University of Nevada
Reno

Hypochlorite Pretreatment in Heap Leaching of a Low Grade Carbonaceous Gold Ore

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Metallurgical Engineering

by
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The dissertation of Mojtaba Ahmadianehrani is approved:

In the Name of God, the Compassionate, the Merciful

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Department Chair

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Dean, Graduate School

I wish to express my deepest appreciation to my wife, Yun, who never lost faith in me and who was always there for me when I was down; to my two beautiful children, Somayeh and Fereydoon, for their happy faces; and to my brothers, Mostafa and Mortaza, for their moral support and encouragement.

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The concept of hypochlorite treatment prior to cyanidation in the heap leaching of low grade carbonaceous gold ores is discussed. Laboratory column leach tests using a low grade Carlin-type carbonaceous ore were performed to investigate the effects of pH, hypochlorite consumption and concentration, solution flow rate, finer grinding, agglomeration, curing time, and bed height on total gold extraction. At high pH, hypochlorite stability increases and thus, hypochlorite consumption decreases. At ambient temperature, total gold extraction is proportional to hypochlorite consumption. However, at some consumption level addition of hypochlorite does not increase gold extraction. Gold recoveries of 10% and 80% are achieved at 12 and 167 lb/ton hypochlorite consumption, respectively. Increasing hypochlorite concentration increases the rate of extraction. Crushing the ore to a finer size and agglomerating with cement decreases hypochlorite consumption by 60%. On the other hand, agglomerating and curing the cement-ore mixture with hypochlorite solution has no significant effect on total gold extraction. Hypochlorite consumption decreases with increasing solution flow rate. In addition, using calcium hypochlorite results in higher gold extraction than using sodium hypochlorite at a fixed hypochlorite consumption.
For a given hypochlorite consumption, gold extraction increases with decreasing ore bed height. The high hypochlorite consumption is due to oxygen depletion as the solution percolates through the column, i.e., oxidation of gangue materials. These side reactions are reduced at sub-ambient temperatures resulting in a substantial further decrease in hypochlorite consumption. The optimum temperature range and additional reduction of hypochlorite consumption by introducing the reagent into the column at different elevations will be discussed. Finally, a brief operating cost evaluation is given.
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The discovery that gold was soluble in alkaline cyanide solutions by the alchemists of the eighteenth century led to developing the cyanidation process for the extraction of gold and silver from their ores. The use of cyanide in commercial processing of gold and silver is generally attributed to MacArthur and the Forrest brothers work in 1887 (Hiskey, 1985; Habashi, 1967). Since then, cyanidation has been the overwhelming option for nearly every gold and silver mining operation in the world because of its economy and process simplicity.

The reactions that take place during the dissolution of gold in an alkaline cyanide solution have been definitely established and presented by the equation that has been known as Elsner's equation (Habashi, 1967),

\[ 4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4NaAu(CN)_2 + 4NaOH \]  

Although a simple reaction, the presence of many complex side reactions causes
no end to the problems. Practically, the system requires certain conditions: gold should be free and clean, cyanide solution should not contain impurities and an adequate supply of oxygen should be present in the solution. Generally, not all gold ores meet all the conditions mentioned, therefore, they may show poor response to conventional cyanidation and are termed "refractory."

The refractoriness is primarily due to the complex nature of the containment of gold in the ore materials. In many cases, native gold is very finely disseminated in a sulfide matrix consisting mostly of pyrite, pyrrhotite, and arsenopyrite. In other cases, gold is associated with tellurides or contained in base metal sulfides of lead, copper and zinc. The finely disseminated gold particles may be locked at the grain boundaries of the minerals and even fine grinding does not expose them in the leaching solution, consequently, poor leaching efficiency results.

Native gold is also found in association with carbonaceous matter. In general, ores containing 0.25-0.8 percent organic carbon are classified as carbonaceous ores.

Refractory behavior of carbonaceous gold ores is fundamentally different from the other refractory gold ores. These types of ores contain an active form of carbon that would adsorb the dissolved gold already present in the leaching solution. This phenomenon, usually referred to as "preg robbing", constitutes loss of gold to the tailing.

The growing number of carbonaceous gold ore stockpiles, the decreasing
availability of more easily processed ores and the relatively high price of gold has drawn many investigators' attention to developing an economical process for these refractory ores.

Various methods have been proposed to treat this type of refractory ores. These include coating the adsorptive carbon compounds with kerosene, rejecting carbon by flotation, cyanide leaching with carbon or resin in pulp, using chelating agents, roasting, chemical oxidation, resin-in-leach, bioleaching, and carbon-in-chlorine (Dorfman, 1922; Heinen et al, 1970; Leaver and Woolf, 1930; Chapman, 1939; Nice, 1971; Friedman and Savari, 1983; Scheiner et al., 1972; Hiskey and Atzure, 1989; Brierley and Wan, 1990; Greaves et al., 1990; Sandberg and Greaves, 1991). Among these methods, only roasting the ore in an oxidizing atmosphere and chemical oxidation treatment prior to cyanidation have shown success on the commercial scale (Guay, 1980, 1981; Brunk and Atwood, 1987). However, due to their high capital and operating costs, these pre-oxidation processes are not economical for low grade carbonaceous gold ores.

Heap leaching provides an economical method for recovering gold from low grade ores. The feasibility of employing hypochlorite pretreatment to the conventional cyanide heap leaching process to treat carbonaceous gold ores has been investigated in a previous study (Sawyer and Hendrix, 1988). Gold recoveries of greater than 85% using hypochlorite pretreatment were achieved. However, the process seems uneconomical because of high hypochlorite consumption.
This study investigates the concept of heap leaching low grade Carlin-type carbonaceous gold ores, employing hypochlorite treatment before cyanidation. The nature and mineralogy of the Carlin-type ore deposit along with the concept of the heap leaching and analytical methods are described in this chapter. The effects of pH, hypochlorite concentration, sodium versus calcium hypochlorite, size reduction, agglomeration, curing, temperature, hypochlorite solution flow rate and bed height on gold extraction at low hypochlorite consumption are presented in chapter 2. The mechanism of hypochlorite treatment and gold extraction behavior are described in chapter 3. Finally, the role of oxygen and some technical improvements are given in chapter 4.

II - THE NATURE OF CARLIN TYPE CARBONACEOUS GOLD ORES

Mineralogy

The Carlin type ore takes its name from the Carlin Mine in northeast central Nevada which is located in the northern portion of the Lynn window along the eastern flank of the Tuscarora anticline in the Silurian Roberts Mountains Formation. The Carlin deposit, which is also referred to as "disseminated Carlin-type" gold deposit, is a sediment-hosted epithermal type deposit. Its formation and characterization are well described by Radtke and others (1970, 1980, and 1985).

Limestone, dolomites, and quartzites of Devonian-Ordovician Age were

...
overthrust by shales, quartzites, and cherts of Ordovician Age along the Roberts Mountain Thrust (Radtke et al., 1980). The Carlin deposit formed by interaction between carbonate-bearing sedimentary rocks and moderately reduced, acidic, gold-bearing fluids at temperatures below 250 °C (Radtke, 1985). Two types of ore are present; lower unoxidized, and upper oxidized. The unoxidized ore consists of 5% siliceous, 5-10% pyritic, 15-20% carbonaceous, 5-10% arsenical types, and 60% normal. The normal ore consists of gold associated with mercury, antimony, and arsenic in fractures and as coatings on pyrite grains in a rock that has lost 25-50% of its primary carbonate content. Oxidized ores contain larger amounts of quartz, 3-10% pyrite, 1-5% carbon, and 0.5-10% arsenic. Oxidized ores were produced by surface weathering as well as by near-surface acid-leaching during the primary stage of ore formation (Radtke et al., 1980).

Gold Occurrence

It has been hypothesized that gold in hydrothermal fluids transported in acid solutions as a chloride complex, along with silica and pyrite, heated by igneous intrusions and precipitated at temperatures above 175 °C (Radtke and Scheiner, 1970). The silty carbonate rocks in the upper Roberts Mountains formation were sufficiently permeable to accommodate hydrothermal fluid flow along beds and grain boundaries (Bakken and Einaudi, 1986). Deposition of gold occurred by one or a combination of the following occurrences: temperature decrease, wall-rock alteration, boiling, and fluid mixing (Radtke et al., 1980).
Native gold grain sizes of minus 10 μm, and infrequently euhedral to oval grains of 5 μm size have been observed in Carlin ore samples (Hausen and Kerr, 1968). Microprobe studies by Wells and Mullens (1973) showed that most of the gold in Carlin ore was associated with pyrite. In contrast, Radtke and Scheiner (1970) reported that gold was chelated to the organic matter.

Puddephatt et al., (1989), demonstrated that gold was selectively deposited from a chlorine vapor phase on all the sulfide minerals tested but was not deposited on quartz. The sulfide mineral acts as a very efficient collector of gold and the gold is present on the mineral surface as small spheres. The order of decreasing collecting efficiency was pyrite > arsenopyrite > pyrrhotite.

Microscopic studies at Newmont have confirmed the auriferous nature of pyrite in Carlin-type gold ores (Hausen, 1981). Two types of auriferous pyrite have been identified by a scanning electron microscope (SEM) in Carlin unoxidized ore. One is spheroidal in shape and porous to spongy in internal appearance. It is made of 0.5 to nearly 2 μm size crystallites that aggregate to form spheroidal clusters of 20 to 30 μm. The other type is the coarse euhedral pyrite, 10 to 50 μm in size, displaying cubic outlines and no internal porosity. Samples from the Carlin deposit showed major concentrations of gold occluded in spheroidal pyrite grains, and in smaller concentrations in thin rims around cubic grains. The same studies have indicated that the more easily oxidized form of auriferous pyrite is the fine spheroidal kind that is amenable to low temperature oxidation.
Carbonaceous Matter

The nature of the carbonaceous material contained in Carlin-type ore deposits has not been fully determined. In early 1944, Schwartz pointed out that various forms of carbonaceous matter were associated with these deposits. Early investigations by Newmont Exploration Limited and the United States Bureau of Mines, in the 1960's, defined activated carbon in the Carlin ores as fine grain amorphous carbon that could adsorb stable gold complexes (Scheiner et al., 1971 and 1972). The term "Preg-Robbing" was then applied to describe the refractory nature of carbonaceous ores that adsorb gold from pregnant cyanide solutions (Hausen and Bucknan, 1985). Radtke and Scheiner (1970) attempted to characterize the carbonaceous matter in Carlin-type ores. They suggested that the carbonaceous matter consists of (1) an activated carbon component that absorbs gold chloride complexes from solution, (2) a mixture of long-chain high molecular weight hydrocarbons that do not interact with gold but are usually associated with the activated carbon, and (3) an organic acid, like humic acid containing functional groups capable of chelating with dissolved gold to form organic gold compounds. These investigators proposed that as the hydrothermal gold-bearing solution comes into contact with humic acids, ligands such as N, S, and O would easily displace the chloride to form a stable chelate. The same authors argued that probably more than 50% of the gold in the Carlin-type ore is associated with these organic acids as an Au(I) complex. However, Wells and Mullins (1973) reported that carbonaceous matter in the Carlin disseminated gold deposits
contain very little gold, contrary to pyrite that may contain gold in relatively high amounts.

Nelson et al., (1986) have characterized carbonaceous matter in Carlin ore using photoacoustic, Raman, and EPR Spectroscopy. These authors have reported that the organic carbon material was not humic acid nor a hydrocarbon, but instead some type of activated carbon. In the same study, these investigators obtained a yellow solid from carbonaceous Carlin ore with hot chloroform extraction in a soxhlet extractor. They described the solid as elemental sulfur based on the melting point determination. The infrared spectrum of this solid was featureless indicating no hydrocarbons were extracted.

Sibrell and Miller (1990) noted the presence of a high rank, naturally-occurring "activated carbon-type" compound in the ore using FTIR spectroscopic methods. They did not find humic acid.

Leventhal and Hofstra (1990) confirm the results of Nelson et al., using Laser Raman Microspectroscopy. These authors believe that the previous report (for example, Radtke and Scheiner, 1970), of hydrocarbons, pyrobitumens, humic acids and anomalous nitrogen are due to contamination by ammonium nitrate and diesel fuel used to blast holes. The same authors identified all forms of preg robbing carbonaceous matter in the sediment-hosted disseminated gold ore deposits as hydrogen-poor, cryptocrystalline graphite.

There is a general agreement among the investigators in this field that the carbonaceous matter in the Carlin-type gold ores is some form of activated
carbon. This black carbonaceous matter has been identified as high rank anthracitic to sub-graphitic pyrobitumens derived mostly from fossil petroleum residues (Hausen, 1991). However, there still are some controversies over the mechanism of adsorption of gold compounds onto the carbonaceous matters and surface characterization of these materials. This subject is discussed in chapter 3.

III - HEAP LEACHING

The actual principle of the heap leaching process dates back to the mid-sixteenth century when copper-bearing solutions recycled through waste heaps in Hungary (Hiskey, 1985). Since then, this technology has been practiced worldwide for low-grade copper and uranium ores using either acid or alkaline solutions.

Heap leaching of precious metal ores using alkaline cyanide solution was originally suggested by the United States Bureau of Mines in the late 1960’s. The first commercial operation of heap leaching of an oxidized gold ore started in 1971 by the Carlin Gold Mining Company in northern Nevada (Hiskey, 1985). Since then, this technology has found considerable acceptance in gold and silver processing because it is an inexpensive method with comparatively low capital and operating costs for extracting precious metals from oxidized ores.

In heap leaching, coarsely ground ore (3/8 - 3 inches maximum) is piled on an impervious pad such as compacted clay or concrete as pictured in Figure 1-1. Commonly, an alkaline cyanide solution consisting of 0.1% NaCN and 1% NaOH is applied on top of the heap to dissolve the gold during percolation
Figure 1-1. Schematic of a heap leaching operation (from Chamberlin, 1981).
through the stacked ore. The pregnant solutions reach the impervious pad at the bottom of the heap and flow to a collection pond. Then, from the pond, solution is processed through carbon adsorption columns, desorption circuits, followed by electrowinning and recovery, or treated by the Merrill-Crowe zinc dust precipitation method. A general description of processing steps and design factors for heap leaching operations is given by VanZyl et al., editors (1988). Final recoveries from 40 to 85 percent are obtained depending on the response of the specific ores to the leaching. Generally, the best recovery would be obtained by using low bed height to permit oxygen penetration, long residence times, smaller particle size and higher cyanide concentrations.

Most heap leach problems are of a physical nature. For example, one of the common problems is lack of permeability and porosity caused either by an excessive amount of fines or by improper heap building techniques (Chamberlain, 1981, 1986). The improvements in the mid-1970's, called agglomeration-heap leaching, have solved percolation problems. In this technique, Portland Cement is mixed with the fine particles and water, the mixture will agglomerate into small lumps that remain intact as the cement cures. Percolation of cyanide solutions has been shown (Heinen et al., 1979; McClelland and Hill, 1981) to be 10-100 times higher in the case of agglomerated gold and silver ores. In improper heap construction, segregation occurs when the material is dumped down the sloping face from the crest of the heap. This segregation causes dispersion of solutions (channelling) due to horizontal zones of low permeability, fines, and alternate
zones of high permeability, coarse (Chamberlin, 1981).

In view of the prevailing gold prices, continued growth and improvements of heap leaching activity are expected.

IV - ANALYTICAL METHODS

Hypochlorite

The concentration of hypochlorite in solution was determined by the standard iodometric titration method using a 0.1 N sodium thiosulfate solution as a titrant and a potato starch solution as an indicator (Vogel, 1958).

Free Cyanide

The standard method, silver nitrate titration, was employed in determination of free cyanide concentration using 0.01 N silver nitrate solution as the titrant and para-dimethylaminobenzylidene rhodanine as an indicator (ASTM, 1981).

