

University of Nevada, Reno

Pressure Cyanidation

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science in
Metallurgical Engineering

by

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THE GRADUATE SCHOOL

We recommend that the thesis
prepared under our supervision by

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requirements for the degree of

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ABSTRACT

Although the effect of high oxygen pressure at elevated slurry temperatures on gold recoveries was previously investigated, the sole effect of the pressure at ambient temperature on cyanide leaching with the presence of nearly enough oxygen for the cyanide reactions to occur has not been found to be studied.

This research work carried out with the objective of investigating the effect of pressure on the recovery of gold from an oxide gold ore and flotation tailings sample the during cyanide leaching process at room temperature.

Pressure cyanidation experiments were run in a laboratory scale autoclave under different oxygen and nitrogen gas pressures and pH conditions. Results showed that, gold recoveries of the pressure cyanidation experiments conducted at room temperature were as much as two times higher than the atmospheric leaching conditions for the same leaching times.

Oxide ore samples leached at ninety (90) psi nitrogen pressure had thirty-six percent (36%) better recovery, carbon in leach (CIL) feed (flotation tailings samples) leached at the same nitrogen pressure had seventy-seven percent (77%) better recovery compared to atmospheric leaching conditions at the same period of leaching time.

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1. INTRODUCTION

The process of cyanidation involves the dissolution of gold containing ores in dilute cyanide solution with the presence of base and oxygen ^[1]. Past studies investigated effects of dissolved oxygen, cyanide concentration, temperature, slurry pH level, agitation speed, particle size of leached ores and slurry densities on the kinetics of gold dissolution reaction ^[2].

The hydrometallurgical processes for the treatment of gold bearing oxide ores has consisted mainly of a cyanide leach followed by solid-liquid separation and has included adsorption, desorption of the precious metal on carbon and recovery of the precious metals by precipitation by zinc ^[3]. For the ores that are not amenable to direct cyanide leaching, various methods such as pressure oxidation, roasting, chlorination, biooxidation, etc. are available to treat these ores to expose the gold particles before cyanidation ^[4].

In the present study, a pressure cyanidation process for gold ores was investigated to determine its effect on recoveries and operating conditions have been identified under which gold is dissolved by pressure cyanidation in an autoclave. The testing focused on standard leaching of ore samples in the presence of pressurized air and nitrogen.

Bottle roll, autoclave tests and chemical analyses for head and tailing samples, leach solutions were conducted on the sample materials for comparison. All preparation and assaying were performed utilizing accepted industry standard procedures ^[5]. The test

work has been applied to a grab sample of an oxide ore samples and flotation tailings in order to show that this technique can be accommodated to samples of different mineralogical compositions.

2. LITERATURE SURVEY

2.1 HISTORY OF CYANIDE

During the eighteenth century, chemists heated dried blood with potash [K_2CO_3] and then treated the aqueous extract with iron vitriol [$FeSO_4$] to obtain an intense blue pigment (Berlin Blue) ^[6]. The main reason why the chemist had this pigment was because the blood contains the red pigment hemin which is iron chelate containing a porphyrin structure with building units of alkylated pyrrol nuclei ^[7]. When it was heated with potash, potassium ferrocyanide was the result ^[8].

In 1752, French chemist Pierre Macquer separated iron oxide by boiling the pigment (Berlin blue) with alkalines. He concentrated the remaining solution by evaporation and obtained potassium ferrocyanide ^[9]. In 1782, Swedish chemist Carl Wilhelm Scheele heated potassium ferrocyanide with dilute sulfuric acid and obtained a dissolved gas in water that he called Berlin blue acid. In 1811, the French chemist Joseph Louis Gay-Lussac (1778–1850) determined that the dissolved gas composition was HCN ^[10]. In 1822, Leopold Gmelin (1788–1853) obtained potassium ferrocyanide by passing chlorine into a solution of potassium ferricyanide ^[11].

The name cyanide comes from the Greek language. According to the terminology Kyanos means blue; the new compounds obtained by this new blue acid was named as cyanide after numerous new compounds of the blue acid became known ^[12]. Following these new discoveries potassium ferrocyanide and potassium cyanide became a commercial product used in different industries by 1830.

2.2 HISTORY OF GOLD CYANIDATION

For the last hundred years amalgamation, gravity concentration, chlorination, cyanide leaching, zinc precipitation and carbon adsorption were the processes used for gold extraction ^[13].

In 1783 Scheele discovered that cyanide solutions had the ability to dissolve gold ^[10]. George and Henry Elkington discovered a new technique for electroplating gold from cyanide solutions in 1836 ^[14].

Processes to remove cyanogens and cyanides formed as by-product in different industries were investigated since the end of 19th century which also contributed to the understanding of the chemistry of cyanides, cyanogens, thiocyanates, cyanates, cyanamides and other related compounds ^[15].

The dissolution reaction of the metal was studied by Prince Bagration, Franz Elsner and Micheal Faraday [16]. John Stewart MacArthur in 1887 applied this knowledge to gold ores. German chemist Guido Bodlander in 1896 proved that oxygen was necessary for the dissolution as declared by Elsner and Faraday ^[17].

MacArthur was the first scientist who used zinc shavings to precipitate gold from cyanide solution. Following his work, Charles W. Merrill used zinc dust, patented it around 1900, Thomas B. Crowe improved the zinc cementation process by removing the air from the solution by passing the solution through a vacuum tank before the cementation process. This combined technique has since been called the Merrill-Crowe process ^[3].

The adsorption of precious metal ions or complexes onto activated carbon was first applied at the end of the 19th century. This method was a very costly process because the only way known to recover the absorbed metal was to burn away the carbon ^[18].

Zadra at the United States Bureau of Mines (USBM) developed an elution technique to desorb the gold from activated carbon by adding sodium hydroxide and a concentrated sodium cyanide solution at atmospheric pressure. This method allowed for the carbon granules to be reused and made the carbon absorption process economical in the 1950s ^[19].

In the 1970s, heap leaching was developed at the USBM and in the 1980s carbon-in pulp, carbon in leach and carbon reactivation technologies were introduced to the gold mining industry ^[20].

2.3 HISTORY OF PRESSURE HYDROMETALLURGY

Pressure hydrometallurgy has been applied in the mining industry for leaching of ores, concentrates and precipitating metals from leach solutions. Pressure leaching has been applied in the industry in the presence and absence of oxygen ^[21]. Pressure leaching at

high temperatures in the absence of oxygen has been applied to solubilizing aluminum, tungsten, nickel, cobalt, titanium and tin oxide from its ores. Pressure leaching in the presence of oxygen is commonly applied to leaching uranium, zinc from sulphide concentrates and liberate gold from pyritic ores ^[22].

The first pressure hydrometallurgy experiments were conducted by Baketoff in 1859. He recovered the silver after heating silver nitrate and hydrogen together in sealed glass tubes ^[23].

The first autoclave was used by Austrian chemist Karl Joseph Bayer to get pure alumina from bauxite ores. In this process, bauxite ore was mixed with concentrated NaOH then fed to a horizontal reactor at 4.5 atm and 240°C ^[24]. This first reactor was 1 m in diameter and 2 meter long. Today there exist horizontal autoclaves up to 6 m in diameter and 40 meter in length ^[21].

In gold ore processing, autoclaves are mostly used for pretreatment of refractory ores in which the metal is found in association with pyrite, arsenopyrite, arsenic sulfides or carbonaceous materials ^[25]. These types of ores are either unresponsive or have very low recoveries to the standard cyanidation processes. Refractory ores are pretreated under high pressures and temperature inside the autoclaves to oxidize sulfides and carbonaceous materials. Many operations in the USA and Australia use this technique with daily ore processing capacities varying between 70 – 1200 tons/day ^[21]. Figure 1 shows three dimensional drawing of a horizontal autoclave manufactured by Outotec ^[26].



Figure 1. Three Dimensional Drawing of a Horizontal Autoclave

The tube autoclaves which have very small diameters and long lengths compared to conventional autoclaves are also used in the industry for treatment of metallic ores. “High pressure low alkalinity cyanidation” was tested on a pilot scale plant in Africa. The plant processed stibnite ores by applying direct cyanidation under high oxygen pressure. In this operation, leaching is conducted at 8.8 MPa oxygen pressure and high temperature inside the tube autoclaves. The recovery values of the process improved from 1% to 85% with the autoclave ^[27].

Recently, a new pressure gold leaching process was also applied to in-situ pressure leaching of heaps by Hydro-Jex® technology. The Hydro-Jex® technology has leached passive inventories of heaps and recovered gold by application of high pressure lixiviant that overcame hydraulic resistivity for the flow ^[28].

2.4 CHEMISTRY OF CYANIDE SOLUTIONS

Sodium cyanide (NaCN) is the major reagent used for cyanide leaching. It dissolves in water forming a metal cation and free cyanide ions (CN⁻) as presented below ^[29].



Hydrolyzed cyanide ions form hydrogen cyanide (HCN) and increase pH of the solution by forming hydroxyl (OH⁻) ions. Hydrogen cyanide dissociates in water to hydrogen and cyanide ions and the direction of this reaction is directly dependent on the pH value of the solution ^[30]. Total cyanide exists as half hydrogen cyanide and half free cyanide ions at pH 9.3 ^[31].

The hydrolysis of cyanide ions and equilibrium constants are shown in Equation (2) ^[32].



$$K_b = \frac{K_w}{K_a} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{K_a} = \frac{10^{-14}}{K_a} = 1.6 \times 10^{-5}$$

The dissociation reaction of hydrocyanic acid in water and dissociation constant of this reaction is presented in Equation (3) ^[33],



$$K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = 6.2 \times 10^{-10}$$

Free cyanide ions compete with OH^- and H^+ during its reaction with water. For this reason the pH of the cyanide solutions will define the amount of free cyanide and HCN formed during the Reactions 2 and 3.

At pH 12 hydrogen cyanide completely dissociates in water and exists as free cyanide ions ^[34]. Above this pH value, the total cyanide exists as free cyanide ions. Figure 2 shows speciation of cyanide and hydrogen cyanide in aqueous solution as a function of pH ^[35].

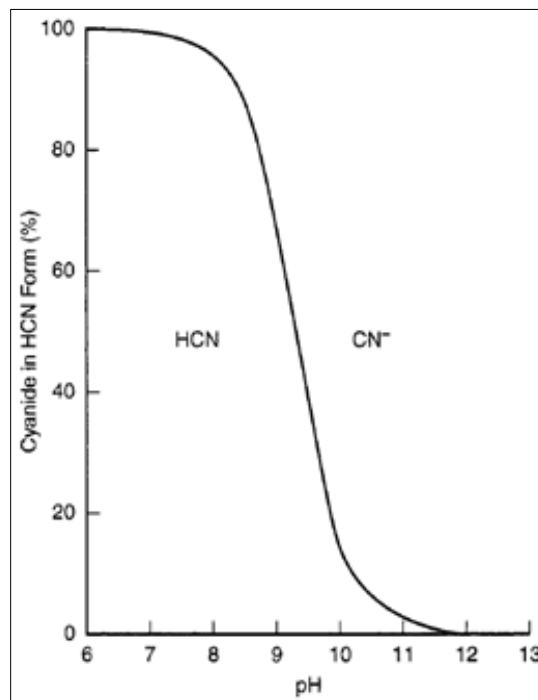


Figure 2. Effect of pH on Formation of CN^- and HCN

Hydrogen cyanide and free cyanide can be oxidized by oxygen to form cyanate (CNO^-) during leaching. Cyanate formation has adverse effects on recovery since it does not

dissolve gold and also decreases free cyanide concentration in the solution. CNO^- forming reactions are shown below ^[36].



The Eh – pH diagram for the CN – H₂O system is given in Figure 3 ^[37]. In this system the cyanide ion concentration is known as 10^{-3} kmol/m^3 .

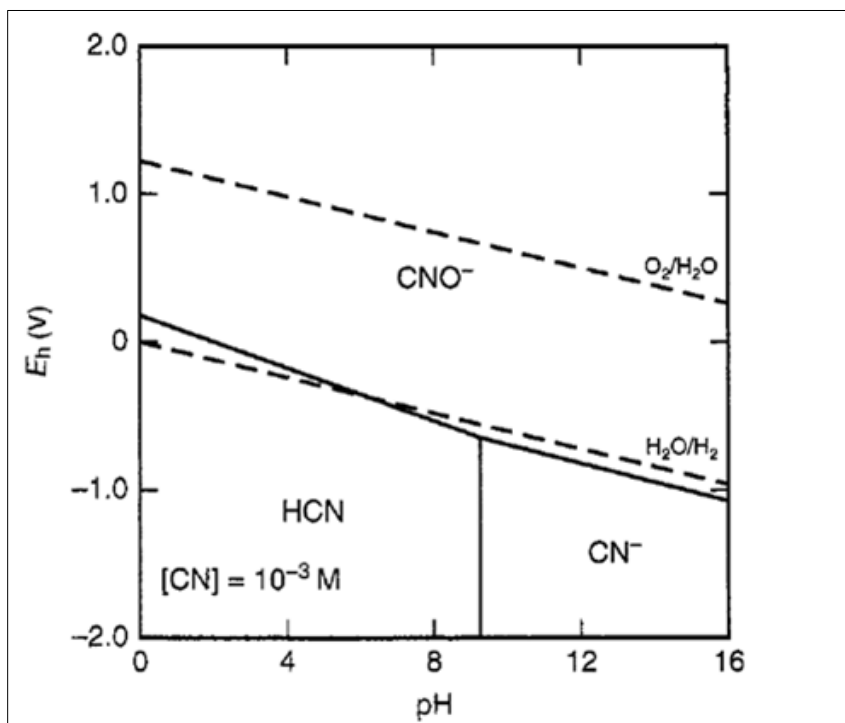


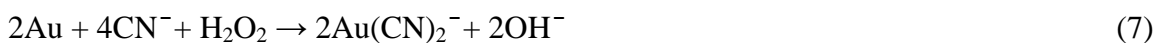
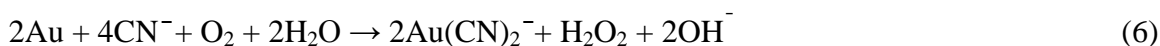
Figure 3. CN – H₂O system E_h – pH diagram at 25 C°

2.5 CHEMISTRY OF GOLD DISSOLUTION IN CYANIDE SOLUTIONS

2.5.1 SOLUBILITY OF GOLD IN CYANIDE SOLUTIONS

Gold dissolves in oxidizing solutions containing leachants such as cyanide, halides, thiourea, thiosulphate and thiocyanate. This noble metal gives the aurocyanide complex $\text{Au}(\text{CN})_2^-$ when it is leached by cyanide ^[38].

During dissolution of gold in cyanide solution, as a first step, oxygen is reduced and hydrogen peroxide is formed as an intermediate product and hydrogen peroxide becomes the oxidizing agent in the second step. The overall chemical reactions are presented below ^[39].



The summation of equations (6) and (7) is presented in the following equation ^[40];



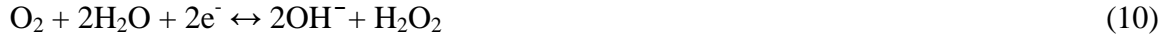
This equation is called the Elsner's equation.

Gold dissolution also involves an anodic reaction of gold oxidation and a cathodic reaction of oxygen reduction ^[41].

The overall anodic reaction is presented in Equation (9) ^[42].



Cathodic reduction reactions of oxygen are shown in Equation (10).



Hydrogen peroxide formed in equation 10 decomposes to H_2O and O_2 , as in Equation (11).



2.6 KINETICS OF DISSOLUTION

The gold dissolution process is electrochemical in nature ^[43]. The mechanism of gold dissolution in an alkaline cyanide solution is a heterogeneous reactions at the solid liquid interfaces. The leach reactions occur by the diffusion of the cyanide ions and the dissolved oxygen through the liquid film on the surface of solid particles. According to this theory the rate of cyanidation is presented by following Equation (12) ^[44] :

$$\text{Rate} = \frac{2 A D_{\text{CN}^-} D_{\text{O}_2} [\text{CN}^-][\text{O}_2]}{\delta\{D_{\text{CN}^-}[\text{CN}^-]+4 D_{\text{O}_2}[\text{O}_2]\}} \quad (12)$$

Where,

$[\text{CN}^-]$ and $[\text{O}_2]$ = Concentrations (in moles/ml) of cyanide and dissolved oxygen

D_{CN^-} and D_{O_2} = Diffusion coefficients of cyanide and dissolved oxygen

A = Surface area of the metal in contact with aqueous phase, in cm^2

δ = Thickness of the boundary layer

The cyanide leaching process is affected by several factors including particle size, cyanide concentration, oxygen concentration, solution temperature, pH, slurry density, speed of agitation factors which are more closely related to the experimental work of pressure cyanidation will be discussed.

2.6.1 EFFECT OF PARTICLE SIZE

The rate of dissolution depends on the surface area of the metal exposed to leaching with the lixiviant. The liberation size of the ore should be reached by a size reduction processes in order to have higher recovery rates of the leaching reactions. According to the study in 1940s ^[45], there is a linear relationship between the gold particle sizes ranging between 10 to 100 μm and the dissolution time required. Another study ^[46] reported similar results on Figure 4 which shows the gold dissolution amounts at the end of the 24 hour leach time at room temperature.

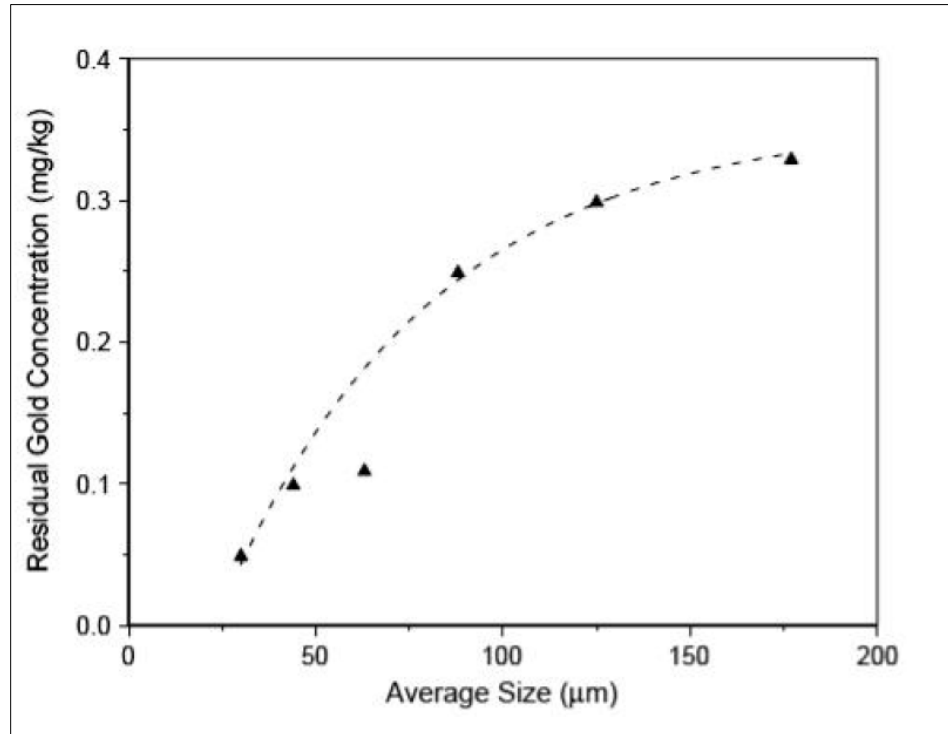


Figure 4. Particle Size Effect on Residual Gold Concentration During Cyanide Leaching

On the other hand, the rate of gold dissolution may decrease with decreased particle size by liberation of other cyanide consuming elements in the ore.

2.6.2 CYANIDE CONCENTRATION

Two moles of cyanide are consumed for one mole of gold dissolved during the dissolution of gold in cyanide solution. This is also shown by Elsner's equation. The rate of gold dissolution is one-half the rate of cyanide consumption [44] :

$$\text{Rate of gold dissolution} = \frac{1}{2} \frac{d(\text{CN}^-)}{dt} \quad (13)$$

Gold extraction increases with increasing cyanide concentration. ^[47]. Gold leaching will increase with increased cyanide concentration in air-saturated solutions when the cyanide concentration is below the critical concentration value 0.1 % by weight of the solution (1000 ppm). Above this molar concentration, increasing the level of cyanide in leach solutions has no positive effect on gold recoveries ^[38]. Also the excess cyanide will cause an increase in cyanide consumption due to formation of cyano complexes from impurities ^[48].

2.6.3 OXYGEN CONCENTRATION

Oxygen is the second most important reagent in leaching of gold bearing ores by cyanide. The concentration of gold determines the concentration of the cathodic reduction of oxygen.

As shown in Equation 2, two (2) moles of gold requires one (1) mole of oxygen gas (O₂). The amount of oxygen dissolved in dilute solution mainly depends on temperature, oxygen partial pressure conditions and agitation speed.

While higher concentrations of oxygen and cyanide increases gold leaching rates, as indicated on the previous section after a certain cyanide concentration level cyanide consumptions will also increase. According to the mixed potential theory oxidation of gold and reduction of oxygen does take place at the same rate. On the basis of this theory the optimum concentration of [CN⁻] / [O₂] has been estimated to be 6 for the maximum

rate of gold dissolution in cyanide solutions ^[49]. According to another study ^[50], the optimum ratio of $[\text{CN}^-] / [\text{O}_2]$ is found as between 4.6 – 6.3.

The diffusion of oxygen to the gold surface is another dissolution rate controlling parameter during gold leaching ^[51]. All particles in slurry should be suspended by sufficient agitation to ensure mass transfer of dissolved O_2 and CN^- ions to be fast enough for the surface reactions during the leaching process. A reaction mechanism to describe rate of gold leaching is presented below ^[52].

$$d[\text{Au(I)}]/dt = k [\text{CN}^-]^{-0.5} [\text{O}_2]^{0.5} \quad (14)$$

This leach rate equation is one-half order in the concentrations of cyanide and oxygen and does take into consideration the transport steps of leaching which are discussed in more detail in the next section.

2.6.4 EFFECT OF LIXIVANT DIFFUSION

Different studies have been done to explain the relationship and diffusivity and the reaction rates of a leaching system. The shrinking core model ^[34] is one of the most the important studies done so far. According to this study, lixivants can diffuse into the solid micropores under a chemical activity gradient. Figure 5 explains the relations between the leached and unreacted parts of the solid particles; lixiviant and leached metal concentrations according to this theory.

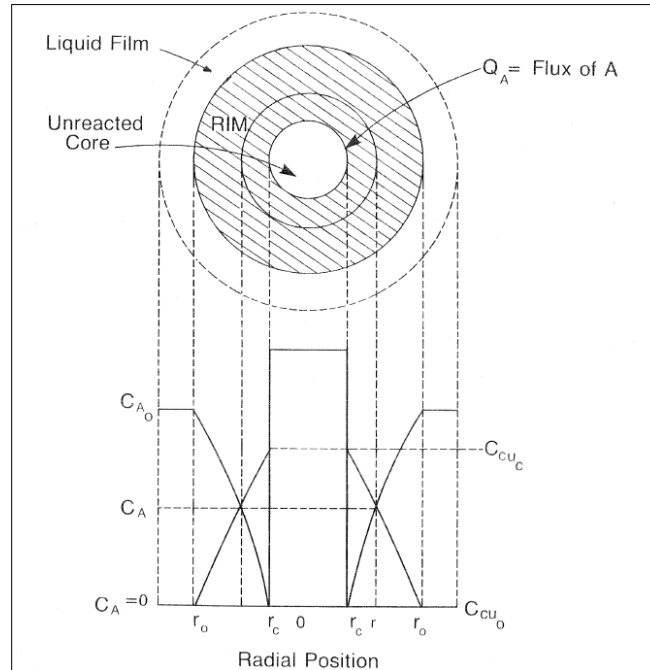


Figure 5. Concentration Gradients for Copper (C_{Cu}) and Lixiviant (C_A) of an Oxide Copper Ore with Representation of Leached Rim and Unreacted Core

According to this theory, the diffusion of the lixiviant into the rock pores will cause the widening of the leached rim and the unleached core shrinks until the completion of the leaching.

He also formulated the effect of lixiviant diffusion on the metal extraction amount by the following formula,

$$F = \left[\frac{2V_{Cu} D_{eff} A_0}{Br_0^2} \right] t \quad (15)$$

Where,

F = Fraction extracted

V_{Cu} = Molar volume of copper in rock

D_{eff} = Effective diffusivity coefficient

A_o = Initial concentration of the lixiviant

B = Chemical leaching reaction constant for the ore

r_o = Initial radius of the rock

t = Leach time

This model is valid for copper oxide ores, not for gold ores, due to the dissolution rate difference between two metals. But the model clearly identifies the direct relationship between diffusion and the leach rates of metals. Because of this, the theory was added to the literature survey part of this study. For the reactions where the reactants and product concentrations are low, the mass transport rate through the liquid film layer may be increased with the following changes ^[53];

- Reduction of the diffusion layer thickness (i.e by mixing)
- Increasing solution flow rate (i.e. higher lixiviant concentrations)
- Increasing shear (i.e. by mixing)

As explained in another study ^[54], leaching kinetics of metals are directly related to the diffusion of lixiviant into the pores of the solids. These steps of the lixiviant diffusion can be summarized as follows;

- 1- Diffusion of the lixiviant through the boundary layer around the solids particles,
- 2- Diffusion of lixiviants though the pores of the solid particles,
- 3- Absorption and desorption reactions between metals and lixiviant,
- 4- Diffusion of leached metal products out of the porous media,
- 5- Diffusion of the leached metal products away from the solid surface through the boundary layer,

2.6.5 EFFECT OF PRESSURE

2.6.5.1 EFFECT ON OXYGEN SOLUBILITY

Oxygen gas solubility in water increases with increased pressure or decreased temperatures. Table 1 shows the oxygen solubility in water under different pressures and temperatures ^[55].

| <i>Temperature (C°)</i> | <i>Pressure (psi)</i> | | | |
|-------------------------|---|-------------|-------------|-----------|
| | 14.7 | 29.3 | 58.7 | 90 |
| | Solubility of oxygen in water (mg/l) | | | |
| 0 | 14.6 | 29.2 | 58.4 | 89.7 |
| 5 | 12.8 | 25.5 | 51.1 | 78.6 |
| 10 | 11.3 | 22.6 | 45.1 | 69.7 |
| 15 | 10.1 | 20.2 | 40.3 | 62.4 |
| 20 | 9.1 | 18.2 | 36.4 | 56.6 |
| 25 | 8.3 | 16.5 | 33.1 | 51.8 |
| 30 | 7.6 | 15.2 | 30.3 | 47.9 |
| 35 | 7.0 | 14.0 | 27.9 | 44.7 |
| 40 | 6.5 | 12.9 | 25.9 | 41.9 |
| 45 | 6.0 | 12.0 | 24.0 | 39.5 |
| 50 | 5.6 | 11.3 | 22.7 | 37.5 |

Table 1. Oxygen Solubility in Water

The mixture of gases also follows the single gas law as described by Boyle's law ^[56].

$$P \cdot V = k \quad (16)$$

Where,

P = Pressure of the system

V = Volume of the gas

k = Constant representing pressure and volume of the system

Application of Boyle's law to the mixture of gases is explained by Dalton's Law of Partial Pressures ^[57] which states,

- Each gas in a mixture exerts a partial pressure that is equal to the pressure the gas would exert if it were the only gas present.
- Total pressure of the mixture is equal to the sum of partial pressures of all gases present.

According to Henry's Law the percent of each gas in the total volume is the same as the percent of each partial pressure in the total pressure ^[58].

$$\frac{V_{gas}}{V_{total}} = \frac{P_{gas}}{P_{total}} \quad (17)$$

The reason why oxygen solubility increases by the increased pressure can be explained by the Dalton's Law of Partial Pressures and Henry's Laws.

Solution of air in water follows Henry's Law that states "The amount of air dissolved in a fluid is proportional with the pressure of the system". This law explains solubility of each gas in a fluid ^[59].

This law is expressed as:

$$c = p_g / k_H \quad (18)$$

c = Solubility of dissolved gas

k_H = Proportionality constant depending on the nature of the gas and the solvent

p_g = Partial pressure of the gas

The solubility of oxygen in water for different temperatures and pressures was presented on Table 1. Table 2 shows the theoretical values of partial pressures of oxygen in water at 25°C for different pressure levels.

| Partial pressure | | Partial pressure of O ₂ (pO ₂) | |
|------------------|-------|---|-------|
| mmHg | psi | mmHg | psi |
| 641 | 12.40 | 130.00 | 2.51 |
| 1551 | 30.00 | 233.50 | 4.52 |
| 3103 | 60.00 | 629.50 | 12.17 |
| 4654 | 90.00 | 944.10 | 18.26 |

Table 2. Partial Pressures of Oxygen in Water at Different Barometric Pressures

2.6.5.2 EFFECT ON DIFFUSIVITY

Pressure will also affect the lixiviant diffusion rate in to micro pore spaces of ground ore. Fick's first law explains the theory of flux diffusion ^[60]. According to Fick's first law, a diffusive flux goes from high concentration regions to low concentration regions. By applying pressure in a reactor diffusion of the lixiviant solution into the micropores of ore particles will increase as the pressure level increases.

This law states that;

$$J = -D \frac{\partial \phi}{\partial x} \quad (19)$$

Where,

J = Diffusion flux per unit area per unit time ($\frac{mol}{m^2 s}$)

D = Diffusivity in dimensions ($\frac{m^2}{s}$)

Φ = Concentration in dimensions ($\frac{mol}{m^3}$)

Diffusivity is an important factor for both materials and geological systems. Dependence of diffusivity on pressure is characterized by the activation volume, (ΔV) by the following formula ^[61],

$$\Delta V = \Delta V_m + \Delta V_f = -k T \left(\frac{\partial \ln D}{\partial P} \right)_T \quad (20)$$

Where,

(ΔV_f) = Formation volume

(ΔV_m) = Migration volume

T = Temperature

D = Material diffusivity

P = Pressure

The volume change in the system upon formation of one defect in its standard state and pressure dependence of the equilibrium point defect concentration is defined by formation volume. The additional volume change when the defect size reaches the end point of micropores and pressure dependence of the equilibrium point is defined by the migration volume ^[61].

2.6.6 EFFECT OF TEMPERATURE

Increasing the temperature in a reactor increases the chemical reaction rates. The temperature effect on reaction rates is formulated by the Arrhenius equation ^[62].

$$k = A e^{-E_a/(RT)} \quad (21)$$

Where,

k = Rate constant of a chemical reaction

T = Absolute temperature

A = Pre-exponential factor

E_a = Activation energy

R = Universal gas constant

Increasing the slurry temperature also causes a decrease in the oxygen solubility thus causing a decrease in the gold dissolution rate after a certain level of temperature. Initially, the reaction rate increases due to faster chemical reaction kinetics caused by increase in slurry temperature but the gold dissolution rate starts decreasing when there is not enough dissolved oxygen in the solution. Another negative effect of increased temperature is it leads to boiling of reagents and volatility of solvents with increased reagent usage.

Figure 6 shows the effect of increased water temperature on oxygen solubility values. As seen on the figure oxygen solubility values decrease with increased temperatures ^[55].

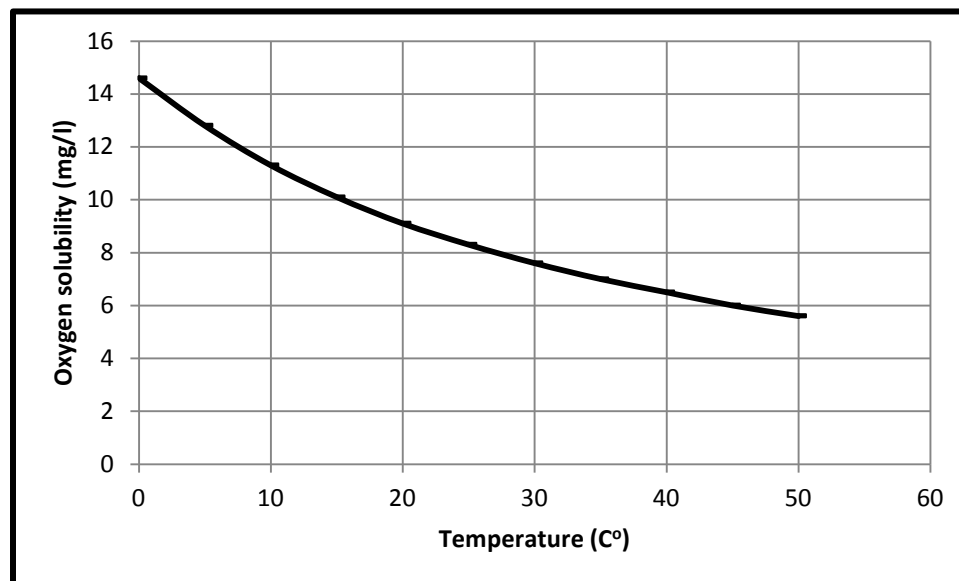


Figure 6. Effect of Temperature on Solubility of Oxygen

2.6.7 EFFECT OF pH

Gold recovery values are maximized at pH values around 9.5 ^[63]. Yet another study ^[64] shows that at the low pH values leached gold values were zero in their static gold disc dissolution experiments. Figure 7 shows the effect of pH on gold recoveries.

