Quantifying the Effect of Competitive Adsorption of Gold Cyanide and Other Metal Cyanides on Activated Carbon in a Carbon in Pulp Circuit

Haleden Chiririwa, Samantha Chivandire and Ochieng Aoyi

Abstract—The effect of Ag, Ni, Fe and Cu cyanides on gold adsorption on activated carbon in cyanide leach solutions was investigated by synthetic cyanide leach solutions containing gold and other metal cyanides. According to the adsorption tests Ag remarkably reduces the gold adsorption on activated carbon by competing with gold for adsorp t sites. Adsorption tests regarding Au concentrations of 5, 10 and 15 ppm were performed. The Au adsorption recoveries were 99.04%, 98.13% and 97.16% for 5, 10 and 15 ppm Au in solution, respectively. The test with 200 ppm Ag showed the strongest decreasing effect on Au adsorption recovery decreasing it from 98.13% to 83.77%. 250 ppm Ni decreased the Au adsorption recovery to 90.63% and 300 ppm Cu decreased it to 94.59%. When metals are added together to the same solution Au adsorption recovery decreased to 74.92%. When the metals are added together, the adsorption recovery of Au decreased more than that of the metals used separately. Also metals prevent adsorption of themselves as well as that of gold, when they are present in solution together.

Keywords—Adsorption, activated carbon, gold, metal cyanides

I. INTRODUCTION

When gold is mined, the ores contain many other metals which are not gold. These and many other metals, such as Ag, Ni, Cu, Fe, Zn are dissolved with gold from ores as cyanide species. Thus, after cyanide leaching of ores, there are many other metal impurities in the leach solution, competing with gold to be adsorbed on activated carbon [1]. Although this process is still being used by artesian mines in third world countries due to its simplicity, the toxic nature of mercury has made it an unpopular route for gold recovery. Today, cyanide leaching is the method of choice for the recovery of most of the world's gold production.

The cyanidation process is used in operations such as agitated tank leaching, heap leaching, zinc precipitation recovery and carbon adsorption recovery. Activated carbon is used to adsorb the gold directly from the cyanided pulp in a series of six to eight large adsorption tanks. These tanks are arranged in a cascade to facilitate the use of gravity for continuous movement of the pulp. Pulp flows continually from the first vessel to the last in the series, and the carbon is transferred intermittently by pumping it in the opposite (counter current) direction inter stage screens between the tanks prevent the carbon from moving downstream. The gold value of the pulp decreases downstream, and the gold loading on the carbon increases upstream with the highest value in the first tank [2]. The pH of the pulp is maintained in the range of 10 to 11 through the addition of lime. The use of activated carbon to adsorb gold from cyanide solutions was patented as early as 1894, but did not receive much attention until the 1950s [3]. The gold reacts with cyanide according to reaction in eqn (1):

\[
\text{Au}(0) + 2\text{CN}^- + \frac{1}{2} \text{H}_2\text{O} + \frac{1}{4} \text{O}_2 \rightarrow \text{Au(CN)}_2^- + \text{OH}^- \quad (1)
\]

The dissolved gold-cyanide complex \( \text{Au(CN)}_2^- \) is adsorbed on the activated carbon. The barren slurry leaves the process from the last tank and gold loaded carbon is driven from the first adsorption tank. Gold loaded carbon is taken to the elution column in which gold is stripped from carbon and directed to the electrolysis process. Thus, after cyanide leaching of ores, there are many other metal impurities in the leach solution, competing with gold to be adsorbed on activated carbon.

II. EXPERIMENTAL

WET SCREEN TEST

A wet screen analysis was carried out on the activated carbon to determine the size of the carbon. This was done using a 475μm screen. 100g of carbon was transferred to a 475μm screen and water from the tap was allowed to pass through the screen. The carbon was dried in an oven for 12hr and weighed.

CARBON ACTIVITY TEST

The activity of the carbon is the amount of gold adsorbed from a 1000ml pregnant solution of 1ppm (1g/t) of gold of a given carbon sample in a minute expressed as a fraction of the concentration of gold adsorbed by virgin carbon. A pregnant solution is a concentrated solution of gold prior to adsorption. Virgin carbon is fresh activated carbon which has never
entered the adsorption tanks before. Its activity is assumed to be 100%.

Procedure

10 ppm Au was prepared in a 1 l volumetric flask and 1 g of the virgin carbon was weighed out. 11 of 10 ppm (pregnant solution) was poured and the bottles were rolled for about an hour. Carbon in each sample was filtered out after which the solutions were aspirated.