Eh and pH Measurements

The redox potential and pH of the effluent were measured potentiometrically using an Orion Ion Analyzer Model EA 940 equipped with combination electrodes. A silver/silver chloride reference electrode filled with a 4M KCl solution was used in oxidation reduction potential (ORP) measurements.
The measured ORP were then converted to standard hydrogen electrode (SHE) values as follow:

\[ E_{\text{SHE}} = E_{\text{meas.}} + E_{\text{ref}} \]

Where, \( E_{\text{ref}} \) is the reduction potential of the reference electrode. For a silver/silver chloride reference electrode with 4M KCl filling solution, \( E_{\text{ref}} \) is equal to 199 mv at 25 °C.

**Elemental Analysis**

A Perkin-Elmer inductively coupled plasma emission spectrophotometer (ICP) Model P2 was employed to determine the common elements' concentration. The instrument operates in a sequential mode. The analytical calibration was made with the custom made standards that contain several elements.

The solid samples (0.5-1.0 grams) were dissolved in a mixture of three acids (2 mL HF, 10 mL HClO₄, and 15 mL HNO₃) at 300 °F for approximately one hour before analysis.

**Gold Analysis**

A Perkin-Elmer 2380 atomic absorption spectrophotometer (AAS) was employed to determine gold concentration in the effluent. The instrument was calibrated with various gold standards according to the manual (Perkin-Elmer, 1973). The standards were made in corresponding matrices (sodium cyanide, sodium and calcium hypochlorite) to eliminate interferences due to the sodium
Standard fire assay techniques (Bergbee, 1933) were employed to determine the gold content of the head and tailing samples. A modified silica flux was employed and its composition for 1 assay ton is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>10.0 g</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>30.0 g</td>
</tr>
<tr>
<td>PbO</td>
<td>70.0 g</td>
</tr>
<tr>
<td>Borax</td>
<td>6.0 g</td>
</tr>
<tr>
<td>Flour</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Silver inquart</td>
<td>1.9 mg</td>
</tr>
</tbody>
</table>

Covered by Borax

The gold-silver bead was dissolved in Aqua-Regia and analyzed by the atomic absorption spectrophotometer.

Anion Analysis

The Dionex Model 2000i and 4000i ion chromatographs (IC) equipped with HPIC-AS4A and MPIC-NS1 columns were employed to determine concentrations of anions (OCl⁻, Cl⁻, ClO₂⁻ and SO₄²⁻) and gold cyanide complex, respectively. The electrochemical, conductivity and UV visible modes of detection were used in this analysis according to the application note 29R (Dionex, 1984) and IC manual (Dionex, 1983) with a minor modification. All standards and reagents were made in distilled deionized water with high quality reagent grade analytical reagents.
Chapter Two

Scope of Hypochlorite Pretreatment

I - INTRODUCTION

The presence of some form of activated carbon and/or organic compounds in carbonaceous gold ores render them not amenable to direct cyanidation. Generally, these ores contain 0.25 to 1.0% organic carbon. The organic carbon material has been identified as activated carbon in nature resembling a cryptocrystalline graphite structure (Nice, 1971; Nelson et al., 1982; Sibrell and Miller, 1990; Leventhan and Hostra, 1990). Conventional cyanidation treatment on these ores is incomplete partially due to the phenomenon designated as "preg robbing" (Hausen and Bucknan, 1985). The adverse interaction of carbonaceous material with dissolved gold in some areas of the Carlin Mine is such that a mixture containing 5% carbonaceous ore and 95% oxidized ore reduces the extraction from 93% to 76.4% gold versus 100% for oxidized ore (Guay, 1981).

In addition to carbonaceous material, submicroscopic to microscopic gold particles are finely dispersed (disseminated) and are associated with pyrite in several gold deposits. The Carlin-type Nevada ores, for instance, contain up to
3% pyrite which has been shown to occlude a majority of gold contained therein (Hausen, 1981). Two types of auriferous pyrite at Carlin have been identified. Most of the auriferous pyrite, which is highly enriched in gold, is fine (1-10 μm), porous and spheroidal in shape. The least auriferous pyrite variety is coarse (10-50 μm), euhedral cubic in shape with no internal porosity (Wells and Mullen, 1973). According to microscopic studies at Newmont (Hausen, 1981), the spheroidal pyrite is amenable to low temperature oxidation whereas the euhedral pyrite is more difficult to oxidize at low temperature and roasting methods would probably be required for complete oxidation. However, locking of disseminated auriferous pyrite in microcrystalline quartz (chert) results in a highly refractory condition that prevents the penetration of oxygen and/or lixiviants, causing low recoveries regardless of treatment. Even fine grinding would not liberate this fine pyrite from gangue minerals.

Various methods have been proposed to solve this problem. These methods usually include some sort of treatment prior to cyanidation. Nice (1971) described both the flotation method to remove carbonaceous materials and the use of organic additives as blanking agents that absorb on carbon in preference to the aurocyanide complex. The use of chelating agents like malononitrile was investigated at the U.S. Bureau of Mines in the late 1960's (Guay, 1981). Abotsi and Osseo-Asare (1987) have shown that some surface active organic compounds enhance the gold uptake in aqueous cyanide solution by a Ghanian carbonaceous ore while the other compounds have a strong opposite effect. The use of carbon
or ion exchange resins to adsorb the aurocyanide complex in preference to natural carbonaceous matter was investigated by Chapman, 1939. Recently, Hiskey and Atluri (1989) studied the use of resin-in-leach cyanidation of a carbonaceous gold ore and obtained 70% gold extraction. Graphite-in-leach was also proposed by Dentan and Attia, 1990 and showed some advantages in comparison to a carbon-in-leach process due to the greater adsorption density of graphite for gold. However, these methods are not applicable to Carlin-type ores because a considerable amount of the refractory gold is occluded in the pyrite lattice (Hausen, 1981; Wells and Mullen, 1973) and would not be liberated by these procedures.

Roasting the ore in an oxidizing atmosphere was practiced at Carlin for some time. Gold extractions of 87% were obtained (Guay, 1981). Roasting was abandoned due to the high capital cost and high process control requirements.

Chemical oxidation of carbonaceous gold-bearing ores began in 1967 by both the Reno, Nevada station of the U.S. Bureau of Mines and Newmont Exploration Limited in a joint research program. After extensive laboratory studies, either chlorine or sodium hypochlorite generated in situ by electrolysis of an ore pulp containing brine was chosen to oxidize Carlin ores (Scheiner et al., 1971). These investigations resulted in gold extractions of 90% or more. Following this work, a commercial plant was started in 1971 (Guay and Peterson, 1973). The process was too expensive due to the high chlorine consumption, 80 to 100 pounds of chlorine per ton of ore. Then, a process named "double
oxidation" was developed by Newmont (Guay, 1980). The commercial plant based on this process started in 1977. In the double oxidation process air is dispersed into a slurry of ground ore with addition of soda ash at a temperature of 86°C followed by chlorination to complete the oxidation. Greater than 85% gold extraction was obtained. This process was abandoned in 1982 due to the equipment failure and increase in the price of fuel.

Yet another chemical oxidation method using chlorine gas was introduced by Brunk and Atwood (1987). This process, flash chlorination, increased gold extraction by 6% and decreased chlorine consumption by 25% per ounce of gold.

Chemical oxidation treatments before cyanidation have shown success on the commercial scale. However, due to their high capital and operating costs, these pre-oxidation processes are not economical for low grade carbonaceous gold ores. Heap leaching, however, provides an economical method for recovering gold from low-grade ores.

The feasibility of employing a hypochlorite pretreatment to the conventional cyanide heap leaching process to treat carbonaceous gold ores was investigated in a previous study (Sawyer and Hendrix, 1988). Gold recoveries of greater than 85% using a hypochlorite pretreatment were achieved. However, the process seems uneconomical because of high hypochlorite consumption.

This portion of the present study describes the concept of heap leaching low-grade Carlin-type carbonaceous gold ores, employing hypochlorite treatment before cyanidation. The effects of hypochlorite solution flow rate, hypochlorite
concentration, pH, temperature, agglomeration, bed height and sodium versus calcium hypochlorite on gold extraction at low hypochlorite consumptions are also investigated.

II - EXPERIMENTAL

Ore Material

Studies were performed on a Carlin-type carbonaceous gold ore supplied by Newmont Gold Company at Carlin, Nevada, in two batches referred to as feed No. 1 and No. 2. The material was collected from the minus 4-inch crushed feed stockpile. Each batch was crushed to minus 1/2-inch and blended thoroughly by the cone and quarter technique. Head samples were taken by using a riffle-type splitter box.

Screen analyses of minus 1/2-inch feed No. 1 and feed No. 2 are presented in Tables 2-I and 2-II, respectively. Feed No. 1 contained 0.075 ounces gold per ton of ore, 2.9% total carbon, 0.9% organic carbon, and 0.35% sulfur (by weight). Whereas feed No. 2 contained 0.09 ounces gold per ton ore, 3% total carbon, 0.98% organic carbon, and 0.35% sulfur (by weight).

The X-Ray powder diffraction study shows that both feeds are composed mainly of quartz with much less dolomite, with kaolinite and illite as minor components together with traces of pyrite.

The trace elemental analyses conducted by an Inductively Coupled Plasma
(ICP) and are presented in Table 2-III for both feeds.

**Table 2-I. Screen analysis on 1/2-inch feed No. 1**

<table>
<thead>
<tr>
<th>Sieve size (Tyler)</th>
<th>Microns</th>
<th>Wt.%</th>
<th>Wt.% Passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4750</td>
<td>41.29</td>
<td>58.71</td>
</tr>
<tr>
<td>12</td>
<td>1700</td>
<td>26.52</td>
<td>32.19</td>
</tr>
<tr>
<td>28</td>
<td>589</td>
<td>13.38</td>
<td>18.81</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>5.72</td>
<td>13.11</td>
</tr>
<tr>
<td>70</td>
<td>212</td>
<td>2.18</td>
<td>10.93</td>
</tr>
<tr>
<td>100</td>
<td>147</td>
<td>1.76</td>
<td>9.17</td>
</tr>
<tr>
<td>140</td>
<td>105</td>
<td>1.60</td>
<td>7.57</td>
</tr>
<tr>
<td>200</td>
<td>75</td>
<td>1.96</td>
<td>5.61</td>
</tr>
<tr>
<td>325</td>
<td>47</td>
<td>2.57</td>
<td>3.04</td>
</tr>
<tr>
<td>-325&lt;47</td>
<td></td>
<td>3.04</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2-II. Screen analysis on 1/2-inch feed No. 2**

<table>
<thead>
<tr>
<th>Sieve size (Tyler)</th>
<th>Microns</th>
<th>Wt.%</th>
<th>Wt.% Passing</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4750</td>
<td>22.90</td>
<td>77.13</td>
</tr>
<tr>
<td>12</td>
<td>1700</td>
<td>21.21</td>
<td>55.92</td>
</tr>
<tr>
<td>28</td>
<td>589</td>
<td>19.26</td>
<td>36.66</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>9.39</td>
<td>27.27</td>
</tr>
<tr>
<td>70</td>
<td>212</td>
<td>4.22</td>
<td>23.05</td>
</tr>
<tr>
<td>100</td>
<td>147</td>
<td>2.38</td>
<td>20.67</td>
</tr>
<tr>
<td>140</td>
<td>105</td>
<td>5.93</td>
<td>14.74</td>
</tr>
<tr>
<td>200</td>
<td>75</td>
<td>6.92</td>
<td>7.82</td>
</tr>
<tr>
<td>325</td>
<td>47</td>
<td>4.64</td>
<td>3.18</td>
</tr>
<tr>
<td>-325&lt;47</td>
<td></td>
<td>3.18</td>
<td></td>
</tr>
</tbody>
</table>
Table 2-III. Elemental analyses of feed No. 1 and 2 carbonaceous Carlin ores by ICP unless otherwise stated.*

<table>
<thead>
<tr>
<th>Element</th>
<th>Feed No. 1</th>
<th>Feed No. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2.1%</td>
<td>2.1%</td>
</tr>
<tr>
<td>Mg</td>
<td>1.8%</td>
<td>2.4%</td>
</tr>
<tr>
<td>Al</td>
<td>3.1%</td>
<td>3.4%</td>
</tr>
<tr>
<td>Zn</td>
<td>200.0</td>
<td>206.0</td>
</tr>
<tr>
<td>As</td>
<td>532.0</td>
<td>612.0</td>
</tr>
<tr>
<td>Sr</td>
<td>116.0</td>
<td>128.0</td>
</tr>
<tr>
<td>Cu</td>
<td>35.0</td>
<td>31.0</td>
</tr>
<tr>
<td>Cr</td>
<td>60.0</td>
<td>65.0</td>
</tr>
<tr>
<td>V</td>
<td>133.0</td>
<td>159.0</td>
</tr>
<tr>
<td>Hg (Hydride/AA)</td>
<td>28.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Au (Fire assay/AA)</td>
<td>0.075-0.085 oz/ton</td>
<td>0.09-0.10 oz/ton</td>
</tr>
<tr>
<td>S (Combustion)</td>
<td>0.35%</td>
<td>0.35%</td>
</tr>
<tr>
<td>C (Total/combustion)</td>
<td>2.92%</td>
<td>2.97%</td>
</tr>
<tr>
<td>C (Organic/combustion)</td>
<td>0.90%</td>
<td>0.98%</td>
</tr>
</tbody>
</table>

*results are reported in ppm unless otherwise indicated.

Column Leaching Tests

Column leach tests were carried out in 6-ft-high columns with an inside diameter of 4 in. Some columns were equipped with water jackets around them in order to control the temperature. The ore was placed into the column in successive lifts by lowering a bag filled with the material to the bottom of the column and then pulling out the empty bag, thus preventing particle segregation.

The ore was pretreated by pumping hypochlorite solution to the top of the
column at a rate of 0.01 gpm/ft². After hypochlorite treatment, the column was
drained for 24 hours and rinsed with water. The ore was then leached with a
cyanide solution at a rate of 0.005 gpm/ft². Cyanidation was continued until gold
extraction changed by less than 0.5% per day (approximately 15 days). Finally, the
residue was rinsed, dried, mixed and fire assayed. The residue was also analyzed
for metal values, total carbon and sulfur content with a Perkin-Elmer ICP Plasma
2 and a Leco CS-46 carbon and sulfur analyzer, respectively. The effluent stream
was analyzed daily for gold and trace metals using an atomic absorption
spectrophotometer (AA) and an inductively coupled plasma (ICP), respectively.
The effluent streams were also analyzed for free cyanide and hypochlorite
concentration using titration techniques. In addition, a Dionex 2000i ion
chromatograph (IC) equipped with an HPIC-AS4A column was employed to
determine [OCI⁻], [Cl⁻], [ClO₃⁻] and [SO₄²⁻]. Eh and pH were also monitored daily.

III - RESULTS AND DISCUSSION

Effect of Hypochlorite Consumption

Results from column leaching of feed No. 1 carbonaceous ore employing
hypochlorite pretreatment are shown in Figure 2-1. Essentially no gold is extracted
by direct cyanidation treatment. For pretreated ore, at room temperature, total
gold extraction is proportional to hypochlorite consumption up to approximately
135 lb/ton, above which no greater gold extraction is realized.
Figure 2-1.Percent gold extraction as a function of hypochlorite consumption (cyanide consumption 0.4-0.6 lb/ton of ore).
Experimental results indicate that hypochlorite consumption is high, whereas cyanide consumption is relatively low. It is possible to use cyanide strength as low as 0.4 lb/ton of solution in this process, which is beneficial for both economical and environmental reasons.