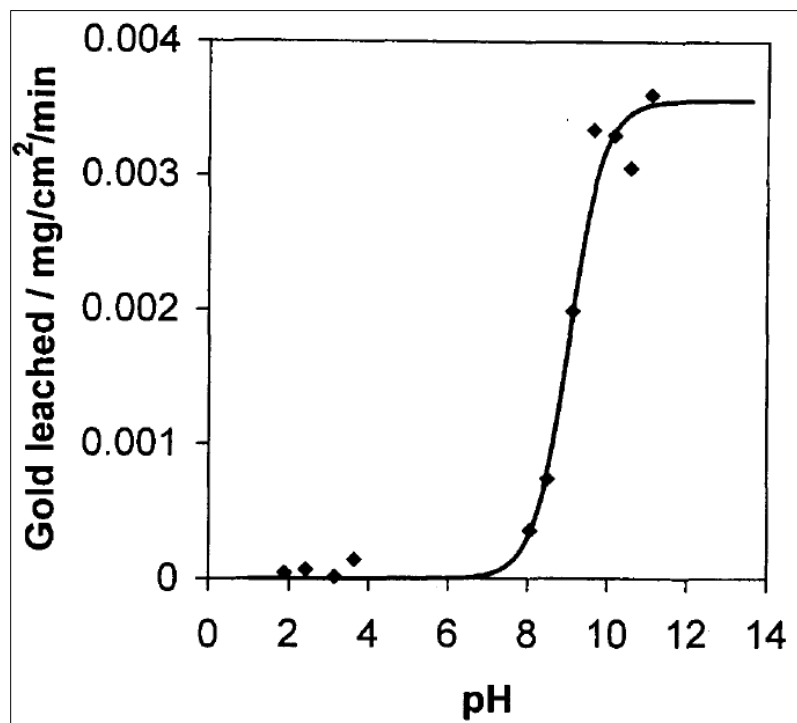


Figure 7. Gold Leaching Rate as a Function of the Ph for the Static Gold Disc
Experiments

Decrease in free cyanide ions also causes a decrease in gold dissolution rate. The effect of pH on formation of free cyanide ion in solutions was presented on Figure 2. Above Figure 7 shows similar relationship between pH and gold recovery. At lower pH values cyanide ions tend to hydrolyze in water and form hydrogen cyanide (HCN), the more HCN formed will cause a resultant decrease of the cyanide ion present in the solution.

In the same study, it is also shown that the effect of presence of cyanide as CN^- on recovery of gold. As shown in Figure 8, the increasing gold recoveries increase by the increase of free cyanide ion presence in the solution.

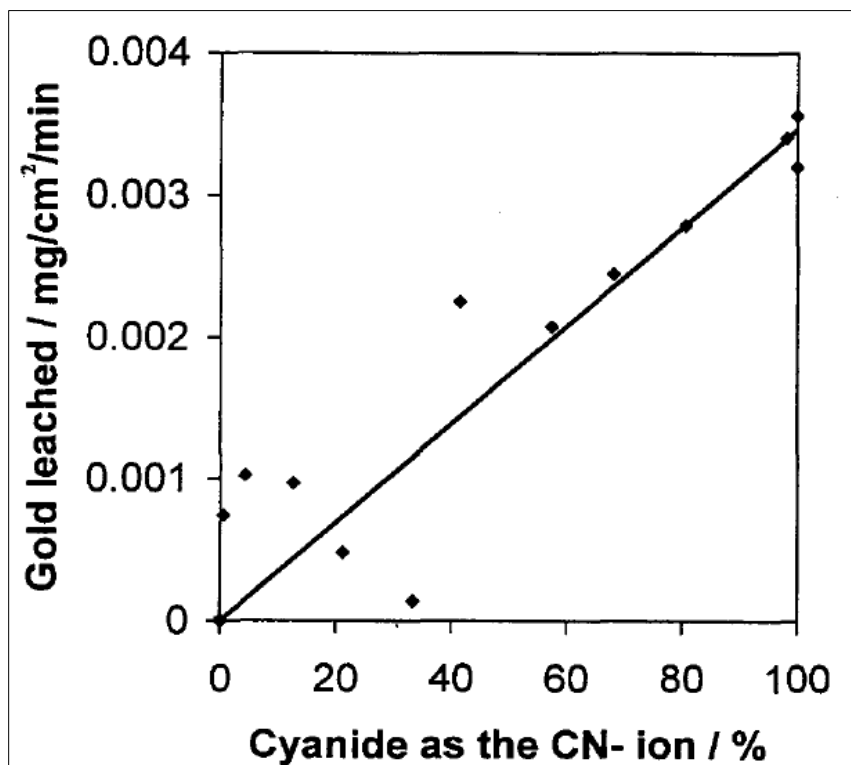


Figure 8. Gold Leaching Rate as a Function of Percentage of CN⁻

2.6.8 EFFECT OF SLURRY DENSITY

Gold recoveries are expected to decrease as the pulp density increases. The main reason for the decrease of gold recoveries with increased slurry densities is because of the poor oxygen dispersion due to increase in apparent viscosity within the system. Figure 9 shows the effect of change in slurry pulp density on the gold and silver extraction values ^[65].

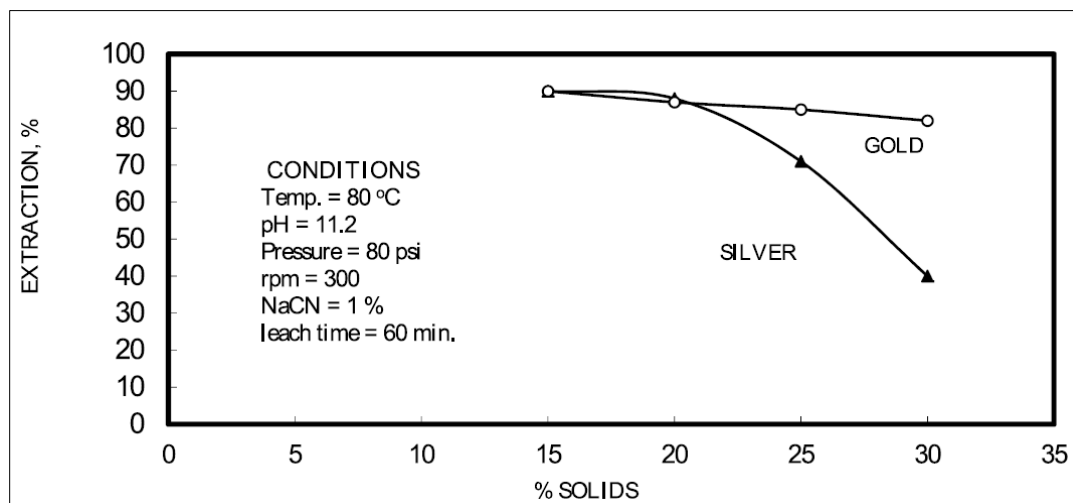


Figure 9. Effect of Percent Solids in the Extraction of Gold And Silver

Increase in slurry density will also decrease the oxygen solubility in the solution. Under room temperature and atmospheric pressure conditions, dissolved oxygen concentration in fresh water is around 8 mg/l as shown on Table 1 whereas during bottle roll tests of an oxide ore this number decreases to as low as 5.8 mg/l when there was a 50% solids (by weight) in the solution and the bottle roll rate was 110 rpm.

2.6.9 EFFECT OF SPEED OF AGITATION

The gold dissolution rate depends on the speed of agitation. Agitation provides suspension of solid particles in slurry allowing reactions between metal, oxygen and cyanide. Increasing agitation speed reduces diffusion layer thickness thus increasing mass transfer rates of oxygen and cyanide during leaching^[66]. Inside of the leaching tanks the diffusion layer thickness is minimized by good mixing by the usage of baffles, oxygen sparge, and high shear impellers^[63].

Many studies in the past reported that increased agitation speed provided higher dissolution rates of gold and silver in cyanide solution. According to another study, silver and copper dissolution rates increase linearly with the square root of speed of the rotating disc where these metals are leached ^[67]. However gold dissolution rate only increases by increasing disc speed up to 150 rpm and no further increased dissolution rates were reported after this point.

Oxygen contact with the leach slurry defines the concentration of dissolved oxygen ^[68]. Figure 10 shows the relationship between agitation speed, dissolved oxygen and gold dissolution rate in a rotating disc. As shown on Figure 10 higher agitation rates cause higher dissolved gold amounts in the solution up to certain levels. At high mixing rates, due to the low contact between oxygen, gold and leaching agent, the dissolved gold rate decreases as shown on the figure.

It can also be concluded from Figure 10 that the higher dissolved oxygen in the slurry will result in a higher gold dissolution rate ^[68]. This second argument is correct as long as there is enough cyanide leachable gold and free cyanide ions present in the slurry to react with the dissolved oxygen.

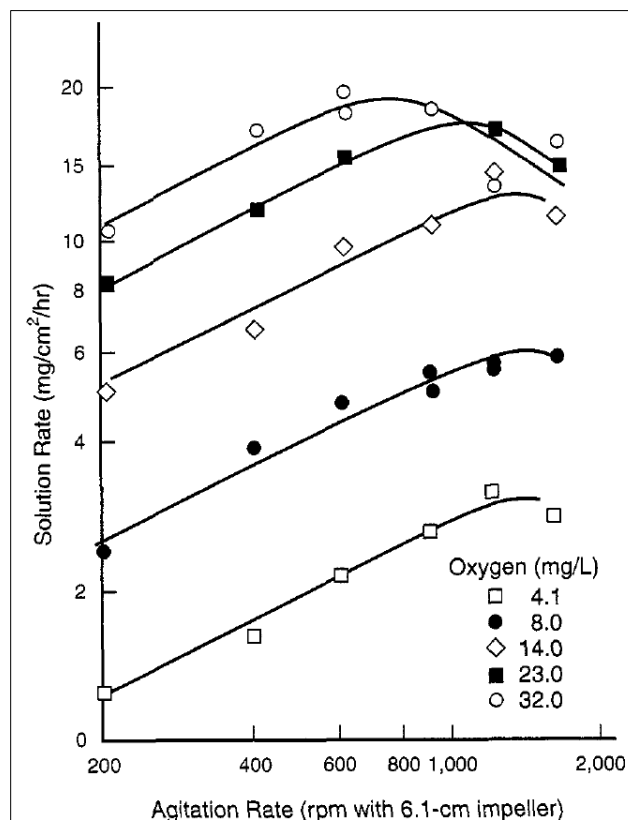


Figure 10. Effect of Agitation Speed on Oxygen Concentration and Gold Dissolution

Rate on y Axis

2.7 SELECTED GOLD EXTRACTION TECHNIQUES

A short summary of gold extraction processes currently applied in the mining industry is presented in this section. Only the related technologies to this study are included throughout the next four sections.

2.7.1 AGITATED LEACHING

In this method, the ore is ground to its liberation size and the formed slurry, generally with 35% to 50% solid content by weight, is pumped to agitated cyanide leaching tanks. These cyanide leach tanks are equipped with agitators, baffles and sparging equipment in order to optimize the cyanidation reaction between the metal and solution. One type of agitated leaching is a continuous operation and at the end of retention time required the leach solution is transferred to solid-liquid separation to separate tails from the leached solution. Following this phase solution clarification, de-aeration and zinc precipitation processes are applied to recover the gold from the solution.



Figure 11. Agitated Leach Tanks in a Merrill-Crowe Plant

2.7.2 CIP/CIL/CIC ADSORPTION CIRCUITS

In carbon in pulp (CIP), carbon in leach (CIL), carbon in columns (CIC) processes where leached gold is absorbed to the molecular surfaces of activated carbon particles.

CIP and CIL units are very similar to the agitated leaching process. Leaching is accomplished in tanks equipped with reagent feeding units, baffles and agitators. However, the recovery of the gold from the solution is accomplished by absorption of gold cyanide complex onto the activated carbon during the leaching or at the end of the leaching. In the CIP units the leached gold is absorbed to activated carbon in separate adsorption tanks which follows leaching tanks. Whereas in the CIL process the leaching of the gold and absorption of the metal to activated carbon is achieved simultaneously [69].

The CIL (Carbon-in-leach) process is fundamentally the same as CIP (Carbon in Pulp) for the fact that leaching of the ground ore is carried out in the presence of carbon and the absorption of gold is simultaneous with leaching. In the CIP process, the dissolved gold is subsequently transferred to an absorption circuit tank where the gold is absorbed onto activated carbon [70].

The CIC process is different than both CIL and CIP since it does not have any leaching function and absorbs gold directly from clarified pregnant solutions obtained from heap leach operations to activated carbon and the carbon is advanced countercurrent to the preg solution [3].

A modular Carbon in Column (CIC) plant is shown on below Figure 12.



Figure 12. Modular Carbon in Column Process (CIC) Plant

2.7.3 REFRACTORY ORE PRE-TREATMENT BY PRESSURE OXIDATION

Refractory ores require pretreatment process before cyanidation ^[71].

The refractoriness of gold ores can be caused by;

1. Presence of other minerals that decompose or react with cyanide.
2. Presence of other minerals that consume oxygen.
3. Insoluble gold tellurides.
4. Encapsulated fine gold in non-porous minerals.
5. Mineral films that avoid the leaching agent reacting with gold.
6. Presence of absorbent materials in the ore as preg rob.

One type of refractory ore is preg-robbing. Presence of preg robbing materials such as carbonaceous materials and clays has a decreasing effect on precious metal recovery from the slurries ^[72]. Preg robbing ores are mostly pretreated by roasting or chlorination.

Another type of refractory ore is gold contained in the sulfide ores such as pyrite (FeS_2), arsenopyrite (FeAsS), sphalerite (Zn,FeS), chalcopyrite (CuFeS_2), pyrrhotite (FeS), galena (PbS), antimonite (NaSbO_2) ^[73]. Pressure oxidation, roasting, biooxidation, nitric acid oxidation are the main methods that are used to reduce refractoriness of this type of gold ores.

One of these methods, pressure oxidation, is carried out in both alkaline and acidic medium. Acid pressure oxidation is generally conducted at temperatures of 100 – 225 °C and pressures of 1000 – 3200 kPa with a retention time of 15 minutes to 3 hours in four to five compartment autoclaves ^[74].

Pressure oxidation is an efficient treatment method compared to biological oxidation and roasting since it achieves almost complete oxidation, high recoveries, shorter residence times and it has very low emission of harmful gases to the atmosphere ^[75]. However pressure oxidation has a limited effect on improved gold extraction for preg robbing ores.

3. EXPERIMENTAL STUDY

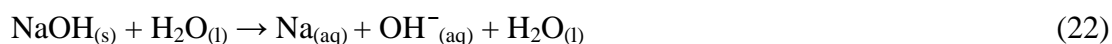
The pressure cyanidation tests were performed with the aim of investigating the effect of pressure on gold recovery from ores at near room temperature (25°C). The main hypothesis of this research was that the cyanidation under higher pressures would result

in an increase in the rate of the lixiviant diffusion into the micro pores of the solid particles and cause higher gold recoveries compared to the atmospheric conditions at the same time of leaching. An oxide ore and flotation tailings of a sulfide ore were used for the experiments.

3.1 CHEMICALS AND PRESURRIZING GASES

3.1.1 SODIUM HYDROXIDE

Sodium hydroxide (NaOH) is highly soluble in water and dissociates in water solutions to form sodium cations and hydroxide anions ^[76]. Sodium hydroxide solubility in water is 109 g/100 ml at 20°C ^[77].



Sodium hydroxide was used as the base to increase the pH of the slurry for bottle roll, autoclave experiments and the standard solution preparation for the AAS.

Table 3 summarizes the properties of the sodium hydroxide used throughout the experiments ^[78].

| | |
|---|-----------|
| Manufacturer | JT Baker |
| Product number | 3722 |
| CAS Number | 1310-73-2 |
| Assay (%) | 98.0 |
| Na₂CO₃ (%) | 0.4 |
| Calcium (%) | 0.005 |
| Chloride (%) | 0.001 |
| Heavy Metals (%) | 0.001 |
| Copper (%) | 0.001 |
| Potassium (%) | 0.01 |
| Nitrogen Compounds (ppm) | 3 |
| Phosphate (ppm) | 2 |
| Sulfate (ppm) | 5 |
| Iron (ppm) | 3 |
| Mercury (ppm) | 0.1 |
| Nickel (ppm) | 5 |

Table 3. Sodium Hydroxide Composition

3.1.2 CALCIUM OXIDE

Calcium oxide was used to increase the pH of the solutions during the bottle roll and autoclave experiments.

Calcium oxide solubility in water is 0.125 g/100 ml of water at 20°C ^[77]. Calcium oxide forms calcium hydroxide in water by the following reaction ^[79].



The calcium oxide used for the experiments was the typical bulk chemical that the mining companies use; the specific material used was from a sample taken from bulk facility outside Carlin, NV. Table 4 summarizes the properties of the calcium oxide used throughout the experiments ^[80].

| | |
|---------------------------------------|---------------|
| Manufacturer | Graymont Inc. |
| Product number | - |
| CAS Number | 1305-78-8 |
| Assay (%) | 90 Min |
| MgO (%) | 1.3 |
| R₂O₃ (%) | 0.7 |
| SiO₂ (%) | 0.5 Max |
| SO₃ (%) | 1.3 Max |
| CO₂ (%) | 2.5 |

Table 4. Calcium Oxide Composition

3.1.3 AMMONIUM HYDROXIDE

Ammonium hydroxide (NH₄OH) was also used as a base for some of the bottle roll and autoclave tests. Table 5 summarizes the properties of the ammonium hydroxide used throughout the experiments ^[81].

| | |
|---------------------------|-----------|
| Manufacturer | EMD |
| Product number | 3722 |
| CAS Number | 1336-21-6 |
| Nominal Molarity | 14.8 |
| Aluminum (ppm) | 0.3 max |
| Calcium (ppm) | 0.3 max |
| Carbon dioxide (%) | 0.002 max |
| Chloride (ppm) | 0.5 max |
| Chromium (ppm) | 0.3 max |
| Copper (ppm) | 0.1 max |
| Gold (ppm) | 0.3 max |
| Heavy metals (ppm) | 0.5 max |
| Iron (ppm) | 0.2 max |
| Lead (ppm) | 0.2 max |
| Magnesium (ppm) | 0.3 max |
| Manganese (ppm) | 0.2 max |
| Nickel (ppm) | 0.1 max |
| Nitrate (ppm) | 2 max |
| Phosphate (ppm) | 2 max |
| Potassium (ppm) | 0.3 max |
| Sodium (ppm) | 0.3 max |
| Sulfate (ppm) | 2 max |
| Tin (ppm) | 0.3 max |
| Titanium (ppm) | 0.3 max |
| Zinc (ppm) | 0.3 max |

Table 5. Ammonium Hydroxide Properties

3.1.4 SODIUM CYANIDE

Sodium cyanide (NaCN) is an inorganic compound that has high reactivity with metals.

Sodium cyanide fully dissociates in water and forms metal cation, free cyanide ions as presented in equation (1).

Sodium cyanide was used to leach gold throughout the bottle roll, autoclave experiments and also for the preparation of the standard solution for the AAS analyses.

Table 6 summarizes the properties of the sodium cyanide used throughout the experiments ^[82].

| | |
|----------------------------------|---------------|
| Manufacturer | Sigma Aldrich |
| Product number | 380970 |
| CAS Number | 143-33-9 |
| Assay (%) | 97 Min |
| Sodium Formate (%) | 0.5 Max. |
| Sodium Hydroxide (%) | 0.5 Max. |
| Sodium Carbonate (%) | 0.3 Max. |
| Sodium Chloride as Cl (%) | 0.05 Max. |
| Water (%) | 0.2 Max. |
| Insoluble Residue (%) | 0.05 Max. |

Table 6. Sodium Cyanide Composition

3.1.5 5-(4-DIMETHYLAMINO BENZYLIDENE) RHODANINE

Dimethylaminobenzylidene rhodanine ($C_{14}H_{16}N_2OS_2$) was used as an indicator in titration experiments used to determine free cyanide concentration in leach solutions during bottle roll and autoclave experiments.

Rhodanine indicator solution was prepared by dissolving 20 mg of dimethylaminobenzylidene rhodanine in 100 mL of another organic compound acetone ($(CH_3)_2CO$).

After sampling the leach solution, samples were centrifuged to obtain a clear solution. Rhodanine indicator was added to the leach solutions to be able to observe color change during silver nitrate titration. Detailed description of the titration process is given in section 4.1.11.

Table 7 summarizes the properties of the rhodanine used throughout the experiments. All percentages are presented by weight ^[83].

| | |
|-----------------------|------------|
| Manufacturer | Alfa Aesar |
| Product number | B23145 |
| CAS Number | 35778-58-6 |
| Assay (%) | 98 Min |

Table 7. Rhodanine Chemical Composition

3.1.6 SILVER NITRATE

Silver nitrate is an inorganic compound with chemical formula AgNO_3 . Silver nitrate was used during titration to quantify free cyanide in the leach solutions ^[84].

Overall chemical reactions occurring between silver nitrate, cyanide ions and rhodanine indicator, are shown by the reactions 24, 25, 26 in section 4.1.11.

Table 8 summarizes the properties of the silver nitrate solution used throughout the experiments ^[85].

| | |
|--------------------------|-------------------|
| Manufacturer | Fisher Scientific |
| Product number | SS72-1 |
| CAS Number | 7761-88-8 |
| Concentration (M) | 0.1 |

Table 8. Silver Nitrate Properties

3.1.7 GOLD, AAS STANDARD SOLUTION

A gold standard solution was used to calibrate the AA spectrometer. A series of calibration standard solutions which was matched the physical and chemical concentration properties of the samples to be analyzed. The standard solution with Au content of 1000 $\mu\text{g/ml}$ diluted to Au concentrations 0.5, 1, 5, 10 $\mu\text{g/ml}$ for the calibration purposes. Table 9 summarizes the properties of the gold standard used throughout the experiments ^[86].

| | |
|---|------------|
| Manufacturer | Alfa Easar |
| Product number | 88068 |
| EINECS Number | 231-595-7 |
| Concentration ($\mu\text{g/ml Au}$) | 1000 |

Table 9. Gold AAS Standard Solution

3.1.8 AIR and NITROGEN GASES

Air and nitrogen gases were used to pressurize the autoclave during leaching experiments. Both properties of air and nitrogen gases used are presented below ^{[87], [88]}.

| | |
|-----------------------|-------------|
| Manufacturer | Airgas |
| Product number | AICZ200 |
| CAS Number | - |
| Nitrogen (%) | 76.5 – 80.5 |
| Oxygen (%) | 19.5 – 23.5 |

Table10. Pressurizing air gas properties

| | |
|-----------------------|-----------|
| Manufacturer | Airgas |
| Product number | NIPP200 |
| CAS Number | 7727-37-9 |
| Nitrogen (%) | 100 |

Table 11. Pressurizing nitrogen gas properties

3.2 SAMPLES

Experiments were conducted on two different samples, Golden Days oxide ore and Newmont Mill#5 flotation tails (CIL Feed). Fire assay, leco, inductively coupled plasma (ICP) and cyanide shake tests were conducted on pulverized dry head samples of the oxide ore and flotation tailings.

The Golden Days ore total gold (AuFA) and cyanide soluble gold (AuCN) contents were 0.222 and 0.213 troy ounce per ton respectively whereas flotation tailings samples AuFA and AuCN amounts were 0.028 and 0.0124 troy ounce per ton, respectively. Fire assay analyses showed that Golden Days oxide ore has nearly eight times more gold content than the flotation tailings. The cyanide shake tests showed that 44% of the total gold amount was amenable to cyanide leaching for flot tails samples. The cyanide leachable gold content for the Golden Days samples was 96% of the total gold content.

The amount of sulfide sulfur content was calculated by subtracting the sulfate sulfur (SRO) from the total sulfur content (STOT) of the samples. The sulfide sulfur content of Golden Days and flotation tailings were found as 0.16% and 0.34%, respectively.

Both Golden Days and flotation tailings samples were primarily selected for the experimental testwork because of their low sulfide sulfur content. The first set of experiments were planned to be conducted on a sample with high grade gold content and the second set of experiments with gold particles locked in silica. The high gold content of Golden Days samples provided better observation of recovery changes during the experiments. A second set of experiments were conducted with flotation tailings samples in order to investigate the effect of pressure cyanidation on the recoveries of the locked gold content. The flotation tailings samples had low cyanide soluble gold content due to the silica locking of the gold particles.

The abbreviations for the chemical analyses made on head samples are given in Table 12. Chemical composition tables for both samples are presented in the following two sections.

| Abbreviation | Unit | Definition |
|---------------------|-------------|----------------------|
| AG | ppm | Silver |
| AL | ppm | Aluminum |
| AS | ppm | Arsenic |
| AUCN | ppm | Cyanide Soluble Gold |
| AUFA1 | ppm | Total Gold |
| AUFA2 | ppm | Total Gold |
| AUPR | ppm | Preg Rob Material |
| BA | ppm | Barium |
| BE | ppm | Beryllium |
| BI | ppm | Bismuth |
| CAI | % | Organic Carbon |
| CA | ppm | Calcium |
| CC | % | Carbonate Carbon |
| CD | ppm | Cadmium |
| CO | ppm | Cobalt |
| CR | ppm | Chromium |
| CTOT | % | Total Carbon |
| CU | ppm | Copper |
| FE | ppm | Iron |
| HG | ppm | Mercury |
| LI | ppm | Lithium |
| MG | ppm | Magnesium |
| MN | ppm | Manganese |
| MO | ppm | Molybdenum |
| NA | ppm | Sodium |
| NI | ppm | Nickel |
| PB | ppm | Lead |
| P | ppm | Phosphorus |
| SB | ppm | Antimony |
| SE | ppm | Selenium |
| SN | ppm | Tin |
| SR | ppm | Strontium |
| SRO | % | Sulfate Sulfur |
| SS | % | Sulfide Sulfur |
| STOT | % | Total Sulfur |
| TE | ppm | Tellurium |
| TI | ppm | Titanium |
| TL | ppm | Thallium |
| V | ppm | Vanadium |
| ZN | ppm | Zinc |
| OPT | | Troy ounce per ton |

Table 12. Chemical Analysis Table Abbreviations

3.2.1 GOLDEN DAYS OXIDE ORE

On 13 October 2013 fifty-two (52) pounds of grab samples from the currently idle Densmore mine in Northern California were received by the staff of the Mining and Metallurgical Engineering Department of the University of Nevada, Reno (UNR). The samples were characterized in the accompanying documentation as oxide material. Bottle roll and autoclave tests were conducted on the head ore. Fire assay, CN shake test, ICP, Leco analyses were performed on head and/or tailing samples. Figure 13 and Table 13 shows Golden Days ore samples and chemical composition.



Figure 13. Golden Days Ore Grab Samples

| TYPE | Weight | Sample Name | Type | AG (PPM) | AL (PPM) | AS (PPM) |
|-----------------------|------------------------|--|-----------------------|---------------------|---------------------|---------------------|
| Head | 300g + | Golden Days Oxide Ore Head Assay | Au/Ag Ore | 3.314 | 576.658 | 61.97 |
| AUCN (OPT) | AUFA1 (OPT) | AUFA2 (OPT) | AUPR (OPT) | BA (PPM) | BE (PPM) | BI (PPM) |
| 0.2126 | 0.2217 | 0.2223 | 0.0098 | 18.729 | 0 | 0.669 |
| CAI (%) | CA (PPM) | CD (PPM) | CO (PPM) | CR (PPM) | CTOT (%) | CU (PPM) |
| 0.08 | 264.081 | 0.581 | 5.263 | 224.263 | 0.048 | 67.2 |
| FE (PPM) | HG (PPM) | LI (PPM) | MG (PPM) | MN (PPM) | MO (PPM) | NA (PPM) |
| 14755.7 | 0.133 | 0.003 | 434.366 | 134.883 | 6.197 | 219.708 |
| NI (PPM) | PB (PPM) | P (PPM) | SB (PPM) | SE (PPM) | SN (PPM) | SR (PPM) |
| 41.774 | 6.098 | 64.337 | 6.059 | 0 | 0.023 | 1.553 |
| SRO (%) | STOT (%) | TE (PPM) | TI (PPM) | TL (PPM) | V (PPM) | ZN (PPM) |
| 0.051 | 0.21 | 14.047 | 27.892 | 0 | 10.645 | 13.108 |

Table 13. Golden Days Samples Chemical Composition

3.2.2 FLOTATION TAILINGS

On 23 January 2014 twelve (12) pounds of dry flotation tailings samples from the Gold Quarry mine of Newmont Mining Corporation were received by the staff of Mining and Metallurgical Engineering Department of University of Nevada, Reno (UNR). The samples were characterized in the accompanying documentation as carbon in leach (CIL) feed flotation tailings. Grinding, specific gravity, bottle roll, autoclave tests were conducted on these ore samples. Fire assay, ICP, Leco analysis were performed on head and/or tailing samples.



Figure 14. Flotation Tailings Samples

| TYPE | Weight | Sample Name | Type | AG (PPM) | AL (PPM) | AS (PPM) |
|-----------------------|------------------------|-------------------------------------|-----------------------|---------------------|---------------------|---------------------|
| Leach Tails | +100g | Flotation Tailings Head Assay | Au Ore | 0 | 3452.55 | 976.179 |
| AUCN (OPT) | AUFA1 (OPT) | AUFA2 (OPT) | AUPR (OPT) | BA (PPM) | BE (PPM) | BI (PPM) |
| 0.0124 | 0.0288 | 0.0271 | 0 | 3440.11 | 0.243 | 3.092 |
| CAI (%) | CA (PPM) | CD (PPM) | CO (PPM) | CR (PPM) | CTOT (%) | CU (PPM) |
| 0.045 | 2969.37 | 2.496 | 6.384 | 16.219 | 0.098 | 64.243 |
| FE (PPM) | HG (PPM) | LI (PPM) | MG (PPM) | MN (PPM) | MO (PPM) | NA (PPM) |
| 12237 | 4.059 | 2.142 | 659.193 | 45.816 | 22.687 | 352.847 |
| NI (PPM) | PB (PPM) | P (PPM) | SB (PPM) | SE (PPM) | SN (PPM) | SR (PPM) |
| 43.713 | 72.598 | 684.768 | 45.343 | 2.572 | 0.039 | 116.836 |
| SRO (%) | STOT (%) | TE (PPM) | TI (PPM) | TL (PPM) | V (PPM) | ZN (PPM) |
| 0.487 | 0.824 | 0 | 25.354 | 6.441 | 140.249 | 375.235 |

Table 14. Flotation Tailings Samples Chemical Composition`

3.3 EQUIPMENTS

3.3.1 CRUSHERS

3.3.1.1 PRIMARY CRUSHER

Size reduction on coarse ore samples was achieved by using 2 stage jaw crushers.

General specifications of the primary jaw crusher are given below ^[89] :

| | |
|-------------------|----------------------------------|
| Manufacturer | : Bico |
| Type | : Badger |
| Crushing Capacity | : 1300 lbs per hour |
| Jaw Capacity | : 5" x 7" |
| Size | : 32" x 24" x 20" |
| Reduction Size | : 1/8" (minimum), 3/4" (maximum) |
| Type of Drive | : V Belt, 1 Phase, 400 rpm |
| Drive Motor | : 5 hp, 110/220 Volt |

Figure 15 shows the Bico crusher used for size reduction of the samples received.



Figure 15. First Stage Jaw Crusher

3.3.1.2 SECONDARY CRUSHER

General specifications of the secondary jaw crusher are given below ^[90]:

| | |
|-------------------|-----------------------------------|
| Manufacturer | : Bico |
| Type | : Chipmunk |
| Crushing Capacity | : 800 lbs per hour |
| Jaw Capacity | : 2.25" x 3" |
| Size | : 25" x 19" x 30" |
| Reduction Size | : 1/16" (minimum), 3/8" (maximum) |
| Type of Drive | : V Belt, 1 Phase, 400 rpm |
| Drive Motor | : 3 hp, 110/220 Volt |

Figure 16 shows second stage crusher used for size reduction of samples received.



Figure 16. Second Stage Jaw Crusher

3.3.1.3 TERTIARY CRUSHER

A dual roll crusher was used as a tertiary crusher. General specifications of the roll crusher are given below.

| | |
|----------------|----------------------------|
| Rolls | : 3" x 8" |
| Size | : 22" x 36" x 20" |
| Reduction Size | : -10 mesh |
| Type of Drive | : V Belt, 1 Phase, 400 rpm |
| Drive Motor | : 3 hp, 110/220 Volt |

Figure 17 shows the roll crusher used as tertiary crusher.



Figure 17. Tertiary Crusher

3.3.2 PULVERIZER

Bico UD pulverizer with V-Belt drive was used to prepare samples for head analysis.

Bico UD pulverizer has material pulverizing capacity of 1 lb/min, max input material size of 1/4", reduction output size of 150 – 200 mesh and physical dimensions of (L) 44" x (W) 15.25" x (H) 25.50". Figure 18 shows the pulverizer.



Figure 18. Bico Pulverizer

3.3.3 HAND MORTAR AND PESTLE

After each leaching experiment, dried tailing samples were ground by using a hand mortar and pestle. In order to make sure no impurities enter the sample during grinding a ceramic mortar and pestle were used due to its resistance to abrasion and chemical action. Below Figure 19 shows the mortar and pestle used for further grinding of the tailings.



Figure 19. Hand Mortar and Pestle

3.3.4 RIFFLE SPLITTER

A riffle splitter was used to reduce the bulk material to a representative split for laboratory analysis. Dry samples were poured through a hopper on top of the riffle having equal amount material flow by chutes into two pans at the bottom of the riffle. The riffle used had 10" by 20" hopper and sixteen chutes with 1" width. Figure 20 shows the riffle splitter.