SAMPLING

The preferred method of obtaining a sample in a processing plant was by obtaining the sample from a moving stream such as a conveyor belt or a slurry pipeline.

SAMPLE PREPARATION

Drying

Before the samples could be analysed, they were dried in a preheated oven at 220 °C for 30-40 minutes.

Crushing and pulverising

Samples were crushed using a laboratory jaw crusher in order to break them down into smaller units which can go through the 8 mm aperture. The ore was further reduced to 75 μ in the pulverising machine.

ADSORPTION

Preparation of pregnant solutions

Standards were prepared by the dissolution of a known amount of the analyte in cyanide solution. A combined stock solution of 1 g/L of Au, Ag, Ni, Fe and Cu was made. Au(CN)₂⁻, Ag(CN)₂⁻, CuCN, Fe(CN)₆³⁻ were added as potassium cyanide salts. Potassium cyanide was added to these standards so that the free cyanide concentration was 300 ppm. Conditions for adsorption were:

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>267.954nm</td>
</tr>
<tr>
<td>Ag</td>
<td>328.605nm</td>
</tr>
<tr>
<td>Fe</td>
<td>259.942nm</td>
</tr>
<tr>
<td>Ni</td>
<td>231.604nm</td>
</tr>
<tr>
<td>Cu</td>
<td>327.385nm</td>
</tr>
</tbody>
</table>

Analysis of loaded carbon using AAS.

Activated carbon was recovered from slurry samples by passing the entire slurry through a 600μm screen. The carbon was collected along with some ore particles from the screen. The ore particles were removed by panning using a gold pan. This technique makes use of the density difference between the activated carbon and the ore particles. Following separation from the ore particles, the carbon was washed thoroughly with water. The carbon was analysed for various metal species to determine carbon loading. Activated carbon was analysed for Au, Ag, Cu, Ni, and Fe in a matrix of 10% HCl.

The carbon was oxidised in an oven at 750 °C for 8 hr. 40ml of aqua regia was used to transfer the ash to a glass beaker. The beaker was covered with a watch glass and gently boiled. Once the volume of solution in the beaker had reached ca 10ml, a further 40ml of aqua regia was added to dissolve any remaining ash. The solution was then filtered into a 100ml volumetric flask and the volume made up to 100ml by the addition of 10% HCl. This solution was analysed by AAS for Au, Ag, Cu, Ni, and Fe.

III. RESULTS AND DISCUSSION

Effect of Nickel Cyanide on Gold Adsorption

Nickel cyanide inhibited the adsorption of gold cyanide by 19% at 200 ppm, 16% at 100 ppm, 12% at 40 ppm and 7% at 20 ppm. Hence the inhibition of gold cyanide adsorption by nickel cyanide depends on the concentration of nickel cyanide in solution. The inhibition increases as the concentration of nickel cyanide increases. Ni dissolves as a Ni(CN)₆³⁻ complex, adsorbs on activated carbon and at high concentrations deceases the Au adsorption [4]. If the gold ore has significant content of Ni that dissolves and adsorbs on activated carbon, Ni comes with gold up to smelting stage and increases the smelting temperature of the metal mixture, because of the high melting point of Ni at 1455°C comparing with Au melting point at 1064°C.
point of 1063°C. Nickel cyanide’s persistence in solution and its competition against gold in adsorption may be due to its stability in solution, its hydration energy may discourage it to compete with gold.

**Effect of Copper Cyanide on Gold Adsorption**

Copper cyanide inhibited adsorption of gold cyanide by 6% at 200 ppm, 6% at 100 ppm and 3% at 40 ppm. Copper cyanides are moderately stable; their formation can cause both operational and environmental concerns, as wastewater or tailings from such operations may have significantly higher cyanide concentrations than would otherwise be present in the absence of copper. High copper concentrations in the ore increase costs and lower recovery efficiencies by requiring higher cyanide application rates to compensate for reagent that complexes with copper rather than gold.

**Effect of Iron Cyanide on Gold Adsorption**

Iron dissolves from the ore as a Fe(CN)₆⁴⁻ strong complex. However this complex does not either adsorb on the activated carbon or prevent the adsorption of gold cyanide even at as high concentrations as 1000 ppm [5].

**Effect of Silver Cyanide on Gold Adsorption**

Silver cyanide inhibited gold cyanide adsorption by 26% at 200 ppm, 17% at 100 ppm, 16% at 40 ppm and by 11% at 20 ppm. In cyanide leaching Ag dissolves as Ag(CN)₂⁻ complex and adsorbs on carbon better than the cyanides of Ni and Cu. When the concentration ratio of [Ag]/[Au] reaches 2:1, Ag starts to inhibit the Au adsorption on activated carbon [6].