Effect of pH on consumption and gold extraction

In highly alkaline solutions, pyrite is oxidized by the adsorption of hydroxyl ions on the surface (i.e., surface alteration), which inhibits any further reaction of the pyrite (Hedley and Tabachmick, 1958).

\[ \text{S - Fe - S + OH}^- \rightarrow [\text{HO - Fe - S}]^+ + S^{2-} \]  \hspace{1cm} (2-1)

Moreover, too alkaline a solution may directly attack sulfides,

\[ 12 \text{Fe}_3\text{S}_6 + 3\text{Ca(OH)}_2 \leftrightarrow 2\text{CaS}_3 + \text{CaS}_2\text{O}_3 + 60\text{FeS} + 3\text{H}_2\text{O} \]  \hspace{1cm} (2-2)

\[ \text{FeS} + \text{Ca(OH)}_2 \leftrightarrow \text{Fe(OH)}_2 + \text{CaS} \]  \hspace{1cm} (2-3)

Additionally, it has been reported that gold adsorption onto activated carbon decreases with increasing pH (Osseo-Asare, Afenya and Abotsi, 1984), and gold extraction is increased following the treatment of the ore with either NaOH or CaO (Radtke and Scheiner, 1970).

Three column leach tests were conducted to study the effect of pH on hypochlorite consumption and gold extraction. In the first test, pH was not adjusted as in previous tests. In the third test, pH was increased using 10 lb. lime per ton of ore. Lime was mixed with the ore, and the ore was pretreated for 15 days. The effluent pH remained neutral throughout the treatment, whereas, when lime was mixed with the ore, the effluent pH decreased from 12, whereas, when lime was mixed with the ore, the effluent pH decreased from...
adjusted. In the second test, pH was increased by adding $1.25 \times 10^3$ M NaOH solution, introduced to the top of the ore charge with the hypochlorite solution. Solution flow rates were adjusted so that the combined total flow rate and concentration of the hypochlorite were the same as previous tests. In the third test, pH was increased using 10 lb. lime per ton of ore. Lime was mixed with the dry ore prior to loading the column. All three tests were pretreated for 15 days. Cyanidation was conducted at pH 10.5 in the tests. Effluent pH and gold extraction as a function of time are shown in Figures 2-2 and 2-3, respectively. When no reagent was added to adjust the pH, the effluent pH remained neutral throughout the hypochlorite solution, the effluent pH increased from neutral to 12; whereas, when lime was mixed with the ore, the effluent pH decreased from 12.2 to 7.0 as the lime was leached from the ore charge.

It appears that gold extraction during the hypochlorite treatment is greater and faster when the pH of the process is made more basic, as evidenced in Figure 2-3. Moreover, more gold is extracted at faster rates during cyanidation when the pH is raised during the hypochlorite treatment. In addition, Table 2-IV shows that the hypochlorite consumption is less when the pretreatment is conducted at alkaline pH compared to the one that is conducted at neutral pH.

In a fourth test, caustic and hypochlorite solutions were added to the ore charge at the same flow rate, each on alternate days. A similar behavior was observed as the previous tests where pH was increased with either caustic or lime addition. The results are presented in Table 2-IV.
Figure 2-2. The effluent pH as a function of time for the hypochlorite treatment process at different test conditions.
Figure 2-3. Effect of alkalinity on percent gold extraction as a function of time: 14 days hypochlorite treatment, 8 days cyanidation.
Table 2-IV. Gold extraction vs. hypochlorite consumption at different test conditions.

<table>
<thead>
<tr>
<th>NaOCl consumption (lb/ton)</th>
<th>secondary reagent</th>
<th>2nd reagent consumption (lb/ton)</th>
<th>percent gold extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>76.8</td>
<td>none</td>
<td>36.0</td>
<td>36.0</td>
</tr>
<tr>
<td>56.2</td>
<td>NaOH</td>
<td>29.3</td>
<td>56.0</td>
</tr>
<tr>
<td>85.0</td>
<td>Lime</td>
<td>10.0</td>
<td>59.7</td>
</tr>
<tr>
<td>51.9</td>
<td>1 day NaOH</td>
<td>53.2</td>
<td>51.9</td>
</tr>
</tbody>
</table>

Effect of Hypochlorite Concentration

The effect of hypochlorite concentration on hypochlorite consumption and total gold extraction was investigated. The results indicate that the rate of the oxidation process increased as the hypochlorite concentration increased, Table 2-V. However, high concentrations of oxidizing agent could result in its being consumed by reacting with ore components. As mentioned earlier, gold extraction is dependent on consumption rather than concentration.

A solution of 1% (10.0 g/L) hypochlorite was used in the normal tests of this investigation unless otherwise stated.
Table 2-V. Effect of the hypochlorite concentration on hypochlorite consumption and gold extraction.*

<table>
<thead>
<tr>
<th>leaching time (days)</th>
<th>NaOCl concentration (g/L)</th>
<th>NaOCl consumption (lb/ton)</th>
<th>percent gold extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>20.0</td>
<td>44.6</td>
<td>35.7</td>
</tr>
<tr>
<td>15</td>
<td>10.0</td>
<td>56.2</td>
<td>56.4</td>
</tr>
<tr>
<td>24</td>
<td>5.0</td>
<td>50.8</td>
<td>47.6</td>
</tr>
</tbody>
</table>

* pH was increased in all tests.

Effect of Bed Height

It was observed that the oxidation of the pyritic material is not uniform throughout the ore charge during pretreatment. The rate of oxidation is more rapid at the top of the ore charge than at the lower portion. This behavior could be the result of oxygen depletion as the solution percolates through the ore charge.

During pretreatment, the material in the column has two distinct portions; it has a light color at the top and a dark brown color at the bottom. This appearance remains unchanged even after cyanidation if the hypochlorite consumption is less than 80-100 lb. per ton of the ore. Fire assay results of the...
residues show that the gold content of the bottom portion was much higher than that of the top, Table 2-VI.

Table 2-VI. Gold extraction of two portions of ore charge for a column leach test. 43.3 lb/ton consumption of Ca(OCl)$_2$, 47.4% total extraction.

<table>
<thead>
<tr>
<th></th>
<th>Wt. (Kg)</th>
<th>F.A.Au (oz/ton)</th>
<th>%Gold Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head</td>
<td>13</td>
<td>0.096</td>
<td></td>
</tr>
<tr>
<td>Tails:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>top portion</td>
<td>7.5</td>
<td>0.029</td>
<td>69.7</td>
</tr>
<tr>
<td>bottom portion</td>
<td>5.5</td>
<td>0.080</td>
<td>16.9</td>
</tr>
</tbody>
</table>

The effect of bed height on total gold extraction was further investigated. Fourteen kilograms of the ore was divided into three different portions and loaded into three columns (A, B and C) with bed heights of 29, 18 and 8 in., respectively. Each was pretreated separately with the same amount of hypochlorite per ton of ore. Residue analysis results (Table 2-VII) show no significant change in the main constituents of materials in columns A, B and C. However, residual sulfur decreased as the bed height is decreased. Moreover, at a fixed consumption, gold recovery increased as the bed height decreased, Table 2-VIII.
Table 2-VII. Selected metals, total C and total S analyses of the ore and residues*

<table>
<thead>
<tr>
<th>NO.</th>
<th>%Fe</th>
<th>%Al</th>
<th>%Mg</th>
<th>As</th>
<th>Zn</th>
<th>Cu</th>
<th>%T.C.</th>
<th>%S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore #1</td>
<td>2.1</td>
<td>3.1</td>
<td>1.8</td>
<td>532</td>
<td>200</td>
<td>35</td>
<td>2.92</td>
<td>0.338</td>
</tr>
<tr>
<td>A(29in.)</td>
<td>2.1</td>
<td>2.8</td>
<td>1.7</td>
<td>496</td>
<td>144</td>
<td>24</td>
<td>2.81</td>
<td>0.333</td>
</tr>
<tr>
<td>B(18in.)</td>
<td>2.1</td>
<td>3.0</td>
<td>1.8</td>
<td>518</td>
<td>157</td>
<td>25</td>
<td>2.85</td>
<td>0.294</td>
</tr>
<tr>
<td>C(8in.)</td>
<td>2.1</td>
<td>3.0</td>
<td>1.8</td>
<td>526</td>
<td>165</td>
<td>25</td>
<td>2.77</td>
<td>0.285</td>
</tr>
</tbody>
</table>

* Reported as ppm unless otherwise stated.

It is apparent that a considerable amount of the hypochlorite is unnecessarily consumed by sulfide as the reagent percolates through the ore charge. Introducing the reagent into the ore charge at different column depths should increase extraction and/or decrease hypochlorite consumption.
Ca(OCl)\textsubscript{2} vs. NaOCl

The effectiveness of Ca(OCl)\textsubscript{2} in comparison to NaOCl on total gold extraction is demonstrated in Figure 2-4. Calcium and sodium hypochlorite concentrations were 20.0 g/L. For the same consumption, pretreatment with calcium hypochlorite resulted in higher gold extraction than with sodium hypochlorite. The reason for this behavior is not clear. Sodium and calcium hypochlorite are both ionic salts. Ca(OCl)\textsubscript{2} is a 2:1 electrolyte, while NaOCl is 1:1. Hence, the ionic strength of the former is greater than the latter for solutions of a given concentration. However, the calculated OCl\textsuperscript{-} activities for 20.0 g/L of Ca(OCl)\textsubscript{2} and NaOCl, using the extended Debye-Huckel law, are nearly the same (0.176 and 0.180, respectively). It has been found that the carbon activity is inhibited by adsorption of inorganic foulant such as CaCO\textsubscript{3} at high pH (Muir, 1987). This behavior might be partially responsible for effectiveness of Ca(OCl)\textsubscript{2} on overall gold extraction. However, Ca(OCl)\textsubscript{2} solutions usually contain an excessive amount of undissolved lime, which can cause percolation problems during pretreatment. Percolation can be improved by agglomerating the ore.

Effect of hypochlorite solution flow rate

Chemical consumption and total gold extraction are also a function of hypochlorite solution flow rate. Figure 2-5 shows the effect of heap leach flow rate on the hypochlorite consumption and the combined hypochlorite/cyanide gold extraction. In these tests, 1% Ca(OCl)\textsubscript{2} solution was used without any
Figure 2-4. Percent gold extraction as a function of sodium and calcium hypochlorite consumption, (pH was increased with lime, 10 lb/ton of ore).
Figure 2-5. Effect of hypochlorite solution flow rate on gold extraction and Ca(OCl)_2 consumption.
modification. As is evidenced, the greater the hypochlorite solution flow rate the lower the chemical consumption and the higher the overall gold extraction. The reason is due to a decrease in residence time, permitting less time for side reactions and possible decomposition to occur.

Effect of agglomeration and curing time

A series of column leaching experiments was conducted to determine the effects of agglomeration, amount of hypochlorite additive during agglomeration and curing time on chemical consumption and overall gold extraction. In these tests, the feed no. 2 that is finer (77% passing 4 mesh, Tyler scale) than previous column charges (59% passing 4 mesh, Tyler scale) was employed. The column charges were initially dry-mixed with 10 pounds per ton of ore Portland Cement Type II on a plastic sheet. Each mixed material was carefully spread out to about a two inch layer. Then, water or hypochlorite solution was added to the mixture in three stages using a plastic garden sprinkling bucket until the moisture content of the mixture was 10% by weight. After each water addition, the material was mixed by rolling once around the square from corner to corner. This rolling procedure more closely simulates plant conditions in which agglomeration is conducted using the rolling action and transfer points. After addition of all the solution, the mixture was cut into 8 pie slices. The agglomerated charge was then carefully placed in the column, taking opposite pie slices, to avoid size segregation. Then, the charges were cured for a specific time in capped leach columns. Finally,
the agglomerated charges were leached with a 1% Ca(OCl)$_2$ solution at the flow rate of 0.01 gpm/ft$^2$ followed by the post cyanidation at 0.15 grams per liter NaCN. The results are illustrated in Figures 2-6, 2-7 and 2-8.

Figure 2-6 shows that wetting the cement ore mixture with hypochlorite solution instead of water during the agglomeration step did not increase the overall gold extraction with respect to a normally agglomerated mixture. The total hypochlorite consumption was nearly the same and the curing time was 7 days for all tests. Simple cyanidation on agglomerated ore did not give appreciable gold extraction, Figure 2-6.

Figure 2-7 shows the effect of curing time after wetting the cement-ore mixture with 20% hypochlorite solution or 20 pounds of Ca(OCl)$_2$ per ton of ore. The longer curing time increased the overall gold extraction slightly for the same hypochlorite consumption.

Figure 2-8 shows the results from tests conducted at a lower temperature, 7 °C. The normal agglomeration gives slightly higher gold extraction versus agglomeration with 10 pounds per ton of ore hypochlorite solution for the same consumption. Furthermore, the results in Figure 2-8 indicate that pretreatment with hypochlorite at 7 °C increased overall gold extraction. The effect of temperature is discussed in the next section. In general, wetting the cement-ore mixture with hypochlorite solution instead of water and curing time had no significant effect on total gold extraction or chemical consumption. However, comparing these results with those from previous tests for non-agglomerated
Figure 2-6. Effect of hypochlorite addition during agglomeration at 24°C.

Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton; 7 days curing.
Figure 2-7. Effect of curing time after agglomeration with 20 lb/ton \( \text{Ca(OCl)}_2 \) at 24°C. Pretreatment: 1% \( \text{Ca(OCl)}_2 \) at 0.01 gpm/ft\(^2\); Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft\(^2\); NaCN consumption 0.15 lb/ton.
Figure 2-8. Effect of hypochlorite addition during agglomeration at 7°C.
Pretreatment: 1% Ca(OCl)\textsubscript{2} at 0.01 gpm/ft\textsuperscript{2};
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft\textsuperscript{2};
NaCN consumption 0.15 lb/ton; 7 days curing.
charges (see Table 2-IX) reveals a sharp decrease in consumption and an increase in gold extraction. This illustrates that crushing the ore to a finer size and agglomeration with cement decreases the pretreatment leaching time from 22 days to 8 days and hypochlorite consumption from 116 pounds per ton to 47 pounds per ton for a 50% plus gold extraction.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Au Head oz/ton</th>
<th>Particle Size wt% passing 4 mesh</th>
<th>Pretreatment Period days</th>
<th>Ca(OCl)_2 Cnsmnt. lb/ton</th>
<th>Gold Recovery Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.084</td>
<td>77.1</td>
<td>None</td>
<td>None</td>
<td>1.6</td>
</tr>
<tr>
<td>Agglomeration with cement and Ca(OCl)_2 solution</td>
<td>0.075</td>
<td>58.7</td>
<td>13</td>
<td>45.9</td>
<td>38.7</td>
</tr>
<tr>
<td>No agglomeration</td>
<td>0.075</td>
<td>58.7</td>
<td>22</td>
<td>116.9</td>
<td>58.7</td>
</tr>
<tr>
<td>Agglomeration with cement and water</td>
<td>0.09</td>
<td>77.1</td>
<td>8</td>
<td>47.2</td>
<td>49.3</td>
</tr>
<tr>
<td>Agglomeration with cement and Ca(OCl)_2 solution</td>
<td>0.09</td>
<td>77.1</td>
<td>4</td>
<td>43.3</td>
<td>47.4</td>
</tr>
</tbody>
</table>
Effect of Temperature

As with most chemical reactions and reactors, temperature plays an important role in heap leaching processes. Most reactions are temperature dependent. For example, in the hypochlorite leaching case, the rates of unwanted reactions are increased at elevated temperature. Consequently, the hypochlorite consumption is increased by these side reactions. Thus, there should be an optimum temperature range in which a maximum production is obtained with the minimum of unwanted side reactions. Although it may take several months for the great mass of heap to reach a steady state temperature, a knowledge of heap leach behavior at different temperatures is useful. Such information can help in choosing the proper operating conditions to minimize chemical consumption.