Figure 20. Riffle Splitter

3.3.5 GRINDING EQUIPMENT

3.3.5.1 GRINDING MILL

For final size reduction of samples, a batch steel mill was used with the roll drives that rotated the mill at a pre-determined speed. Table 15 and Figure 21 shows the mill specifications and the picture, respectively.

| | |
|-------------------------------------|-----|
| Grinding Mill Inner Diameter (inch) | 7.5 |
| Grinding Mill Inside Length (inch) | 9 |
| Net weight (lb) | 45 |
| Total Volume (Liters) | 4.2 |

Table 15. Grinding Mill Dimensions



Figure 21. Grinding Mill

3.3.5.2 MILL ROLL DRIVES

Mill roller mechanism consists of a work shelf, rollers and drive motor. Drive rolls have variable speed drive, for operating the mill at the desired revolutions. General specifications of the system are given below^[91].

| | |
|-----------------------------------|--------------------------|
| Drive motor | 1/2 HP |
| Drive speed | Adjustable, 40 – 110 rpm |
| Roll diameters (inch) | 5 |
| Roll length | 45 |
| Number of rolls | 4 |
| Roll cover | Rubber |
| Overall dimensions (LxHxW) (inch) | 72 x 42 x 53 |

Figure 22. Roll Drive Specification



Figure 23. Mill Roll Drives

3.3.5.3 GRINDING MEDIA

Steel balls with diameters 1, 3/4 , 1/4 inch diameter and specific gravity of 7.9 were used with the mill for further size reduction by grinding. A general specification of the grinding media is shown in Table 16.

| | |
|--|-------------|
| Grinding media charge : | |
| 1" Balls | |
| # of Balls | 42 |
| Weight of each ball (gr) | 67.7 |
| Total weight of 1" balls (kg) | 2.84 |
| 3/4" Balls | |
| # of Balls | 73 |
| Weight of each ball (gr) | 24.6 |
| Total weight of 3/4" balls (kg) | 1.80 |
| 1/4" Balls | |
| # of Balls | 720 |
| Weight of each ball (gr) | 1.0 |
| Total weight of 1/4" balls (kg) | 0.72 |
| Total weight of grinding media (kg) | 5.36 |

Table 16. Grinding Media Specifications

Grinding media charge is shown in Figure 24.



Figure 24. Grinding Media

3.3.6 SCREENING EQUIPMENT

A Tyler rotap test sieve shaker and 200 mesh screen was used to measure particle size. Figure 25 shows the sieve and shaker system used. During the experiments, the top three compartments of the shaker was used and the third (bottom) sieve was replaced with a closed bottom pan.



Figure 25. Rotap and Dry Screening Equipment

3.3.7 HIGH PRESSURE REACTOR

Pressure cyanidation tests were conducted in order to determine the kinetics of the gold extraction with pressures higher than atmospheric conditions at room temperatures. Ore was fed to the reactor vessel with reported amounts of water, cyanide and lime. The pH level of the slurry and cyanide consumptions were monitored throughout the experiments by taking solution samples from the leach solution.

The pressure leaching experiments were carried out in a stainless steel Parr Instrument pressure reactor. The reactor vessel has a capacity of 1900 ml and a maximum pressure rating of 3600 psi and temperature rating of 100 °C.

Pressure reactor specifications are summarized in Table 17.

| | |
|--------------------------------------|-------------------------------|
| Vessel | |
| Model | Parr Instrument A1120HC |
| Style | Moveable |
| Material of construction | T316 Stainless Steel |
| Fe(%) | 65 |
| Ni (%) | 12 |
| Cr (%) | 17 |
| Mo (%) | 1.2 |
| Mn (%) | 2 |
| Si (%) | 1 |
| Inside Diameter (inch) | 4 |
| High Pressure inside diameter (inch) | 3.75 |
| Inside depth (inch) | 10.5 |
| Weight of vessel (pounds) | 6 |
| Reactor dimensions | |
| Width (inch) | 11.5 inch |
| Height | 6.4 |
| Weight (pounds) | 11 |
| Reactor Mounting | Bench Top |
| Closure | Split-Ring (6 Cap Screws) |
| Valve Connections | 1/8" Male NPT |
| Impeller | |
| Type | Turbine |
| Number of blades | 6 |
| Diameter (inch) | 2.28 |
| Pressure Gage | |
| Type | Analog |
| Size | 4.5 inches |
| Range | 0 - 300 psi |
| Stirrer | |
| Manufacturer | Fisher Scientific |
| Model | Steadystir analog – 24 511 55 |
| Speed | 1/8 hp variable speed |
| Electrical Supply | AC 230 Volts |

Table 17. Pressure Reactor Specifications

The rotational speed of the impeller inside the vessel was controlled by a variable stirrer motor. The internal stirring system consists of a motor drive mechanically coupled to an internal stirrer shaft with attached turbine-type impellers.

Air and pure nitrogen gas was supplied from a standard commercial cylinder and desired pressure was maintained by means of a two-stage regulator mounted on the cylinder. Gas was charged into the reactor by the gas inlet valve on the reactor. This inlet valve connects to a dip tube which extends to the bottom of the vessel. The pressure gage on the reactor was used to check the pressure within the vessel at all times.

During the experiments, slurry samples were withdrawn from the reactor through a dip tube shared with a gas inlet valve. This tube was cleared by applying pressurized gas at the end of the each experiment. Autoclave and the inner section of the reactor were shown in Figure 26 and Figure 27, respectively^[92].

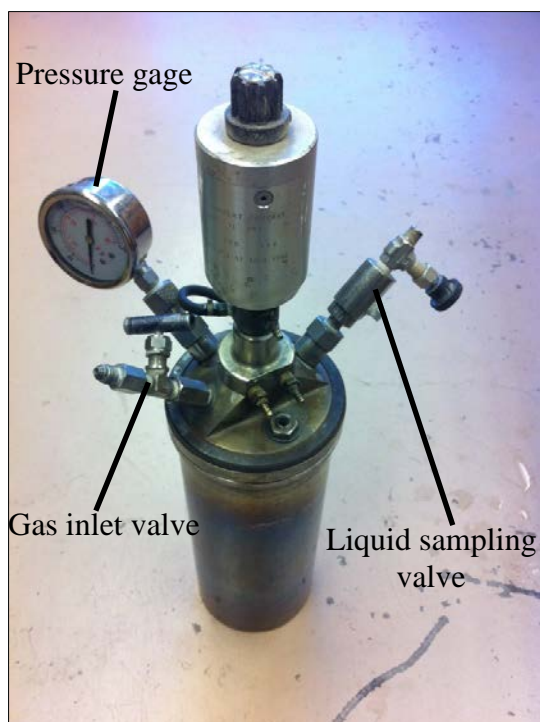


Figure 26. Autoclave

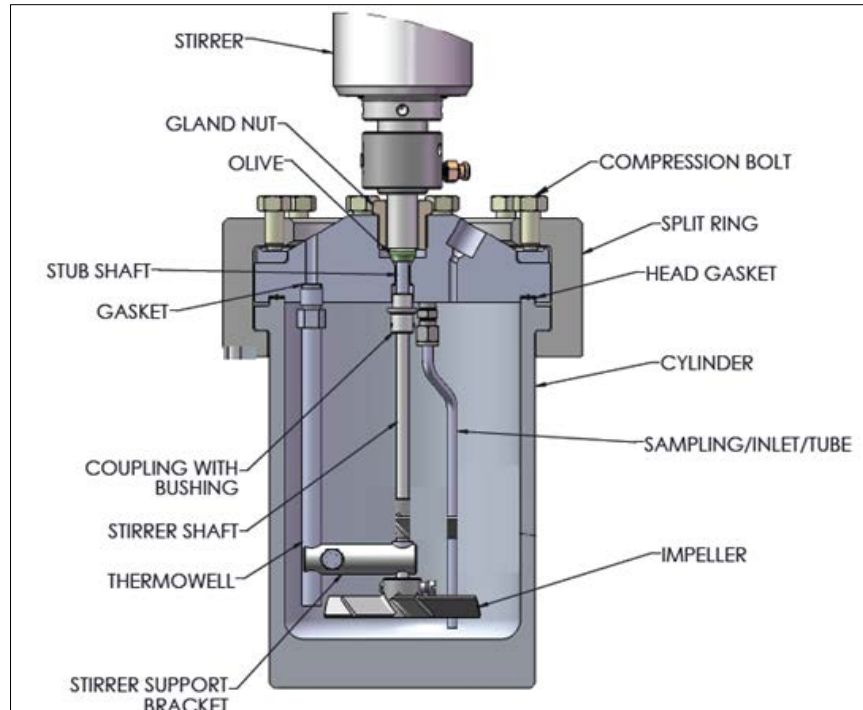


Figure 27. Autoclave Cross Section

3.3.8 BOTTLES

Cyanide bottle roll tests were conducted in order to assess gold recoveries by the standard cyanide leaching technique. Ore was fed to a 1 gallon glass bottle with pre-determined amounts of water, cyanide and lime. Base and cyanide consumptions were monitored throughout the experiments by taking solution samples from the leach solution.

One gallon bottles were used in order to have more efficient sample collection throughout the experiments. The glass bottles used had a height of 11.35 inches and diameter of 6.57 inch. A hole was drilled into each bottle' cap to maintain atmospheric pressure throughout the bottle roll tests. Mill rollers were used for continuous mixing of the slurry.



Figure 28. Bottle Roll Set-up

3.3.9 PRESSURE FILTER

A batch, 3 gallon, 8 inch diameter pressure filter was used for filtration of slurry samples under air pressure of 30 psi. The filtration cycles were 10 minutes to obtain cake filtrate. The collected filtrate from the leach solutions was sampled and tagged to calculate the final gold content of the tailings for each experiment.

The filter used throughout experiments features a removable cylinder, square base plate, a swing away lid for filling and emptying, quick connect air coupling for air supply, polypropylene filter cloth, rubber gasket at the bottom for sealing, valve for charging or discharging air and a safety relief valve.

| | |
|------------------------------------|----------------------|
| Manufacturer | Sepor |
| Model | 070B-010 |
| Maximum pressurizing capacity | 60 psi |
| Material of construction | T316 Stainless Steel |
| Dimensions (inch) | |
| Diameter | 8 |
| Height | 24.5 |
| Base Plate Thickness | 10 |
| Filter cloth pore opening (micron) | 25 |

Table 18. Pressure Filter Specifications

Each grind product and leach tails were dewatered by using the pressure filter after each experiment. The pressure filter equipment is shown in Figure 29.

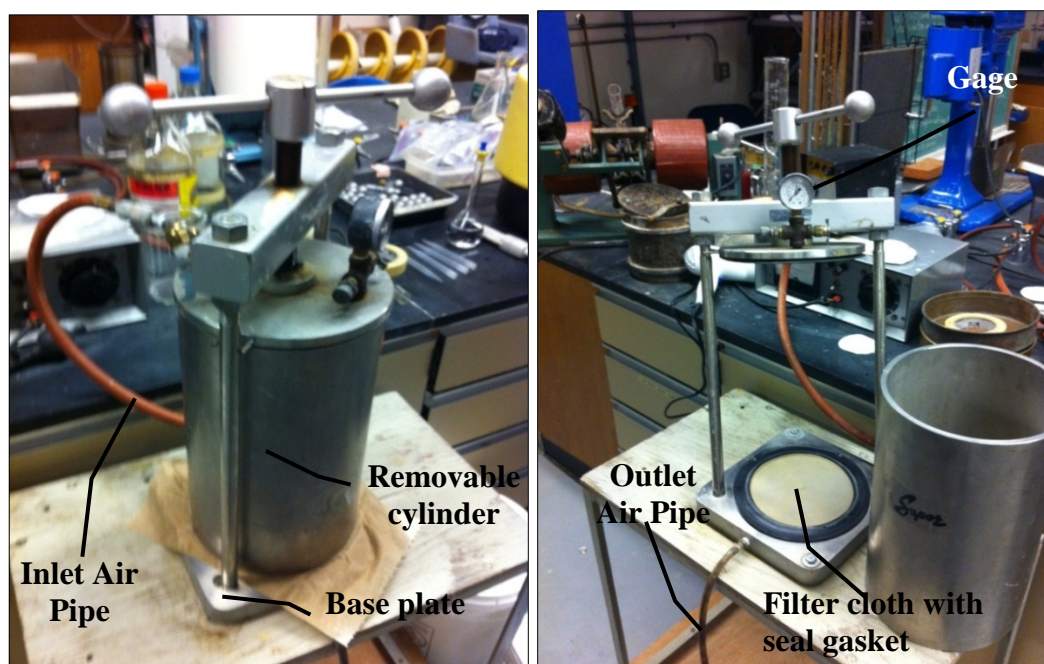


Figure 29. Filtration Equipment

3.3.10 DRYING OVEN

A benchtop analog controlled compact oven was used to dry the samples. After filtrating the grind and leach slurries, the obtained cakes from each slurry had

moisture content of less than 20%. Further drying was accomplished in drying the samples at the drying oven at 35 °C for 24 hours. The low temperature drying was applied in order to avoid any oxidation in the ore. Table 19 summarizes the oven specifications.

| | |
|---------------------------------|--------------------|
| Manufacturer | Thermo Scientific |
| Model | Precision |
| Operation status control | Pilot light |
| Insulation | Silica based |
| Temperature range | 0 – 180 °C |
| Capacity (L) | 113 |
| Exterior Dimensions (L x W x H) | 71 x 110 x 73 |
| Interior Dimensions (L x W x H) | 48 x 48 x 48 |
| Certifications | ASTM E145 Type IIA |

Table 19. Drying Oven Specifications



Figure 30. Drying Oven

3.3.11 pH METER

The hydrogen-ion activities in solutions were measured by a Accumet AP85 portable pH meter. The portable pH meter consists of a voltmeter attached to a glass pH-responsive electrode and a reference mercury-mercurous chloride electrode.

The pH meter was calibrated every seven days. A three point calibration method and buffers at pH 4, 7, 10 at room temperature was used for the most accurate pH measurements. Figure 31 shows the Accumet pH meter used in these experiments ^[93]



Figure 31. Accumet AP85 portable pH meter

3.3.12 CENTRIFUGE

A Model 225 Fisher scientific bench top centrifuge was used for solid-liquid separation of the slurry samples collected during autoclave and bottle roll tests. Each sample was centrifuged at 4000 rpm for 8 minutes in order to obtain a clear solution for silver nitrate titration and AAS analysis. Figure 32 shows the centrifuge equipment used during the experiments.



Figure 32. Centrifuge

3.3.13 ATOMIC ABSORPTION SPECTROMETER

A Varian Spectra 55B model atomic absorption spectrometer was used for the leach solution gold content analysis. Model specifications are summarized in Table 20 and a photo of the AAS is provided in Figure 33.

| | |
|---------------------------------------|---------------------------------------|
| Beam | True double |
| Display | Built-in LCD screen |
| Gas controllers | Manual control |
| Ignition control | Push button, automatic flame off |
| Burner-Atomizer | Changeable, premix universal atomizer |
| Au detection limit (micro gram/Liter) | 9 |
| Wave length range (nm) | 185 – 425 |
| UV Radiation intensity | 185 – 900 |
| Scattering (nm/mm) | 3.2 – 2.4 |
| Replicates | 1 – 10 |
| Working curve | Blank and 5 standards, 1 algorithm |

Table 20. Varian Spectra 55B AAS Specifications



Figure 33. Varian Spectra 55B AAS

4. EXPERIMENTAL PROCEDURES

The specific gravity, grinding, bottle roll, autoclave experiments were conducted on the Golden Days ore samples. Only autoclave experiments were conducted on flotation tailings samples due to limited amount of samples received.

The Golden Days grab samples were crushed by three stage crushing. The crushed ore product was weighed and fed to the ball mill. The mill product was collected and left to dry in an oven at 35°C for 24 hours to avoid any sulfur sulfide oxidation. The dry grind product was used as feed for autoclave and bottle roll tests. Newmont Mill#5 flotation tailings samples were only ground in order to ensure $P_{80} < 200$ mesh particle size distribution.

In order to investigate any change in the leaching kinetics for different base usage, bottle roll and autoclave experiments were repeated by adding three different types of bases, calcium oxide (CaO), sodium hydroxide (NaOH), ammonium hydroxide (NH₄OH), to the solution. However, calcium oxide was used as a pH modifier for all of the pressure cyanidation experiments, since it is the most common pH modifier used in the cyanide leaching industry. Table 21 summarizes bottle roll experiment conditions.

| Pressure(psi) | Type of base added | | |
|--|---|--|--|
| <p style="text-align: center;">12.4 (Atmospheric Pressure)</p> | <p style="text-align: center;">CaO</p> | <p style="text-align: center;">NaOH</p> | <p style="text-align: center;">NH₄OH</p> |

Table 21. Bottle Roll Experiments Summary

Autoclave experiments were conducted at pressures of 90, 60, 30, 12.4 psi (atmospheric pressure). During the experiments the autoclave was pressurized by using pure nitrogen gas or air. Pressure leaching experiments were conducted with addition of a base or under neutral pH conditions of the samples without any addition of base. Table 22 summarizes pressure cyanidation experimental conditions for both ore types.

| | Air pressure | | Nitrogen gas pressure | |
|--------------------------------|-------------------------|-----|-----------------------|-----|
| Pressure(psi) | Type of base added | | Type of base added | |
| 90 | None (Natural pH) | CaO | None (Natural pH) | CaO |
| 60 | | | | |
| 30 | | | | |
| 12.4 (Atmospheric Pressure) | | | | |

Table 22. Autoclave Experiments Summary

None of the pressurizing gases were purged through the pulp inside the autoclave. Pressurizing gases were injected to the autoclave through the pressure inlet valve on top of the autoclave and the gases accumulated above the slurry inside the autoclave.

Nitrogen gas was used as a pressurizing agent in order to minimize effect of increased dissolved oxygen amount in the solution and to be able to observe the pressure effect on gold leaching. However, at the beginning of each experiment, 1350 cubic centimeter of air was present in the empty portion of the autoclave under atmospheric conditions. The air left in the autoclave was not purged by nitrogen gas out of the autoclave in order to ensure the presence of enough oxygen for the cyanide leaching reactions to occur.

Before starting the autoclave tests, bottle roll leaching tests were run in order to determine the mixing rate of the autoclave under atmospheric pressure to give nearly the same recoveries to compare with bottle roll experiments. At the end of these experiments, both bottle roll and autoclave mixing rates, gave the same recoveries over the same period of time. The optimum bottle roll and autoclave mixing rates 81 and 400 rpm respectively.

Figure 34 and Figure 35 presents the procedures followed for the bottle roll and autoclave experiments respectively.

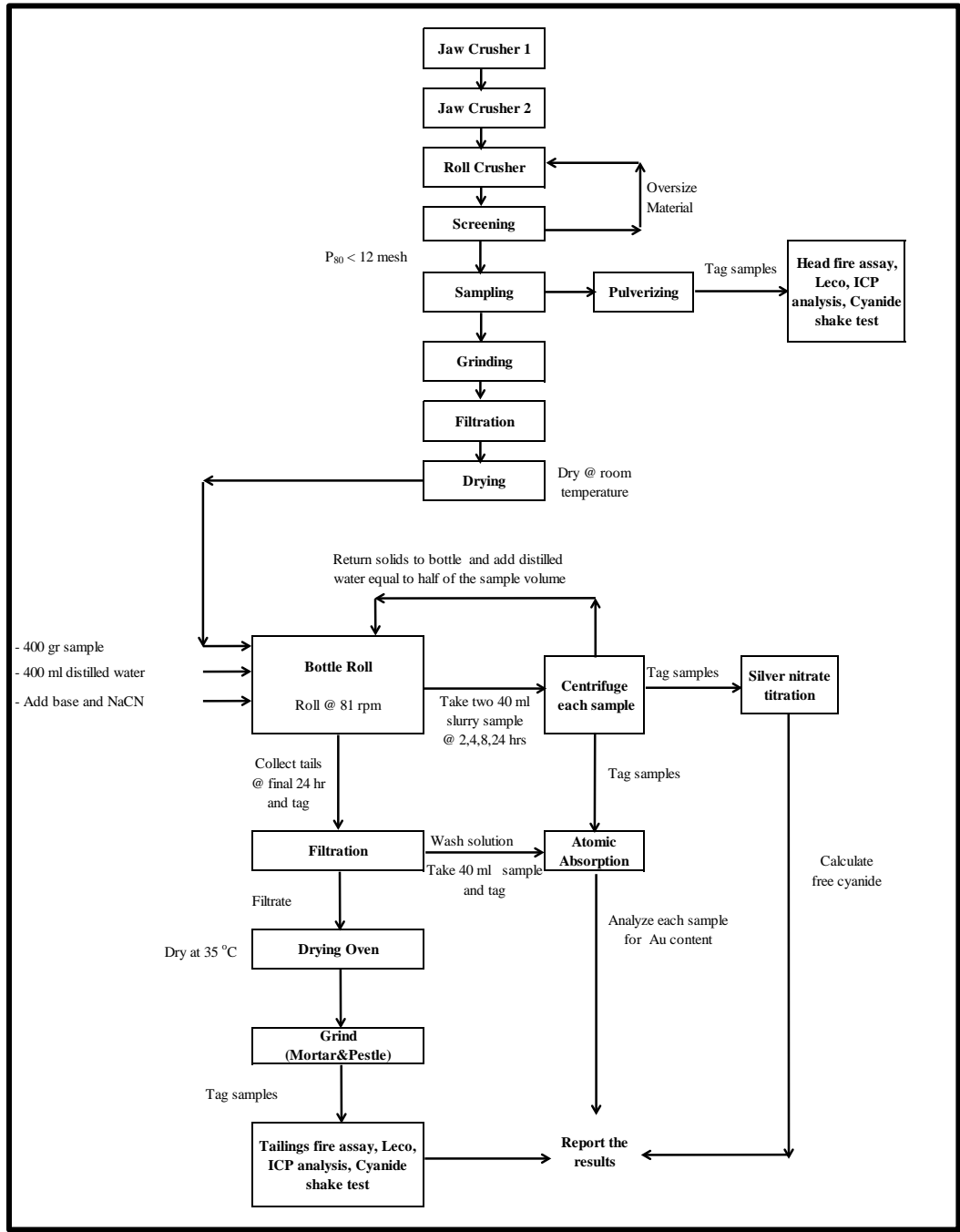


Figure 34. Bottle Roll Experimental Procedure

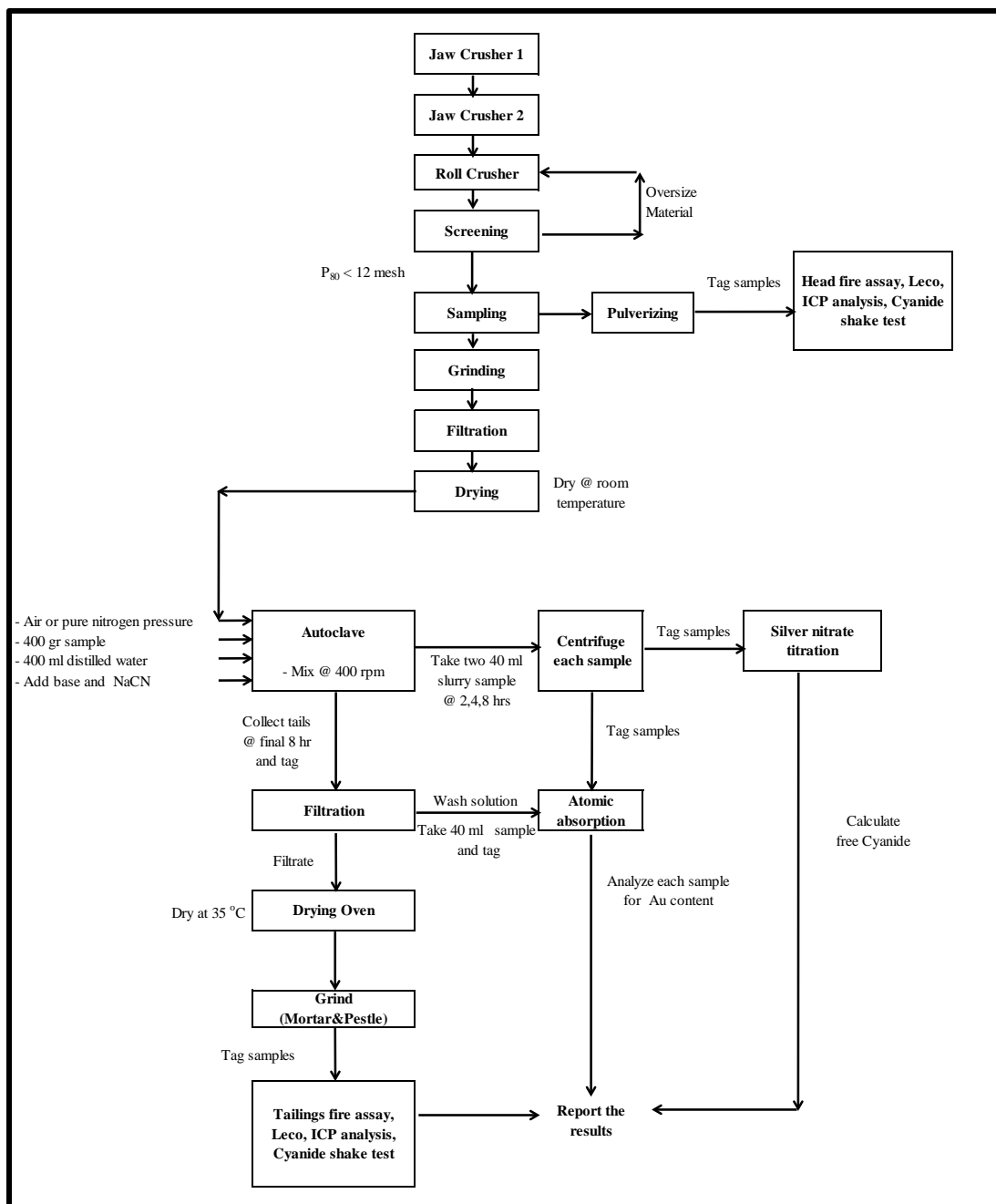


Figure 35. Autoclave Experimental Procedure

4.1.1 SAMPLE SIZE REDUCTION

Prior to sample preparation, specimens were selected and stored for the crushing process. Sample size reduction by crushing was completed to provide 80 % minus 12 mesh material for grinding mill feed.

The crushing procedure followed is summarized below,

1. The grab samples were fed to the lab scale jaw crusher with closed side opening set to approximately 3/4 inch.
2. Product of first jaw crusher was fed to second jaw crusher with closed size opening 3/8 inch.
3. Product of the second jaw crusher was fed to the roll crusher. Roll mill product screened to 12 mesh screen. All oversized material was returned to the roll crusher until 80% of the material passed through the 12 mesh screen.
4. Crushed ore was split by riffle and combined. Combined samples were split again to provide samples for the head analyses and grinding tests.

4.1.2 SAMPLE SPLIT

Sample split procedure were applied in order to maintain homogeneity of the samples and avoid the nugget effect during sample size reduction. The sampling procedure applied is summarized below ^[5],

1. Entire sample was passed four times over the top of the riffle splitter for blending purposes.
2. As the sample was passed over the riffle, samples were recombined from the two catch pans at the bottom of the riffle.
3. After the blending, a split was taken from one side only. Repeatedly the content of only one pan was passed over the riffles.
4. As shown in Figure 36 each split was combined and split again to ensure the material blending.
5. The splitter and pans were cleaned between each sample using compressed air.

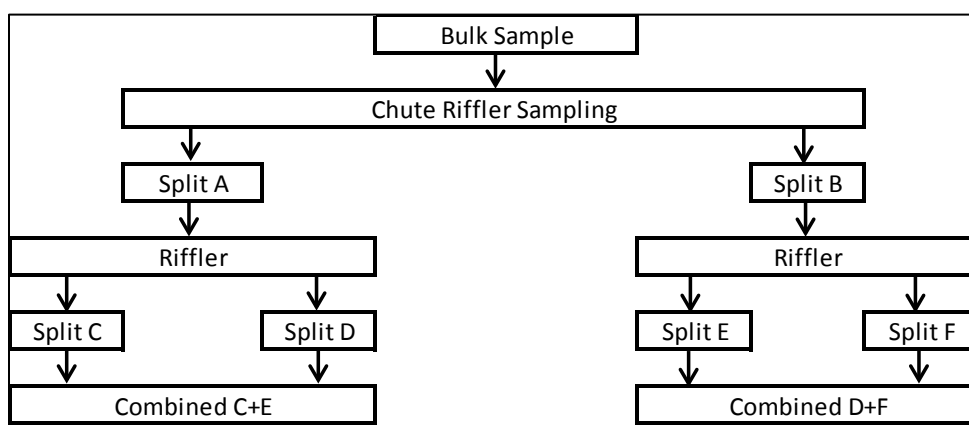


Figure 36. Sampling Procedure

4.1.3 PULVERIZING

A disc pulverizer was used to reduce the material size to a fine powder sample (minus 200 mesh) for the head analysis. The procedure followed for pulverizing is presented below,

1. Prior to pulverizing, samples were thoroughly dried in order to avoid any sample contamination.
2. Split samples were fed to the pulverizer slowly to prevent binding of the plates.
3. Pulverized samples were collected from the retrieval cup at the bottom of the pulverizer.

4.1.4 GRINDING TESTS

Grinding tests were applied to the crushed samples in order to determine the grindability of the samples as a function of grinding duration. Once the required time to have the target product size ($P_{80} < 200$ mesh) was calculated, each crushed product was ground using this time.

The following procedure applied for the grinding tests.

1. Three equal sized samples of 400 gr from the three stage crushed ore sample were split.
2. The grinding media was placed inside of the mill.
3. The ball mill was loaded with one of the samples and 400 mL water was added to make the slurry 50% (w/w) solids.
4. Grinding mill lid was fasten securely.
5. The mill was run on the roller table for the determined durations.

6. When each grinding time was complete, all sample were rinsed into a bucket and the grinding media was removed and the sample residue on the media was rinsed to the same bucket.
7. The screening procedure in section 4.1.7 was applied to find the oversize and undersize particle amounts of the grind product.
8. Steps 1 - 3 were repeated for different grinding time interval.
9. Percent passing 200 mesh vs. grinding time was graphed.

4.1.5 FILTRATION

At the end of the bottle roll and autoclave experiments leach slurries were filtered under pressures of 30 psi. Two products, the cake and wash solution were obtained at the end of the filtration process and both of them were analyzed for their gold content. Filtration procedure is presented below,

1. Lids, filter cloths, hoses, gaskets, drain hose and relief valves were checked and in order to prevent contamination, necessary cleaning was done prior to operating the filtration equipment.
2. Filter cloth and two layers of filter paper were placed over the press base
3. The filter cloth and the paper were wetted with a minimum amount of water improve the filter seal.
4. The cylinder was placed slowly inside the knobs of the press in order to not tear the filter paper.
5. Slurry was poured slowly into the cylinder.

6. The swing frame was centered over the lid and hand tightened.
7. Air relief valve of the filtration equipment was closed prior to pressurizing the filter.
8. Air inlet valve was opened and the press was pressurized slowly until the pressure inside the vessel reached 30 psi.
9. Filtration continued until a very small amount of solution was coming out the drain valve.
10. Air inlet valve was shut down and air relief was opened in order to depressurize the filtration equipment.
11. The lid and the cylinder were removed.
12. The cake and the solution were retrieved from the filter base and the drain bottle, respectively.

4.1.6 DRYING

Following the filtration samples were dried in a lab oven. Drying procedure was as follows,

1. Batch oven temperature controller was adjusted for desired drying oven temperature.
2. At the end of the drying period samples were removed from the oven, stirred and check for any water condensation under a watch glass.
3. Any sample with moisture content was returned to the oven for further drying.

4.1.7 PARTICLE SIZE ANALYSIS

The procedure for the size analysis of samples being processed was as follows:

1. Dry weight of the samples were recorded.
2. The sample was placed in a 500 ml beaker to make a 20% solid by weight slurry.
3. Small quantities of the slurry were placed onto the sieve and sprayed with wash water (Wet screening).
4. Periodically +200 mesh material was unloaded to a separate pan. No more than 50 g of material was loaded on the screen at any given time to protect the screen from not overloading it.
5. +200 and -200 mesh fraction were dried in an oven at 35 °C for 24 hours.
6. The dried +200 mesh material was used as feed material for dry screening tests.
7. +200 mesh material was loaded into rotap screen. And the rotap was run for 10 minutes. Only 200 mesh screen was and two pans (above and below the screen) was placed into the rotap for size analysis purposes.
8. Sieves were unloaded and the weights of the retained samples were recorded.
9. Oversize and undersize materials were combined separately.
10. Weights of dry screening material were reported.

Screen analysis report for the grinding tests is presented on results and discussion section. Figure 37 shows summary of the particle size analysis procedure.

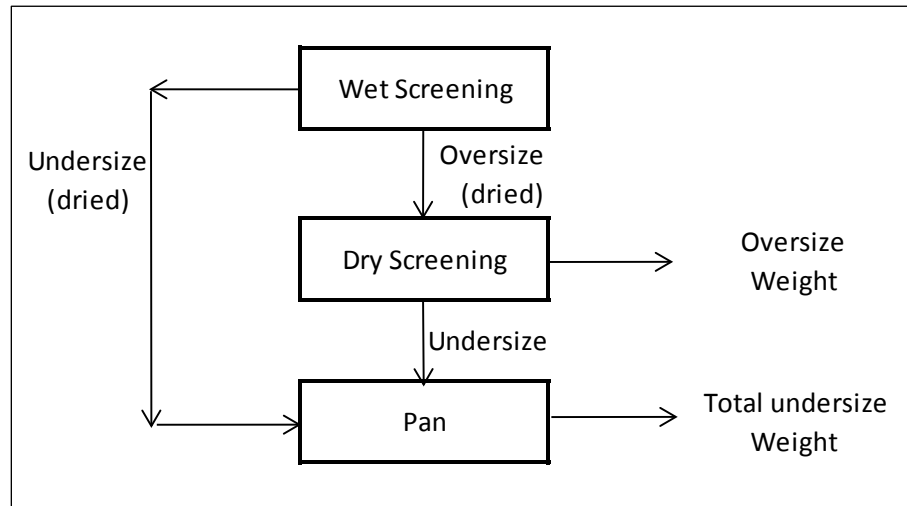


Figure 37. Particle Size Analysis Procedure

4.1.8 ROCK DENSITY DETERMINATION TESTS

The density measurement procedure was as follows:

1. The weight of the empty clean and dry pycnometer was determined and recorded.
2. Between 20 - 30 gr of a dry sample (80% passing 200 mesh) was placed in the pycnometer. The weight of the pycnometer containing the dry sample was measured and recorded (W_{PS}).
3. Distilled water was added to fill about half of the pycnometer, then the sample was allowed to soak for 10 minutes.
4. A partial vacuum was applied to the contents for 10 minutes, to remove the entrapped air.
5. The vacuum was stopped and the vacuum line was removed from the pycnometer.

