

# TREATMENT OF A COPPER - RICH GOLD ORE BY AMMONIA ASSISTED CYANIDE LEACHING

A D Bas<sup>1,\*</sup>, E Y Yazici<sup>2</sup> and H Deveci<sup>3</sup>

## ABSTRACT

Copper minerals present difficulties during the cyanide leaching of gold ores leading to excessively high consumption of cyanide (and oxygen) coupled with low extraction of gold. Copper cyanide species, if present at high levels, adversely affects the downstream processes such as the activated carbon adsorption and the effluent treatment. In this study, the extraction of gold from a copper-bearing gold ore by ammoniacal cyanide leaching was studied. Furthermore, ammonia leaching as a pretreatment process ahead of cyanide leaching was also examined. Only ~12% of gold was extracted by direct cyanide leaching of the ore. The addition of lead nitrate did not affect the leaching of gold. When ammoniacal cyanide leaching system was used, the extraction of gold was significantly improved to >90%. Similarly, the pretreatment of the ore by ammonia leaching was shown to lead to high gold extractions (98%), in subsequent cyanide leaching with significant reductions in the consumption of cyanide. This appeared to be linked with the ready dissolution/removal of copper during ammonia leaching.

**Keywords:** ammoniacal cyanide leaching, pre-treatment, lead nitrate, copper-gold ore, gold

## INTRODUCTION

Cyanidation process is extensively used for leaching of gold from ores since cyanide forms strong complexes with gold. In this process, some impurities such as copper and arsenic problems are present (Hayes and Corrans, 1992; Bas *et al*, 2011; Muir, 2011). The copper minerals have often a detrimental effect on the cyanide of gold resulting in low extraction of gold and high consumption of cyanide (Dawson *et al*, 1997, Almore and Muir, 2001; Breuer *et al*, 2005; Adams, 2005). The solubility of copper minerals in cyanide solutions is shown in Table 1. Copper minerals consume 30 kg/ton NaCN for each 1% copper reagent present, which often makes the process uneconomic (Muir, 2011). Alternative processes for the treatment of copper bearing gold ores are flotation (Bulatovic, 1997 Forrest *et al*, 2001), alternative lixivants such as thiosulphate (Bas *et al*, 2011), alkaline or ferric leaching prior to cyanidation (Dawson *et al*, 1997) and ammonia pre leaching ahead of cyanidation (Muir *et al*, 1991).

1. Mineral Processing Div., Dept. of Mining Eng., Karadeniz Technical University, 61080, Trabzon, Turkey. Email: [adenizbas@gmail.com](mailto:adenizbas@gmail.com)

2. Mineral Processing Div., Dept. of Mining Eng., Karadeniz Technical University, 61080, Trabzon, Turkey. Email: [eyazici@ktu.edu.tr](mailto:eyazici@ktu.edu.tr)

3. Mineral Processing Div., Dept. of Mining Eng., Karadeniz Technical University, 61080, Trabzon, Turkey. Email: [hdeveci@ktu.edu.tr](mailto:hdeveci@ktu.edu.tr)

**Table 1.** Solubility of copper minerals (in 0.1% NaCN solutions) (Marsden and House, 2006 after Hedley and Tabachnick, 1958)

Mineral	Formula	%Cu dissolved	
		23°C	45°C
Azurite	$2\text{Cu}(\text{CO}_3) \cdot \text{Cu}(\text{OH})_2$	94.5	100.0
Malachite	$2\text{CuCO}_3(\text{OH})_2$	90.2	100.0
Chalcocite	$\text{Cu}_2\text{S}$	90.2	100.0
Covellite	$\text{CuS}$	-	-
Native copper	$\text{Cu}$	90	100.0
Cuprite	$\text{Cu}_2\text{O}$	85.5	100.0
Bornite	$\text{FeS} \cdot 2\text{Cu}_2\text{S} \cdot \text{CuS}$	70	100.0
Chalcopyrite	$\text{CuFeS}_2$	5.6	8.2
Tetrahedrite	$(\text{Cu}, \text{Fe}, \text{Ag}, \text{Zn})_{12}\text{Sb}_4\text{S}_{13}$	21.9	43.7