**Overall effect of competitive metal cyanides on gold adsorption**

The adsorption of metal-cyanide species on activated carbon occurs selectively. Firstly, it was thought that it is because of the difference between ionic diameters of the metal-cyanide complexes. However, although strongest adsorption on activated carbon occurs for the Au(CN)₂⁻ complex, the ionic diameter is higher than many other cyanide species. Thus, according to the recent studies, the reason for the selective adsorption of metal-cyanide species would be the differences in the levels of hydration of the metal-cyanide molecule. Due to the hydration of the metal-cyanide complex in solution, a water shell occurs around the molecule increasing their diameter at different degrees. The hydration of the molecule relates to the cyanide molecules binding to the metal ion. Thus, increased quantity of CN⁻ of a metal-cyanide complex will lead to increased hydration level and thus, increased diameter of metal-cyanide molecule. So metal-cyanide could not enter through the micro pores of the activated carbon and adsorption of the metal cyanide species will decrease.

On the other hand hydrophobicity increases by decreasing hydration level. Hydrophobic metal-cyanide species tends to form clusters by binding together. Forming clusters is another
mechanism of adsorption of the metal-cyanides that they settle down to the activated carbon to increase the adsorption of these metal-cyanide species. Confirming these results of the studies, for example $\text{Fe(CN)}_6^{4-}$ and $\text{Ni(CN)}_4^{2-}$ complexes are found to adsorb more weakly on activated carbon that these species contain 6 and 4 $\text{CN}^-$ molecules, and thus, have increased hydration level and decreased hydrophobicity. As a result they are well dispersed in the solution without forming clusters. The $\text{Ni(CN)}_4^{2-}$ complex can serve as a similar example but it has not been studied in the literature as to the hydration levels. Also, $\text{Cu(CN)}_3^{2-}$ complex is well dispersed in water and its hydration level is relatively high. Three cyanide bearing complexes, $\text{Au(CN)}_2^-$, $\text{Ag(CN)}_2^-$ and $\text{Cu(CN)}_2^-$, have the lowest hydration state and form clusters adsorbed on activated carbon. They can be classified from the strongest adsorbed to the least strong: $\text{Au} > \text{Ag} > \text{Cu}$ [7].

The adsorption of metal-cyanides on activated carbon is selective and the strongest adsorbed complex is $\text{Au(CN)}_2^-$. The $\text{Ag(CN)}_2^-$ complex adsorbs strongly but not as strong as $\text{Au(CN)}_2^-$ [1]. The $\text{Cu(CN)}_2^-$ and $\text{Cu(CN)}_3^{2-}$ complexes shows different adsorption features; $\text{Cu(CN)}_2^-$ complex adsorbed strongly while the adsorption of $\text{Cu(CN)}_3^{2-}$ complex is insignificant. The $\text{Ni(CN)}_4^{2-}$ complex adsorbs weaker than $\text{Au(CN)}_2^-$, $\text{Ag(CN)}_2^-$, $\text{Cu(CN)}_2^-$ complexes but stronger than $\text{Cu(CN)}_3^{2-}$, and $\text{Ni(CN)}_4^{2-}$ can reduce $\text{Au(CN)}_2^-$ adsorption significantly when there is as much as 200ppm in leach solution. $\text{Fe(CN)}_6^{4-}$ adsorption and effects on gold adsorption are insignificant.

The iron complexes shows that they are strong in solution, followed by nickel cyanide. The results of this project depend to a very large extent on the accuracy of the solution analysis. Therefore it was essential that the details of the solution analytical procedures had to be given in the methodology. The solution analysis method in cyanide solutions required a number of operating parameters to be constant for accurate results to be obtained and as such the pH had to be strictly within the limits in as much as the concentration.

IV. CONCLUSION

The effect of Ag, Ni and Cu on the Au adsorption on activated carbon has been quantified with synthetic cyanide solutions. The stability of free cyanide concentration is to a large extent controlled by the pH of the solution. Low pH levels results in a significant decrease in cyanide concentration. The pH can however be regulated by the constant addition of lime. The lime, however contributes to the formation of carbonates which cause major fouling of the carbon and prevents the gold from adsorbing on the surface of the carbon due to the reduction in surface area. Copper affects the CIP circuit to a greater extent than the other metals nickel, silver and iron because of cyanide’s lack of selectivity for gold over copper.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to Duration and Blanket Mine Laboratories were most of the experimental work was carried out.

REFERENCES