- Pycnometer was filled with distilled water. The weight of the pycnometer and contents was determined.

The pycnometer was emptied and cleaned. Then it was filled with distilled water. The weight of the pycnometer and distilled water was determined^[94].

The specific gravity of the sample solids was calculated using the following formula:

$$\text{Specific gravity} = \frac{W_s}{W_s + (W_{pw} - W_{psw})} \quad (24)$$

Where:

W_{psw} = The weight of the pycnometer filled with water plus the dry sample

W_{pw} = Weight of pycnometer filled with water

W_{ps} = The weight of the pycnometer plus the dry sample

W_p = The weight of the empty pycnometer

W_s = Weight of the dry sample = $W_{ps} - W_p$

4.1.9 AUTOCLAVE EXPERIMENTS

The following procedure was followed for the autoclave tests,

- 400 gr of dry ground ore was added to the autoclave with 400 mL distilled water.
- Before addition of cyanide or base, the slurry was stirred for an hour of conditioning time and the pH of the pulp was recorded and adjusted as needed.

3. After addition of cyanide, the lid of the autoclave was closed, the two piece of clamp was attached and 6 screws on the clamps were tighten, then the ring around the clamps was placed and tightened.
4. All valves were closed except the gas inlet valve.
5. The tubing of compressed air or nitrogen from the cylinder was connected to the autoclave and tightened.
6. The compressed air or nitrogen cylinder valve was opened and the regulator was adjusted to the desired pressure.
7. After pressurizing, the autoclave was put into a water bath to check if there were any gas leakage.
8. The overhead stirring mechanism was placed on the driving shaft of the autoclave.
9. The overhead stirring was adjusted to 400 rpm and turned on.
10. The autoclave was stirred for 2 hours, then it was stopped and a sample was taken by the following procedure:
 - a) Sample was extracted from the autoclave using the sampling valve to fill a centrifuge test tube.
 - b) 80 mls of clarified solution was centrifuged and decanted.
 - c) Sample solution was checked for pH, Au content, free cyanide.
11. Step 10 was repeated and samples are taken at 4, 8 and 24 hours.
12. At end of each test, the gas valve and the overhead drive were shut off. The gas relief valve was opened to release the pressure. After all of the pressure in the autoclave was relieved, the tubing for the gas cylinders was disconnected.

13. The slurry was collected from the autoclave.
14. The collected tailings were filtered, washed and weighed.
15. The dried tailings were fire assayed in duplicate for Au.
16. All filtrate and wash volumes were recorded. The final wash solution was assayed for Au. Metal recovery was calculated as metal extracted via solution versus metal extracted via solution plus tailings assay. Chemical consumptions were calculated as NaCN, pounds/dry short ton of ore and CaO, pounds/dry short ton of ore.
17. The amount of gold, silver and NaCN removed from the bottle roll tests during the sampling procedures were determined and used to determine metal recovery and chemical consumptions.

4.1.10 BOTTLE ROLL TESTS

Cyanide bottle roll experiments were performed on Golden Days samples in order to provide evidence for the amenability of leaching gold from its ore. A total of twelve (12) cyanide bottle roll leach tests were conducted on the composite samples on the Golden Days oxide ore samples. The tests were conducted on material ground to 80% passing 200 mesh.

The experimental procedure is summarized below.

1. 400 g 80% passing 200 mesh ore was placed into a clean 1 gallon bottle.
2. 400 mL of distilled water was placed into the bottle and agitated thoroughly.

3. After 1 hour conditioning stage, with addition of only lime as a reagent, pH was checked. The amount of lime added and the value of the pH was recorded.
4. Sodium Cyanide (NaCN) was added to the solution to a concentration of 0.1%.
5. The bottle was placed on a standard roller to agitate the slurry.
6. The bottle was rolled for 2 hours, then it was stopped and a sample was taken, as follows:
 - A) 80 ml of sample was transferred to a centrifuge test tube.
 - B) 80 mls of clarified solution was centrifuged and decanted. Reject pulp was returned to the bottle and 40 ml of D.I. H₂O was added to the bottle leach test.
 - C) The sample solution was analyzed for pH, free cyanide and Au content.
7. Step 6 was repeated and samples were taken at 4, 8 and 24 hours.
8. At the end of each test, dry tailings were filtered, washed and weighed. Tailings were submitted for assay analyze. The dried tailings were fire assayed in duplicate for Au.

All filtrate and wash volumes were recorded. The final wash solution was assayed for Au/Ag. Metal recovery was calculated as metal extracted via solution versus metal extracted via solution plus tailings assay. Chemical consumptions were calculated as NaCN, lb/st ore and CaO, lb/st.

The amount of gold, silver and NaCN removed from the bottle tests during the sampling procedures were determined and added back into the calculations to determine metal recovery and chemical consumptions.

Bottle Roll tests were conducted at atmospheric pressure. At Reno, Nevada the atmospheric pressure was calculated by the following formula and noted accordingly on the experiment reporting sheets.

$$p = 101,325 \times (1 - 2.25577 \times 10^{-5} \times h)^{5.25588}$$

p = air pressure (Pa)

h = altitude above sea level (m)

Since the city is at 1300 m elevation, atmospheric pressure value is calculated as 12.4 psi (0.855 bar; 85,495 pascals).

4.1.11 SILVER NITRATE (AgNO₃) TITRATION

The silver nitrate with p-dimethylaminobenzylidene rhodanine indicator was used to measure free cyanide in leach solutions. Initially rhodanine is added to the sample leach solution that turns the solution color into yellow. Since silver cyanide complex is more stable than silver rhodanine complex, silver ions first form silver nitrate complex with the free cyanide in the solution. Once all the free cyanide complexes with silver, the excess silver complexes with the rhodanine and at that point the solution color changes to pink [95]. The overall reactions forming silver complexes are presented below.



Further Silver nitrate addition causes precipitation of silver cyanide.



Detailed description of the chemical used for the titration experiments given in the sections 3.1.5 and 3.1.6. Figure 38 shows the titration equipment set-up.



Figure 38. Titration Setup

The experimental procedure applied for free cyanide measurements is summarized below,

1. Exactly 25 mls clear solution was collected from the previously centrifuged slurry solution by a graduated cylinder.

2. 5 drops of Rhodanine indicator solution was added to the sample which turned the solution color to yellow.
3. The metal mixing pill was placed into the solution sample and placed under the digital burette.
4. The silver nitrate was added slowly by drop to the sample until the sample solution color was changed to a salmon pink color.
5. The display on the burette was recorded. This was used to calculate the free cyanide concentration.

4.1.12 FIRE ASSAY

The gold content of head and tail samples was determined by conventional fire assay method. Fire assaying consists of sample preparation, fluxing and fusion, cupellation, parting and annealing ^[96].

Sample preparation: Received samples were crushed, split and pulverized. If the samples were from the leach tailings they were directly pulverized for further assaying

Fluxing and Fusion: Samples were melted with the proper flux in a crucible at 1100°C inside the fire assaying oven. Assay fluxes are composed of litharge, borax, silica sand, sodium carbonate and wheat flour. Wheat flour acts as a reducing agent and forms metallic lead, sodium carbonate is added for de-sulfurization, borax and silica modify the melting point and helps control the viscosity of the melted impurities. An amount of sodium carbonate (NaCO_3), litharge (PbO), silica (SiO_2), borax ($\text{Na}_2\text{B}_4\text{O}_7$) and wheat

flour added was 27%, 53.5%, 13.5%, 4.5%, 1.5%, respectively. Figure 39 shows the fire assaying oven where fluxes and samples is melted inside the crucibles.



Figure 39. Fire Assaying Oven

After complete melting of the samples, the crucibles were removed from the furnace and the contents were poured into a mold. After solidification of all contents of the crucible, a lead button forms on the bottom of the crucible and a slag forms above it. The slag and the lead button formed were broken by hammer and separated from each other. The lead button obtained, is used for the cupellation process^[97]

Cupellation: Lead buttons were placed into the cupels that were made of bone ash and cement than the cupels were loaded into the cupellation kiln at 950°C. At his temperature lead buttons were melted and lead oxide absorbed into the cupel leaving behind a tiny doré bead containing gold and silver. After the cupellation has been completed, the cupel was removed from the furnace and allowed to cool. The doré beads derived from

cupellation were weighed. One mg doré represents one troy ounce per ton of ore. The hot cupels and the formed dore beads are shown in Figure 40 and Figure 41.



Figure 40. Removed Cupels from the Furnace



Figure 41. Doré Bead Containing Gold and Silver in Cupels

Determination of the Gold and Silver Amount of the Buttons: The doré was placed in a porcelain cup. Nitric acid (15% by volume) was added to the cup and heated on a

hotplate. The nitric acid dissolved the silver and left a gold sponge behind. The sponge was washed with de-ionized water and left to dry. The gold sponge was annealed and then weighed by using a microbalance ^[98].

4.1.13 LECO ASSAYING

Sulfide sulfur, total carbonaceous matters (TCM) and carbonates are assayed by Leco analysis. The Leco method consists of burning sulfur and carbon to SO₂ and CO₂ respectively, in an induction furnace and analyzing the off-gas for these species ^[99].

All samples submitted for either a short or long method Leco analysis were run for total carbon (carbonate + TCM) and total sulfur (sulfate sulfur + sulfide sulfur).

All samples submitted for any Leco suite have a HCl digestion step followed by Leco bum to determine carbonate carbon by dissolving out the carbonates, i.e., calcite, dolomite and siderite, in the ore and then determining the total carbonaceous matter remaining (TCM).

4.1.14 INDUCTIVELY COUPLED PLASMA

Inductively coupled plasma spectrometry (ICP) was used for chemical analysis of leach tailings obtained at the end of the bottle roll and autoclave experiments.

ICP detection limit of 10 ppb for metals and several non-metals. In this method the solid samples were ionized with inductively coupled plasma and then by using a spectrometer the ions were separated and quantified ^[100].

4.1.15 ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Atomic absorption spectroscopy (AAS) is a spectro analytical procedure for determining chemical elements quantities. This is accomplished by the measurement of absorbed radiation by the chemical elements' free atoms in the gaseous state ^[101].

The gold amount (analyte) in leach solutions was assessed by the absorption spectrometry technique. A standard with known analyte content was initially measured in order to define a relation between the measured absorbance and analyte concentration.

Overall analysis procedure followed is summarized below,

The amount of gold in the sodium cyanide solution of the samples was determined by atomic absorption spectrophotometry at a wavelength of 242.8 nm in an oxidizing air-acetylene flame.

After turning on the compressed air and acetylene cylinders valve connected to the AAS instrument, it was turned on. Following the display on instrument screen, below instrument parameters were entered for gold analysis of the solutions sampled during autoclave and bottle roll experiments.

Instrument mode, choose: Absorbance

Active lamp : 2 (Gold lamp)

Active current : 4.0 (mA)

Standby current : 0 (mA)

D2 correction : No
Gas type : Air acetylene
Wave length : 242.8
Slit : 1

Measurement parameters were set up as follows:

Next sample : 1
Batch number : 1
Pre-read delay : 10 sec
Read time : 4 sec
Replicates : 3

After setting up the spectrometer parameters, a Varian card was used to make light beam alignment and additional 45 minutes spent for the gold lamp to warm up until the readings were stable before analysis gold content of samples.

Once the readings were stable the spectrometer was calibrated using 0, 0.5, 1, 5, 10 ppm gold standards in 0.1% NaCN and 1% NaOH solution.

After completing sample analysis each standard used for calibration of the spectrometer was analyzed again and the correction factor for samples analyzed was found and applied to the results.

4.1.16 LEACHABLE GOLD IN PULP BY CYANIDE SHAKE TEST

A shake test was applied to analyze the ore samples' refractory nature and response to cyanidation.

Shake test experimental procedure is presented below,

1. All test tubes were numbered and labeled.
2. 15 gr of pulverized samples were added to 50 mL glass test tubes.
3. 30 mL of caustic cyanide solution with the concentration of 0.5% NaCN and 0.8% NaOH was added to the test tubes
4. All the glass tubes were tapped, placed on a shaker table and agitated for 1 hour.
5. If any sample was not wetted, sample number was noted and rerun using half of the sample weight.
6. All the samples were centrifuged for 10 minutes at 3200 rpm.
7. The solution was collected from the tubes and analyzed for its gold content by AAS.

5. RESULTS AND DISCUSSION

Bottle Roll experiments and a grinding study was only conducted for Golden Days ore samples. These experiments were not conducted for flotation tailings samples due limited amount of the samples received.

The flotation tailings samples were ground for forty-eight (48) minutes by the same procedures applied to Golden Days ore samples prior to leaching. The resulting particle size distribution obtained was $P_{90} < 200$ mesh for the ground flotation tailings. However, the methods used for the pressure cyanidation experiments were the same for both flotation tailings and Golden Days ore samples.

5.1 GRINDING EXPERIMENTS

Grinding experiments were conducted in order to determine grinding time required to obtain 80% passing 200 mesh size from the crushed Golden Days ore samples. Total of four (4) grinding experiments were conducted. Experiment results are provided in Table 23 and Figure 42 presents.

| Exp # | Sample weight (gr) | Grinding time | + 200 mesh | - 200 mesh | % Passing |
|-------|--------------------|---------------|------------|------------|-----------|
| | | (min) | (gr) | (gr) | 200 mesh |
| 1GD | 400 | 20 | 249.76 | 149.2 | 37.39 |
| 2GD | 400 | 31 | 169.04 | 229.44 | 57.45 |
| 3GD | 400 | 55 | 52.88 | 346.08 | 86.95 |
| 4GD | 400 | 90 | 4.32 | 394.56 | 98.91 |

Table 23. Golden Days Samples - Grinding Study Results

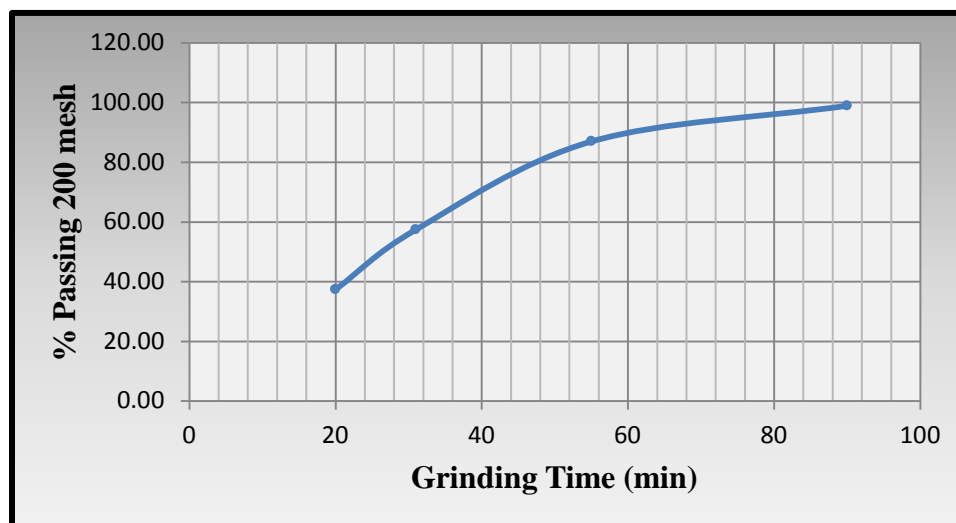


Figure 42. Golden Days Samples – Grind Study Results

It was concluded that Golden Days ore samples were to be ground for 48 minutes in order to have 80% of the particles passing 200 mesh.

5.2 ROCK DENSITY DETERMINATION

Golden Days oxide ore ($P_{80}<200$ mesh) and flotation tailings ($P_{90}<200$ mesh) specific gravities were found as 2.52 and 2.22 respectively. The experiments were conducted in 500 ml pycnometer.

5.3 BOTTLE ROLL EXPERIMENTS

Bottle roll experiments were conducted in order to determine cyanide leachability of the samples by the industry accepted standard technique. Initial bottle roll and autoclave experiments were conducted for different mixing rates in order to determine a mixing rate

both for autoclave and bottle rolls that would give similar recovery values for the same leaching time at atmospheric pressure.

Table 24 summarizes the bottle roll experiment results for Golden Days samples. Sodium cyanide (NaCN) consumptions are calculated in pounds NaCN per ton of Golden Days ore. AuCN recovery represents the % gold recovery of the cyanide shake test whereas AuFA recoveries represent the % gold recovery of the fire assay value.

As shown in Table 24, bottle roll tests resulted in recoveries of more than 90% for the cyanide soluble gold (AuCN) amount at the end of the 24 hours at atmospheric conditions.

| Exp. # | Leach Time (hr) | Pressure (psi) | Base | pH | NaCN Cons. (lb/st of ore) | AuCN Rec. (%) | AuFA Rec. (%) |
|---------------|------------------------|-----------------------|--------------------|-----------|----------------------------------|----------------------|----------------------|
| 1 | 24 | 12.4 | CaO | 11.5 | 2.31 | 94.5 | 87.4 |
| 2 | 24 | 12.4 | NaOH | 11.1 | 1.88 | 92.5 | 89.0 |
| 3 | 24 | 12.4 | NH ₄ OH | 10.7 | 1.75 | 95.6 | 93.3 |
| 5 | 24 | 12.4 | NaOH | 11.1 | 2.28 | 92.9 | 88.6 |
| 6 | 24 | 12.4 | CaO | 11.6 | 1.60 | 92.4 | 89.1 |
| 8 | 24 | 12.4 | CaO | 11.7 | 1.65 | 93.8 | 90.5 |
| 9 | 24 | 12.4 | NaOH | 10.9 | 1.07 | 93.9 | 91.3 |
| 10 | 24 | 12.4 | NH ₄ OH | 10.6 | 1.74 | 92.6 | 89.8 |

Table 24. Golden Days Samples Bottle Roll Experiments Conditions, Cyanide Consumption Values and Recoveries at Atmospheric Conditions

Throughout the bottle roll tests lime addition amount was 0.2 grams per 400 grams of dry sample feed (1 pounds per dry short ton of ore).

The bottle recoveries and the mixing rates were compared to the autoclave tests in order to find a mix rate for each system that would result in the similar recoveries. The findings of these experiments are compared in section 5.4.

Table 25 shows the resulting gold recoveries for different bottle mixing rates. These experiments were conducted with mixing rates at 81, 98, 110 rpm.

| Exp. # | Base | % AuFA Recovery @ 8 hr leaching | Bottle Roll, rpm |
|---------------|--------------------|--|-------------------------|
| 8 | CaO | 71.0 | 110 |
| 6 | CaO | 67.6 | 98 |
| 1 | CaO | 66.4 | 81 |
| 9 | NaOH | 70.8 | 110 |
| 2 | NaOH | 69.3 | 98 |
| 5 | NaOH | 67.0 | 81 |
| 3 | NH ₄ OH | 71.7 | 110 |
| 10 | NH ₄ OH | 66.5 | 81 |

Table 25. Bottles Roll Agitation Rate Effects on Gold Recoveries

Kinetics of bottle roll experiments at different rolling rates are presented in

Figure 43. The bottle roll experiments where ammonium hydroxide was used as pH modifier gave slightly higher gold recoveries compared to the experiments where calcium oxide (CaO) and sodium hydroxide (NaOH) were used for 24 hour leaching period at the bottle mixing rates of 81 and 110 rpm. Cyanide leaching kinetics curves for the experiments where NaOH was used as a base resulted in higher leaching rates compared to experiments conducted with CaO addition as a base. Between 65% to 72% of the total gold (AuFA) contained in Golden Days ore was leached at the end of the 8 hr cyanide

bottle roll experiments. Bottle roll tests showed that at the end of the 24 hour period 87% of the total gold was recovered by adding CaO as a base and rolling the bottles at 81 rpm. As expected higher mixing rates resulted in higher gold dissolution rates by reducing diffusion layer thickness and increasing mass transfer rates of oxygen and cyanide during leaching.

As it can be observed from the Figure 43, bottle roll leaching experiments where CaO was used as a base has slower gold dissolution kinetics and lower recoveries at the end of the 24 hours leaching period. This can be explained by the retarding effect the lime on gold dissolution. Formation of calcium peroxide film on the surface of the gold particles occurs when lime reacts with hydrogen peroxide (H₂O₂) in the slurry solution by the following reaction ^[102];



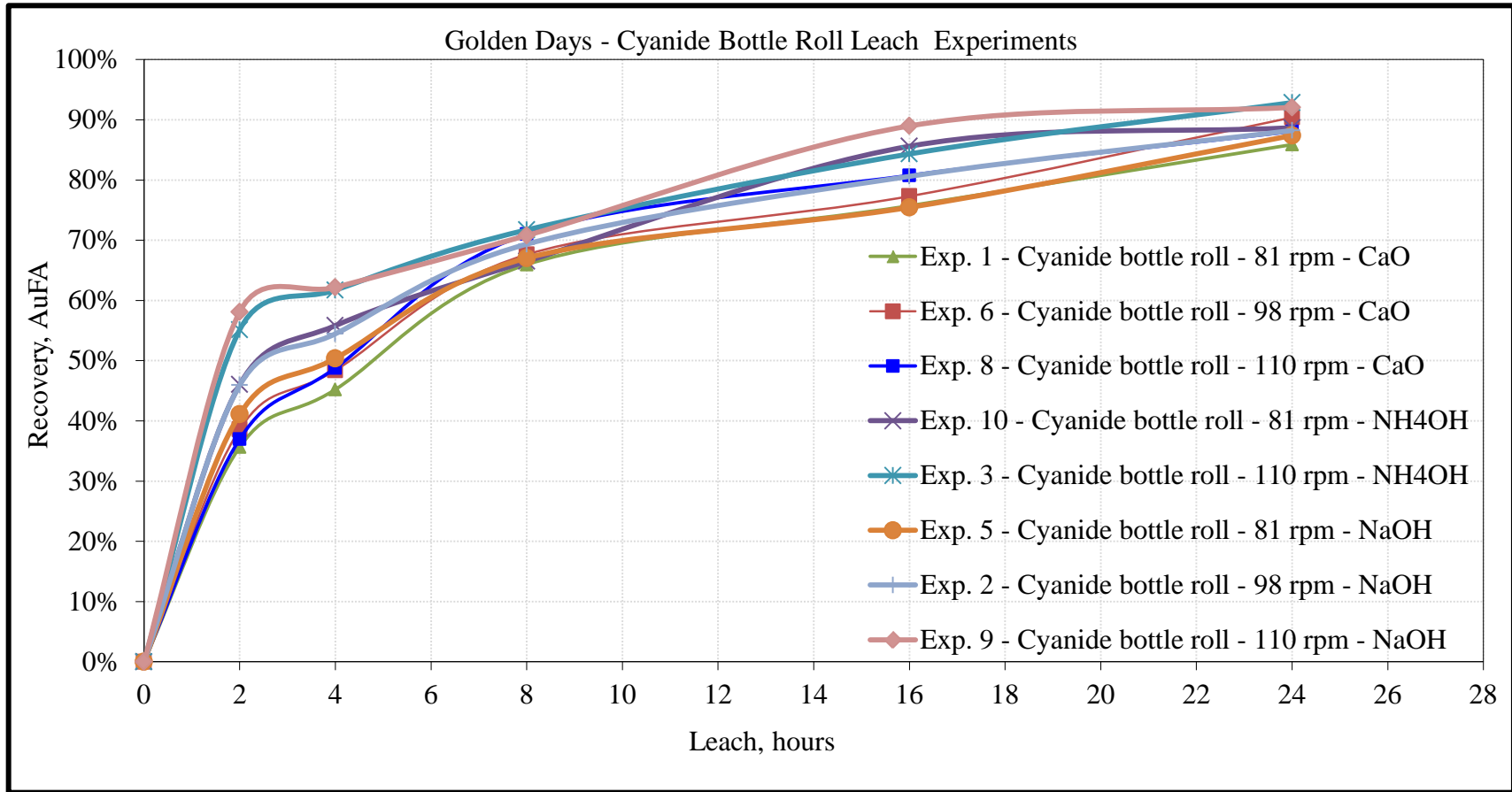


Figure 43. Golden Days Bottle Roll Test Results – Recoveries versus Time

5.4 AUTOCLAVE TESTS

Autoclave experiments were conducted in order to investigate room temperature pressure cyanidation effects on gold recoveries. Experimental work proved that there is a direct relationship between the leaching environment pressure level and gold recovery rates.

5.4.1 GOLDEN DAYS SAMPLES

Initial autoclave experiments were conducted at 200, 350 and 400 rpm impeller mixing rates in order to find the right mixing rates that would give similar recovery values with the bottle roll experiments.

Two hundred (200) rpm impeller mixing rate was not enough to suspend the particles and caused settling of the solid particles to the bottom of the autoclave. The minimum impeller mixing rate was found to be 300 rpm in order to have all solid particles suspending in the solution. Table 26 summarizes recoveries obtained for different autoclave mixing rates.

| Golden Days Autoclave Tests | | | | |
|------------------------------------|--------------------|-----------------------------------|------------------------------------|-----------------------|
| Test # | Base | % Recovery @ 8 hr leaching | % Recovery @ 24 hr leaching | Autoclave, rpm |
| 4 | NH ₄ OH | 63 | 89 | 350 |
| 7 | NaOH | 64 | 91 | 350 |
| 11 | NaOH | 67 | 92 | 400 |

Table 26. Agitation Rate Effects on Gold Recovery

By comparing the results on Table 26 and Table 25, mixing rates for bottle roll and autoclave experiments for the same recoveries were found to be 81 rpm and 400 rpm respectively. In other words, the autoclave 400 rpm impeller agitation rate gave the nearly the same gold recoveries to the bottle roll experiments at 81 rpm under the atmospheric conditions.

Figure 44 presents the gold recovery comparison for the bottle roll and autoclave experiments at 81 rpm and 400 rpm respectively.

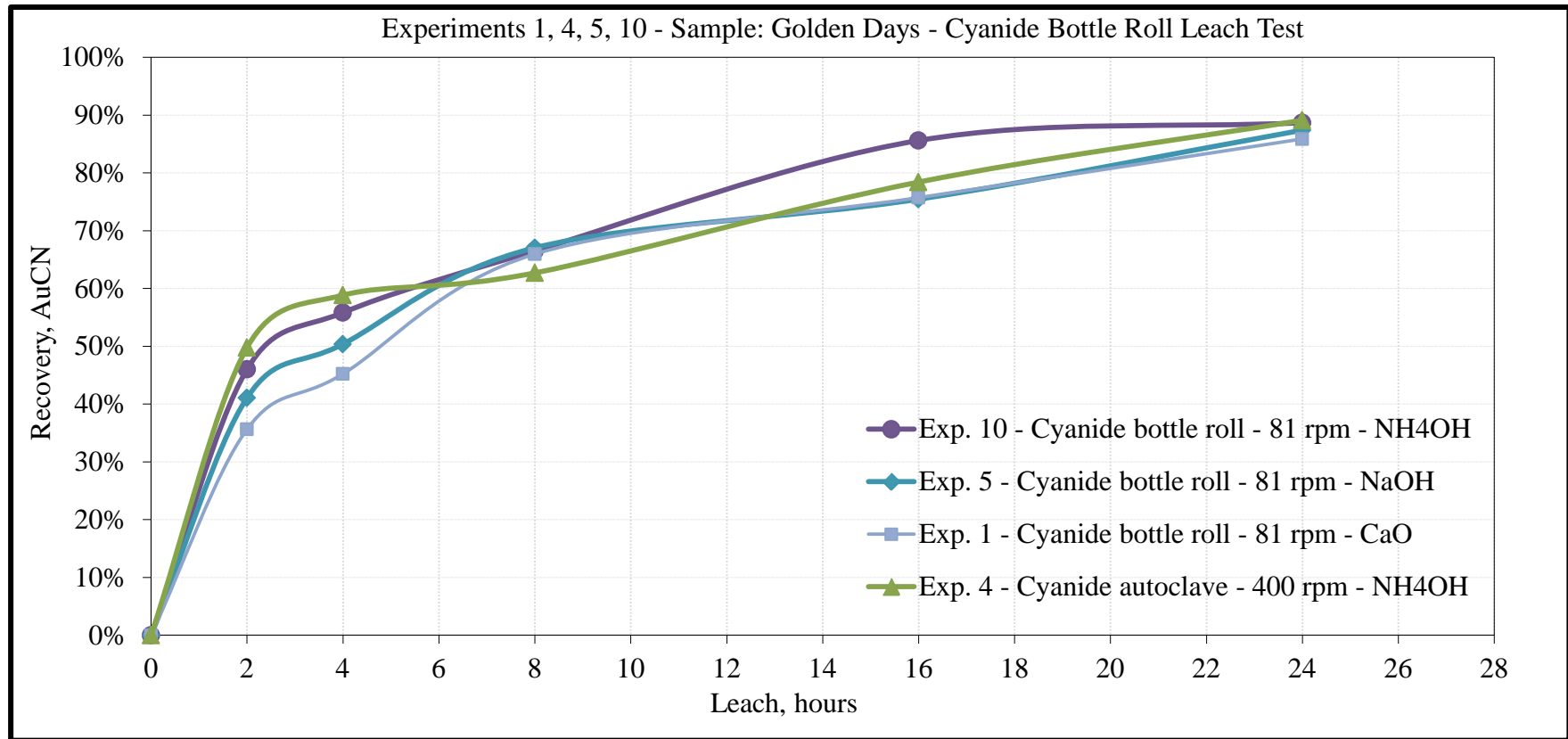


Figure 44. Comparison of Recoveries between Bottle Roll and Autoclave for Different Impeller Mixing Rates

Bottle roll experiment #1 had 66.4% of AuFA recovery after eight hours of leaching. The gold recoveries increased with the increased pressure levels by the pressure cyanidation when compared with the total gold (AuFA) and the cyanide shake test (AuCN) as shown on Table 26. The resulting gold recoveries from both bottle roll and autoclave experiments and percent gold recovery increases for the pressure cyanidation experiments are presented on below Table 27. Pressure cyanidation leaching experiments resulted in 40% higher total gold (AuFA) recoveries compared to bottle roll experiments. The comparison of the recoveries between the bottle roll and autoclave experiments for different pressure levels are presented in Figure 45.

It is expected that increased gold recoveries would result in higher cyanide consumption. But examining all pressure leaching experiments that resulted in higher recoveries, the cyanide usage of these experiments showed lower cyanide consumptions compared to bottle roll experiments.

Golden Days ore has natural pH values of 8.3. During gold dissolution by cyanide (Equation 8) the leach solution becomes more basic due to formation of hydroxide ions (OH^-). As a result of this, the pH of the solution for the experiments conducted with Golden Days samples under air pressure without addition of base rose to 10.1 which is very close to the optimum pH value (10.3) for gold cyanide leaching. The experiments at natural pH values which were close to optimum pH value showed higher gold recoveries compared to the ones conducted with base addition resulting in higher pH plus lower NaCN consumption.

However, the pH – cyanide consumption – gold recovery relationship observed for the experiments conducted under nitrogen pressure with addition of CaO (Experiment

sets 17, 18, 19) and without addition of CaO (Experiment sets 38, 39, 40) were opposite of the ones conducted under air pressure. The experiments conducted under nitrogen pressure and without any base resulted in higher cyanide consumptions and reduced gold recoveries compared to the experiments conducted with base addition as shown on Table 27.

Prior to pressurizing of the autoclave, there was oxygen as air present in the empty portion of the autoclaves (1350 ml @ 12.4 psi) since the oxygen was not flushed out prior to experiments. Following the pressurization of the autoclave, the partial pressure of the oxygen increased and as a result, the dissolved oxygen amount in the slurry would be expected to increase. But the dissolved oxygen amount in the slurry was lower when the reactor was pressurized with pure nitrogen gas compared to when the air was the pressurizing agent since the contained oxygen in the pressurized air would cause more oxygen dissolution into the slurry. The higher cyanide consumption and lower gold recoveries observed in nitrogen pressurization experiments may be due to the non optimal $[CN^-/O_2]$ ratio in the slurry causing lower gold dissolution rates and enhancing the decomposition of cyanide due to reactions with other metals, i.e. iron, present in the ore.