Ammonia as a modifying agent to mitigate copper interferences in cyanide leaching of gold has been known for over 100 years as it was discovered by Hunt in 1901 (Adams, 2005; Muir, 2011). Ammonia is added to stabilize  $\text{Cu}^{2+}$  Eq. (1). In the absence of ammonia,  $\text{Cu}^+$  tends to form strong complexes with cyanide Eq. (2) thus leading an increase in the consumption of cyanide (Hayes *et al*, 1992). The beneficial effect of ammonia for improving the extraction of gold Eq. (3) and reducing the consumption of cyanide has been reported (Hayes and Corrans, 1992; Breuer *et al*, 2005; Muir, 2011 and Dai *et al*, 2012).

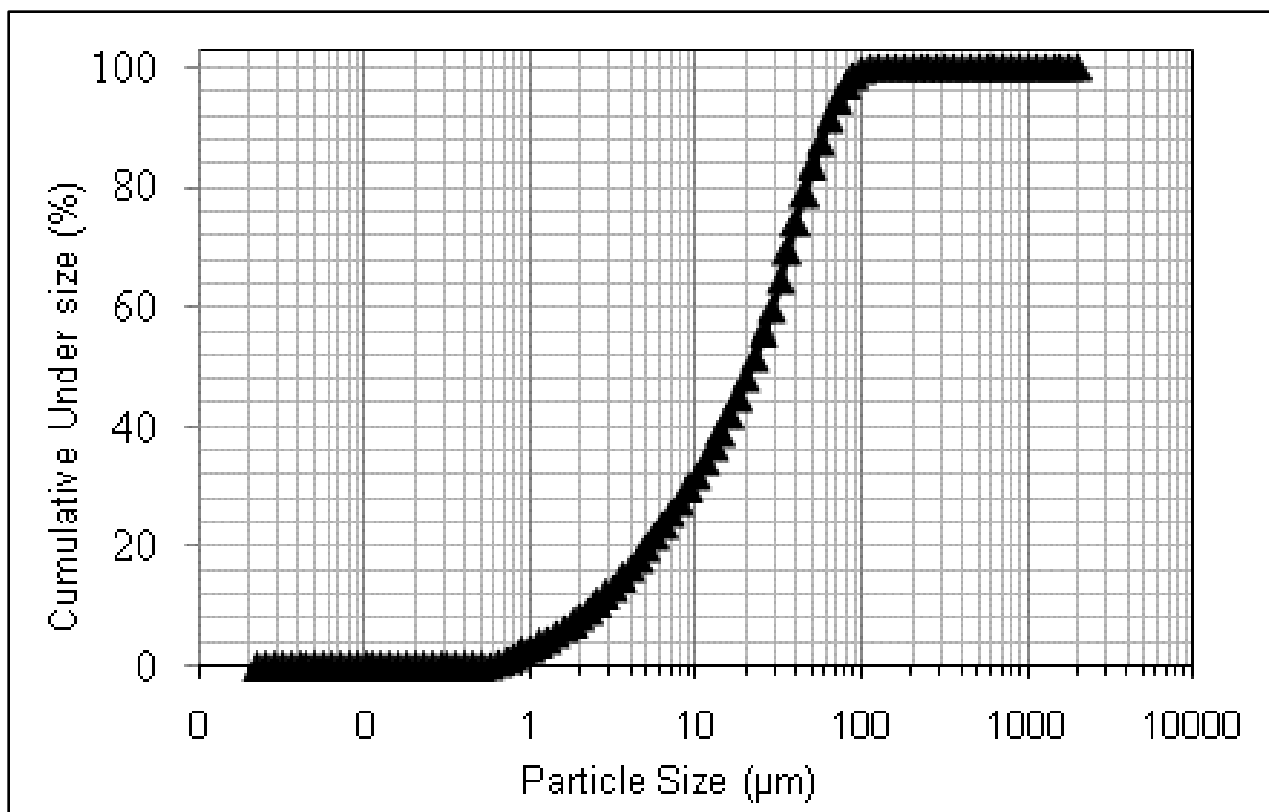


In this study, ammoniacal cyanide leaching of gold for the treatment of a copper-rich refractory gold ore was investigated. Ammonia leaching as a pretreatment process ahead of cyanidation was also examined. Some additives were tested to reduce the copper interferences. Direct cyanide leaching of gold was carried out for comparison.

