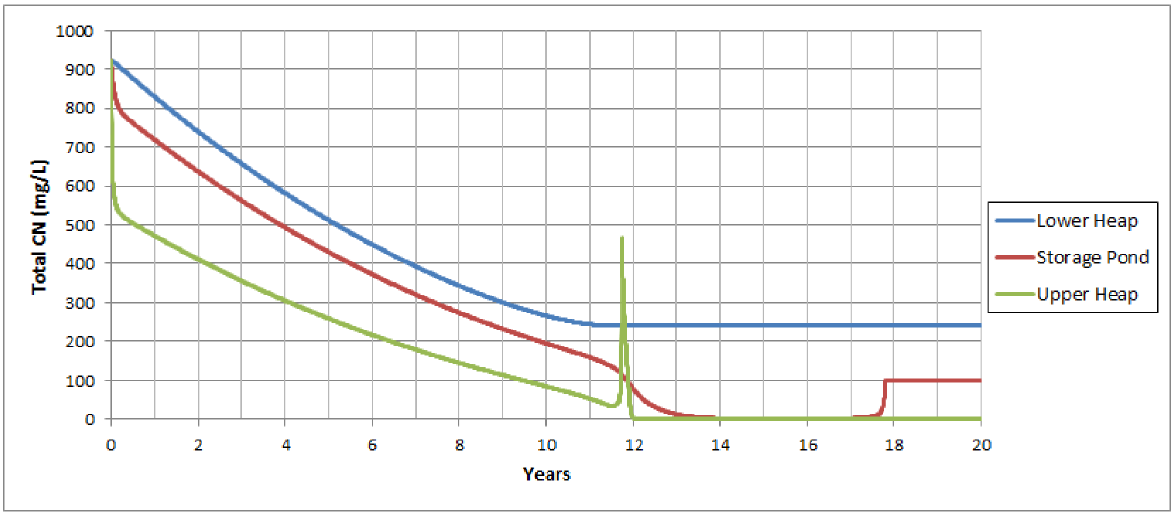

Figure 5 *: Base Case cyanide concentrations in the Heap Leach Pad and Storage Pond*

Conclusion

This study shows a certain cyanide distribution within the heap system due to both the degradation and the management strategy modeled here. Cyanide is shown to be present in lower concentrations in the upper part of the heap due to the volatilization and UV degradation while the main reservoir is the lower heap where the conditions prevent volatilization and UV degradation and consequently higher cyanide concentrations are observed.

From an initial Total cyanide concentration in excess of 900 mg CN/L at closure, the simulations predict cyanide concentration to remain above local discharge values for up to 10 years.

Based on the approach here, closure of this heap will require significant inventory reduction through evaporation or water usage or active treatment prior to environmental release.

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