As shown in Table 28 in the next section, this same trend was also observed for the experiment sets 22, 23, 24 and 25, 26, 43 conducted with flotation tailings samples where nitrogen was used as the pressurizing agent.

| Exp # | Leach Time (hr) | Press. (psi) | Gas type | Base | NaCN Cons. (lb/st of ore) | pH | AuCN Rec. (%) | AuFA Rec. (%) | % Increase in AuCN Rec. | % Increase in AuFA Rec. |
|-------|-----------------|--------------|----------------|------|---------------------------|------|---------------|---------------|-------------------------|-------------------------|
| 1 | 8 | 12.4 | - | CaO | 2.32 | 11.5 | - | 66.4 | - | - |
| 14 | 8 | 90 | Air | CaO | 2.14 | 11.5 | 93.5 | 88.8 | 40.76 | 33.73 |
| 15 | 8 | 60 | Air | CaO | 2.25 | 11.4 | 89.4 | 87.7 | 34.59 | 32.08 |
| 16 | 8 | 30 | Air | CaO | 2.28 | 11.9 | 97.7 | 82.4 | 38.13 | 24.10 |
| 18 | 8 | 90 | N ₂ | CaO | 1.3 | 11.0 | 96.4 | 90.6 | 45.15 | 36.45 |
| 17 | 8 | 60 | N ₂ | CaO | 0.98 | 11.1 | 91.7 | 87.6 | 38.13 | 31.93 |
| 19 | 8 | 30 | N ₂ | CaO | 1.32 | 11.3 | 90.7 | 85.9 | 36.65 | 29.37 |
| 35 | 8 | 90 | Air | - | 1.79 | 10.1 | 97.6 | 93.1 | 46.92 | 40.21 |
| 36 | 8 | 60 | Air | - | 1.55 | 9.8 | 90.4 | 87.9 | 36.08 | 32.38 |
| 37 | 8 | 30 | Air | - | 1.21 | 10.1 | 87.0 | 85.6 | 31.05 | 28.92 |
| 38 | 8 | 90 | N ₂ | - | 1.92 | 10.0 | 91.0 | 90.0 | 37.02 | 35.54 |
| 39 | 8 | 60 | N ₂ | - | 2.18 | 10.2 | 87.2 | 86.0 | 31.33 | 29.52 |
| 40 | 8 | 30 | N ₂ | - | 2.01 | 10.1 | 84.7 | 83.0 | 27.51 | 25.00 |

Table 27. Golden Days – Autoclave and Bottle Roll Experiments Recovery

Comparison

As presented on the above table recovered cyanide soluble (AuCN), total (AuCN) gold and the recovery increases for AuCN and AuFA at each pressure level are close to each other when compared to the experiments with flotation tailings. This is due to the non-refractory nature of the Golden Days ore and refractory nature (gold particles locked in silica) of the flotation tailings.

Figure 45 compares effect of pressure on total gold recoveries (AuFA) among the selected bottle roll test and each pressure cyanidation experiment conducted under different conditions. The direct relationship between applied pressure at room temperature and total gold recoveries was observed in each experimental condition.

The leaching kinetic curves of the bottle roll and autoclave experiments are presented on Figures 46, 47, 48, 49, 50. Figure 46 shows the dissolution kinetics of experiments where lime (CaO) was added to the solution and air used as a pressurizing agent. Whereas Figure 47 shows the gold dissolution kinetics when the nitrogen gas was used as a pressurizing agent. Figure 48 shows the case where applied gas was air without the addition of base into the solution. Figures 49 and 50 compares the effect of the pressurizing gas on the leach kinetics for the same experimental conditions

The leach kinetic curves presented below also points out a higher kinetic rate with the increase in pressure levels. Also all five presented curves shows that the gold recovery increase with increased pressure levels are independent from the solution pH values since the pressure effect on gold recoveries resulted from a physical effect (increased lixiviant diffusion rate into the micropores of the solids) not a chemical effect on the gold dissolution rates.

All of the leach kinetic curves for the experiments conducted by Golden Days samples are presented in Appendix A of this report.

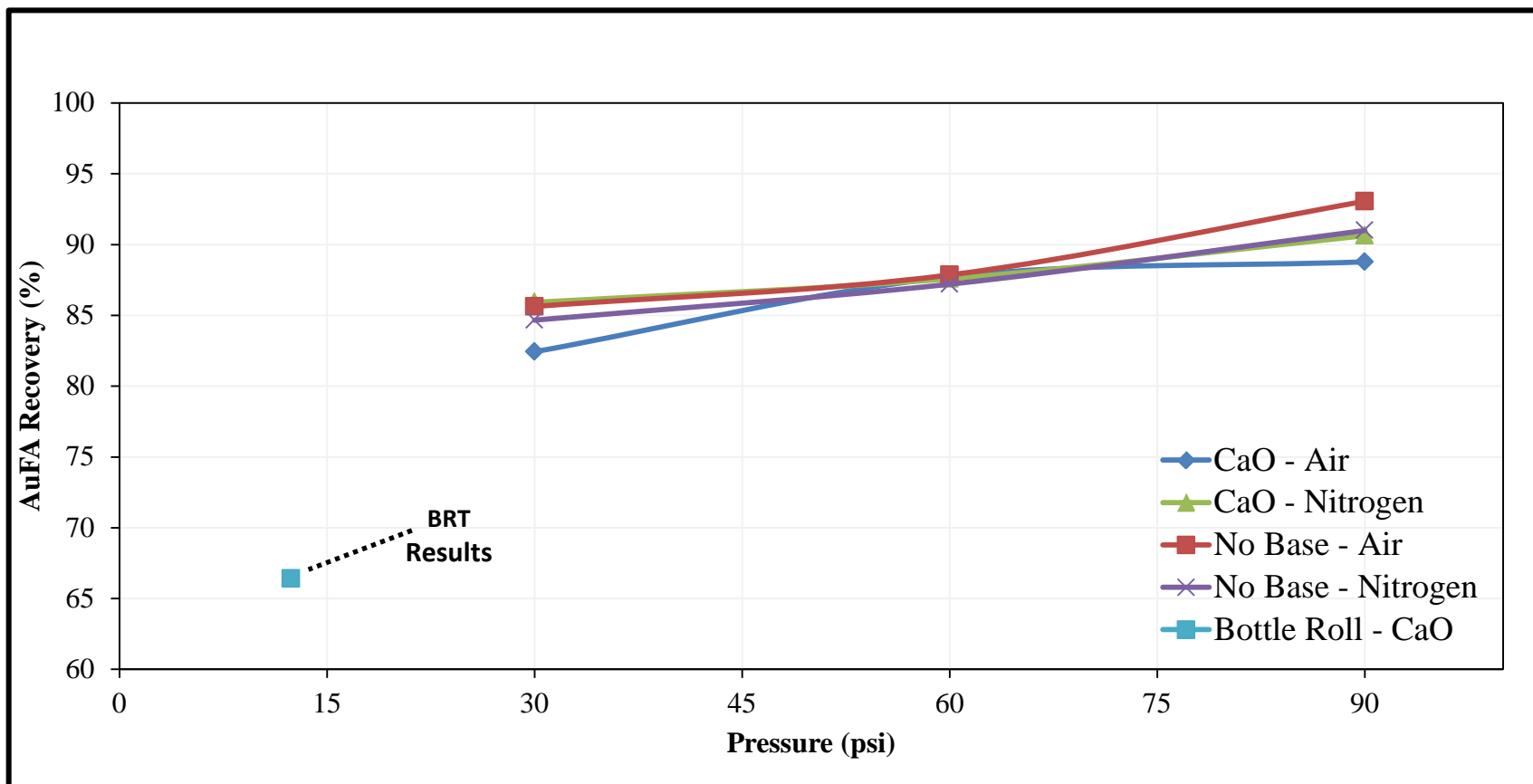


Figure 45. Golden Days 8 hr Bottle Roll and Pressure Leaching Recoveries

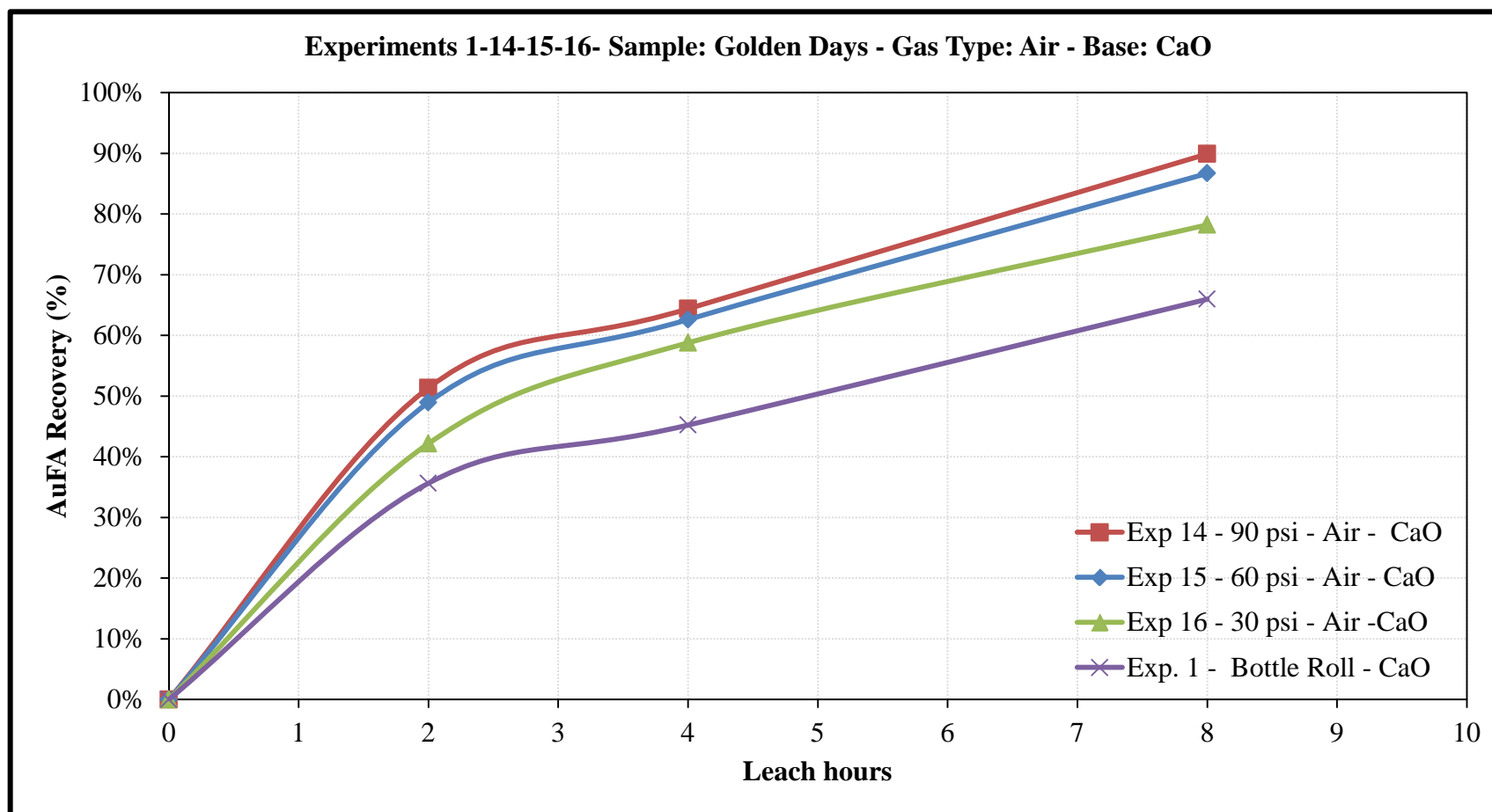


Figure 46. Leaching Kinetic Curves – Experiments 1, 14, 15, 16 - Golden Days Samples

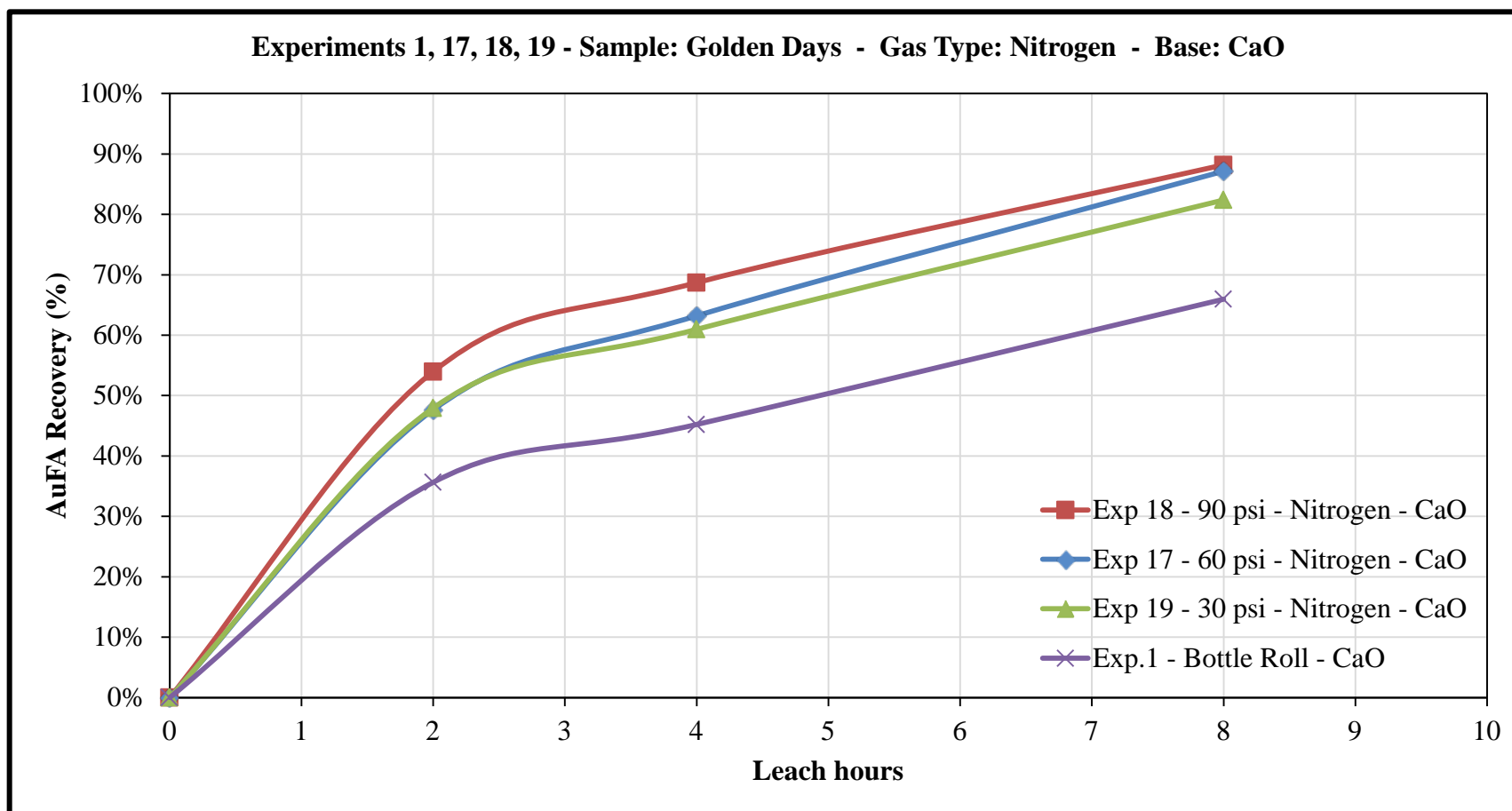


Figure 47. Leaching Kinetic Curves – Experiments 1, 17, 18, 19 – Golden Days Samples

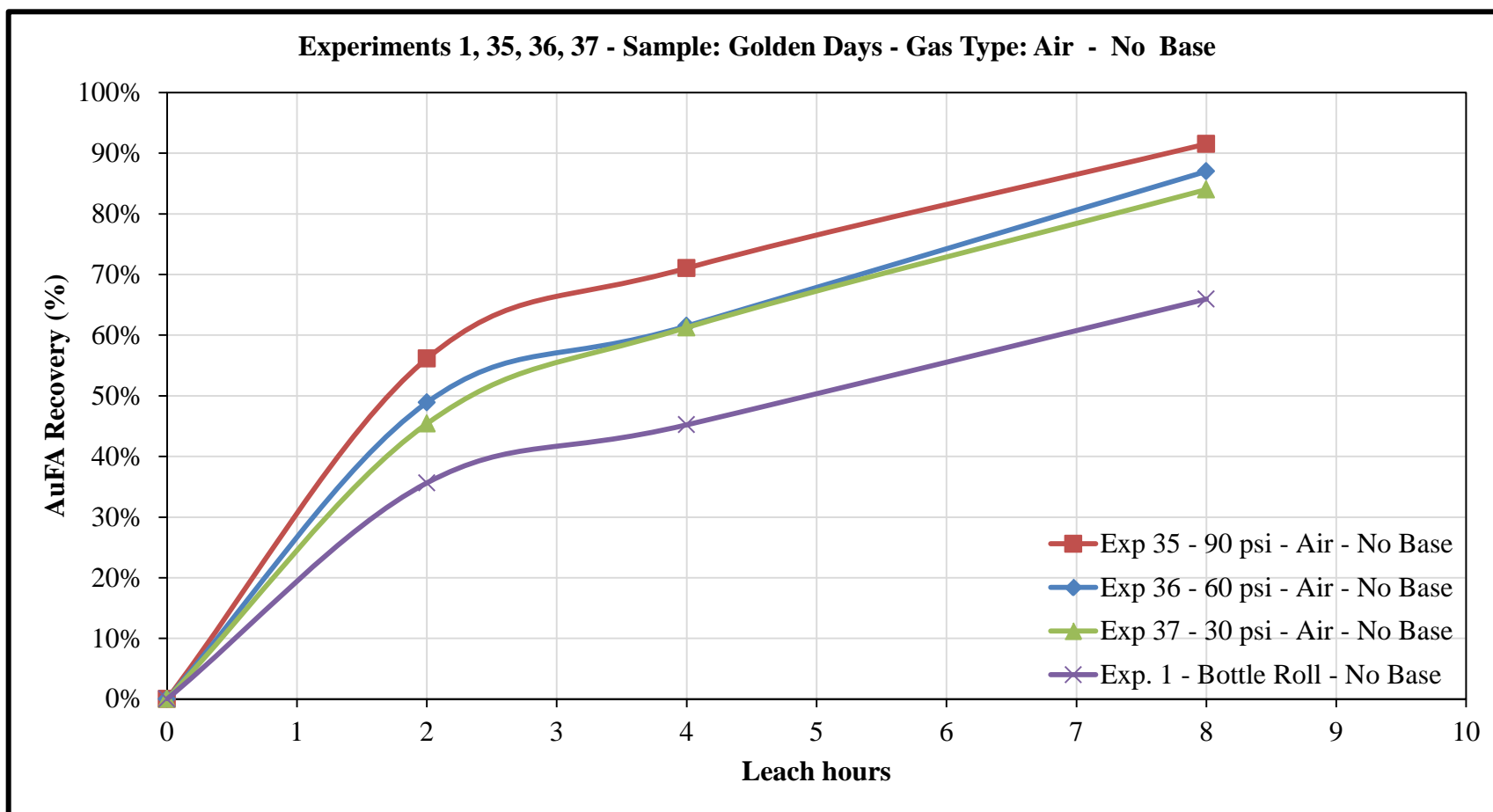


Figure 48. Leaching Kinetic Curves – Experiments 1, 35, 36, 37 – Golden Days Samples

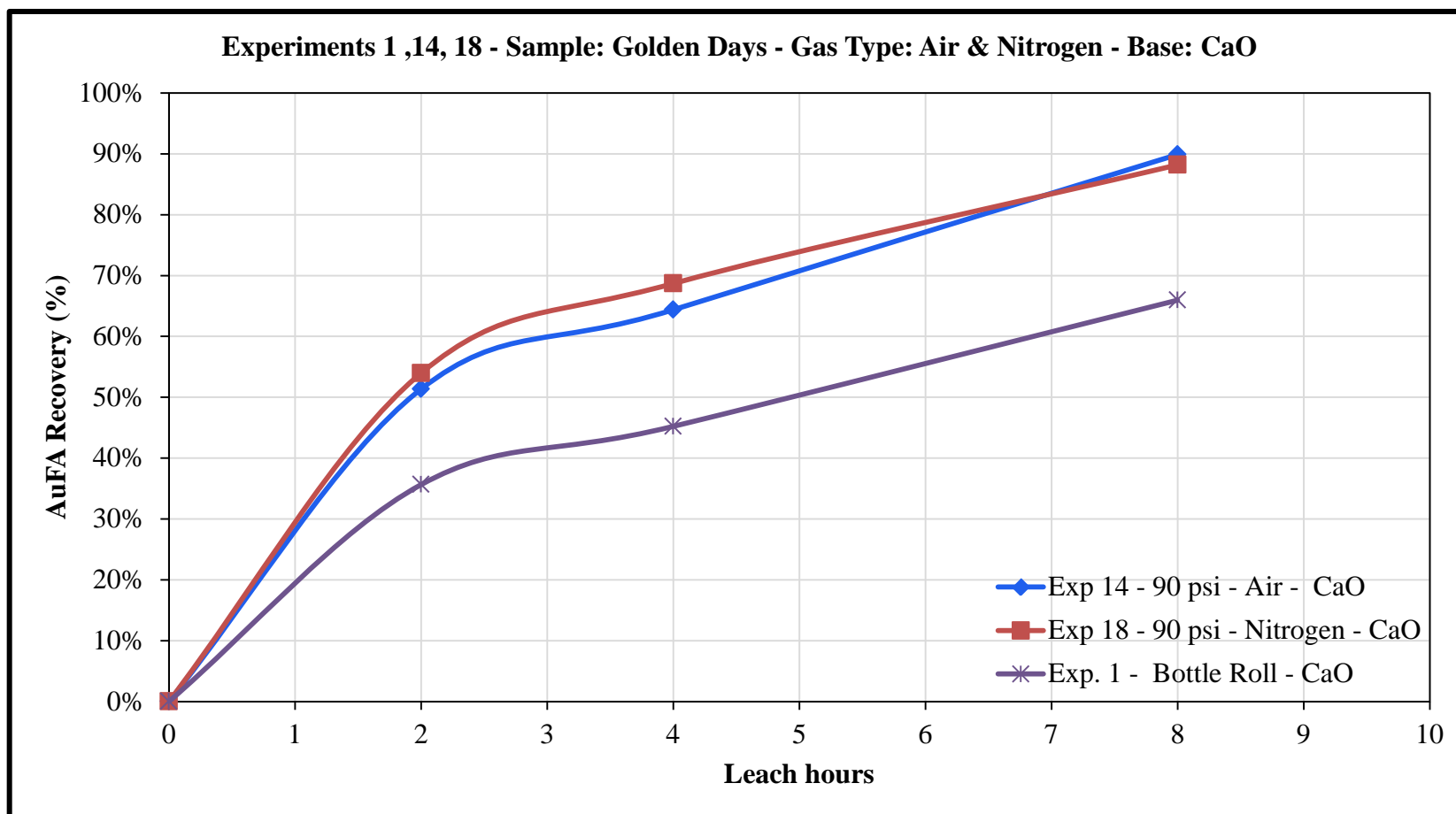


Figure 49. Leaching Kinetic Curves – Experiments 1, 14, 18 – Golden Days Samples

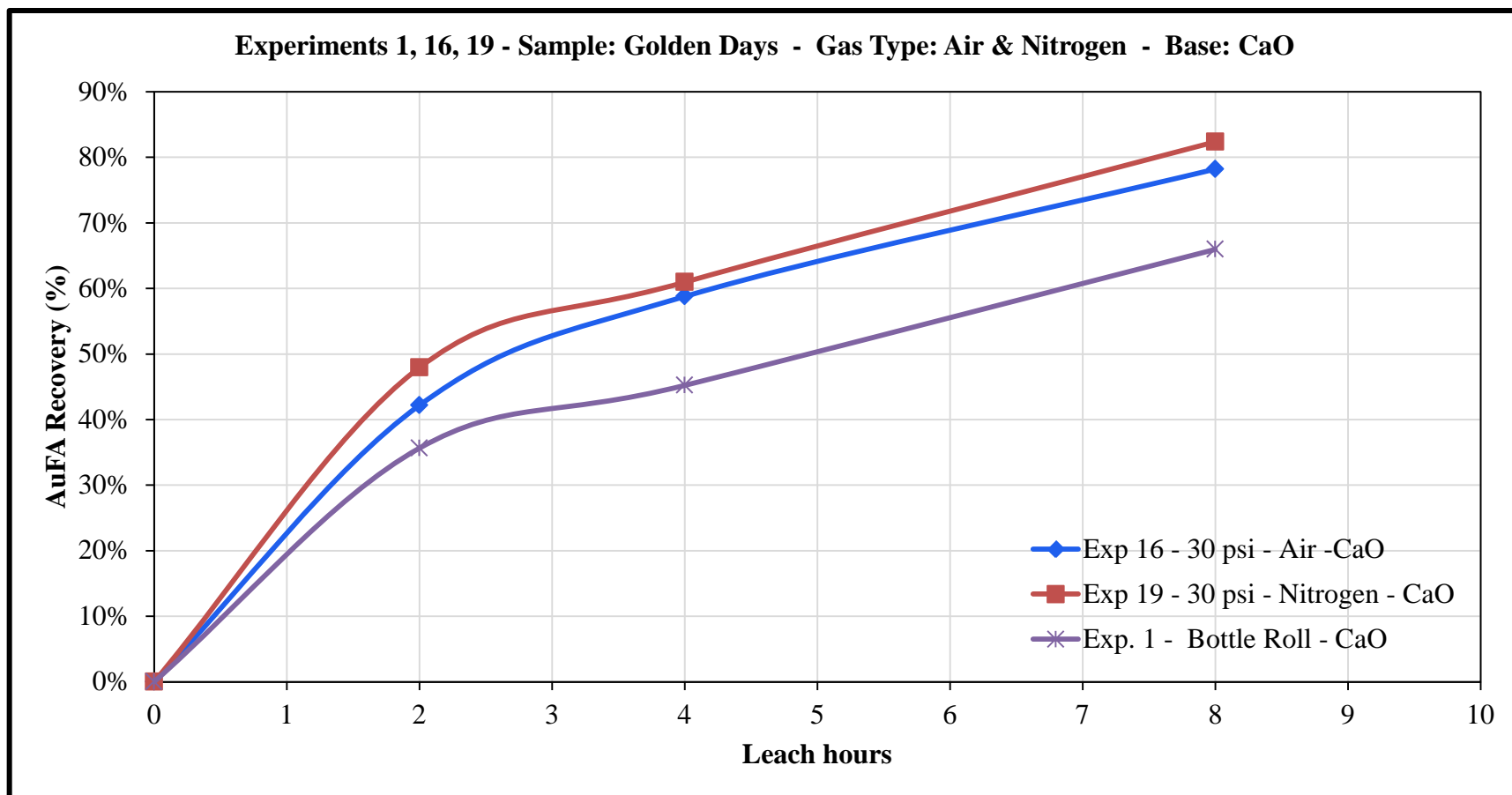


Figure 50. Leaching Kinetics Curves – Experiments 1, 16, 19 – Golden Days Samples

5.4.2 FLOTATION TAILINGS

Additional experiments with flotation tailings (CIL feed) samples were conducted in order to compare the pressure effect on recoveries for the samples with different mineralogical composition. The main difference in the results between Golden Days samples and flotation tailings were the overall sample cyanide soluble gold (AuCN) and total gold (AuFA) values. Experimental results are presented with and without base addition for the leaching of the flot tails at atmospheric and elevated pressures. The flotation tailing samples had lower natural pH values around 6.8 compared with Golden Days ore samples. Due to lower natural pH value of the flotation tailings samples, higher lime amounts were added to the solution in order have similar pH conditions with the Golden Days pressure leaching experiments. The amount of calcium oxide (CaO) added during the flotation tailings pressure leaching experiments was 0.55 grams per 400 grams of dry sample feed (2.75 pound per dry short ton of float tailings) whereas this amount was 0.15 gr CaO for 400 gr dry sample feed (0.75 pounds per dry short ton of ore) for Golden Days. The pressure leaching experiments conducted by adding lime to the leach slurry showed higher gold recoveries than experiments with no base addition due to the increase from the natural pH of the flotation tailings slurry to close to optimum cyanide leaching pH values (10.3).

The flotation tailings samples fed to autoclave had smaller particle sizes ($P_{90} < 200$ mesh) compared to the Golden Days ore samples ($P_{80} < 200$ mesh) more than 98% of the cyanide soluble gold was leached from the flotation tailings at elevated pressure at room temperature, with base.

The results of experiment set 25, 26, 43 are presented in Table 28 showed similar recoveries, around 99%, for the cyanide soluble (AuCN) gold at the end of the 8 hr leaching period for each pressure level (30-60-90 psi). Experimental results were nearly at their maximum gold recoveries when compared to the AuCN recoveries and kept increasing with higher pressure levels when compared to the total gold (AuFA) as well. This also proved that pressure cyanidation had limited or no effect on the recovery of the gold particles locked in silica. Similar results were also obtained for the experiment sets in Table 28 where no lime added to the solution and air was used for pressurizing the reactor.

Pressure cyanidation experiments conducted at pH values less than 10 caused a decrease in gold recoveries and increase in cyanide consumption compared to experiments conducted with average pH values between 10.6 – 11.0. This could be explained by the effect of the pH values on formation of cyanide compounds and the activities and reactions of other metals consuming cyanide.

On the other hand, most pressure cyanidation experiments at any pH value resulted in higher gold recoveries compared to autoclave experiments conducted at atmospheric pressures. As presented on Table 28, gold recoveries increased up to 105% for the same time of leaching at elevated pressure levels (90 psi) compared to the autoclave experiments conducted at atmospheric conditions. This proves that the pressure cyanidation process was able to recover more cyanide soluble gold than the amount projected by the cyanide shake tests.

| Exp. # | Leach Time (hr) | Press. (psi) | Gas type | Base | NaCN Cons. (lb/st of ore) | pH | AuCN Rec. (%) | AuFA Rec. (%) | % Change in AuCN Rec. | % Change in AuFA Rec. |
|--------|-----------------|--------------|----------------|------|---------------------------|------|---------------|---------------|-----------------------|-----------------------|
| 28 | 8 | 12.4 | - | CaO | 1.76 | 10.9 | 87.10 | 16.80 | - | - |
| 29 | 8 | 90 | Air | CaO | 1.68 | 10.6 | 99.40 | 34.50 | 14.12 | 105.36 |
| 30 | 8 | 60 | Air | CaO | 1.36 | 10.7 | 99.60 | 29.00 | 14.35 | 72.62 |
| 44 | 8 | 30 | Air | CaO | 1.25 | 10.6 | 98.70 | 23.00 | 13.32 | 36.90 |
| 25 | 8 | 90 | N ₂ | CaO | 1.30 | 10.7 | 99.40 | 29.70 | 14.12 | 76.79 |
| 26 | 8 | 60 | N ₂ | CaO | 1.58 | 10.6 | 99.50 | 25.20 | 14.24 | 50.00 |
| 43 | 8 | 30 | N ₂ | CaO | 1.57 | 11.0 | 99.20 | 18.80 | 13.89 | 11.90 |
| 32 | 8 | 90 | Air | - | 2.21 | 8.1 | 99.00 | 26.80 | 13.66 | 59.52 |
| 33 | 8 | 60 | Air | - | 2.23 | 8.1 | 98.80 | 25.90 | 13.43 | 54.17 |
| 34 | 8 | 30 | Air | - | 2.33 | 8.0 | 98.50 | 21.30 | 13.09 | 26.79 |
| 22 | 8 | 90 | N ₂ | - | 2.27 | 7.7 | 98.40 | 22.00 | 12.97 | 30.95 |
| 23 | 8 | 60 | N ₂ | - | 2.17 | 8.4 | 97.40 | 17.00 | 11.83 | 1.19 |
| 24 | 8 | 30 | N ₂ | - | 2.18 | 7.9 | 98.30 | 16.00 | 12.86 | -4.76 |

Table 28. Flotation Tailings – Gold Recovery Values for Different Pressure Levels

Pressure cyanidation experiments conducted with air pressure resulted in higher total gold (AuFA) recoveries compared to the experiments where nitrogen gas was used for pressurizing the autoclave.

Experiment 24 (No base, 30 psi N₂ pressure) and 23 (No base, 60 psi, N₂ pressure) gave similar total gold (AuFA) recoveries when compared to the experiment that was run under atmospheric conditions. It is hypothesized that combination of low pH and low dissolved oxygen amount in the solution caused the low reaction rates for gold dissolution.

Figure 51 presents the recoveries on the flotation tailings samples for each pressure level. The leaching kinetic curves of the reactions for different pH and pressure levels are shown on below Figures 52, 53, 54. Kinetic curves for pressure cyanidation of flotation tails also show the same relationship between recoveries and pressure levels as the rest of the experimental work, except the experiments when no base was added.

All of the leach kinetic curves of the experiments conducted by flotation tailings are presented in Appendix A of this report.