## EXPERIMENTAL

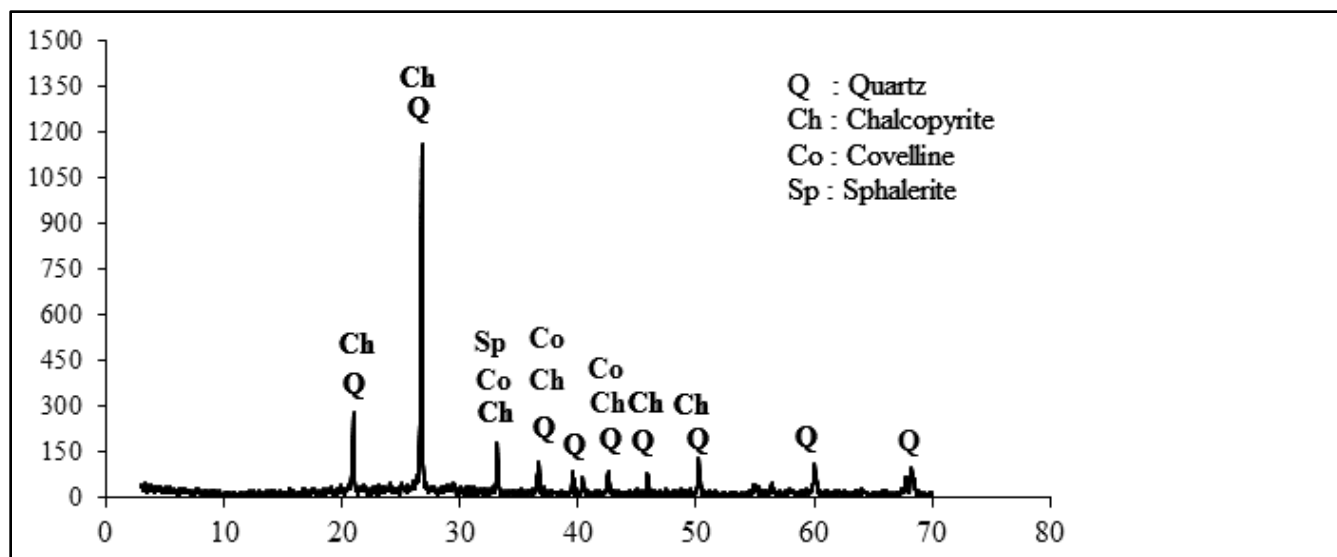
### Ore sample

The ore sample was obtained from Mastra Gold Mine, located in Gümüşhane, Turkey. The sample was crushed to -4 mm by using a jaw and then a roll crusher. The crushed ore sample was ground in a rod mill to 80% passing -75  $\mu\text{m}$  ( $d_{80}$ ) (refer Figure 1). The ground ore was riffled to 120 g portions and used in the leaching experiments.



**Figure 1.** Particle size distribution of the ore

Mineralogical analysis (refer Figure 2) showed that the ore sample consisted predominantly of quartz. Chalcopyrite and Covellite were also identified to be present as the main copper minerals in the ore (refer Figure 2). Previous studies have reported the presence of pyrite, galena and sphalerite as the other sulphide phases in the ore (Serbest, 2010; Ozdemir, 2011). The ore sample was determined to contain 85%  $\text{SiO}_2$ , 1.1% Cu, 3.1% S, 56 g/ton Au and 10 g/ton Ag.