A series of column leaching experiments were conducted to determine the effect of temperature on hypochlorite consumption during the pretreatment step. These experiments were performed on feed no. 2, which was agglomerated with cement and water. The temperature was controlled by means of a water circulating constant temperature bath and a column equipped with a water jacket around it. The temperature was controlled only during the pretreatment period after which cyanidation was conducted at ambient temperature. The results are presented in Figures 2-9 and 2-10 for overall gold extraction and hypochlorite consumption, respectively. These results show that the hypochlorite consumptions are decreased at temperatures below 16°C while total gold extractions are increased. The maximum extraction was 81% for the test conducted at 14°C with
Figure 2-9. Effect of pretreatment temperature on gold extraction. Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$; NaCN consumption 0.15 lb/ton.
Figure 2-10. Effect of pretreatment temperature on hypochlorite consumption. Pretreatment: 1% Ca(OCl)\(_2\) at 0.01 gpm/ft\(^2\); Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft\(^2\); NaCN consumption 0.15 lb/ton.
a 20% reduction in consumption compared to the test conducted at 24°C. The minimum hypochlorite consumption was 17.3 pounds per ton of ore for the test conducted at 3°C with a 67% extraction. These results further show that a portion of hypochlorite input remained unreacted in the test conducted at temperatures below 18°C, Figure 5. The unreacted hypochlorite could be recycled back into the column which results in an increase in the gold extraction.

Higher hypochlorite consumptions at elevated temperatures are due to the side reactions. The rate of these side reactions is increased in accordance with two principles: (1) the activation energy requirement and (2) the increase in solubility of the products of these reactions with increased temperature.

Dolomite, CaMg(CO₃)₂, constitutes a large fraction of the total composition of the Carlin-type ore. Hypochlorite decomposes dolomite and forms calcium and magnesium chlorides. The rate of dolomite decomposition and the solubilities of chlorides are both increased with increasing temperature.

Figure 2-11 shows magnesium concentration in the column effluent versus leaching time at different temperatures. The dissolution of dolomite occurred during the hypochlorite pretreatment and its dissolution rate increased with increasing temperature. Dolomite dissolution, however, stopped after cyanide addition. This is opposite to the dissolution of sulfidic minerals in which their dissolutions begun with introduction of cyanide solution, Figures 2-12 through 2-16. As shown in these figures, the magnitude of the metals dissolutions in the cyanidation step increases with increasing temperature.
Less dolomite decomposed to Mg$^{2+}$ at temperatures below 16 °C for a given hypochlorite consumption which results in a further increase in gold extraction.

It is known that dolomite stability increases with increasing Ca$^{2+}$ concentration and increasing pH values above 7.8 (Stumm and Morgan, 1981). This behavior might be partially responsible for the high gold extraction and low consumption that resulted by employing Ca(OCl)$_2$ and high pH, respectively, in the previous tests.

Figure 2-11: Effect of temperature on CaMg(CO$_3$)$_2$ decomposition.

Pretreatment: 1% Ca(OCl)$_2$ at 0.04 gpm/ft$^2$;
Cyanidation: 0.15 g/l NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton.
Figure 2-11. Effect of temperature on CaMg(CO$_3$)$_2$ decomposition.

Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton.
Figure 2-12. Arsenic concentration as a function of leaching time at various temperatures.

Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton.
Figure 2-13. Iron concentration as a function of leaching time at various temperatures.
Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton.
Figure 2-14. Nickel concentration as a function of leaching time at various temperatures.

Pretreatment: 1% Ca(OCl)_2 at 0.01 gpm/ft²;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft²;
NaCN consumption 0.15 lb/ton.
Figure 2-15. Copper concentration as a function of leaching time at various temperatures. Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$; NaCN consumption 0.15 lb/ton.
IV - CONCLUSIONS

Figure 2-16. Zinc concentration as a function of leaching time at various temperatures.

- Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
- Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
- NaCN consumption 0.15 lb/ton.
IV - CONCLUSIONS

The following conclusions may be drawn from this part of this investigation:

- Hypochlorite pretreatment process can be used effectively in heap leaching of the low grade Carlin-type carbonaceous gold ores. Gold recovery as high as 80% is achieved by combining the hypochlorite treatment and conventional cyanidation. However, chemical costs may be high due to the high hypochlorite consumption despite low cyanide consumption. An 80 percent gold extraction is achieved for 160 lbs./ton NaOCl and 0.4 lb/ton NaCN consumptions using the standard solution percolation technique with no modifications.

- The hypochlorite consumption, however, can be reduced by increasing the pretreatment pH. This modification could be done either by addition of lime powder to the ore charge before hypochlorite treatment or by addition of sodium hydroxide solution while pretreating the ore charge.

- Calcium hypochlorite yields a 10% higher gold extraction than sodium hypochlorite for a given consumption. The effectiveness of Ca(OCl)₂ on the overall gold extraction might be partially due to the formation of CaCO₃. Calcium carbonate is known to inhibit the adsorption behavior of active carbon.

- The rate of oxidation depends on the hypochlorite concentration. However, higher concentrations could result in higher consumption.
• The hypochlorite consumption decreases with increasing hypochlorite solution flow rate. The residence time is decreased at the high solution flow rates, permitting less time for side reaction to occur.

• Crushing the ore to a finer size and agglomeration with cement decreased consumption by 60% for a 50% gold extraction. However, addition of a hypochlorite solution to the cement-ore mixture during the agglomeration step and curing the mixture for a period of time has no significant effect on the overall gold extraction.

• The pretreatment process strongly depends on the temperature. Hypochlorite consumption increases with increasing pretreatment temperature. The high hypochlorite consumption at elevated temperature is due to side reactions as the hypochlorite solution percolates through the column.

• Although an optimization for an operating temperature was not made, however, the best operating temperature range found to be between 3 and 16°C. The observed maximum gold recovery occurred at 14°C with 38 lbs/ton of ore Ca(OCl)₂ consumption for an 81 percent gold extraction.
Chapter Three

Mechanisms of the hypochlorite pretreatment

1 - INTRODUCTION

Pretreatment of carbonaceous gold ores by direct injection of chlorine gas or hypochlorite at an alkaline condition has been investigated for many years with little understanding of the basic chemistry of the oxidation mechanism involved. In the earliest studies by U.S. Bureau of Mines, Scheiner et al. (1971, 1972) suggested that the carbonaceous material contained two different types of carbon which prevented favorable gold extraction: (1) An activated type of carbon which physically adsorbed the gold cyanide complex, and (2) a hydrocarbon type which formed a gold compound during hydrothermal deposition that was not attacked by cyanide. These investigators concluded that the low extraction of gold from carbonaceous material could not be attributed wholly to physical adsorption of the Au(CN)$_2^-$ complex on carbon, but that in certain of these materials, a substantial amount of the gold was locked in the form of a chelate containing CO-N-S ligand. Therefore, a chemical oxidation treatment could liberate the gold from gold-organic compounds, and could passivate the adsorptive properties of the ore.
Moreover, these researchers could not obtain appropriate recoveries after blanking out the activated carbon component by coating it with kerosene, a technique known as the Dorfman Process. A similar result was found by Nice (1971). This indicates that the preg robbing properties of the carbonaceous gold ores is not the only problem.

Work by Wells and Mullens (1973) showed that most of the gold in Carlin ore is occluded in pyrite grains. Later this result was confirmed by Hausen (1981). Therefore, it was concluded that a complete oxidation of the carbonaceous materials and pyrite is necessary to obtain high gold extraction.

A process named "Double Oxidation" was then developed (Guay, 1980). In this process, which was in operation commercially until 1982, air is dispersed in an aqueous slurry of ground ore at temperatures of plus 80°C followed by chlorination. In the improved version of this process, soda ash was also added to the slurry during the air oxidation. It was hypothesized that the air and the soda ash react with pyrite to form soluble sulfates and iron oxides which enhance the exposure of fresh gold surfaces to oxidation (Guay, 1980). During aeration some carbonaceous material was oxidized, but most of it was unaffected. No further detail of oxidation mechanisms was given.

Brunk and Atwood (1987) investigated the chlorination process at Newmont Gold Company. According to this investigation, as much as 85% of the gold is dissolved during the chlorination. However, the gold precipitates as fine elemental gold as the results of Eh drops and the pH rises during this phase of
process. Then, the addition of cyanide to the pretreated ore solubilizes the elemental gold. Pyrite was oxidized to geothite, FeO(OH), and other sulfides were oxidized as well and consumed large quantities of chlorine.

According to Scheiner (1987), the hypochlorite reacts with carbonaceous material in the ore, passivating activated-type carbon and converting the metal sulfides to chlorides by reaction 3-1.

$$\text{MS} + 4\text{OCl}^- \rightleftharpoons \text{MCl}_2 + \text{SO}_4^{2-} + 2\text{Cl}^- \quad (3-1)$$

Then, the metal chlorides can hydrolyze to a metal hydroxides depending on the pH of the slurry.

Arslan and Duby (1991) studied the mechanism of electrooxidation of refractory gold ores using petroleum coke and pyrite as a model. These workers concluded that hypochlorite reacts with pyrite by reaction 3-2,

$$2\text{FeS}_2 + 15\text{OCl}^- + \text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons 2\text{Fe}^{3+} + 4\text{HSO}_4^- + 15\text{Cl}^- \quad (3-2)$$

and with carbonaceous material by reaction 3-3.

$$\text{C} + 2\text{OCl}^- \rightarrow \text{CO}_2 + 2\text{Cl}^- \quad (3-3)$$

The solution pH's for reactions 3-2 and 3-3 were 1 and 6, respectively. Hypochlorite is not stable under these conditions and reactions 3-2 and 3-3 could
not occur to any great extent. Brunk and Atwood (1987) also did not believe that reaction 3-3 could occur. Instead, they noted that chlorohydrocarbon compounds are present on the carbonaceous materials after chlorination which renders these surfaces non-preg robbing.

It is also reported that the organic carbon had not been removed entirely by oxidation during chlorination, but was simply passivated by the interaction of the oxidizing agent with carbon surfaces (Tseng, Wert and Hausen, 1987).

FTIR spectroscopic analysis of organic matter isolated from Carlin ores after passivation treatments with sodium hypochlorite, chlorine gas, and autoclaving with oxygen indicated the presence of carbonyl structure (Sibrell, Wan and Miller, 1990). These investigators concluded the carbonyl structure formed by oxidation of functional groups on the surface of the organic matter.

In order to understand the mechanism of the oxidiation process more precisely one should consider not only the oxidation and/or passivation of carbonaceous matter, but also the oxidation of sulfidic materials. Since gold is somehow associated with these ore's constituents and moreover, it interacts with the former after dissolution.

The purpose of this chapter is to discuss, in a broader sense, the oxidation mechanisms of carbonaceous gold ore employing an alkaline hypochlorite solution. The results of oxidation during pretreatment and cyanidation are also given.
II - MECHANISM OF THE PROCESS

Redox mechanism of hypochlorite solutions

Hypochlorite ion can be produced by dissolving chlorine gas in cold base according to the reaction

\[ \text{Cl}_2 + 2\text{OH}^- \rightleftharpoons \text{OCl}^- + \text{Cl}^- + \text{H}_2\text{O} \]  \hspace{1cm} (3-4)

the equilibrium constant for this reaction is \( 7.5 \times 10^{15} \) and the reaction is rapid (Cotton and Wilkinson, 1988).

Hypochlorite solutions, however, are unstable. At pH levels above neutral, solutions undergo disproportionation to generate chlorite and chlorate:

\[ 3\text{OCl}^- \rightleftharpoons 2\text{Cl}^- + \text{ClO}_3^- \]  \hspace{1cm} (3-5)

The equilibrium constant for this reaction is \( 10^{27} \). The reaction is slow at and below room temperature. However, in hot solution (75°C) the rate of disproportionation is fairly rapid (Cotton and Wilkinson, 1988).

A typical IC analysis of 10 g/L (1%) NaOCl solution, along with pH and redox potential, are presented in Table 3-I.
Table 3-1. Analysis of a 1% NaOCl solution.

<table>
<thead>
<tr>
<th>pH (SHE)</th>
<th>Eh(V)</th>
<th>[OCl⁻] (g/L)</th>
<th>[Cl⁻] (g/L)</th>
<th>[ClO₃⁻] (g/L)</th>
<th>[SO₄²⁻] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.5</td>
<td>0.84</td>
<td>6.8</td>
<td>2.3</td>
<td>0.64</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Hypochlorite in solution forms an equilibrium with hypochlorous acid:

\[
\text{HOCl}^⁻ \rightleftharpoons H^+ + \text{OCl}^⁻ \quad pK_a = 7.5
\]  

(3-6)

At pH equal to pKₐ, hypochlorite concentration is equal to the hypochlorous acid concentration. Figure 3-1 shows the relative concentrations of each species as a function of pH. Hypochlorite ion predominates at higher pH's and hypochlorous acid predominates at lower pH's.

Hypochlorites and hypochlorous acid are thermodynamically unstable in water. These species oxidize the water with the release of oxygen because the position of the stability-domains of HClO and ClO⁻ are above the domain of stability of the water as shown in Figure 3-2 (Pourbaix, 1974).
Figure 3-1. Concentration diagram for hypochlorous acid species as a function of pH.
Figure 3-2. Stability of the hypochlorites; equilibria between dissolved Cl\(^-\), Cl\(_2\), HClO, ClO\(^-\) (from Pourbaix, 1974).
The reactions under different conditions are as follows:

At pH below approximately 4

\[
4\text{HClO} + 4\text{H}^+ + 4e^- \leftrightarrow 2\text{Cl}_2 + 4\text{H}_2\text{O}
\]

\[
2\text{H}_2\text{O} \leftrightarrow \text{O}_2 + 4\text{H}^+ + 4e^-
\]

At pH between approximately 3.3 and 7.5

\[
2\text{HClO} + 2\text{H}^+ + 4e^- \leftrightarrow 2\text{Cl}^- + 2\text{H}_2\text{O}
\]

\[
2\text{H}_2\text{O} \leftrightarrow \text{O}_2 + 4\text{H}^+ + 4e^-
\]

\[
2\text{HClO} \leftrightarrow \text{O}_2 + 2\text{Cl}^- + 2\text{H}^+
\]

At pH above approximately 7.5

\[
2\text{ClO}^- + 4\text{H}^+ + 4e^- \leftrightarrow 2\text{Cl}^- + 2\text{H}_2\text{O}
\]

\[
2\text{H}_2\text{O} \leftrightarrow \text{O}_2 + 4\text{H}^+ + 4e^-
\]

\[
2\text{ClO}^- \leftrightarrow \text{O}_2 + 2\text{Cl}^-
\]
In the absence of suitable catalysts (MnO₂, NiO₂, and CoO₂) or the action of light, however, these reactions are extremely slow; especially in alkaline solution (Pourbaix, 1974).

The reduction mechanism of hypochlorite in the presence of a surface capable of conducting electrons involves separate anodic and cathodic reactions (Wu, 1987). At above pH 7.5, anodic and cathodic sites are developed at the solid-liquid interface. The cathodic reaction is the reduction of hypochlorite ion to chloride ion, and the anodic reaction is oxidation of water to oxygen. A schematic of the reaction sequence incorporated into a mechanistic model is shown in Figure 3-3. Overall reactions at both cathode and anode, respectively, are:

\[
\begin{align*}
\text{OCl}^- + \text{H}_2\text{O} + 2\text{e}^- &\rightarrow \text{Cl}^- + 2\text{OH}^- \quad \text{E}_b^0 = +0.89\text{v} \quad (3-10) \\
2\text{OH}^- &\rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^- \quad \text{E}_b^0 = -0.40\text{v} \quad (3-11)
\end{align*}
\]

The reactions occur simultaneously, i.e., the electrons liberated at the anodic site are consumed completely at the cathodic site. The system rest potential is a mixed potential, according to Wu (1987), and is given by

\[
E_m = \frac{2.3RT}{(1+\alpha^-_a-\alpha^-_c)F} \log \frac{\phi_a K_a a_{\text{ClO}^-}^-}{\phi_a K_a a_{\text{OH}^-}^2} 
\]  (3-12)
and the corresponding rate expression for the reduction of hypochlorite ion is

\[ i_c = -Fk_cK_1a_{\text{ClO}^-}\cdot a_{\text{OH}^-} \exp\left[\frac{-\left(1-\alpha\right)F}{RT}E_c\right] \]  

(3-13)

where:  
- \( k_a \) and \( k_c \) = the anodic and cathodic rate constants
- \( \alpha \) = transfer coefficient,
- \( K_1 \) = equilibrium constant,
- \( a \) = activity,
- \( F \) = Faraday constant,
- \( \Phi_a \) and \( \Phi_c \) = fraction of total surface area that exhibits anodic and cathodic behavior,
- \( E_c \) = cathodic overpotential,
- \( i_c \) = cathodic current density.