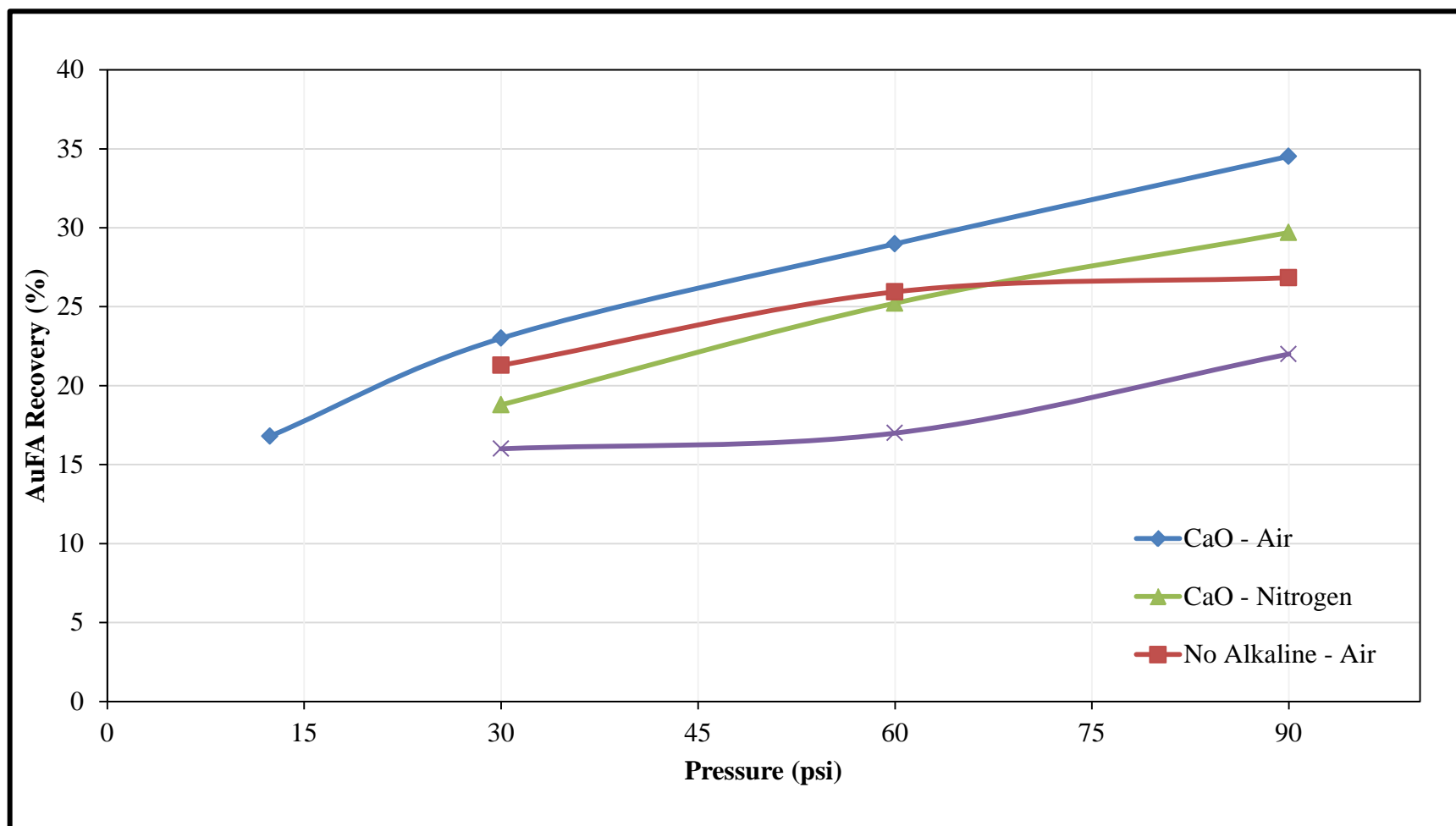


Figure 51. Pressure Effect on Gold Recoveries – Flotation Tailings

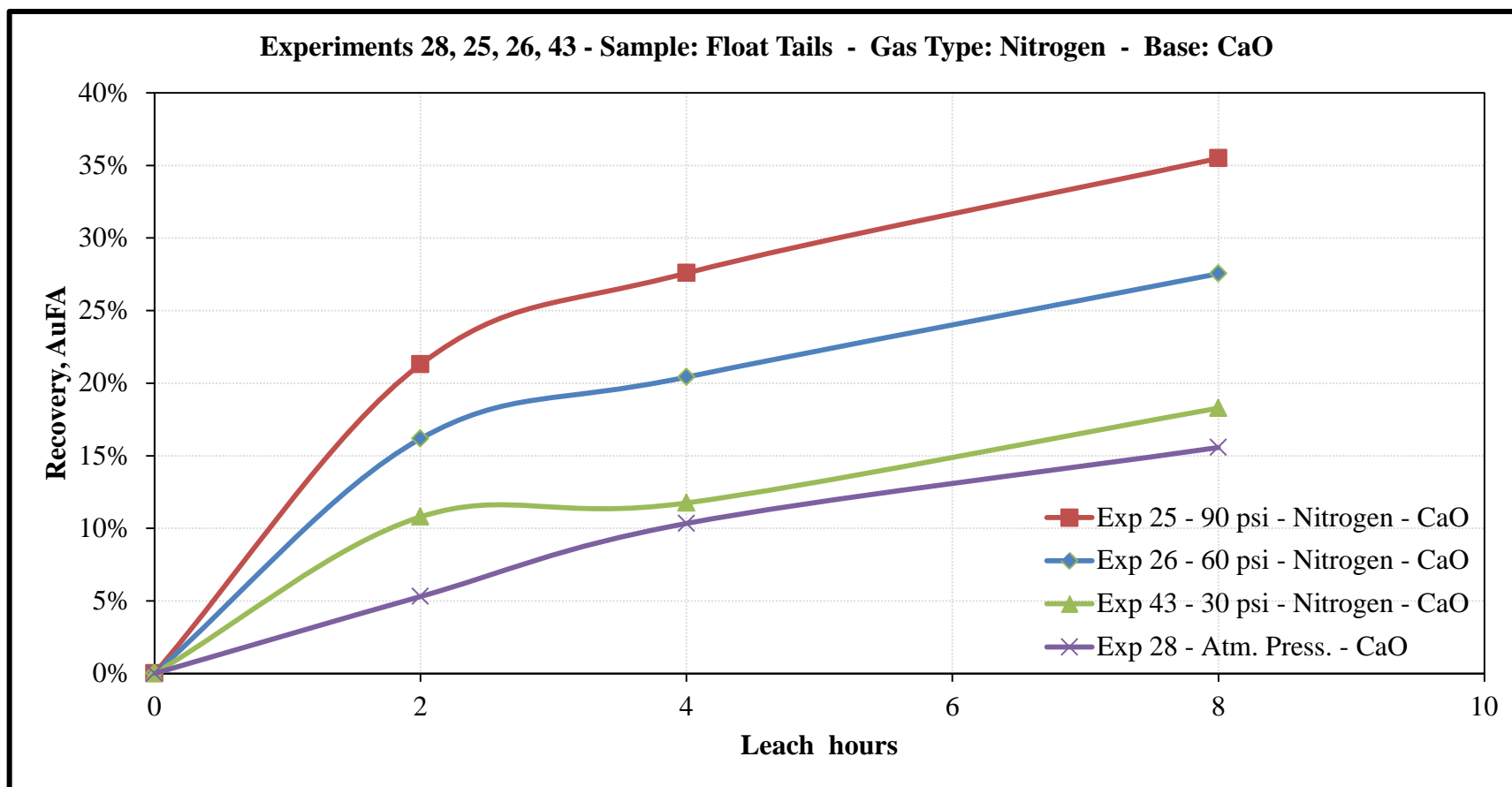


Figure 52. Leaching Kinetic Curves – Experiments 28, 25, 26, 43 – Flotation Tailings Samples

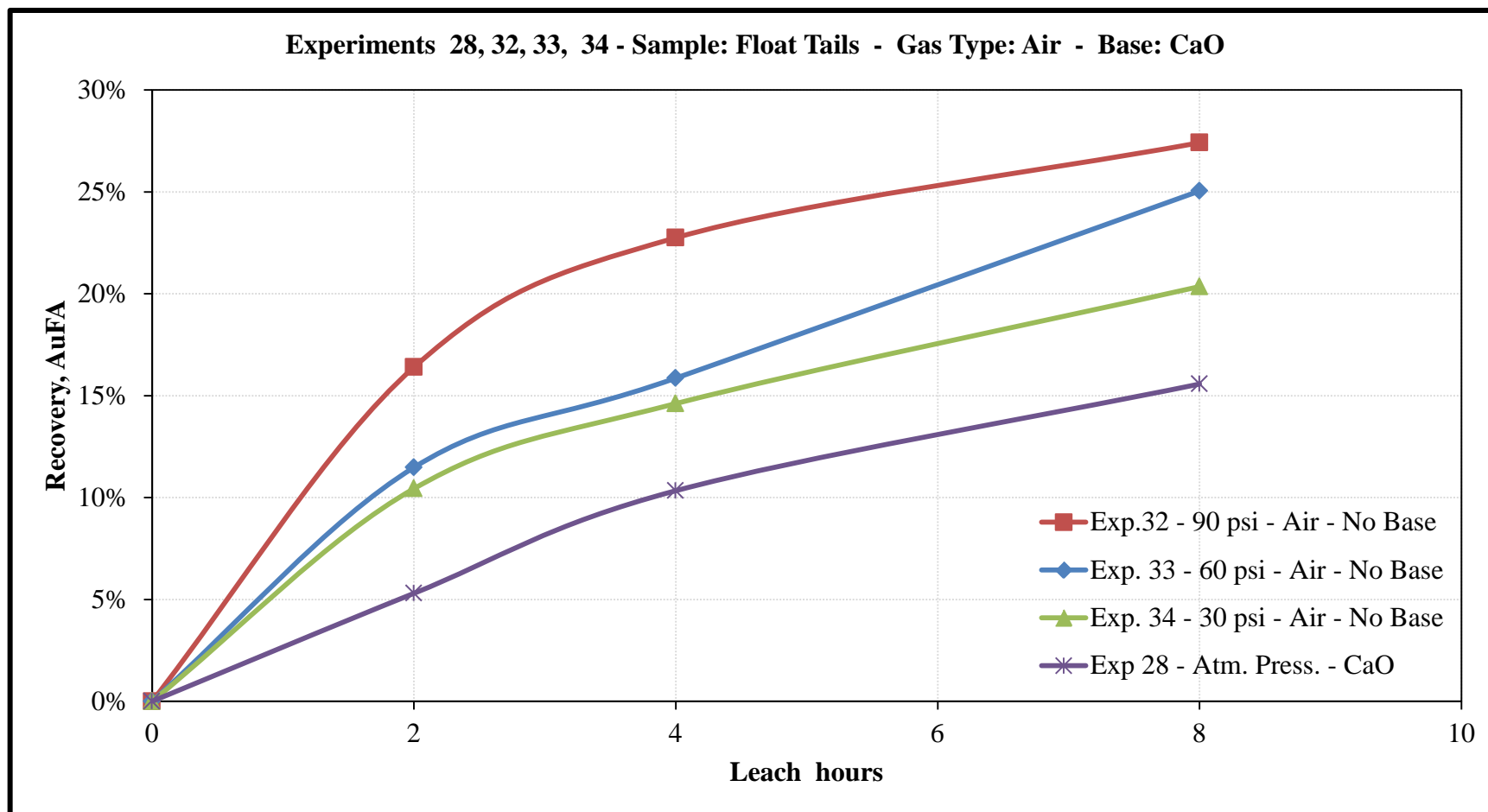


Figure 53. Leaching Kinetic Curves – Experiments 28, 32, 33, 34 – Flotation Tailings Samples

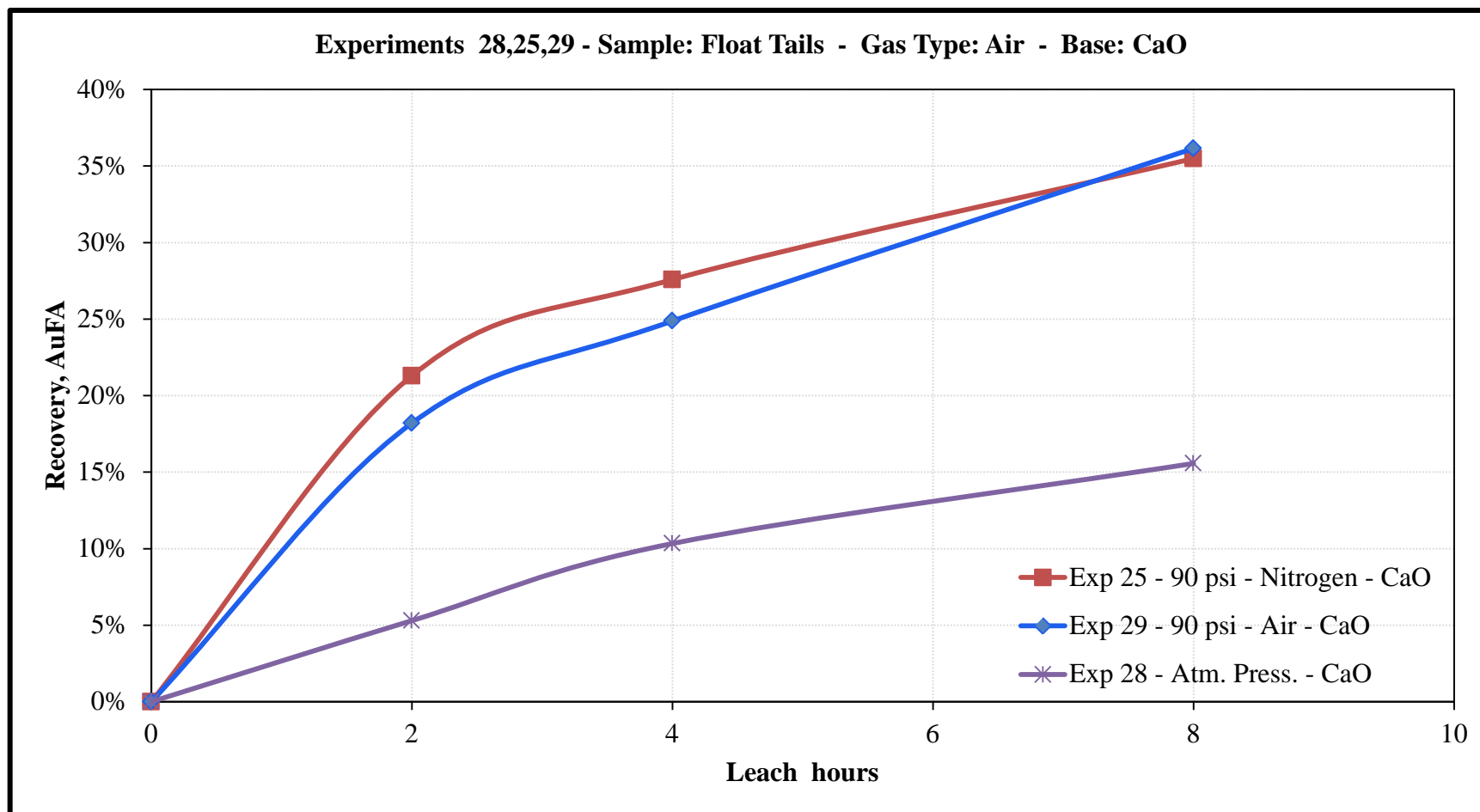


Figure 54. Leaching Kinetic Curves – Experiments 28, 25, 29 – Flotation Tailings Samples

As discussed further in sections 2.6.2 and 2.6.3 leaching of ore particles is a diffusion controlled reaction. It was hypothesized that higher pressure levels cause an increase in the lixiviant diffusion in and out of the micropores of the solids. As a result, reaction rates and gold recoveries were higher for the pressure cyanide leaching experiments than the atmospheric leaching conditions at the same time of leaching at room temperature.

Another effect of the increased pressure was the increase in oxygen partial pressures which causes higher dissolved oxygen concentrations in leach solution. Increase in the dissolved oxygen concentration can improve the reaction rates as long as the free cyanide ions are not the limiting factor and the solid particles are suspending in solution with the sufficient amount of leachable metal.

Explaining the recovery increase by the increase in dissolved oxygen amount and its effect on the mineralogy is a valid argument if applied pressurizing gas which contains oxygen. For this reason, an inert gas, pure nitrogen was added as a pressurizing agent for a set of autoclave tests, in order to investigate the pure effect of pressure on leachant diffusivity into the solid particle micropores with a minimal amount of air present. The experiments conducted with the nitrogen gas pressure also resulted in higher gold recoveries compared to atmospheric leaching experiments for the same leaching time and proved the pressure effect on the diffusivity during cyanide leaching.

6. CONCLUSION

The pressure cyanidation experiments were conducted with the primary aim of investigating the pressure effect on the gold dissolution rate for the cyanide soluble gold. The secondary aim of the test work conducted was to see the effect of pressure cyanidation on recovery of silica locked gold particles. The findings of this study are summarized as follows:

- (1) The rate of gold dissolution increases with the increased pressure levels inside the reactor at ambient temperatures.
- (2) The pH level has an effect on gold dissolution rate and the optimum pH level for the gold dissolution was observed between pH values 10.0 and 10.5.
- (3) The oxygen content of the pressurizing gas has effect on gold dissolution rates since it changes the amount of the dissolved oxygen in the slurry.
- (4) Effect of pressure on recoveries cyanide leaching experiments was observed on cyanide soluble gold amounts for both of the samples. The pressure cyanidation has no effect on recovery of the silica locked gold particles.
- (5) Pressurizing a reactor during cyanidation has an effect on cyanide consumption that is not consistent. But cyanide consumption was not greater than atmospheric leaching when using a base.
- (6) Higher slurry mixing rates during cyanidation improve the rate of gold leaching.
- (7) Bottle roll leach experiments where lime (CaO) was used as base resulted in lower gold dissolution kinetics due to the retarding effect of lime.

7. FUTURE WORK

This study investigated the effect of pressure on recoveries of gold cyanidation at ambient temperatures. This initial research has only been undertaken at a laboratory scale in an autoclave. Additional test work in a closed circuit pilot plant is recommended to determine the impact of a closed circuit system on gold recovery values, retention times and industrial applicability of the process.

Additionally, further research on pressure leaching with alternative lixiviants such as thiosulfate, thiocyanate, thiourea in both base and acidic solutions should be investigated in order to determine economical competitiveness of these reagents to cyanide, using this high pressure process.

The effect of pressure leaching at room temperature should also be investigated on different metallic ores beneficiation processes such as sulfuric acid (H_2SO_4) leaching of copper ores. These experiments can be further applied to non-conventional methods such as bio-oxidation in order to investigate various potential process improvements.

Pressure cyanidation leaching experimental work can be further expanded in order to optimize parameters such as; the pulp density, pH, pressure level, leach time, cyanide consumption and dissolved oxygen. At the end of this test work an industry applicable flowsheet can be generated to use this technology.

At very low pH values, HCN gas will be formed during cyanidation process. Since vapor pressure of HCN gas is 100 kpa (14.5 psi) at room temperature^[103], there is the possibility of the HCN bubble formation to be reduced in leach solution and at

elevated pressures where HCN will not volatilize and thus will stay in solution inside the reactor. Additional pure gold pressure leaching experiments with acidic solution conditions should be conducted in order to investigate gold dissolution by dissolved HCN, its effects on reagent consumption and on the activity coefficient of the reagent ions.

8. REFERENCES

- [1] J. Park, *The cyanide process of gold extraction*, Auckland: Champtaloup and Cooper, 1897.
- [2] N. Arbiter and K. N. Han., *Gold: Advances in Precious Metals Recovery*, Philadelphia: Gordon and Breach, Science Publishers, 1990.
- [3] A. L. Mular, D. N. B. Halbe and J. Derek, *Mineral Processing Plant Design, Practice, and Control Proceedings*, vol. 2, Littleton: Society for Mining, Metallurgy, and Exploration (SME), 2013, pp. 1663-1666.
- [4] D. Sinadinovic, Z. Kamerovic and B. Vakanjac, "Proceedings of 8th Balkan Mineral Processing Conference," in *Refractory gold ores, characteristics and methods of their procession*, Belgrade, 1999.
- [5] Z. M. Abouzeid, *Mineral Processing Laboratory Manual*, Clausthal: Trans Tech Publications, 1990, pp. 11-23.
- [6] J. Wagner, F. Fischer and W. Crookes, *Manual of chemical technology*, New York: D. Appleton & Co., 1900, p. 478.
- [7] M. Ware, "Prussian Blue: Artists' Pigment and Chemists' Sponge," *Journal of Chemical Education*, p. 612, 2008.
- [8] "Prussian Blue," 28 September 2014. [Online]. Available:

http://en.wikipedia.org/w/index.php?title=Prussian_Blue&oldid=631209249.

- [9] C. Lehman, "Pierre-Joseph Macquer an Eighteenth-Century Artisanal-Scientific Expert," *Annals Of Science*, vol. 69, no. 3, pp. 307-333, 2012.
- [10] G. Williams, "The cyanides of gold," *Gold Bulletin*, vol. 11, no. 2, pp. 56-59, 1978.
- [11] "Hydrogen Cyanide," 12 September 2014. [Online]. Available: http://en.wikipedia.org/w/index.php?title=Hydrogen_cyanide&oldid=630340984.
- [12] "The Blue History of Cyanide," 1 September 2014. [Online]. Available: <http://scienceblogs.com/speakeasyscience/2010/02/26/the-blue-history-of-cyanide>.
- [13] T. McNulty, "A Metallurgical History of Gold," in *American Mining Congress*, San Francisco, 1989.
- [14] L. Hunt, "The early history of gold plating," *Gold Bulletin*, vol. 6, no. 1, pp. 16-27, 1973.
- [15] "Hydrogen Cyanide," 13 September 2014. [Online]. Available: http://en.wikipedia.org/wiki/Hydrogen_cyanide.
- [16] F. Habashi, "Gold Through Ages," *CIM Bulletin*, vol. 88, no. 990, pp. 60-69, 1995.

- [17] F. Habashi, "One Hundred Years of Cyanidation," *CIM Bulletin*, vol. 80, no. 905, pp. 108-114, 1987.
- [18] R. Bansal and M. Goyal, *Activated Carbon Adsorption*, Boca Raton: Taylor & Francis, 2005.
- [19] J. B. Zadra, L. Engel and H. J. Heinen, "Process for Recovering Gold and Silver from Activated Carbon by Leaching and Electrolysis," United States Bureau of Mines, Butte, 1952.
- [20] D. Hausen, *Gold '90*, Littleton: Society for Mining Metallurgy and Exploration, 1990.
- [21] F. Habashi, *A textbook of Hydrometallurgy*, Quebec City: Metallurgie Extractive Quebec, 1993.
- [22] F. Habashi, ""Pressure Hydrometallurgy" Key to better and non-polluting processes," *Eng. & Min. J.*, vol. 172, no. 2, pp. 88-94, 1971.
- [23] C. Gupta, *Extractive Metallurgy of Molybdenum*, Boca Raton: CRC Press, 1992.
- [24] N. Board, *Products from Waste (Industrial Agro Waste)*, Delhi: National Institute of Industrial Research, 2000.
- [25] G. P. Demopoulos and V. G. Papangelakis, "Recent Advances in Refractory Gold Processing," *CIM Bulletin*, vol. 82, no. 931, pp. 85-91, 1989.

- [26] "Qutotec Global Products," 14 September 2014. [Online]. Available: http://www.outotec.com/Global/Products%20and%20services/Gold%20processing/autoclave_01_hires.png.
- [27] M. S. Prasad, R. Mensah-Biney and R. S. Pizarro, "Modern Trends in Gold Processing," *Minerals Engineering*, p. 1262, 1991.
- [28] T. Seal and D. F. Rucker, "Enhancing Gold Recovery using Hydro-Jex at Cripple Creek and Victor Gold Mine Co.," *Metal Recovery Solutions*, Spring Creek, 2010.
- [29] H. Aman, "Molecular Neuroscience and General Chemistry Notes," Chem 1180, 3 October 2010. [Online]. Available: <http://chem1180.blogspot.com/2010/10/163-164-base-ionization-equilibria.html>. [Accessed 1 10 2014].
- [30] C. A. Fleming, "Hydrometallurgy of Precious Metals Recovery," *Hydrometallurgy*, pp. 127-137, 1992.
- [31] P. Verhoeven, G. T. Hefter and P. M. May, "Dissociation Constant of Hydrogen Cyanide in Saline Solutions," *Minerals and Metallurgical Processing*, pp. 185-188, 1990.
- [32] S. Zumdahl, *Chemical Principles*, Boston: Houghton Mifflin, 2009, p. 265.
- [33] S. Zumdahl and S. Zumdahl, *Chemistry*, Belmont: Brooks Cole, 2008, p. 657.
- [34] R. W. Barlett, *Solution Mining: Leaching and Fluid Recovery of Materials*,

Netherlands: Psychology Press, 1998, p. 60.

- [35] J. Marsden and L. House, in *The Chemistry of Gold Extraction*, Littleton, Society of Mining, Metallurgy and Exploration Inc., 2006, p. 19.
- [36] M. Adams, "The chemical behaviour of cyanide in the extraction of gold. 1. Kinetics of cyanide loss in the presence and absence of activated carbon," *J.S. Afr. Inst. Min. Metall.*, vol. 90, no. 2, pp. 37-44, Feb. 1990.
- [37] K. Osseo-Asare, T. Xue and V. S. T. Ciminelli, "Solution Chemistry of Cyanide Leaching Systems," *Precious Metals: Mining Extraction and Processing*, pp. 173-197, 1984.
- [38] H. Kellogg and V. Kudryk, "Mechanism and rate-controlling factors in the dissolution of gold in cyanide solution," *Journal of metals*, vol. III, no. 2, pp. 540-548, 1954.
- [39] G. Senanayake, "Kinetics and reaction mechanism of gold cyanidation: Surface reaction model via Au(I)-OH-CN," *Hydrometallurgy*, vol. 80, p. 2, 2005.
- [40] L. Elsner, "Über das Verhalten verschiedener Metalle in einer wässrigen Lösung von Zyankalium," *J. Prakt. Chem.* 37, pp. 441 - 446, 1846.
- [41] G. Senanayake, "Kinetics and Reaction Mechanism of Gold Cyanidation: Surface Reaction Model via Au(I)-OH-CN Complexes," *Hydrometallurgy*, vol. 80, no. 1-2, pp. 1-12, 2005.
- [42] M. E. Wadsworth, "Gold Dissolution and Activation in Cyanide Solution,"

Hydrometallurgy, vol. 57, no. 1, pp. 1-11, 2000.

- [43] V. Kudryk and H. H. Kellog, "Mechanism and Rate Cotrolling Factors in the Dissoltion of Gold in Cyanide Solution," *Journal of Metals*, vol. 6, pp. 541-548, 1954.
- [44] F. Habashi, "Kinetics and Mechanicsm of Gold and Silver Dissolution in Cyanide Solution," State of Montana, Breau of Mines and Geology, Butte, 1967.
- [45] M. Kameda, "Fundemental Studies on Solution of Gold in Cyanide Solutions, Effects of Alkalines, Lead Acetate and Some Impurities contained in foul," The Research Instiute of Mineral Dressing and Metallurgy, 1949.
- [46] L. R. P. de Andrade Lima and D. Hodouin, "A Lumped Kinetic Model for Gold Ore Cyanidation," *Hydrometallurgy*, vol. 79, pp. 121-137, 2005.
- [47] J. Marsden and I. House, "Chemistry of gold extraction," Ellis Horwood, West Sussex, 1992.
- [48] P. Kondos, G. Deschenes and G. Morrison, "Process optimization studies in gold cyanidation," *Hydrometallurgy*, pp. 235-250, 1995.
- [49] F. Habashi, Principles of Extractive Metallurgy. Hydrometallurgy vol. 2., New York: Gordon and Breach, 1970.
- [50] L. Lorenzen and J. S. J. van Deventer, "Electrochemical interactions between gold and its associated minerals during cyanidation," *Hydrometallurgy* 30, pp.

177-194 , 1992.

- [51] J. Li, T. K. Zhong and M. E. Wadsworth, "Application of mixed potential theory in hydrometallurgy," *Hydrometallurgy* 30, pp. 47 - 60, 1992.
- [52] F. K. Crundwell and S. A. Godorr, "A mathematical model of the leaching of gold in cyanide solutions," *Hydrometallurgy*, vol. 44, pp. 147 -162, 1997.
- [53] J. Marsden and I. House, *The Chemistry of Gold Extraction*, Littleton: Society for Mining, Metallurgy, and Exploratin, Inc., 2006, p. 136.
- [54] V. N. Misra, "Pressure Leaching Kinetics of Multimetallic Sulphide Concentrates in H₂SO₄ + O₂ Solution," *GMPR*, vol. 9, no. 1, pp. 223-232, 1992.
- [55] "Oxygen Solubility in Fresh and Sea Water," 30 September 2014. [Online]. Available: http://www.engineeringtoolbox.com/oxygen-solubility-water-d_841.html.
- [56] J. Daintith, *Dictionary of Chemistry*, Oxford University Press, 2008, p. 82.
- [57] J. Daintith, *Dictionary of Chemistry*, Oxford University Press, 2008, p. 161.
- [58] R. Myers, *The Basics of Chemistry*, Westport: Greenwood Publishing Corp, 2003.
- [59] R. Battino and H. L. Clever, "The solubility of Gases in Liquids," *Chemical Reviews*, vol. 66, no. 4, pp. 406-453, 1966.

- [60] J. Philiert, "One and a Half Century of Diffusion: Fick, Einstein, before and beyond," *Basic principles of Diffusion Theory*, pp. 1-2, 2005.
- [61] S. Mitha, M. J. Aziz, D. Schiferl and D. B. Poker, "Activation Volume for Arsenic Diffusion Germanium," *Applied Physics Letters*, vol. 69, no. 7, pp. 922-924, 1996.
- [62] K. J. Laidler, *Chemical Kinetics*, New York: Harper & Row, 1987.
- [63] J. Marshden and L. House, in *Chemistry of Gold Extraction*, Littleton, Society of Mining, Metallurgy and Exploration Inc., 2006.
- [64] R. Perry, R. E. Browner, R. Dunne and N. Stoitis, "Low pH Cyanidation of Gold," *Minerals Engineering*, vol. 12, no. 12, pp. 1431-1440, 1999.
- [65] J. R. Parga, J. L. Valenzuela and D. J. A, *New Technology for Recovery of Gold and Silver by Pressure Cyanidation*, Rijeka: In Tech, 2012, pp. 71-94.
- [66] S. Ellis and G. Senanayake, "The effects of Dissolved Oxygen and Cyanide Dosage on Gold Extraction from Pyrrhotite - Rich Ore," *Hydrometallurgy*, vol. 72, pp. 39-50, 2004.
- [67] I. A. Kakovskii and Y. B. Kholmanskikh, "The Kinetics of the Silver Cyaniding Process," *Tekh. Nauk. Met. i Toplivo*, pp. 98-102, 1959.
- [68] K. J. Cathro and A. Walkley, *The Cyanidation of Gold*, Melbourne: CSIRO, 1961.

- [69] S. R. La Brooy, H. G. Linge and W. G. S, "Review of gold extraction from ores," *Minerals Engineering*, vol. 7, no. 10, pp. 1213-1241, 1994.
- [70] W. Stange, "The process design of gold leaching and carbon in pulp circuits," *The Journal of The South African Institute of Mining and Metallurgy*, no. January/February, pp. 13-26, 1999.
- [71] D. S. Barr, M. D. J and G. R. O'neil, "The Various Forms of Refractoriness in Nevada Gold Ores," *Process Minerology VII: Applications to Mineral Benefication Technology and Mineral Exploration with Special Emphasis on Disseminated Carbonaceous Gold Ores*, pp. 81- 97, 1987.
- [72] W. R. Goodall, L. J. D and P. J. Scales, "A new method for determination of preg-robbing in gold ores," *Minerals Engineering*, vol. 18, pp. 1135-1141, 2005.
- [73] M. C. Jha, "Refractoriness of certain gold ores to cyanidation: Probable causes and possible solutions," *Mineral Processing and Extractive Metallurgy Review*, pp. 330-349, 1987.
- [74] R. M. G. S. Berezowsky and D. R. Weir, "Pressure Oxidation Pretreatment of Refractory Gold," *Minerals and Metallurgy Processing*, vol. 1, no. 1, pp. 1-4, 1984.
- [75] G. P. Demopoulos and V. G. Papangelakis, "Recent Advances in Refractory Gold Processing," *CIM Bulletin*, vol. 82, no. 931, pp. 85-91, 1989.

- [76] S. S. Zumdahl and D. J. DeCoste, *Basic Chemistry*, Stamford: Cengage Learning, 2011, p. 136.
- [77] A. M. Comey, *A Dictionary of Chemical Solubilities*, New York: The Macmillian Company, 1921.
- [78] J.T.Baker, "Sodium Hydroxide Baker Analyzed Reagent Pellets, Low in Carbonate," Avantor Performance Materials, Center Valley, 2011.
- [79] S. S. Zumdahl and D. J. DeCoste, *Basic Chemistry*, Stamford: Cengage Learning, 2011, p. 217.
- [80] Graymont, "High Calcium Quicklime Material Safety Data Sheet," Salt Lake City, 2014.
- [81] E. Millipore, "Ammonium Hydroxide," Billerica, 2014.
- [82] SigmaAldrich, "Sodium Cyanide," 14 September 2014. [Online].Available: <http://www.sigmaaldrich.com/catalog/product/sial/380970lang=en®ion=US>
- [83] AlfaEasar, "Rhodanine Safety Data Sheet," Ward Hill, 2014.
- [84] FischerScience, "A review of the methods available for the detection and determination of small amounts of cyanide," *Analyst*, vol. 88, no. October, pp. 756-758, 28 August 1963.
- [85] FischerScience, "Silver Nitrate Material Safety Data Sheet," Nazareth, 2013.

- [86] AlfaAesar, "Gold, AAS Standard Solution," 29 August 2014. [Online]. Available: <https://www.alfa.com/en/catalog/88068>.
- [87] Airgas, "Air Safety Data Sheet," Radnor, 2014.
- [88] Airgas, "Nitrogen Gas Safety Data Sheet," Radnor, 2014.
- [89] "Badger Crusher," 12 September 2014. [Online]. Available: <http://www.bicoinc.com/badger.html>.
- [90] "VD Chipmunk," 12 September 2014. [Online]. Available: <http://www.bicoinc.com/vd.html>.
- [91] "Sepor Inc.," 19 September 2014. [Online]. Available: <http://www.sepor.com/wp-content/uploads/2013/10/5-In-Jar-Drive-1.pdf>.
- [92] "4550 Floor Stand Reactors Operating Manual," Moline, 2014.
- [93] "Fisher Scientific," 2 August 2014. [Online]. Available: <http://www.fishersci.com/ecom>.
- [94] K. R. Reddy, "Specific Gravity Determination," Chicago, 2014.
- [95] P. L. Breuer, C. A. Sutcliffe and R. L. Meaking, "Cyanide measurement by silver nitrate titration: Comparison of rhodanine and potentiometric endpoints," *Hydrometallurgy*, vol. 106, no. 3-4, pp. 135-140, 2011.
- [96] E. E. Bugbee, *A Textbook of Fire Assaying*, London: John Wiley & Sons Inc.,

1922.

- [97] O. C. Shepard and W. F. Dietrich, *Fire Assaying*, New York: McGraw-Hill, 1940.
- [98] "Fire Assaying: An Overview," Reno, 2007.
- [99] R. F. Lee, "Simultaneous Determination of Carbon and Sulphur in Geological Material Using Inductive Combustion," *Chemical Geology*, vol. 31, pp. 145-151, 1980.
- [100] ThermoFisherScientific, "Elemental Spectroscopy ICP-OES," 2014.
- [101] M. A. Farrukh, *Atomic Absorption Spectrometry (AAS), Atomic Absorption Spectroscopy*, Mexico City: InTEch, 2012.
- [102] G. Barsky, "Dissolution of gold and silver in cyanide solution," *AIME Trans.*, vol. 112, pp. 673-677, 1934.
- [103] A. Smith and T. Mudder, *The Chemistry and Treatment of Cyanidation Wastes*, London: Mining Journal Books Limited, 1991, p. 102.

9. APPENDIX

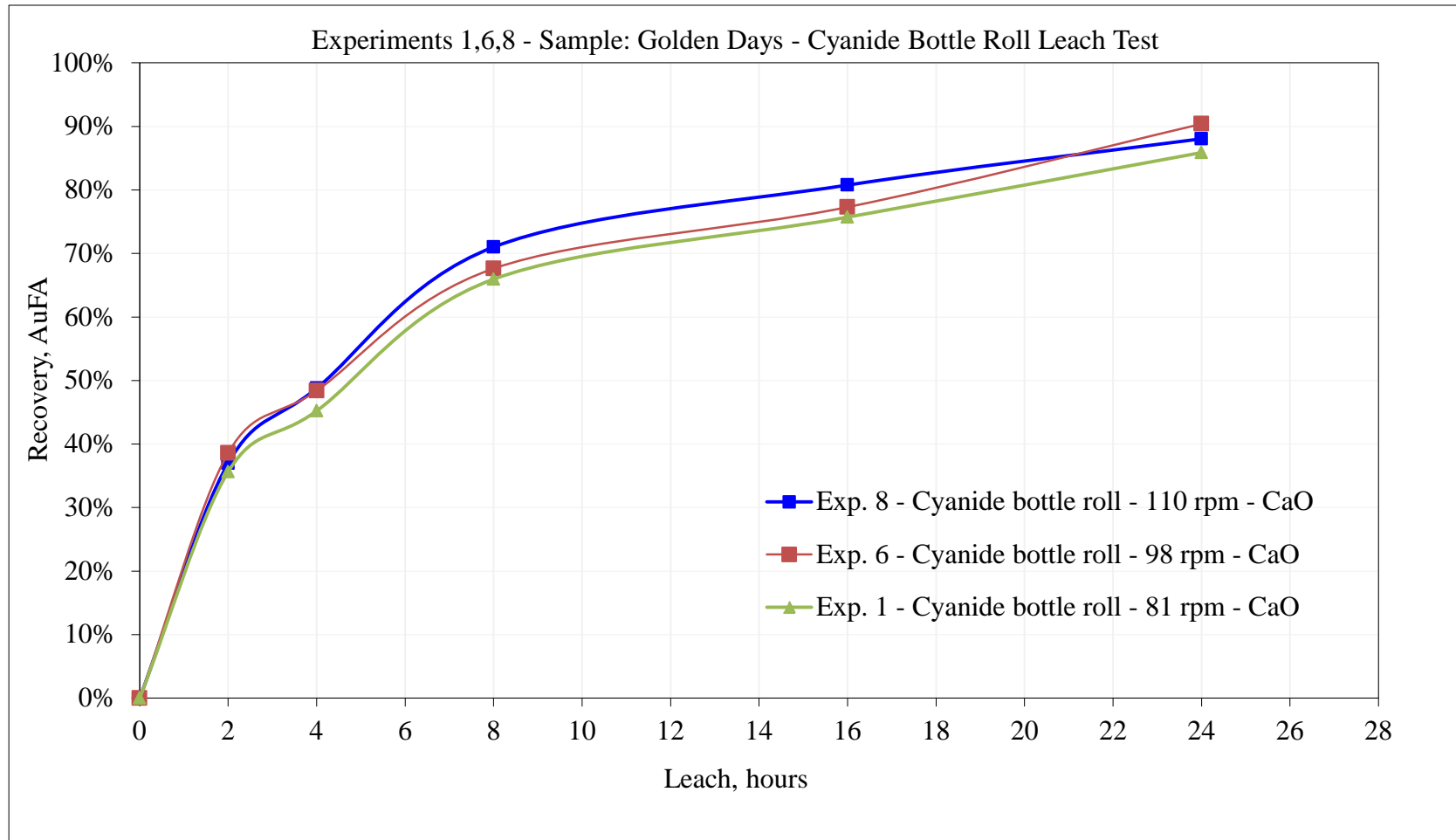


Figure 55. Golden Days Ore Bottle Roll Tests - AuCN Recoveries under Different Mixing Rates - Base: CaO

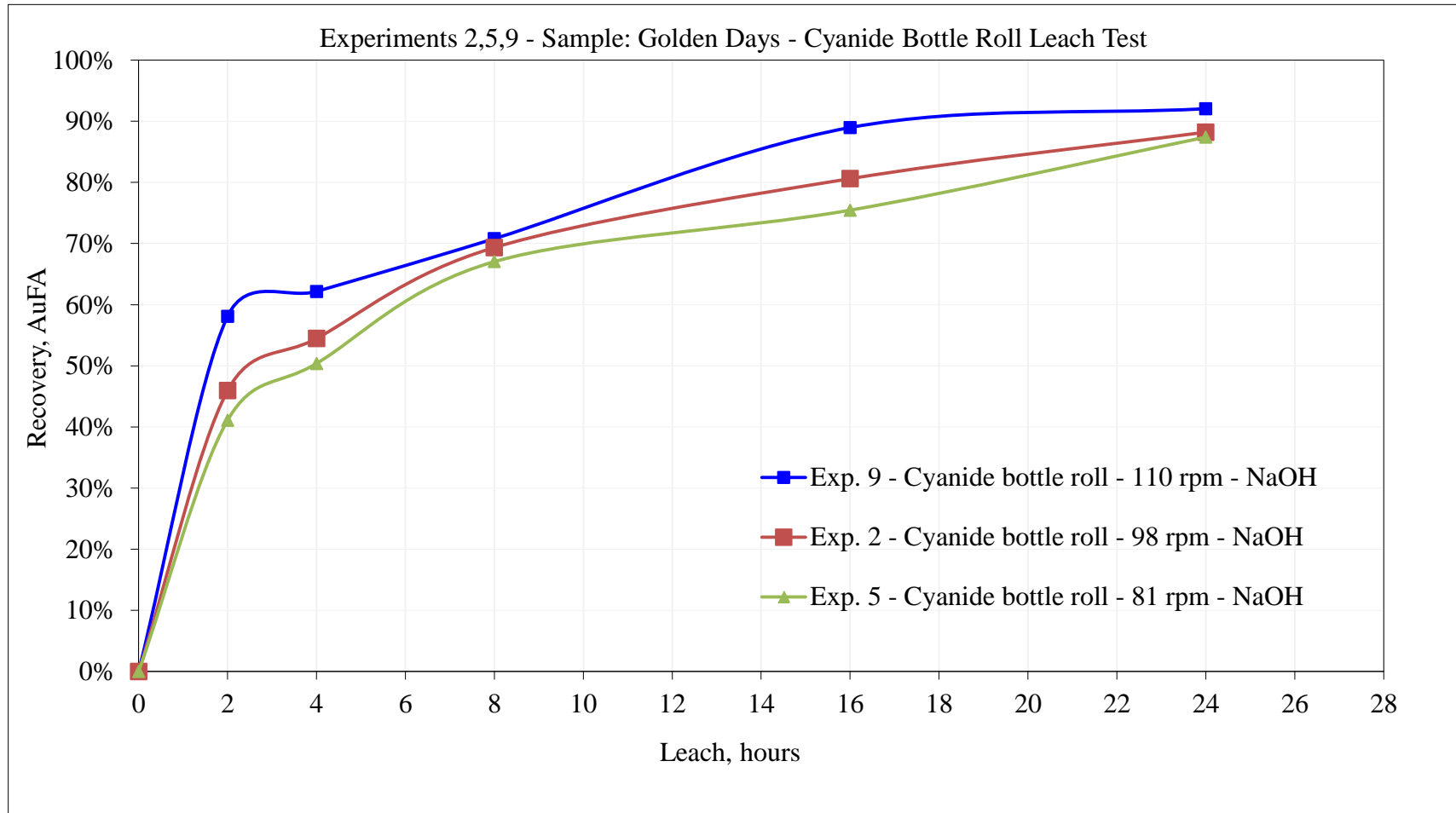


Figure 56. Golden Days Ore Bottle Roll Tests - AuCN Recoveries under Different Mixing Rates - Base: NaOH

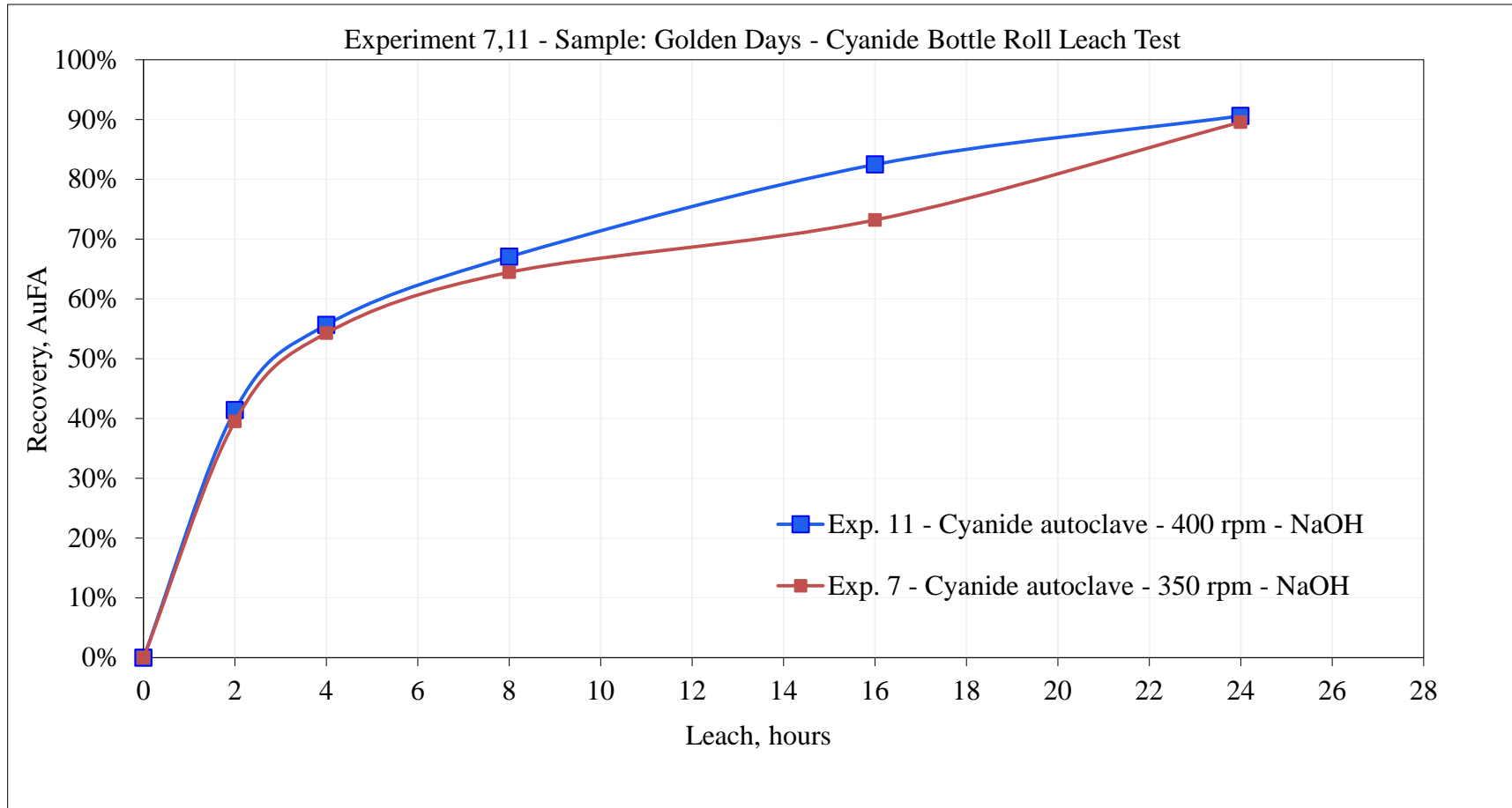


Figure 57. Golden Days Ore Autoclave Tests - AuCN Recoveries under Different Mixing Rates - Base: NaOH

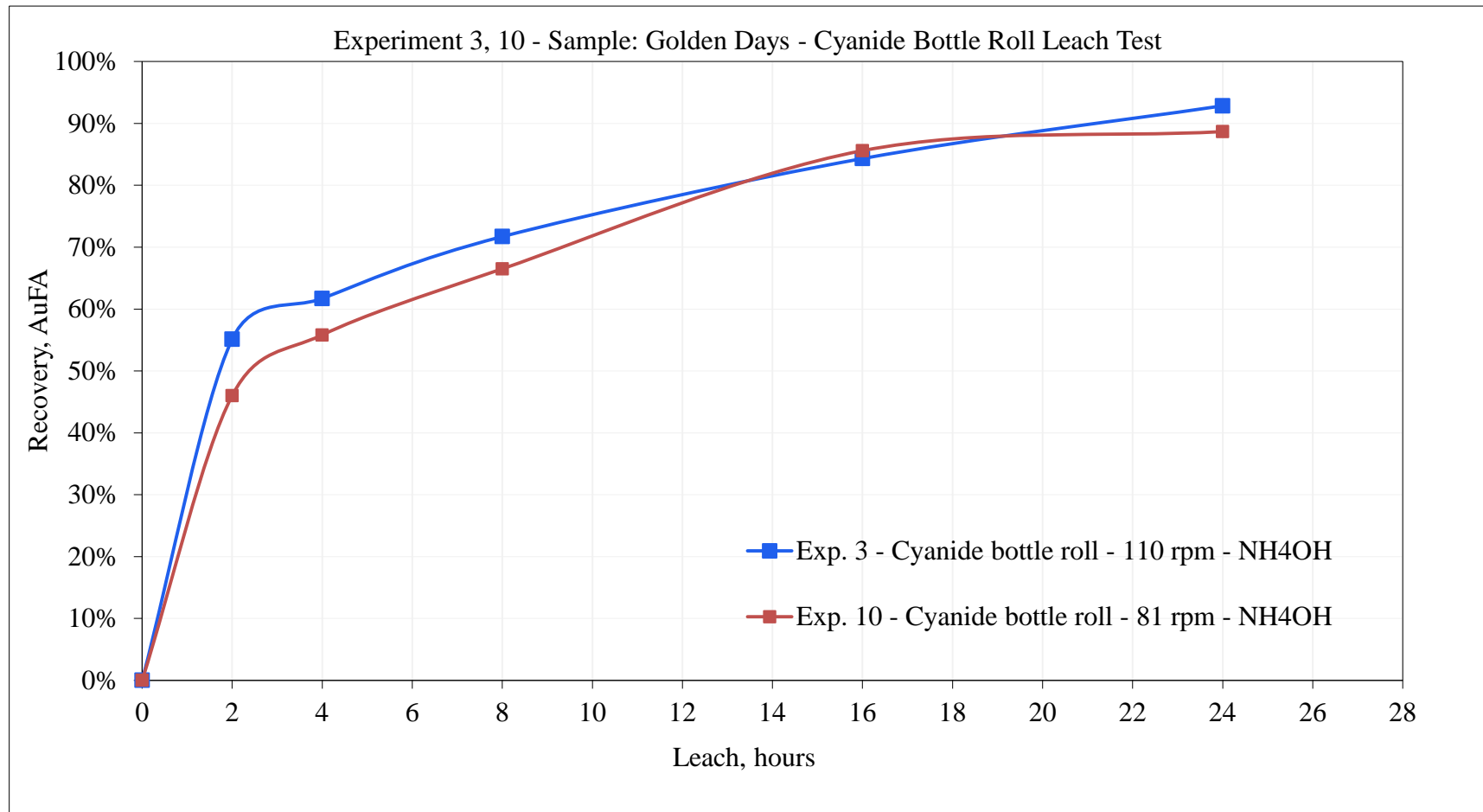


Figure 58. Golden Days Ore Bottle Roll Tests - AuCN Recoveries under Different Mixing Rates - Base: NH₄OH

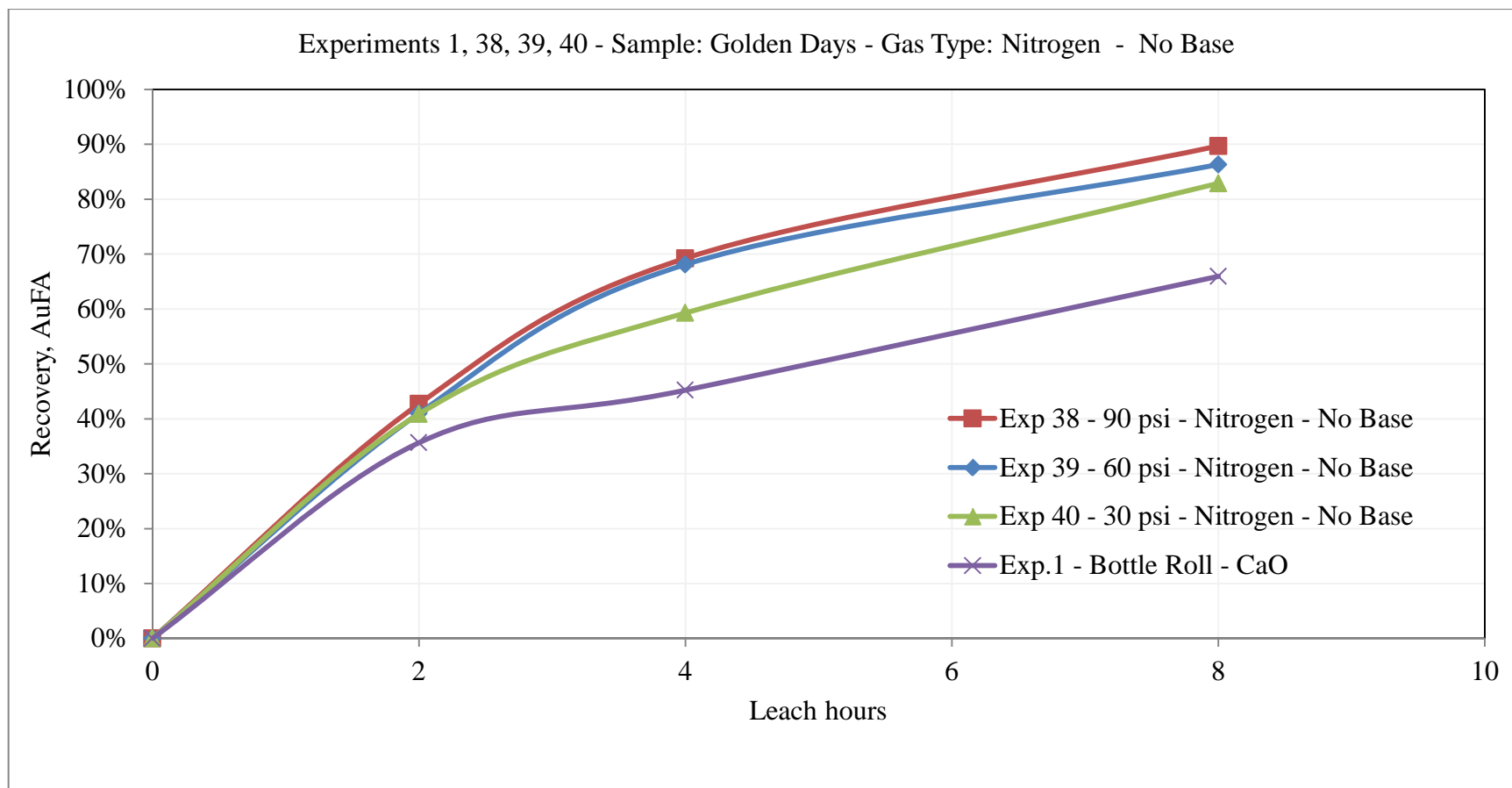


Figure 59. Experiments 1, 38, 39, 40 - Sample: Golden Days - Gas Type: Nitrogen - No Base

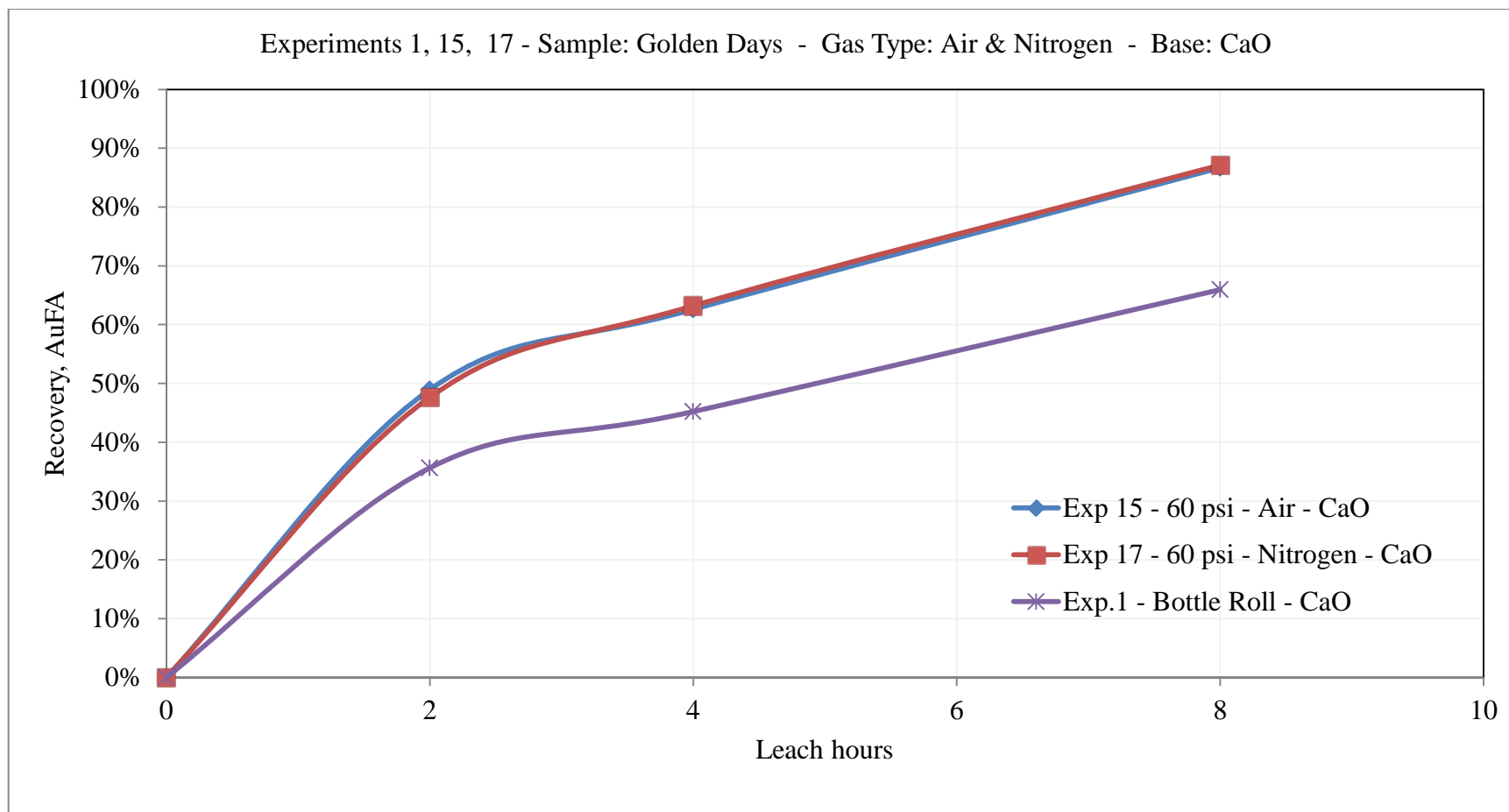


Figure 60. Experiments 1, 15, 17 - Sample: Golden Days - Gas Type: Air & Nitrogen - Base: CaO

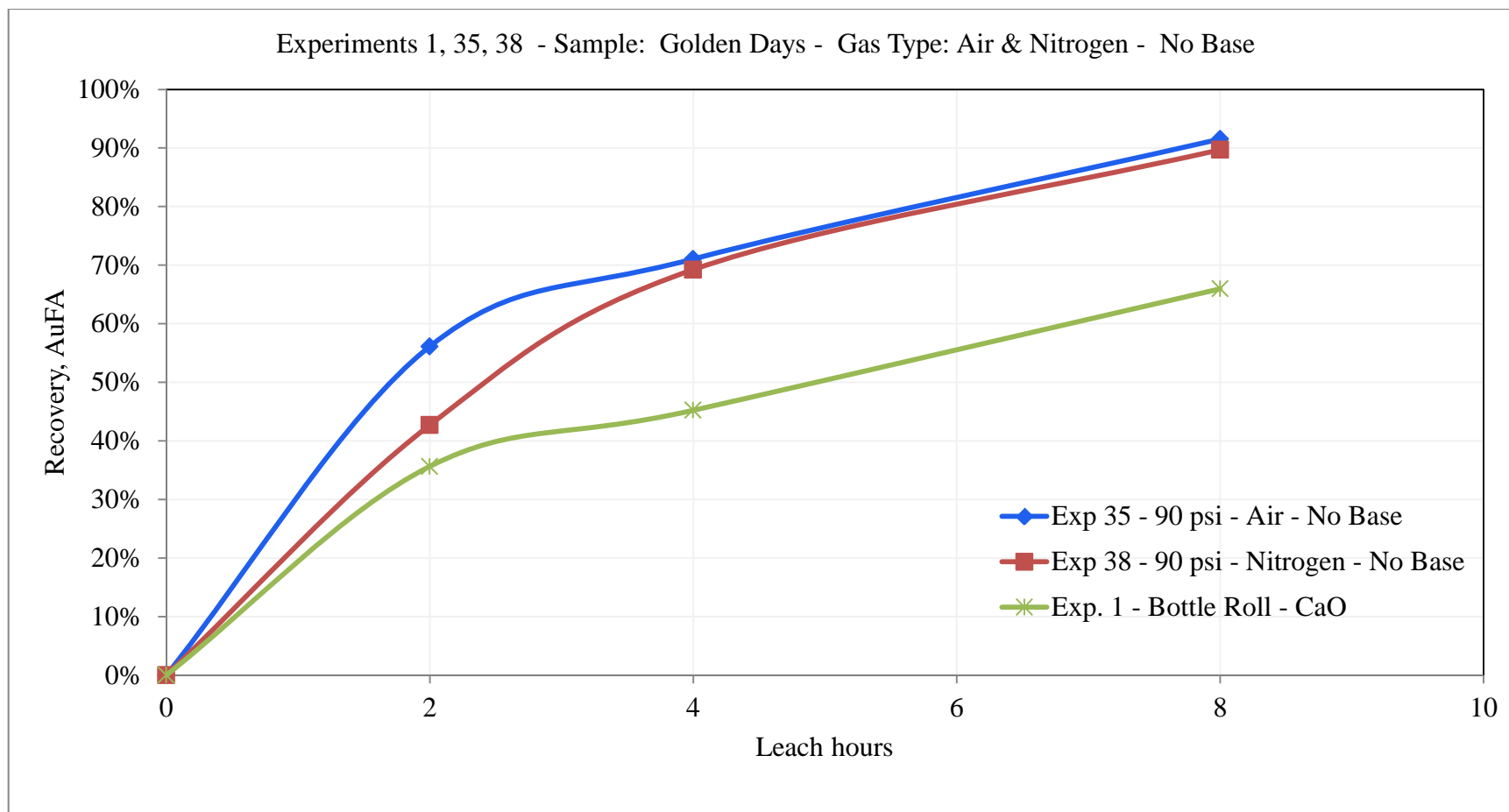


Figure 61. Experiments 1, 35, 38 - Sample: Golden Days - Gas Type: Air & Nitrogen - No Base

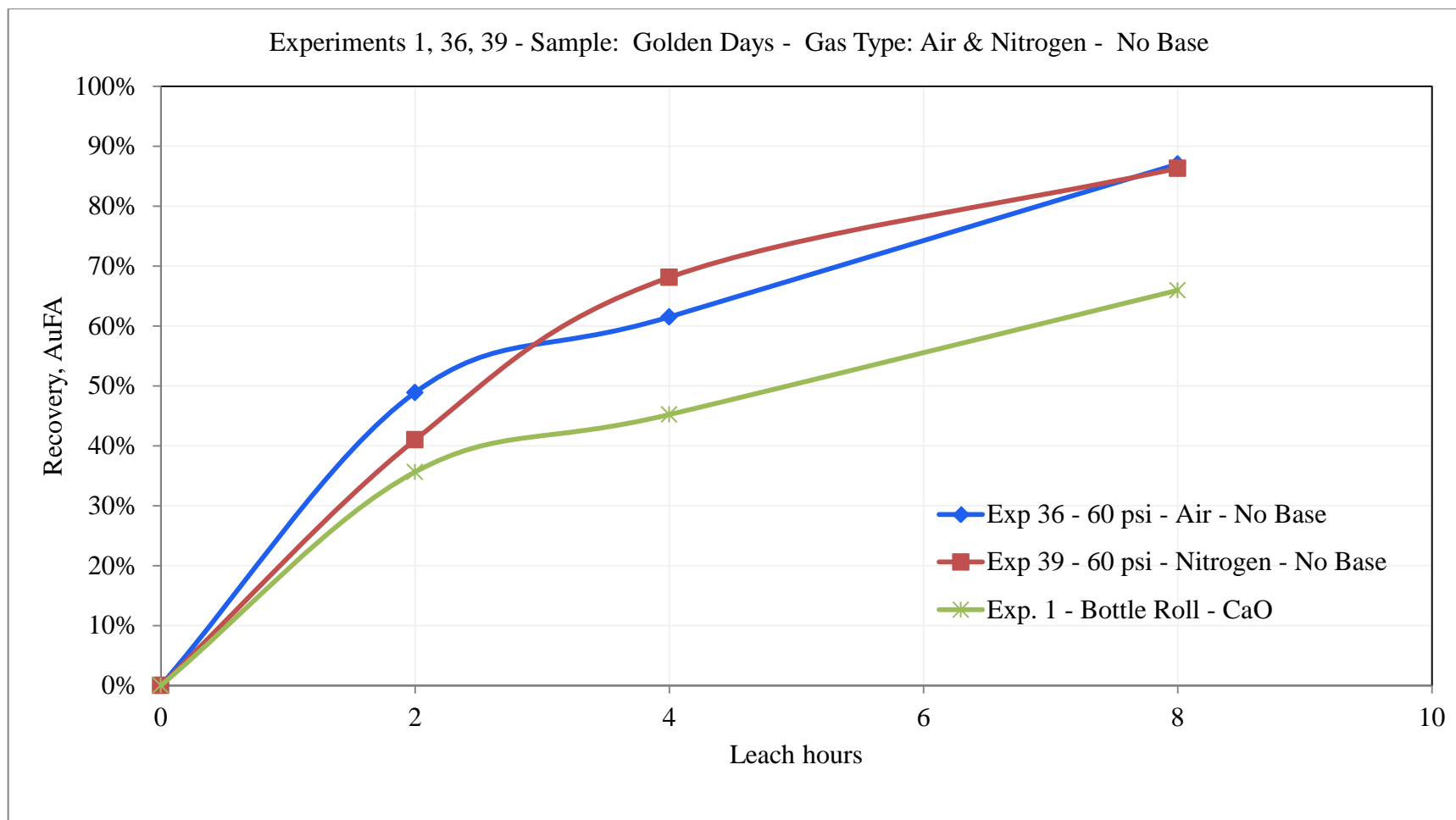


Figure 62. Experiments 1, 36, 39 - Sample: Golden Days - Gas Type: Air & Nitrogen - No Base