Wu (1987) has also shown that the rest potential, \( E_m \), depends on pH and \([\text{OCl}^-]\) but is independent of the \([\text{Cl}^-]\). In addition, the cathodic reaction rate increases as \([\text{OCl}^-]\) increases. Conversely, the rate of the cathodic reaction decreases as the system pH increases (Wu, 1987). The measured value of the rest potential is 0.86 volts (SHE) for the system at pH 11.
Figure 3-3. Schematic of the electrochemical reduction of hypochlorite at rest potential.
Oxidation of Sulfidic Materials

As mentioned previously, it has been confirmed that most of the gold in Carlin ore is associated with sulfidic materials, namely pyrite (Wells and Mullens, 1973; Hausen, 1981). Therefore, knowledge of the factors affecting the rate of oxidation of sulfidic materials is essential for the effective control of pretreatment process.

Figure 3-4 shows dissolution behavior of base metals during cyanidation of the untreated carbonaceous ore. Despite much lower concentration in the ore with respect to the other metals (Table 3-II) copper dissolution is predominate as evidenced in Figure 3-4. The other metals were not detected in the column effluent in an appreciable amount. However, zinc began to appear in the effluent at the end of the leaching period. About 13.8% copper and only 1.6% gold were extracted during this cyanidation process with 0.23 lb NaCN per ton of ore consumption which is 36.5% of the sodium cyanide used.

<table>
<thead>
<tr>
<th>% Fe</th>
<th>% Al</th>
<th>% Mg</th>
<th>As</th>
<th>Zn</th>
<th>Cu</th>
<th>Ni</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>3.1</td>
<td>1.8</td>
<td>532</td>
<td>200</td>
<td>35</td>
<td>45</td>
<td>28</td>
</tr>
</tbody>
</table>

* Reported as ppm unless otherwise stated.
Figure 3-4. The dissolution behavior of base metals during cyanidation of the untreated carbonaceous ore.
This is in agreement with the work of Leaver and Woolf (1931) who have shown that copper minerals, with the exception of chalcopyrite (CuFeS₂) and chrysocolla (CuSiO₃) which are the least soluble, are readily soluble in cyanide solution. They also have shown that the rate of dissolution of all copper minerals increases with an increase in the temperature.

Generally, the greater part of the copper dissolved in cyanide solution exists in the form of complex ions such as Cu(CN)₂⁻, Cu(CN)₃²⁻ and Cu(CN)₄³⁻. The IC analysis of the column effluent confirmed the presence of Cu(CN)₄³⁻ species. It is interesting to note that despite the tendency of Cu(CN)₄³⁻ to adsorb onto the activated carbon, this species was not adsorbed by the graphitic constituents of the ore.

Leaver and Woolf (1931) have also shown that zinc minerals dissolved in cyanide only to some extent. According to these workers, percent extraction of zinc from sphalerite, ZnS, in cyanide solution was only 18.4.

Sphalerite dissolves in cyanide solution according to the reversible reaction:

\[
\text{ZnS} + 4\text{NaCN} \leftrightarrow \text{Na}_2\text{Zn(CN)}_4 + \text{Na}_2\text{S}
\]  (3-14)

which depends on the strength of the cyanide solution in the absence of oxygen.

Thermodynamically, zinc sulfide is the most stable compound in the Zn-S-CN-H₂O system at 25°C (Osseo-Asare, Xue and Ciminelli, 1984). This behavior could lead to the formation of insoluble sulfide instead of soluble zinc cyanide.
Iron sulfide minerals tend to decompose in cyanide solution with an order of reactivity pyrrhotite > marcasite > pyrite. Generally, the end products of decomposition in aerated alkaline cyanide solutions are ferric hydroxide and either sulfate ion or calcium sulfate (Adamson, 1972; Hedley and Tabachnick, 1958). For example, pyrrhotite reacts with sodium cyanide according to reaction

\[
\text{Fe}_5\text{S}_6 + \text{NaCN} \rightleftharpoons \text{NaCNS} + 5\text{FeS}
\] (3-15)

The ferrous sulfide oxidizes rapidly to ferrous sulfate:

\[
\text{FeS} + 2\text{O}_2 \rightleftharpoons \text{FeSO}_4
\] (3-16)

In alkaline solutions, ferrous hydroxide is precipitated and finally oxidized to ferric hydroxide:

\[
\text{FeSO}_4 + \text{Ca(OH)}_2 \rightleftharpoons \text{Fe(OH)}_2 + \text{CaSO}_4
\] (3-17)

\[
2\text{Fe(OH)}_2 + 1/2 \text{O}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{Fe(OH)}_3
\] (3-18)

The insoluble ferrous and ferric hydroxides are adsorbed as a coating on the sulfide surface which retard further decomposition of the sulfide (Hedley and Tabachnick, 1958).

Of three arsenical common minerals, orpiment (As$_2$S$_3$) decomposes most...
readily in cyanide solution followed by realgar (As$_2$S$_3$) to a lesser extent. The decomposition products are attached to the gold surface and thereby prevent the interaction of CN ions, oxygen, and gold. The third mineral, arsenopyrite (FeAsS or FeS$_2$, FeAs$_2$), is attacked very slowly by typical cyanidation solutions and has no effect on gold dissolution (Hedley and Tabachnick, 1958). However, gold may be present in fine grain size in these minerals, thus complete destruction of these minerals is necessary.

It is apparent from the above discussions and the results shown in Figure 3-4 that the base metals in the ore are mainly present in the form of sulfide minerals. These sulfidic minerals either did not dissolve during cyanidation or if dissolved, they precipitated in the other forms.

Sulfide minerals, however, are thermodynamically unstable. In the presence of sufficient oxygen or an oxidizing agent, the oxidation of these minerals proceed to completion by an exothermic reaction (Woodcock, 1961).

It is known that sulfide minerals conduct electricity and exhibit electron conductivity. Thus, reduction of hypochlorite could take place at the surface of sulfide minerals. Oxygen evolved from the hypochlorite reduction, Figure 3-3; is reduced at the preferred sites on the mineral surface. The process is analogous to the corrosion of metals involving two simultaneous reactions according to Woodcock (1961), and the rate is chemically controlled.

The suggested mechanism for oxidation of pyrrhotite by oxygen (Woodcock, 1961) is given as follows:
The initial step is anodic dissolution of mineral and liberation of elemental sulfur from the lattice

\[
\text{FeS} \rightarrow \text{Fe}^{2+} + S^0 + 2e^- \quad (3-19)
\]

Simultaneously, electrons are transferred through the mineral lattice, and are consumed in the cathodic reduction of oxygen to water

\[
\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (3-20)
\]

followed by two additional simultaneous reactions in which ferrous ion is oxidized to ferric ion

\[
\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad (3-21)
\]

\[
\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (3-20)
\]

Finally, the hydrolysis of ferric ion to ferric oxide

\[
\text{Fe}^{3+} + 3H_2O \rightarrow 6H^+ + \text{Fe}_2O_3 \quad (3-22)
\]

The overall oxidation is given by

\[
4\text{FeS} + 3O_2 \rightarrow 2\text{Fe}_2O_3 + 4S^0 \quad (3-23)
\]
A similar mechanism for oxidation of pyrite to ferric hydroxide and sulfate ion is described by Stumm and Morgan (1981).

Figure 3-5 shows the base metal concentrations in a column effluent as a function of time for a pretreated ore charge at 24°C followed by a post cyanidation. The metal concentrations are nil during hypochlorite pretreatment, but increased rapidly after cyanide application. These results suggest that the unstable sulfidic minerals are oxidized to their correspondingly more stable and insoluble oxides by the action of hypochlorite according to the mechanism described above. During cyanidation, Cu, Zn, Ni, and As oxides react with cyanide to form soluble cyano-metal complexes. Thermodynamically, the oxides of these metals are the most stable species in the presence of oxygen (Peters, 1976). In the presence of cyanide, however, the region of stabilities of oxides is covered by cyano-metal complexes (Osseo-Asare, 1984; Wang and Forssberg, 1990).

The proposed mechanism for oxidation of sulfide minerals, MS, in alkaline hypochlorite solution may be summarized in a general form as follows:

(cathodic) \[ \text{OCI}^- + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{Cl}^- \quad (3-24) \]

(anodic) \[ \text{MS}_{(s)} + 10\text{OH}^- \leftrightarrow \text{MO} + \text{SO}_4^{2-} + 5\text{H}_2\text{O} + 8e^- \quad (3-25) \]

The overall reaction for this oxidation can be written as

\[ \text{MS}_{(s)} + 4\text{OCI}^- + 2\text{OH}^- \leftrightarrow \text{MO} + \text{SO}_4^{2-} + 4\text{Cl}^- + \text{H}_2\text{O} \quad (3-26) \]
Elemental sulfur may also be formed as a consequence of incomplete oxidation. Chappin and Paulikerberry (1937) studied the oxidation of sodium sulfide solution by sodium hypochlorite. They concluded that at low hypochlorite concentrations, elemental sulfur may be formed. Whereas high hypochlorite concentrations increase the sulfate formation. These investigators reported that sulfur production increases as the alkalinity of the solution increases up to pH 10. Above which sulfate production is increased. Therefore, the elemental sulfur production on the mineral surface could result at the rate of oxygen diffusion through the sulfur layer which results in less consumption. Hypochlorite consumptions are lower and overall pulp densities are higher when the pretreatment temperature is below 15°C. The reverse is true for higher pretreatment temperatures. This is evident from these results that the total amount of metal ions extracted increases with an increase in pretreatment temperature. This means that more sulfur is deflated at higher temperatures.

Figure 3-5. Metal dissolution during cyanidation as a result of metal sulfide oxidation during pretreatment at 24°C. Pretreatment: 1% Ca(OCl)₂ at 0.01 gpm/ft²; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft²; NaCN consumption 0.15 lb/ton.
This is similar to the reaction proposed for the dissolution of molybdenite, MoS$_2$, in alkaline hypochlorite solution (Bhappu et al., 1963).

Elemental sulfur may also be formed as a consequence of incomplete oxidation. Choppin and Faulkenberry (1937) studied the oxidation of sodium sulfide solution by sodium hypochlorite. They concluded that at low hypochlorite concentrations, elemental sulfur may be formed. Whereas high hypochlorite concentrations increase the sulfate formation. These investigators reported that sulfur production increases as the alkalinity of the solution increases up to pH 10, above which sulfate production is increased. Therefore, the elemental sulfur precipitation on the mineral surface could reduce the rate of oxygen diffusion through the sulfur layer which results in less oxygen consumption.

It is illustrated in chapter 2 that temperature plays an important role in the pretreatment step. Hypochlorite consumptions are lower and overall gold extractions are higher when the pretreatment temperature is below 16°C. Whereas the reverse is true for higher temperatures. Figures 3-6 through 3-10 are produced from the same results and show accumulated amounts of metal ions extracted as a function of time at various temperatures. It is evident from these results that the total amount of metal ion extracted increases with an increase in pretreatment temperature. This means that more sulfide is oxidized at higher temperatures and thus, results in more hypochlorite consumption. This phenomenon is due to a high apparent activation energy of reaction of sulfides being oxidized by dissolved oxygen (Woodcock, 1961). In these types of reactions,
Figure 3-6. Accumulative arsenic extraction at various temperatures.

Pretreatment: 1% Ca(OCl)₂ at 0.01 gpm/ft²;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft²;
NaCN consumption 0.15 lb/ton.
Figure 3-7. Accumulative copper extraction at various temperatures.
Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton.
Figure 3-8. Accumulative nickel extraction at various temperatures.
Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$; NaCN consumption 0.15 lb/ton.
Figure 3-9. Accumulative zinc extraction at various temperatures. 
Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$; NaCN consumption 0.15 lb/ton.
Figure 3-10. Accumulative iron extraction at various temperatures.

Pretreatment: 1% Ca(OCl)₂ at 0.01 gpm/ft²;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft²;
NaCN consumption 0.15 lb/ton.
the rates are increased by an increase in temperature. The sulfate productions as a function of time for different pretreatment temperatures are presented in Figure 3-11. Due to the presence of soluble sulfate in the ore body, the differences are not significant. However, sulfate productions are slightly higher for higher temperatures. Choppin and Faulkenberry (1937) have also noted that high temperatures increase the sulfate production.

An interesting result regarding the oxidation of base metals during hypochlorite pretreatment is the association of gold with mercury. Figures 3-12 and 3-13 illustrate the dissolution behavior of mercury and gold, respectively, as a function of time at various temperatures. These results indicate that mercury dissolution follows the same behavior as gold dissolution. The dissolution has a maximum at 14°C and decreases rapidly as temperature of pretreatment increases.

The presence of mercury in Carlin carbonaceous gold ore has not been addressed in the literature. Therefore, the nature of this element in the ore is not clear. Mercury is a very noble metal and can exist in non-oxidizing aqueous solutions of all pH's (Pourbaix, 1974), provided that they are free from complexing agents. Thus, it is encountered in nature in the elementary state along with cinnabar, HgS. Mercury and cinnabar are oxidized in water and alkaline solutions in the presence of oxygen and form HgO which is slightly soluble in water. However, in the presence of complexing agents; Hg and HgO forms soluble complexes which are often quite stable.
Figure 3-11. Sulfate concentration in the effluent as a function of time at various temperatures.
Figure 3-12. Accumulative mercury extraction at various temperatures. Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$; NaCN consumption 0.15 lb/ton.
Figure 3-13. Accumulative gold extraction at various temperatures.

Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton.
It can be hypothesized that mercury exists on the surface of the gold particles as an insoluble film in forms of amalgam or cinnabar. This insoluble film is oxidized to HgO by hypochlorite and is finally dissolved in cyanide solution.

The overall percent extraction of base metals at various temperatures, along with that of gold are compared in Table 3-III. These results show that hypochlorite consumption increases with increasing sulfide dissolution. Contrary to the metal sulfide dissolution, gold and mercury dissolution is not increased by an increase in pretreatment temperature. This phenomenon could be explained in terms of selective oxidation. The metal sulfides are oxidized selectively at elevated temperatures by hypochlorite, leaving little or no oxidizing power to passivate the carbonaceous matter. Consequently, gold and mercury cyanide complexes could be adsorbed by these materials.

Moreover, the insoluble iron oxides such as goethite and iron hydroxides can be formed as the result of the rapid oxidation. The formation of iron oxide coatings around the pyrite particles is reported (Hausen, 1981; Brunk and Atwood, 1987). This could prevent the dissolution of gold.

Oxidation of Carbonaceous Materials

It has been known for many years that chlorine gas and hypochlorite passivate carbonaceous matter contained in gold ores. Consequently, the preg robbing action of the carbonaceous matter is rendered non-preg robbing after these treatments. However, the mechanism of the passivation is not clearly
Table 3-III. Percent base metal and gold extraction in the effluent solutions at various pretreatment temperatures.

<table>
<thead>
<tr>
<th>Metal</th>
<th>3</th>
<th>7</th>
<th>14</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.5</td>
<td>3.7</td>
<td>6.3</td>
<td>7.6</td>
</tr>
<tr>
<td>Cu</td>
<td>13.8</td>
<td>18.8</td>
<td>21.3</td>
<td>30.6</td>
</tr>
<tr>
<td>Ni</td>
<td>3.0</td>
<td>2.4</td>
<td>6.7</td>
<td>8.6</td>
</tr>
<tr>
<td>As</td>
<td>0.3</td>
<td>2.2</td>
<td>1.7</td>
<td>2.5</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Hg</td>
<td>23.5</td>
<td>22.4</td>
<td>31.5</td>
<td>10.9</td>
</tr>
<tr>
<td>Au</td>
<td>67.1</td>
<td>64.2</td>
<td>81.7</td>
<td>49.3</td>
</tr>
<tr>
<td>Ca(OCl)₂ Consumption (lb/ton)</td>
<td>17.3</td>
<td>39.2</td>
<td>37.8</td>
<td>47.2</td>
</tr>
</tbody>
</table>

understood. This is due to the lack of knowledge about the mechanics of gold adsorption onto these materials (preg robbing) themselves.

There is a general agreement that the carbonaceous matter in the Carlin-type gold ores is activated carbon in nature resembling a graphite structure.

The exact mechanism of adsorption of gold cyanide complex onto the activated carbon remains a subject of much debate. Some have suggested that adsorption of ion pairs is the predominant mechanism (Adams et al, 1987; Adams and Fleming, 1989; Adams, 1990). Principally, this mechanism involves the formation of ion pairs of the type $M^{n+} [Au(CN)₂]_n$, where $M^{n+} = Na^+, K^+, Ca^{2+},$...
Mg$^{2+}$, etc, in alkaline solution; and where $M^{n+} = H^+$ in acidic solution. Under high ionic strength conditions, $M^{n+}$ [Au(CN)$_2$]$_n$ ion pairs are adsorbed onto the carbon surface without chemical change and oxygen has an insignificant effect.

An alternative view presented by others is the formation of surface oxide sites from functional groups present on the surface of activated carbon (Tsuchida and Muir, 1986; Muir, 1987; Abotsi and Osseo-Asare, 1986, 1987). According to this theory, aurocyanide is adsorbed onto the surface oxide sites via ion-exchange with OH$^-$ of the functional groups. The proposed mechanism for chromene groups that are assumed to be present on the carbon surface is shown in scheme I below:

Scheme I

\[
\text{Scheme I}
\]

- chromen group

\[
\begin{align*}
&\text{CO}_2 + \quad \begin{array}{c}
\text{O} \\
\text{C}^+ \\
\text{R} \\
\end{array} \quad \begin{array}{c}
\text{O} \\
\text{C}^+ \\
\text{R} \\
\end{array} \\
&\quad \text{OH}^{-} + \quad \text{KAu(CN)$_2$} \\
&\quad \text{KHCO}_3
\end{align*}
\]
However, this model does not offer an explanation for the enhanced loading which is observed from acidified cyanide solutions nor for adsorption of neutral inorganic molecules such as Hg(CN)$_2$. The neutral mercury complex was found to compete directly with Au(CN)$_2^-$ anions for adsorption sites (McDougal and Hancock, 1981; Adams, 1991).

A series of experiments was conducted to study the effect of hypochlorite on the carbon gold loading using a packed column. The column consisted of a piece of polypropylene tube (5 mm I.D., 9 mm O.D.) approximately 5 cm long. The bed support consisted of a filter assembly made of a piece of teflon and tube fitting which was screwed on at both ends of the column (Figure 3-14). The column was packed with 0.25 grams of coconut shell activated carbon (Fisher Scientific). The carbon was crushed and sieved to give a 110-53 μm (-100 x 200 mesh, Tyler scale), rinsed with DI/distilled water and was dried in the air at 70°C for two hours before usage. The surface area of the crushed samples was determined by the BET method to be 1114 ± 40 m$^2$ per gram of carbon. Inductively Coupled Plasma emission spectrometry (ICP) analysis of the carbon is listed in Table 3-IV.

Gold cyanide solutions were prepared by dissolving potassium dicyanoaurate (I), obtained from Johnson Matthey Company, in the 0.04 M NaOH solution. Similarly, gold chloride solutions were prepared by diluting the atomic absorption gold standard (Aldrich) in the 2.4 M HCl. Solutions were pumped through the column at a flow rate of 1 ml/min. The concentrations of Au and
Figure 3-14. Schematic of the experimental setup for carbon adsorption/desorption study.

C = carbon column, P = peristaltic pumps, S = gold or eluent solution, V = injection valve, R = recorders, F = filter, MS = magnetic stirrer, RS = reclaim solution, W = waste, IC = ion chromatograph, ICP = inductively coupled plasma.

Although the assembly was assembled in this study, the experiments were conducted continuously, this feature was not used in this study.
Table 3-IV. Inductively coupled plasma analysis of activated carbon

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount (ppm)</th>
<th>Element</th>
<th>Amount (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>370.0</td>
<td>Ba</td>
<td>5.6</td>
</tr>
<tr>
<td>Ca</td>
<td>520.0</td>
<td>Cr</td>
<td>6.9</td>
</tr>
<tr>
<td>K</td>
<td>27.0</td>
<td>Mg</td>
<td>600.0</td>
</tr>
<tr>
<td>Mn</td>
<td>0.6</td>
<td>Na</td>
<td>400.0</td>
</tr>
<tr>
<td>Ni</td>
<td>27.0</td>
<td>Sn</td>
<td>730.0</td>
</tr>
<tr>
<td>Sr</td>
<td>4.6</td>
<td>Zn</td>
<td>21.0</td>
</tr>
</tbody>
</table>

Au(CN)$_2^-$ in the initial solution and in the column effluent were measured by ICP and the ion chromatography (IC), respectively. The measurements were made after a volume of solution (100 mL) was pumped through the packed column. Although the assembly was such that the gold concentration could be monitored continuously, this feature was not used in this study.

In the first test, 100 mL of a 20% HCl solution containing 105 ppm Au was passed through the column. No gold was detected in the effluent after one volume pass indicating 100% gold adsorption. The Eh dropped from 0.85 V (SHE) to 0.62 V (SHE) whereas pH remained constant at 0.7. Then, the loaded carbon was rinsed with 200 mL DI water in order to raise the pH. Finally, gold was eluted with 100 mL 972 ppm CN$^-$ solution in 0.04 M NaOH, followed by elution with 100 mL DI water. The Eh and pH of the cyanide solution remained unchanged at 10.7 and 0.2 V (SHE).
unchanged at 10.7 and 0.2 V (SHE), respectively, whereas cyanide concentration dropped to 885 ppm. Gold elution as a function of time is illustrated in Figure 3-15. About 100% of the gold was eluted in the form of \( \text{Au(CN)}_2^- \) by combined cyanide and water elution. It is known that gold in gold chloride complex is reduced on the activated carbon surface and is adsorbed as the elemental gold (deSiegel and Soto, 1984).

In the second test, gold was loaded in the same manner as the first test, but eluted by a 150 ppm \( \text{CN}^- \) solution. Gold elution did not go to completion (Figure 3-16) as it did in the previous test. Then, the carbon was subjected to elution with 1% \( \text{NaOCl} \) followed by DI water and cyanide elution. About 80% of the gold was eluted by combined elution and was rinsing gradually.

These results indicate that the elemental gold can be extracted from activated carbon by a strong cyanide solution, Figure 3-15. However, the extraction is incomplete and the system approaches an equilibrium when a weak cyanide solution is used, Figure 3-16. Treating the carbon with the hypochlorite, prevents readsorption of gold cyanide complex and the extraction proceeds again, Figure 3-16.

In the third test, 100 mL of a solution containing 126 ppm gold cyanide solution was passed through the carbon. Sixty-four percent of the gold cyanide was adsorbed onto the carbon. This is equal to gold loading of 25.8 mg Au per gram of carbon. The pH of the solution decreased from 10.5 to 10.1 whereas Eh increased from 0.31 V (SHE) to 0.34 V (SHE). Then, the loaded carbon was
eluted by a 150 ppm CN\(^{-}\) solution followed by a 1 g/L CN\(^{-}\) solution. Only 20% of the Au(CN)\(_2\)^{2-} complex was eluted by the cyanide solution, Figure 3-17. No significant changes in pH's or Eh's were observed during cyanide elution. This result indicates that the elution of gold cyanide complex from activated carbon is more difficult than elution of the adsorbed metallic gold. Finally, the carbon was eluted with 50 mL of 1% NaOCl solution followed by a 150 ppm cyanide solution. The pH dropped from 11.8 to 8.0 and Eh rose from 0.7 V (SHE) to 1.1 V (SHE) during NaOCl elution. A total of 56% of the loaded Au(CN)\(_2\)^{2-} eluted in this test. Further gold elution could be achieved, if the test was continued.

In the fourth and fifth tests, activated carbon was treated with 100 mL of the 5 and 1 percent NaOCl solutions, respectively. About one-third of the carbon mass was lost during treatment with 5% NaOCl solution and the column effluent color was dark brown. No mass losses were observed when carbon was treated with 1% NaOCl and the column effluent was light yellow in color. These column effluents were similar in appearance to the effluent of carbonaceous ore column tests when they were treated with hypochlorite solutions. The pH of the NaOCl solution dropped from 11.8 to 9.2 and its Eh rose from 0.7 V (SHE) to 0.9 V (SHE). About 50% of the NaOCl was consumed in this treatment. After rinsing the treated carbon with DI water, a 100 mL solution containing 12.6 ppm Au(CN)\(_2\)^{2-} was passed through the carbon bed. No adsorption was observed in the case of 5% NaOCl treatment and only 2.4% of the Au(CN)\(_2\)^{2-} was adsorbed when carbon was treated with 1% NaOCl. The results are presented in Table 3-V.
Figure 3-15. Gold extraction from a loaded activated carbon as a function of elution time.
Figure 3-16. Gold extraction from a loaded activated carbon as a function of elution time.
Figure 3-17. Gold extraction from a loaded activated carbon as function of elution time.
The effect of acids on Au(CN)$_2^-$ loading was also investigated. In these tests, 10 g/L Cl$^-$ and 0.15 g/L CN$^-$ were passed through the carbon followed by Au(CN)$_2^-$ solution. The results are presented in Table 3-VI, indicating no effect by these ions on Au(CN)$_2^-$ loading and no adsorption of these ions onto the carbon.

### Table 3-V. Passivation of activated carbon by NaOCl solution at 25°C.

<table>
<thead>
<tr>
<th>Treatment of carbon before loading</th>
<th>Au(CN)$_2^-$ concentration after carbon loaded (mg/L)</th>
<th>Percent Au(CN)$_2^-$ loaded</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>100 ml 5% NaOCl followed by rinsing with water</td>
<td>12.6</td>
<td>0.0</td>
</tr>
<tr>
<td>100 ml 1% NaOCl followed by rinsing with water</td>
<td>12.3</td>
<td>2.4</td>
</tr>
</tbody>
</table>

**Loading Conditions:**
Carbon mass 0.25g; initial Au(CN)$_2^-$ 12.6 mg/l or 10.0 mg/l Au in .02M NaOH; solution volume 100 ml; flow rate 1 ml/min.
The effect of anions on \( \text{Au(}CN\text{)}_2^- \) loading was also investigated. In these tests, 10 g/L \( \text{Cl}^- \) and 0.15 g/L \( \text{CN}^- \) were passed through the carbon followed by \( \text{Au(}CN\text{)}_2^- \) solution. The results are presented in Table 3-VI, indicating no effect by these ions on \( \text{Au(}CN\text{)}_2^- \) loading and no adsorption of these ions onto the carbon.

Table 3-VI. Effect of \( \text{Cl}^- \) and \( \text{CN}^- \) on \( \text{Au(}CN\text{)}_2^- \) adsorption by activated carbon at 25°C.

<table>
<thead>
<tr>
<th>Treatment of carbon before loading</th>
<th>Percent anion adsorbed</th>
<th>( \text{Au(}CN\text{)}_2^- ) concentration after carbon (mg/L)</th>
<th>Percent ( \text{Au(}CN\text{)}_2^- ) loaded</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-</td>
<td>45.0</td>
<td>64.0</td>
</tr>
<tr>
<td>10 g/L ( \text{Cl}^- ) in NaOH</td>
<td>0.0</td>
<td>45.0</td>
<td>64.0</td>
</tr>
<tr>
<td>0.15 g/L ( \text{CN}^- ) NaOH</td>
<td>0.0</td>
<td>44.8</td>
<td>64.2</td>
</tr>
</tbody>
</table>

Loading Conditions:
Carbon mass 0.25g; initial \( \text{Au(}CN\text{)}_2^- \) 125.0 mg/l or 99.0 mg/l Au in .02M NaOH; solution volume 100 ml; flow rate 1 ml/min.
The adsorption action of activated carbon is complex due to the surface properties and pore structure of this unique substance.

The existence of macropores (pores greater than 1000 Å diam.) and micropores (10-100 Å diam.) in activated carbon introduce the distinctive molecular screening properties. According to this phenomenon, the larger adsorbate molecules may be screened out by those smaller than a certain minimum diameter due to the steric effect. In addition, the surface of activated carbon is composed primarily of oxygen-containing organic functional groups. These two properties of carbon, which are directly attributed to the process of activation, are responsible for a variety of carbons showing different behavior in adsorption. The most frequently suggested functional groups according to McDougall and Hancock (1981) are:

- Carboxyl groups
- Phenolic hydroxyl groups
- Quinone - type carbonyl groups
In general, activated carbons are excellent adsorbents of neutral and organic substances but poor adsorbents of inorganic electrolytes. This is because the surfaces of active carbon show hydrophobic characteristics and thus any molecule with limited solubility in water is preferentially adsorbed onto the carbon.

In light of the above discussion, experimental results and results found in the literature, a mechanism could be suggested for adsorption of gold onto the activated carbon.

In this view, the proposed adsorption is via reversible van der Waal's forces whose strengths are inversely proportional to the ionic strength of the solution. In the case of gold cyanide adsorption, the linear and relatively hydrophobic Au(CN)$_2^-$ ion is physically adsorbed from neutral end onto the graphitic planes via van der Waal's force, Figure 3-18.

**Figure 3-18.** Schematic depiction of the Au(CN)$_2^-$ adsorbed on a graphitic plane.
The zeta-potential studies have shown that the negative potential of activated carbons increases with increasing pH (Adams and Fleming, 1989). Moreover, the gold loading increases in acidic solution and decreases at high pH's. This behavior could be explained in terms of ionization of the phenolic and/or carboxylic groups on the carbon surface via

\[
\text{OH} + \text{OH}^- \rightleftharpoons \text{O}^- + \text{H}_2\text{O}
\]

The pKa of this ionization is 9.89. Thus, at pH's higher than 10 carbon surface becomes more negative. Therefore, due to the electrostatic repulsion, \(\text{Au(CN)}_2^-\) ion could not approach carbon surface easily. This is in agreement with the result of the study conducted by Gallager et. al.(1989) on the affinity of carbon for gold complexes. These investigators concluded that extraction of disseminated gold from activated carbon matrix could be accomplished with activated carbon maintained at a negative potential.