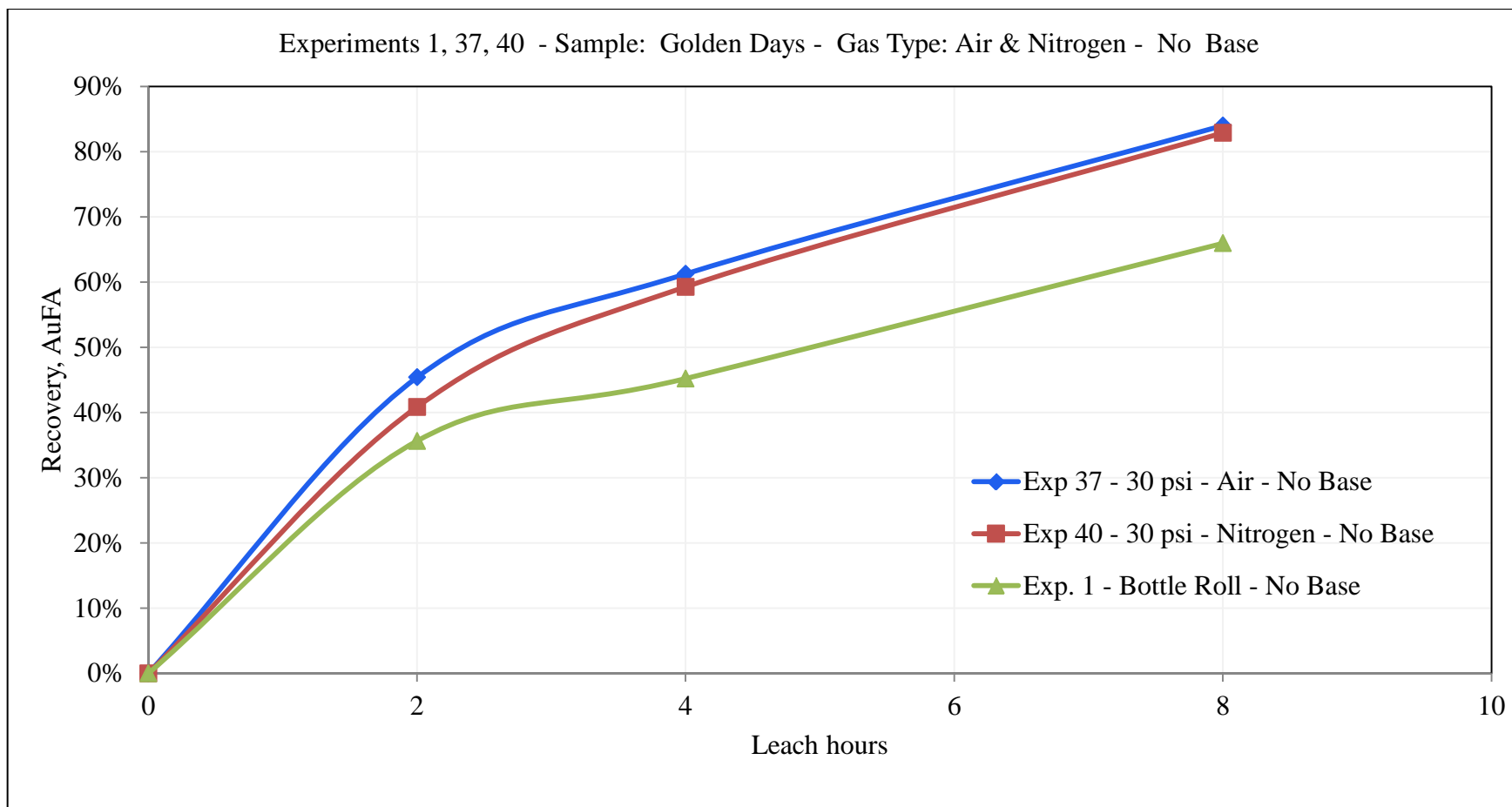


Figure 63. Experiments 1, 37, 40 - Sample: Golden Days - Gas Type: Air & Nitrogen - No Base

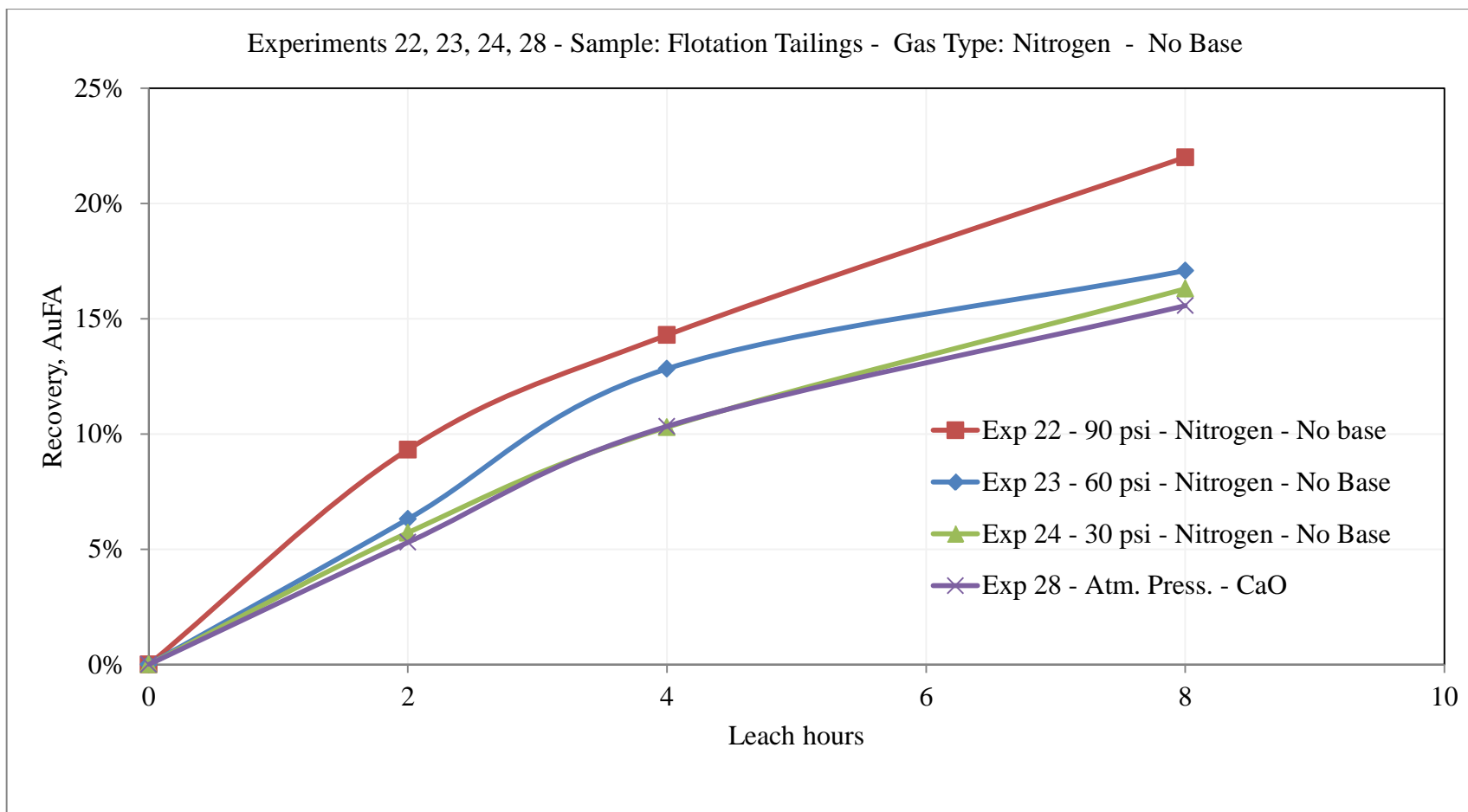


Figure 64. Experiments 22, 23, 24, 28 - Sample: Flotation Tailings - Gas Type: Nitrogen - No Base

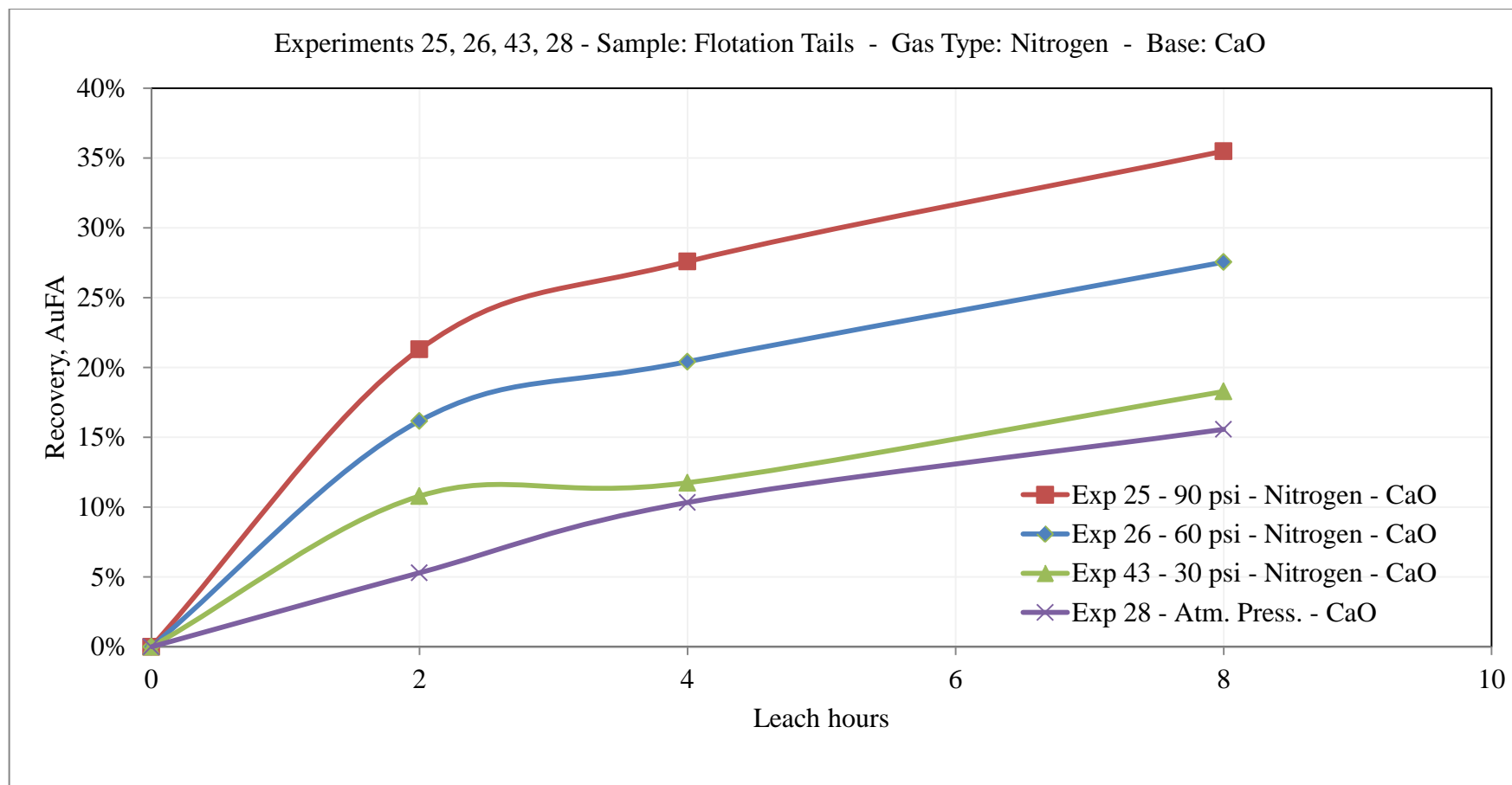


Figure 65. Experiments 25, 26, 43, 28 - Sample: Flotation Tails - Gas Type: Nitrogen - Base: CaO

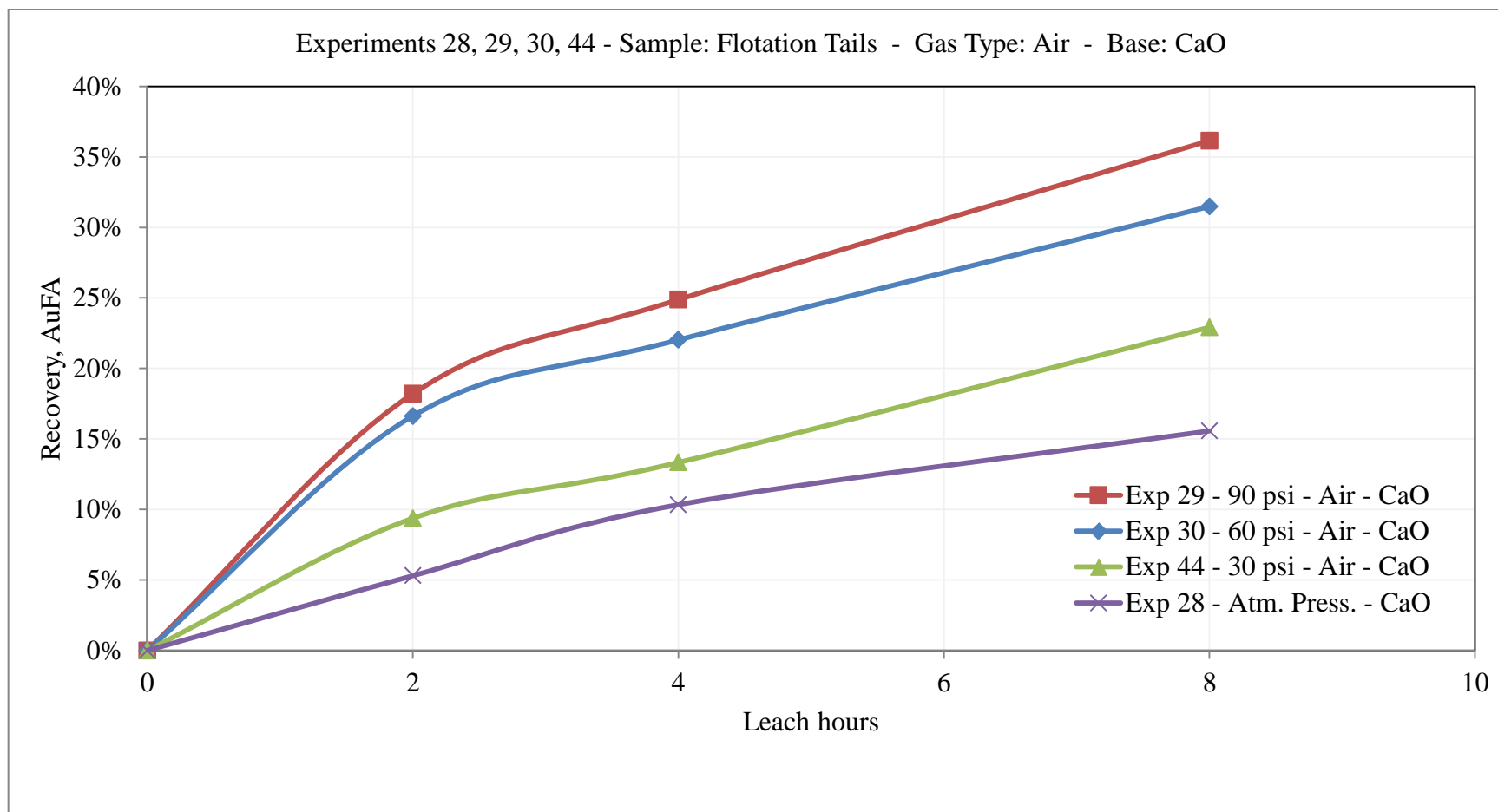


Figure 66. Experiments 28, 29, 30, 44 - Sample: Flotation Tails - Gas Type: Air - Base: CaO

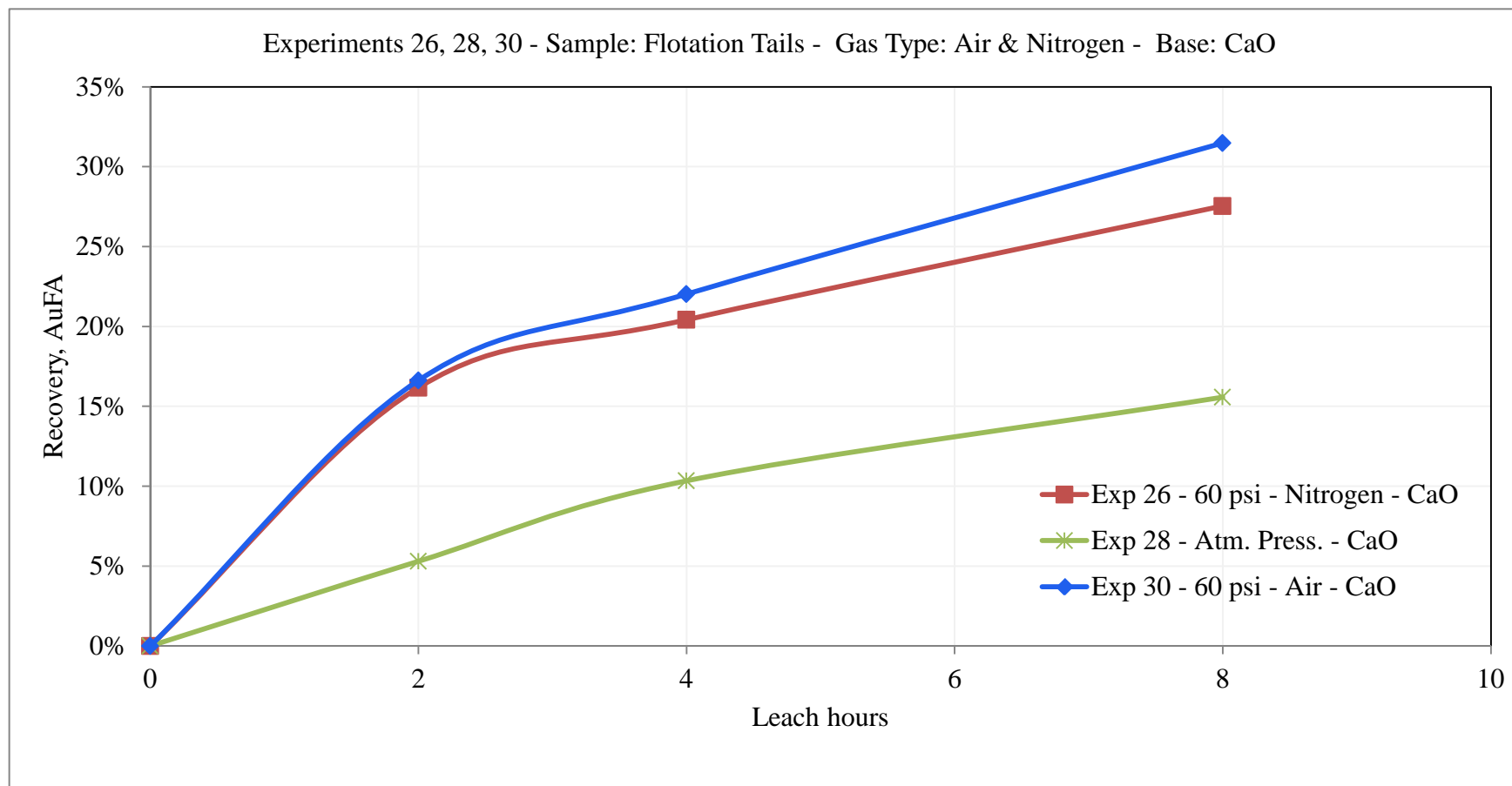


Figure 67. Experiments 26, 28, 30 - Sample: Flotation Tails - Gas Type: Air & Nitrogen - Base: CaO

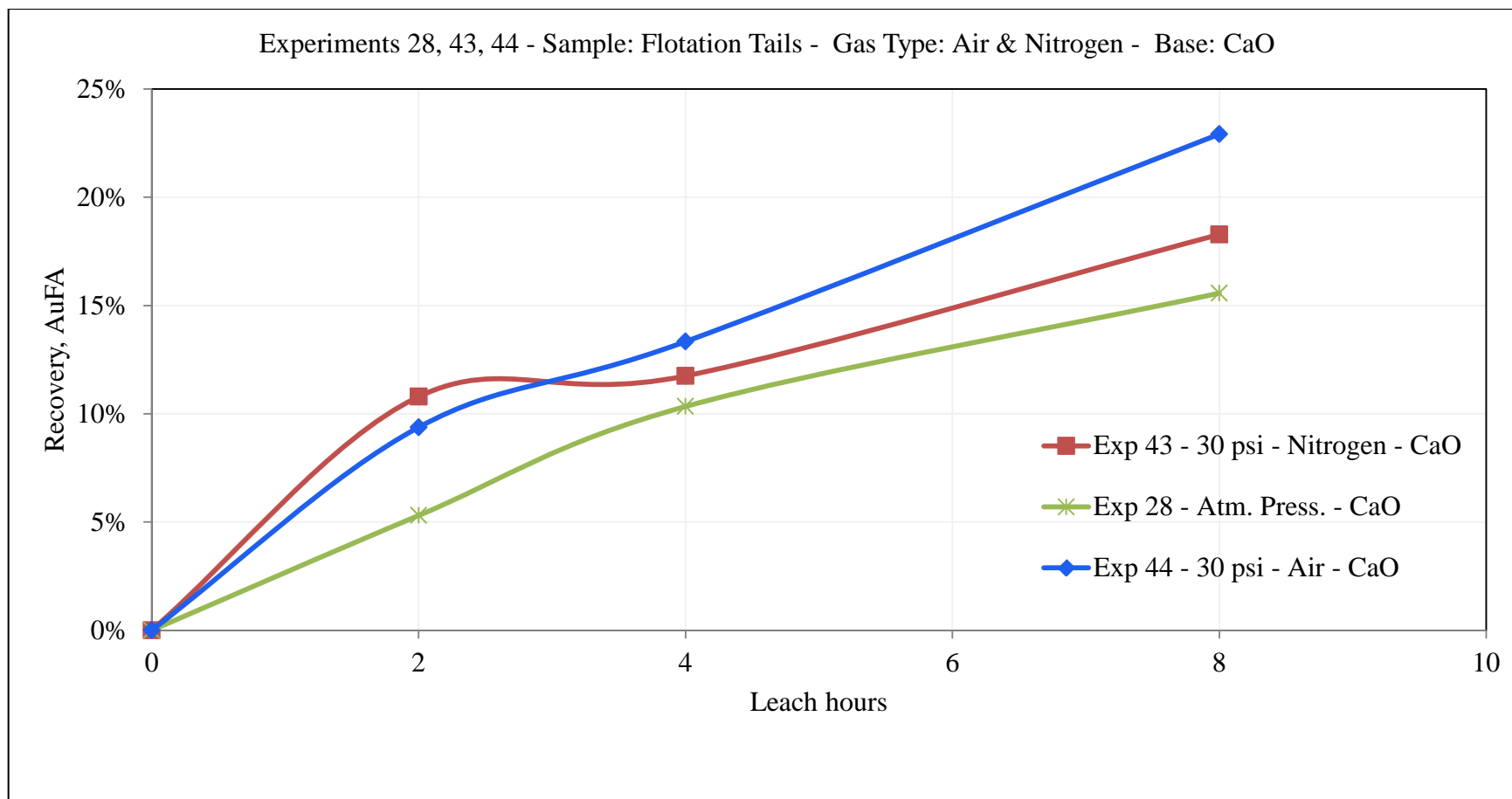


Figure 68. Experiments 28, 43, 44 - Sample: Flotation Tails - Gas Type: Air & Nitrogen - Base: CaO

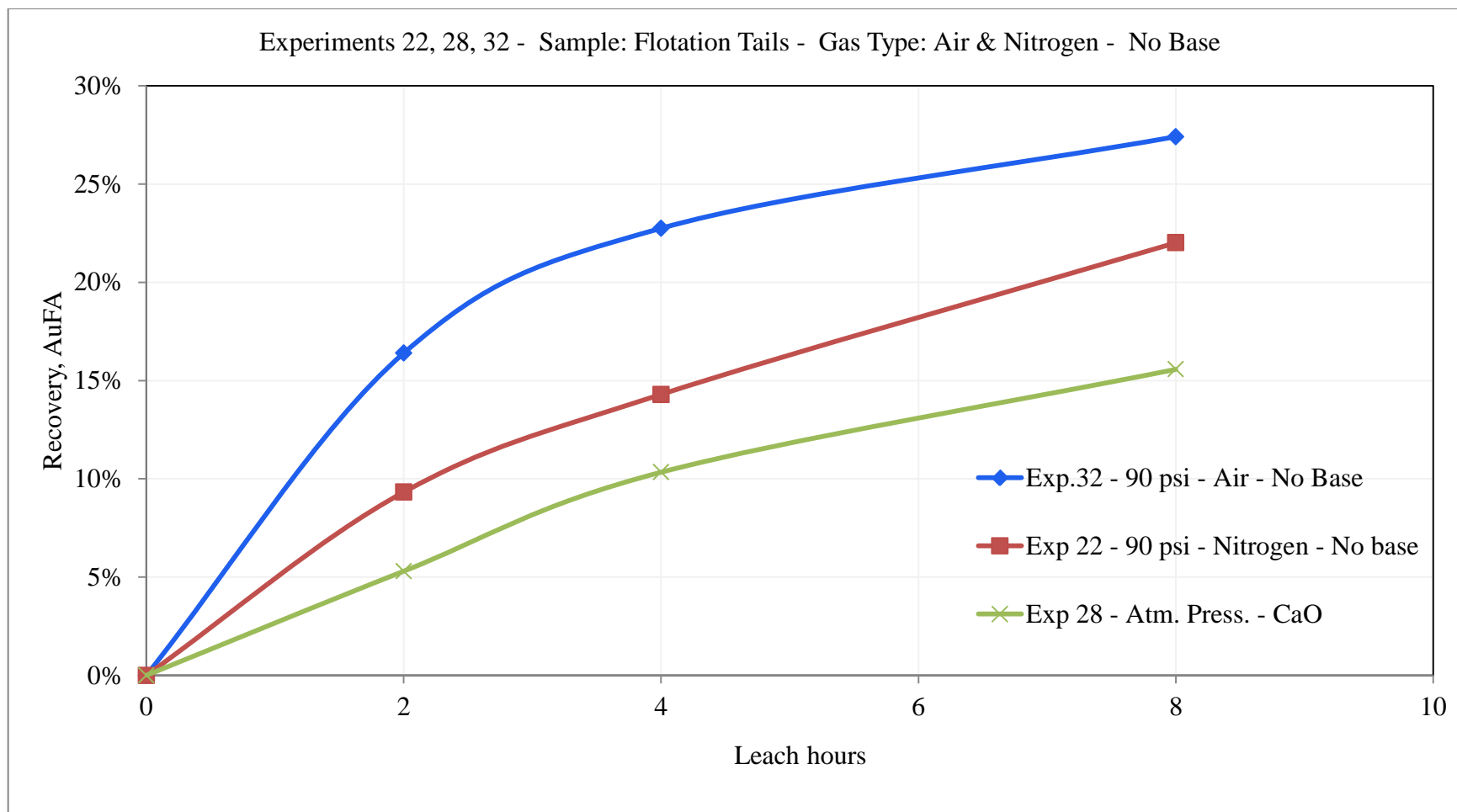


Figure 69. Experiments 22, 28, 32 - Sample: Flotation Tails - Gas Type: Air & Nitrogen - No Base

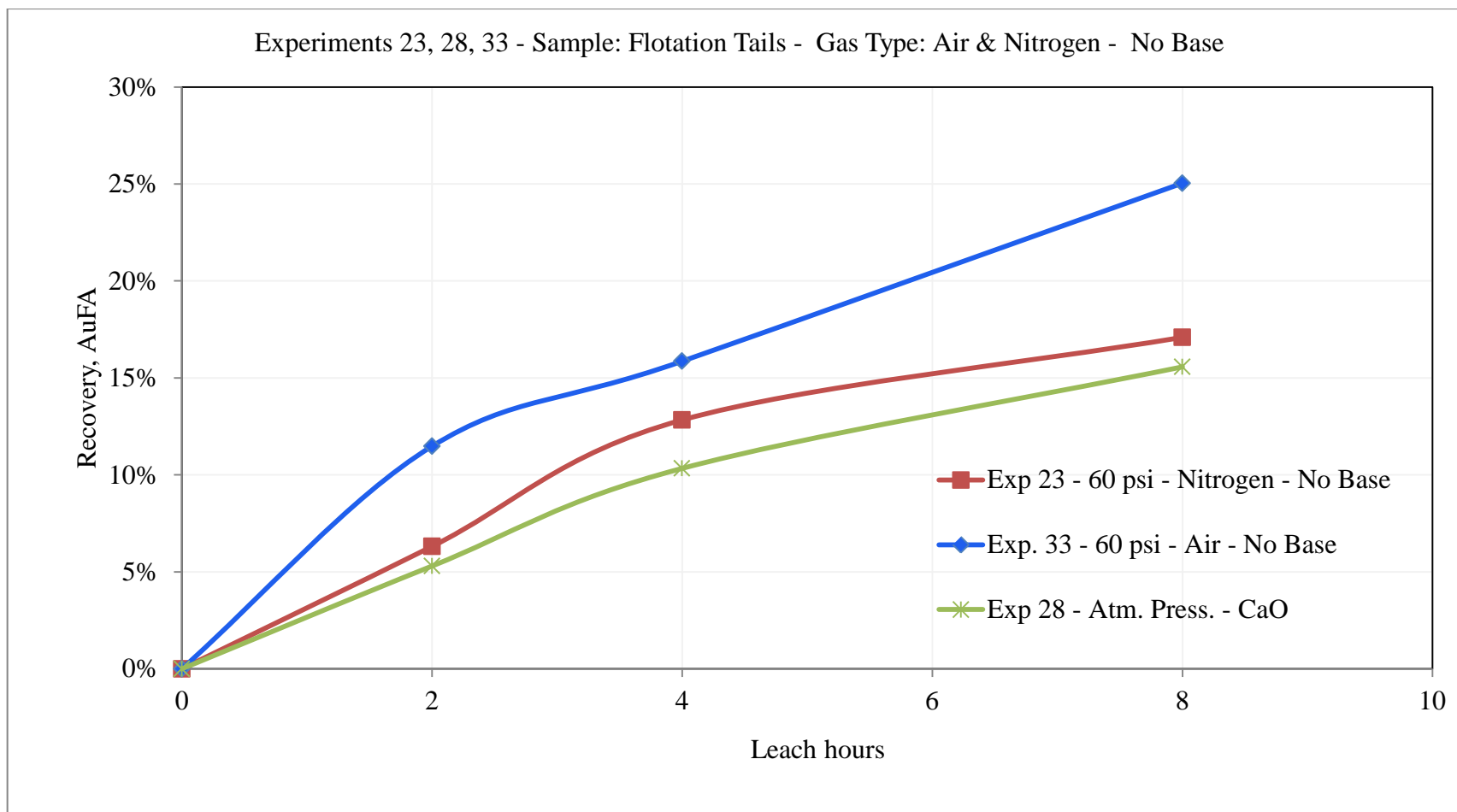


Figure 70. Experiments 23, 28, 33 - Sample: Flotation Tails - Gas Type: Air & Nitrogen - No Base

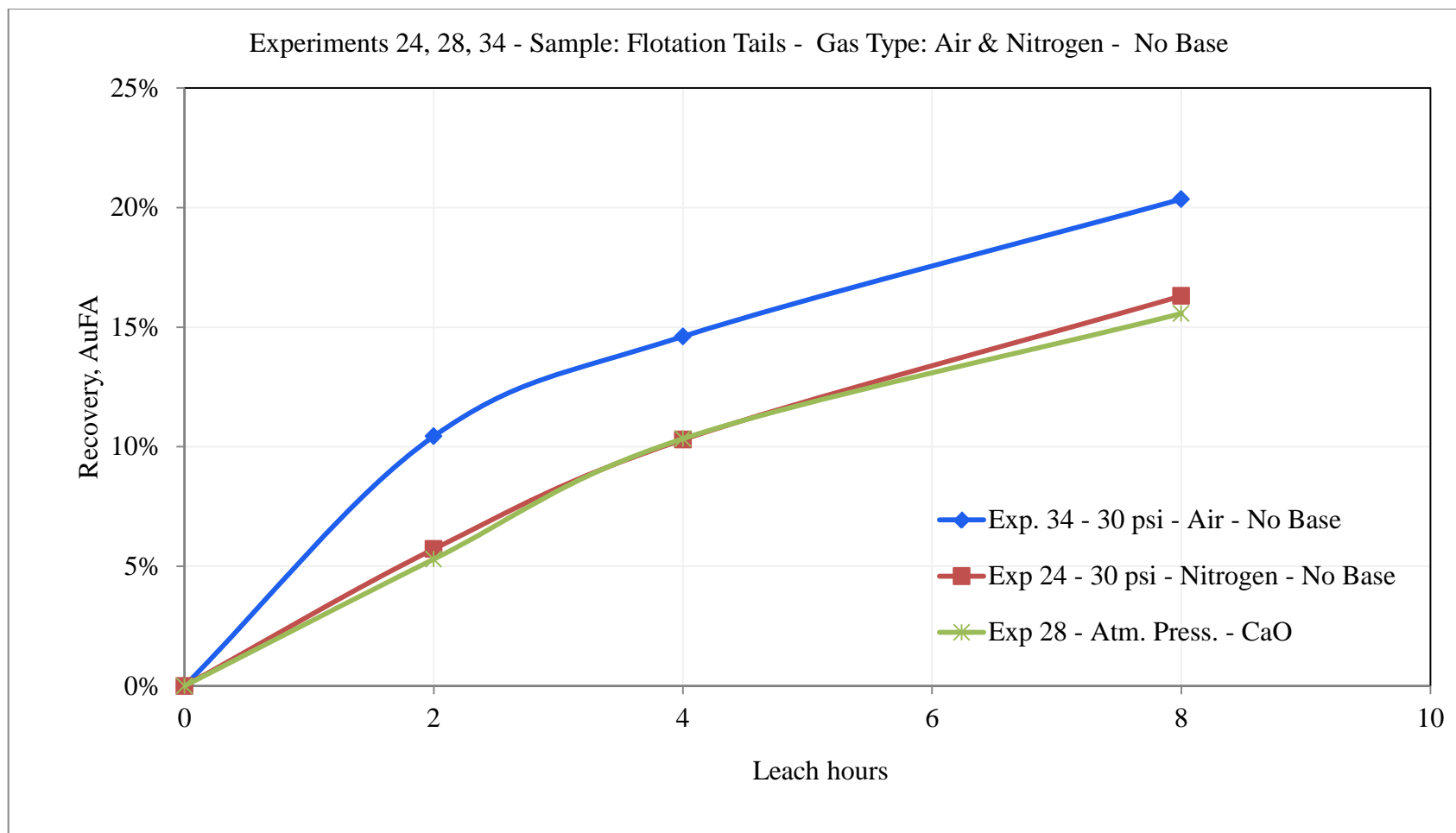


Figure 71. Experiments 24, 28, 34 - Sample: Flotation Tails - Gas Type: Air & Nitrogen - No Base