On the basis of the mechanism suggested, hypochlorite destroys the hydrophobic sites as well as micropore structures of the active carbon by dissolving portions of the graphitic structure when used excessively.
Gold Extraction Behavior

As illustrated by the Eh-pH relationships for the Au-H$_2$O system, gold is an extremely noble metal. Its domain of stability covers a very large area including the whole of the domain of stability of water at all pH's in the absence of a complexing ligand, Figure 3-19. However, gold is dissolved in the presence

![Equilibrium diagram for the gold-water system, dissolved gold species = 10$^{-4}$ M, (from Hiskey and Atluri, 1988).](image)

Figure 3-19. Equilibrium diagram for the gold-water system, dissolved gold species = 10$^{-4}$ M, (from Hiskey and Atluri, 1988).
Like the other corrosion processes, the dissolution of solid metallic gold is best described in terms of an electrochemical model which involves separate anodic and cathodic reactions, (Habashi, 1967; Hiskey and Atluri, 1988). The schematic of the electrochemical dissolution of gold is illustrated in Figure 3-20. The anodic step involves oxidation and complexation of gold with a complexing ligand, $X^-$, according to the following general reaction

$$ Au + 2X^- \rightarrow Au X^- + e^- \quad (3-25) $$

The cathodic reaction involves the reduction of an oxidant, $O$, which complements reaction (3-25).

$$ O + e^- \rightarrow O^- \quad (3-26) $$

![Figure 3-20. Schematic of the electrochemical microcell describing the dissolution of gold.](image-url)
A mixed potential is developed which is dependent on the pH of the system, oxidant concentration and/or complexing ligand concentration.

According to Habashi (1967) the gold dissolution process is a heterogeneous reaction, which is controlled by the diffusion of both of the reacting species through the Nernst boundary layer.

Gold dissolves in the presence of chloride ion and a strong oxidant when the solution is highly acidic. The mixed potential is 1.1 V (SHE) and the AuCl₄⁻ complex is the only gold species stable under these conditions (Hiskey and Atluri, 1988). Figure 3-21 shows the Eh-pH diagrams for the Au-Cl-H₂O system for 10⁻² M Cl⁻; the shaded area shows a small portion of the water domain occupied by dissolved gold. However, increasing the chloride concentration increases the Au/AuCl₄⁻ boundary to the lower potentials and the higher pH's. In addition, the formation of AuCl₂⁻ would be possible under these conditions.

Gold extraction behavior in the pretreatment step was studied in a typical column leach test. In this test, 132 lb Ca(OCl)₂ per ton of ore was used. This is the approximate quantity of hypochlorite required for maximum gold extraction without any modifications (agglomeration, pH adjustment, etc.). The material was rinsed with water after pretreatment and fire assayed for gold content. The gold dissolution behavior and effluent pH-Eh for this test are presented in Figures 3-22 through 3-24, respectively. Gold is not dissolved in the early stages of the hypochlorite pretreatment. During this time, oxygen generated at the anodic sites (Figure 3-3) presumably oxidizes sulfidic materials to their corresponding oxides
Figure 3-21. Equilibrium diagram for the gold-chloride system, [Au] = 10^{-5} M and [Cl] = 10^{-2} M (from Hiskey and Atluri, 1988).
Figure 3-22. Gold concentration in the effluent as a function of time in the pretreatment process of a column leach test, 131.6 lb/ton Ca(OCl)$_2$, 32% gold extraction.
Figure 3-23. Effluent pH as a function of time in the pretreatment process of a column leach test, 131.6 lb/ton Ca(OCl)$_2$, 32% gold extraction.
and passivates the activated carbon; thus blunts the preg-robbing behavior of the ore. Gold dissolution begins after passivation of the activated carbon. About one-fourth of the hypochlorite is consumed at this time. Gold concentration is initially high but decreases rapidly, Figure 3-23. The maximum hypochlorite gold extraction occurred at the lowest effluent pH just before the pH started to rise (see Figures 3-23 and 3-25). This is in agreement with the stability domain of gold chloride, hydroxide and oxide complexes, Figure 3-21. The rise in pH is due to the decrease in hypochlorite consumption as the pretreatment progresses.

Figure 3-24. Redox potential of the effluent as a function of time in the pretreatment process of a column leach test, 131.6 lb/ton Ca(OCl)₂, 32% gold extraction.

In a series of bottle roll tests, 10 mg metallic gold powder (<25 mesh) was placed in the bottle and leached for twenty-four hours. The leach solutions were treated with a standard cyanide test. The results which are shown in Table 3-VII indicate clearly that gold could not be dissolved in hypochlorite leach solutions. The overall gold extraction profile for a typical column leach test is shown in Figure 3-25. Shortly after the introduction of cyanide solution, the liberated
and passivates the activated carbon; thus hindering the preg-robbing behavior of the ore. Gold dissolution begins after passivation of the activated carbon. About one-fourth of the hypochlorite is consumed at this time. Gold concentration is initially high but decreases rapidly, Figure 3-23. The maximum hypochlorite gold extraction occurred at the lowest effluent pH just before the pH started to rise (see Figures 3-22 and 3-23). This is in agreement with the stability domain of gold chloride, hydroxide and oxide complexes, Figure 3-21. The rise in pH is due to the decrease in hypochlorite consumption as the pretreatment progresses.

Approximately one-third of the total gold was extracted after all the hypochlorite was consumed. Further hypochlorite pretreatment does not increase the overall gold extraction.

One explanation for this behavior could be the surface retardation of metallic gold at high Eh and pH as it is demonstrated in the following experiments.

In a series of bottle roll tests, 10 mg metallic gold powder (-325 mesh) was placed in a 100 mL of 1% Ca(OCl)₂ solution and agitated on a rolling mill for twenty-four hours. The pH was adjusted by means of sulfuric acid. A standard cyanidation test was also conducted in the same way for a baseline. The results which are shown in Table 3-VII indicate clearly that gold could not be dissolved in hypochlorite solution at high pH.

The overall gold extraction profile for a typical column leach test is shown in Figure 3-25. Shortly after the introduction of cyanide solution, the liberated
gold particles, having exposed and fresh surfaces, are dissolved rapidly. The magnitude of extraction during cyanidation depends on the degree of oxidation during pretreatment.

In addition, IC analyses of the column leach effluent (Table 3-VIII) indicate production of sulfate ions throughout the experiment. These analyses further show that \( \text{ClO}_3^- \) ions are not produced during pretreatment since \([\text{ClO}_3^-]\) was essentially the same as in the head solution throughout leaching. This indicates that hypochlorite ion is not degraded via reaction (3-5).
Figure 3-25. Percent gold extraction as a function of time for a complete leaching process, 22 days pretreatment, 15 days cyanidation.
Consumption: 116 lb/ton hypochlorite, 0.29 lb/ton cyanide.

Table 3-VIII. The IC analysis of the effluent of a typical hypochlorite leaching test.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>ClO⁻ (g/L)</th>
<th>Cl⁻ (g/L)</th>
<th>ClO₂⁻ (g/L)</th>
<th>SO₄²⁻ (g/L)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head</td>
<td>6.8</td>
<td>2.3</td>
<td>0.64</td>
<td>0.97</td>
<td>11.5</td>
</tr>
<tr>
<td>1</td>
<td>0.0</td>
<td>7.9</td>
<td>0.58</td>
<td>0.94</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>7.8</td>
<td>0.61</td>
<td>0.25</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>8.1</td>
<td>0.64</td>
<td>0.27</td>
<td>4.5</td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>8.2</td>
<td>0.73</td>
<td>0.28</td>
<td>6.4</td>
</tr>
<tr>
<td>8</td>
<td>0.0</td>
<td>8.0</td>
<td>0.61</td>
<td>0.34</td>
<td>5.5</td>
</tr>
<tr>
<td>10</td>
<td>5 ppm</td>
<td>8.4</td>
<td>0.74</td>
<td>0.28</td>
<td>6.6</td>
</tr>
<tr>
<td>11</td>
<td>3 ppm</td>
<td>8.3</td>
<td>0.76</td>
<td>0.28</td>
<td>6.7</td>
</tr>
<tr>
<td>12</td>
<td>5 ppm</td>
<td>8.5</td>
<td>0.74</td>
<td>0.28</td>
<td>6.7</td>
</tr>
<tr>
<td>13</td>
<td>0.1</td>
<td>8.0</td>
<td>0.67</td>
<td>0.99</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Table 3-VIII. The IC analyses of the effluent of a typical hypochlorite leaching test.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>ClO^- (g/L)</th>
<th>Cl^- (g/L)</th>
<th>ClO_3^- (g/L)</th>
<th>SO_4^{2-} (g/L)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head</td>
<td>6.8</td>
<td>2.3</td>
<td>0.64</td>
<td>0.07</td>
<td>11.5</td>
</tr>
<tr>
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<td>7.9</td>
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<td>0.86</td>
<td>7.5</td>
</tr>
<tr>
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<td>0.0</td>
<td>7.8</td>
<td>0.61</td>
<td>0.25</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>8.1</td>
<td>0.64</td>
<td>0.27</td>
<td>6.5</td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>8.2</td>
<td>0.73</td>
<td>0.28</td>
<td>6.4</td>
</tr>
<tr>
<td>8</td>
<td>0.0</td>
<td>8.0</td>
<td>0.61</td>
<td>0.34</td>
<td>6.4</td>
</tr>
<tr>
<td>10</td>
<td>4 ppm</td>
<td>8.0</td>
<td>0.67</td>
<td>0.32</td>
<td>6.5</td>
</tr>
<tr>
<td>11</td>
<td>5 ppm</td>
<td>8.4</td>
<td>0.74</td>
<td>0.28</td>
<td>6.6</td>
</tr>
<tr>
<td>12</td>
<td>5 ppm</td>
<td>8.3</td>
<td>0.76</td>
<td>0.23</td>
<td>6.7</td>
</tr>
<tr>
<td>13</td>
<td>5 ppm</td>
<td>8.5</td>
<td>0.74</td>
<td>0.36</td>
<td>6.7</td>
</tr>
<tr>
<td>14</td>
<td>0.1</td>
<td>8.0</td>
<td>0.67</td>
<td>0.49</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Side Reactions

Side reactions during pretreatment processes include the oxidation of sulfidic materials and dolomite. Oxidation mechanisms of the former were discussed previously.

It was illustrated in Chapter 2 that dolomite decomposition is increased with increasing temperature. Consequently, hypochlorite consumption is increased.

The dolomite decomposition mechanism can be described by the reactions as follows:

\[
\text{Ca}^{++} + \text{MgCO}_3 \text{CaCO}_3 \rightleftharpoons \text{Mg}^{++} + 2\text{CaCO}_3
\]
Hypochlorite reduces at the surface of a solid according to reactions (3-27) through (3-30)

\[
\text{Ca(OCl)}_2 \rightleftharpoons \text{Ca}^{++} + 2\text{Cl}^- \quad (3-27)
\]
(cathodic)

\[
2\text{Cl}^- + 2\text{H}_2\text{O} + 4e^- \rightleftharpoons 2\text{Cl}^- + 4\text{OH}^- \quad (3-28)
\]
(anodic)

\[
4\text{OH}^- \rightleftharpoons 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \quad (3-29)
\]

The overall reaction combining equation (3-26) with (3-30)

\[
\text{MgCO}_3 \cdot \text{CaCO}_3 + \text{Ca(OCl)}_2 \rightleftharpoons \text{MgCl}_2 + 2\text{CaCO}_3 + \text{O}_2 \quad (3-31)
\]

The solubility of MgCl\textsubscript{2} increases with increasing temperature (Linke, 1965), which means reaction (3-31) proceeds to the right rapidly at high temperatures. As a result, more hypochlorite is consumed at high temperatures. The oxygen generated could be consumed by the ore components at the top portion of the ore charge leaving little or no oxidizing power to oxidize the bottom portion. This is what was observed in the tests which were conducted at ambient temperature.
In addition, the decomposition of hypochlorite is catalyzed by the oxides of transition metals. The catalytic activity increases in the order Mn $<$ Fe $<$ Cu $<$ Co $<$ Ni (Lister, 1956; Warren and King, 1977). It is well known that oxides of these metals are oxidized to higher oxides by hypochlorite (Pourbaix, 1974). The suggested mechanism of this catalysis reaction is reported to be in the stages (Lister, 1956) with loss of oxygen as follows:

\[
2\text{MO} + \text{ClO}^- \leftrightarrow \text{M}_2\text{O}_3 + \text{Cl}^- \quad (3-32)
\]

\[
\text{M}_2\text{O}_3 + \text{ClO}^- \leftrightarrow \text{M}_2\text{O}_5\text{ClO}^- \text{(adsorbed)} \quad (3-33)
\]

\[
\text{M}_2\text{O}_5\text{ClO}^- \leftrightarrow 2\text{MO} + \text{Cl}^- + \text{O}_2 \quad (3-34)
\]

Where M is any catalytic metal. According to this report, manganese and iron do not catalyze the reaction. This is attributed to their oxidation to stable states.
III - CONCLUSIONS

The following conclusions may be drawn from this part of investigation:

• The base metals of the Carlin-type ore tested are mainly present in the form of sulfides. These sulfides neither dissolve by cyanide nor by hypochlorite solutions. However, hypochlorite selectively oxidizes metal sulfides to their correspondingly insoluble oxides at elevated temperatures. This phenomenon is due to the high apparent activation energy of sulfides reaction with dissolved oxygen. The overall reaction for oxidation of sulfide minerals, MS, in an alkaline hypochlorite solution may be summarized as:

\[
\text{MS(s)} + 4\text{OCl}^- + 2\text{OH}^- \leftrightarrow \text{MO} + \text{SO}_4^{2-} + 4\text{Cl}^- + \text{H}_2\text{O}
\]

• Hypochlorite consumption increases with increasing sulfide dissolution at elevated temperatures which results in a low gold extraction.

• Mercury dissolution follows the same behavior as gold dissolution. It can be hypothesized that mercury exists on the surface of gold particles as an insoluble film.

• The elemental gold can be eluted from activated carbon by a strong cyanide solution. The elution is incomplete when a weak cyanide solution is used instead. However, the elution proceeds to completion when the carbon is treated with a hypochlorite solution.

• The elution of gold cyanide from a loaded activated carbon by means of
a cyanide solution is more difficult than elution of the adsorbed metallic gold.

- Aurocyanide ion adsorbs onto the graphitic planes of carbonaceous materials from its end via reversible van der Waal's forces.

- Hypochlorite destroys the hydrophobic sites and micropore structures of the activated carbon, preventing readsorption of gold cyanide complex onto the carbon.

- Gold is not dissolved in the early stages of the hypochlorite pretreatment. However, gold dissolution begins after passivation of all of the carbonaceous matter. The maximum hypochlorite gold extraction occurs at the lowest effluent pH just before the pH starts to rise.

- Gold cannot be dissolved in the hypochlorite solutions at high pH's.

- The prime side reactions during pretreatment processes include the oxidation of sulfidic materials and decomposition of dolomite.

- Dolomite, CaMg(CO$_3$)$_2$, constitutes a large fraction of the total composition of the Carlin-type ore. Hypochlorite decomposes dolomite and forms calcium carbonate and magnesium chloride. The overall reaction for this decomposition can be summarized as

$$\text{MgCO}_3\text{.CaCO}_3 + \text{Ca(OCl)}_2 \leftrightarrow \text{MgCl}_2 + 2\text{CaCO}_3 + \text{O}_2$$

The solubility of MgCl$_2$ increases with increasing temperature, resulting in a high hypochlorite consumption.
Role of Oxygen in the Pretreatment Process

I - INTRODUCTION

From earlier discussions, it can be seen that the concentration of oxygen is critical for oxidation of carbonaceous matter. However, the oxygen concentration in the bottom portion of the ore charge is much less than in the upper portions and consequently oxidation of the carbonaceous matter decreases with increasing bed height. This is attributed primarily to impurities present in the ore charge. The use of air in chlorination processing of a highly refractory carbonaceous gold ore "Double Oxidation", decreased chlorine consumption (Guay, 1980). Aeration serves to reduce chlorine consumption, largely by oxidizing the sulfide species contained in the ore.

The high demand for oxygen in the oxidation of both the carbonaceous and sulfidic material results in high hypochlorite consumption. Moreover, oxygen availability can be limited by the reaction of oxygen with gangue materials. For example, pyrrhotite oxidizes rapidly to sulfate (Hedley and Tabachmick, 1958),
FeS + 2O₂ ⇌ FeSO₄ (4-1)

and in an alkaline medium it converts to ferrous hydroxide,

FeS + 2OH⁻ ⇌ Fe(OH)₂ + S²⁻ (4-2)

which is easily oxidized to ferric hydroxide (Habashi, 1967)

2Fe(OH)₂ + 1/2O₂ + H₂O ⇌ 2Fe(OH)₃ (s) (4-3)

Pyrite oxidizes to ferrous and ferric sulfate (Bartlett, 1990)

2FeS₂ + 7O₂ + 2H₂O ⇌ 2FeSO₄ + 2H₂SO₄ (4-4)

4FeSO₄ + 2H₂SO₄ + O₂ ⇌ 2Fe₂(SO₄)₃ + 2H₂O (4-5)

Also, arsenopyrite consumes oxygen in highly alkaline solutions (Dorr and Basque, 1950)

4FeAsS + 4Ca(OH)₂ + 11O₂ ⇌ 4FeSO₄ + 4CaHAsO₃ + 2H₂O (4-6)

In addition, sulfide ion is partly oxidized to thiosulfate and polysulfide (Habashi, 1967)
The oxygen demand for adequate pretreatment is proportional to the amount of sulfide mineral and organic material. An insufficient contact of oxygen with these materials will not adequately oxidize them.

The relation of dissolved oxygen with the bed height and effect of solution application into the ore charge are investigated and described in this chapter.

**Experimental**

Special columns were designed with injection and sampling ports along both sides at 2 and 3 foot intervals, respectively. The ports' construction was such that it did not prevent water circulation around the inner tube of the water jacket columns, Figure 4-1.

Each sampling device consists of a plastic funnel (10ml capacity) filled with glass wool. The tip of the funnels were connected to the teflon tubing and then were passed through the sampling ports. The tubing lines from two sampling devices plus those from the bottom of the column and head solution were connected to a selector valve which has a single output port. In addition, lines from distilled water and pH buffer containers were connected to the selector valve for the baseline adjustments (see Figure 4-1). The single output port of the valve
Figure 4-1. Schematics of the experimental setup for the multi-levels injection study. 

S = sampling port, I = injection port, G = glass wool
F = flow-through cell, V = injection valve, W = waste,
P = peristaltic pumps, M = potentiometer, R = recorder,
H = head solution, WI and WO = cooling water in and out.
was attached to a peristaltic pump to produce a solution flow rate of one mL per minute. Then, the output line of the pump was connected to three flow-through cells in series. The first cell consisted of a pH electrode. The second cell consisted of a platinum working electrode plus a Ag/AgCl reference electrode separated from the flowing solution by means of a Nafion membrane to measure potentials, and the third cell consisted of a YSI Micro Oxygen Probe Model 5357 equipped with a constant temperature circulating block to measure dissolved oxygen. The first and second cell electrodes were connected to the Orion meters Model 500 and 940, respectively. The oxygen probe was connected to the YSI Model 5300 Oxygen Monitor. Finally, all three cell output signals were recorded on a three pen strip chart recorder simultaneously. The flow diagram of the complete system is shown in Figure 4-1.

The sampling devices plus Tygon tubing for hypochlorite injection were placed inside of the ore charge as the column was gradually filled with the material.

Before each measurement, the air equilibrated distilled water was circulated through the cells and the oxygen monitor was set to 100.0%. All dissolved oxygen measurements were made relative to this baseline.

II - RESULTS AND DISCUSSION

In the first series of experiments, hypochlorite solution was simply pumped to the top of the column as in the normal pretreatment.
The relative dissolved oxygen in the leach solution at different elevations for tests conducted at 24, 14, and 7°C is illustrated graphically in Figures 4-2, 4-3, and 4-4, respectively. The oxygen content of the leach solution for the test conducted at 24°C (see Figure 4-2) is less than for those tests conducted at sub-ambient temperature, Figures 4-3 and 4-4. In addition, the dissolved oxygen decreased as the ore charge depth increased. The oxygen content of the leach solution in the lower portion of the bed is essentially the same as for air-equilibrated distilled water for the test conducted at 24°C, Figure 4-2. This indicates that the oxygen generated from reduction of hypochlorite is consumed in the upper portion of the bed. On the other hand, the dissolved oxygen in the leach solution is higher than in the hypochlorite feed solution (120%) in the case of sub-ambient experiments. Moreover, the redox potentials for sub-ambient tests, Figures 4-5 and 4-6, are approximately the same at all elevations indicating a continuous redox reaction throughout the ore charge. Whereas, in the high temperature test (Figure 4-7) the redox potentials are lower in the lower portion than in the upper portion of the ore charge indicating that the oxidation is not uniform throughout the packed material. This phenomenon suggests that the activated carbon content of the organic material is not completely passivated and/or gold content of organic matter is not released in the lower portion of the column. The gold extracted from the top portion could be readsorbed in lower portions whenever the oxidation is incomplete. The data presented in Table 2-VI of Chapter 2 support this hypothesis.
Figure 4-2. Relative percent dissolved oxygen in the hypochlorite effluent at various bed height locations as a function of leaching time at 24 °C.
Figure 4-3. Relative percent dissolved oxygen in the hypochlorite effluent at various bed height locations as a function of leaching time at 14 °C.
Figure 4-4. Relative percent dissolved oxygen in the hypochlorite effluent at various bed height locations as a function of leaching time at 7 °C.
Figure 4-5. Redox potential of the hypochlorite effluent at various bed height locations as a function of leaching time at 24 °C.
Figure 4-6. Redox potential of the hypochlorite effluent at various bed height locations as a function of leaching time at 14 °C.
The pH of leach solutions at different elevations for tests conducted at 24, 14, and 7°C is shown in Figures 4-8, 4-9, and 4-10, respectively. It is evidenced that solution pH's are more basic and uniform for sub-ambient temperatures than at 24°C. It is shown in Chapter 8 (see Figure 2-3) that hypochlorite consumption decreases at high pHs. In addition, pH decreased to 7 in the middle of the bed height for the test conducted at 24°C, Figure 4-8. At this pH, gold chloride could be produced which may be adsorbed by oxidized carbonaceous matter. This again supports the argument stated in the previous paragraph.

In the second series of experiments, hypochlorite solution was pumped initially to the top of the column for two days, then to the second port (from the top of the column) for two days, next to the second port and so on. As usual, aeration followed this treatment. Figures 4-11, 4-12, and 4-13 show the solution pH, redox potential, and dissolved oxygen at different elevations for the tests conducted at 24°C using multi-level injection technique. All three parameters (pH, Eh, and D.O.) increased from 49.3% to 74.0% for the same hypochlorite consumption using this solution application technique.

Figure 4-7. Redox potential of the hypochlorite effluent at various bed height locations as a function of leaching time at 7 °C.
The pH of leach solutions at different elevations for tests conducted at 24, 14, and 7°C is shown in Figures 4-8, 4-9, and 4-10, respectively. It is evidenced that solution pH's are more basic and uniform for sub-ambient temperatures than at 24°C. It is shown in Chapter 2 (see Figure 2-3) that hypochlorite consumption decreases at high pH's. In addition, pH decreased to 7 in the middle of the bed height for the test conducted at 24°C, Figure 4-8. At this pH, gold chloride could be produced which may be adsorbed by unoxidized carbonaceous matter. This again supports the argument stated in the previous paragraph.

In the second series of experiments, hypochlorite solution was pumped initially to the top of the column for two days, then to the first port (from the top of the column) for two days, next to the second port and so on. As usual, cyanidation followed after this treatment.

Figures 4-11, 4-12, and 4-13 show the solution pH, redox potential, and dissolved oxygen, respectively, at different elevations for the tests conducted at 24°C using multi-level injection. All three parameters (pH, Eh, and D.O.) increased using this technique compared to the test in which a normal pretreatment was applied (figures 4-2, 4-5, and 4-8). In addition, gold extraction increased from 49.3% to 74.0% for the same hypochlorite consumption using this solution application technique.

Figures 4-14 and 4-15 show that the oxidation of sulfide decreased substantially by using the multi-level injection technique compared to the normal
pretreatment technique (figures 4-16 and 4-17). Moreover, Figure 4-18 shows that dolomite decomposition is much lower in comparison with the test in which this injection technique was not used (Figure 4-19). As a result, gold hypochlorite consumption even further decreased for tests conducted at sub-ambient temperatures.

Table 4-I shows a comprehensive comparison between these results and the previous ones. The results indicate that a combination of the finer material, agglomeration, low temperatures and introduction of hypochlorite solution at different elevations reduce hypochlorite consumption and increase gold extraction.

![Graph showing leaching time vs. pH at various bed height locations](image)

*Figure 4-8: The hypochlorite effluent pH at various bed height locations as a function of leaching time at 34 °C.*
Figure 4-8. The hypochlorite effluent pH at various bed height locations as a function of leaching time at 24 °C.
Figure 4-9. The hypochlorite effluent pH at various bed height locations as a function of leaching time at 14 °C.
Figure 4-10. The hypochlorite effluent pH at various bed height locations as a function of leaching time at 7 °C.
Figure 4-11. The hypochlorite effluent pH at various bed height locations as a function of leaching time at 24 °C, using multi-level injection technique.
Figure 4-12. Redox potential of the hypochlorite effluent at various bed height locations as a function of leaching time at 24 °C, using multi-level injection technique.
Figure 4-13. Relative percent dissolved oxygen in the hypochlorite effluent at various bed height locations as a function of leaching time at 24 °C, using multi-level injection technique.
Figure 4-14. Accumulative metal extraction at 24°C using the multi-level injection technique.
Pretreatment: 1% Ca(OCl)_2 at 0.01 gpm/ft^2;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft^2;
NaCN consumption 0.15 lb/ton.
Figure 4-15. Accumulative metal extraction at 14°C using the multi-level injection technique.
Pretreatment: 1% Ca(OCl)₂ at 0.01 gpm/ft²; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft²; NaCN consumption 0.15 lb/ton.
Figure 4-16. Accumulative metal extraction at 24 °C.
Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton.
Figure 4-17. Accumulative metal extraction at 14 °C. Pretreatment: 1% Ca(OCl)₂ at 0.01 gpm/ft²; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft²; NaCN consumption 0.15 lb/ton.
Figure 4-18. Dolomite decomposition at different temperatures using the multi-level injection technique. 
Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$; Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$; NaCN consumption 0.15 lb/ton.
Figure 4-19. Dolomite decomposition at different temperatures.
Pretreatment: 1% Ca(OCl)$_2$ at 0.01 gpm/ft$^2$;
Cyanidation: 0.15 g/L NaCN at 0.005 gpm/ft$^2$;
NaCN consumption 0.15 lb/ton.
Table 4-1. Comparison between test results conducted with different hypochlorite pretreatment conditions.

<table>
<thead>
<tr>
<th>Hypochlorite Pretreatment Conditions</th>
<th>Ca(OCl)_2 Used (lb/ton)</th>
<th>Ca(OCl)_2 Consumed (lb/ton)</th>
<th>Gold Extraction Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>No agglomeration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No side injection</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at: 24°C</td>
<td>117.0</td>
<td>117.0</td>
<td>57.2</td>
</tr>
<tr>
<td>Agglomeration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No side injection</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at: 24°C</td>
<td>49.0</td>
<td>47.2</td>
<td>49.3</td>
</tr>
<tr>
<td>Agglomeration plus side injection</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at: 24°C</td>
<td>42.1</td>
<td>42.1</td>
<td>74.0</td>
</tr>
<tr>
<td>14°C</td>
<td>26.1</td>
<td>22.0</td>
<td>67.2</td>
</tr>
<tr>
<td>7°C</td>
<td>26.9</td>
<td>15.3</td>
<td>66.0</td>
</tr>
</tbody>
</table>

At the first look, the application of solution to different elevations seems impractical. However, the installation of pressure emitters at a burial depth of 3 feet at the Coeur-Rochester Mine near Lovelock, Nevada has proved very successful (Wilder and Dixon, 1989). The use of pressure emitters which operate based on the drip irrigation system allowed this mine to operate in an efficient and cost-effective way all winter long. Not only the formation of ice due to the...
sprayed solution application in cold weather was prevented by use of this technique, but also solution evaporation and heat loss in hot weather were also eliminated. The other benefits of using drip irrigation as found by these investigators is a reduction in maintenance, improved environmental controls, reduction in reagent (cyanide) consumption, and optimization of solution control (flow rate) on the heap. These operational benefits offset the tubing costs for the buried emitter system. Moreover, the present technology is able to produce an inexpensive net type irrigation tubing for this purpose.

Another alternative technique would be to pretreat the materials with hypochlorite solution in a multi-lift heap construction during the colder months followed by a one long post cyanidation treatment during the warmer months.

IIl - ECONOMIC CONSIDERATIONS

Sodium or calcium hypochlorite does effectively oxidize the refractory carbonaceous ore and achieves an overall 80% gold extraction. However, the process seems uneconomical because of high hypochlorite consumption. Although this study shows that the hypochlorite consumption can be reduced from 160 to 20 lb/ton of ore using the improved techniques. Yet, the operating cost could be high for the low grade ores due to the price of hypochlorite (1.00 per pound of Ca(OCl)_2). The average operating cost for a standard cyanide heap leach ranges from $10.00 to $15.00 per ton of ore. Assuming a grade of 0.08 ounce per ton and
80% recovery, the operating cost per ounce of gold produced would be $156.25 to $234.40. The addition of $20.00 per ton to this operating cost for hypochlorite cost would increase the operating cost per ounce of gold produced to $468.75 - $546.90. Compared to the present gold price, $380.00 per ounce, this operating cost is not profitable. However, the process becomes economical for the ores with a grade higher than 0.15 oz/ton.

A further improvement in technology is needed to produce hypochlorite at a cheaper price.
IV - CONCLUSIONS

The following conclusions may be drawn from this part of this investigation.

• The oxygen content of the leach solution is higher for tests conducted at sub-ambient temperatures than for tests conducted at ambient temperature.

• The dissolved oxygen in the leach solution decreases as the solution percolates through the ore charge. The high demand for oxygen in the oxidation of both the carbonaceous and sulfidic materials results in high hypochlorite consumption. Moreover, the metal oxides are oxidized to higher oxides by catalytic action which results further decrease in the dissolved oxygen.

• The pH's and redox potentials are not uniform throughout the ore charge in the tests conducted at ambient temperature.

• Introducing hypochlorite solution into the ore charge at different column depths decreases reagent consumption and increases gold extraction.
Hypochlorite pretreatment of refractory carbonaceous gold ore shows promise as a method for oxidizing sulfidic and carbonaceous materials prior to conventional cyanide leaching. However, a successful application of this technology would require the following considerations:

The best gold recovery and lowest hypochlorite consumption would be obtained by increasing pH, pretreating at sub-ambient temperatures, finer grinding and agglomeration, increasing hypochlorite solution flow rate, and using low lifts (pad height). These conditions decrease the hypochlorite consumption by gangue materials as it percolates through the ore charge. The side reactions are decreased further by application of hypochlorite solution at different elevations. In addition, calcium hypochlorite yields higher gold extraction than sodium hypochlorite.

The implementation of all conditions stated above could add to operation cost and decrease throughput. Further research should be done for regenerating and recycling hypochlorite solutions to reduce the chemical costs. The plant site generation of the hypochlorite solution should be also implemented to produce inexpensive reagent.

Overall, it appears that hypochlorite pretreatment of carbonaceous gold ores may become one of the best alternative methods for processing these
refractory ores in the years to come. Moreover, this process becomes more attractive when the price of gold increases as a result of a decrease in availability of more easily processed ores and an increase in the number of carbonaceous gold ore stockpiles.


Kongolo, K., et al., 197 , "Au Mossbauer Study of the Gold Species Adsorbed on


Oseoo-Asare, K., Afenya, P. M., and Abotsi, G. M. K., 1984, "Carbonaceous