**Figure 2.** XRD profile of the gold ore  $2\theta$  (°)

## Leaching tests

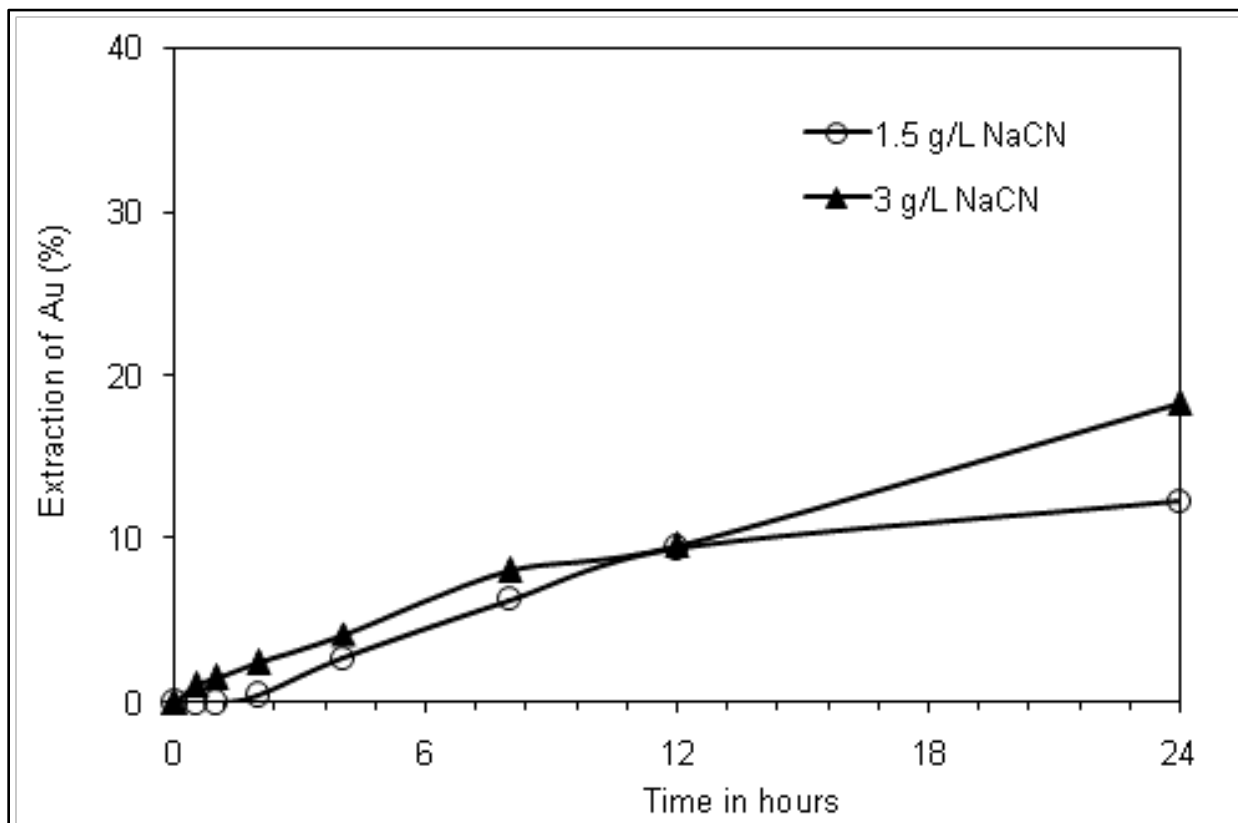
Leaching tests were carried out in 1000-ml beakers. Leach solutions (480 mL) were prepared to use deionised-distilled water at the required strengths of cyanide (0-3 g/L), ammonia (0-1 M  $\text{NH}_3$ ), and lead nitrate (0-1000 g/ton ( $\text{Pb}(\text{NO}_3)_2$ ). The ore (120 g, 25% wt/vol) was then added into the beakers, which were agitated by overhead stirrers at a constant stirring speed of 600 rpm. The top of the beakers were kept covered during the experiments and pH was controlled at 10.5-11 by the addition of 1 M NaOH. Samples were taken at predetermined intervals and centrifuged to obtain clear supernatants for analysis of gold and copper. The concentration of free cyanide was monitored by titration with silver nitrate using p-dimethylamino-benzal-rhodanine (0.02% w/w in acetone) as the indicator. Carboxymethyl cellulose (CMC) and polycarboxylate condensate (SP2) were also tested in the cyanide leaching of the ore.

After the leaching period (24 h), leaching residues were collected by filtration and dried. They were then digested in hot aqua-regia for the analysis of metals (gold, silver and copper), which was performed using an atomic absorption spectrophotometer (Perkin Elmer Analyst 400). Metal extraction in the tests was calculated based on the analysis of residues.

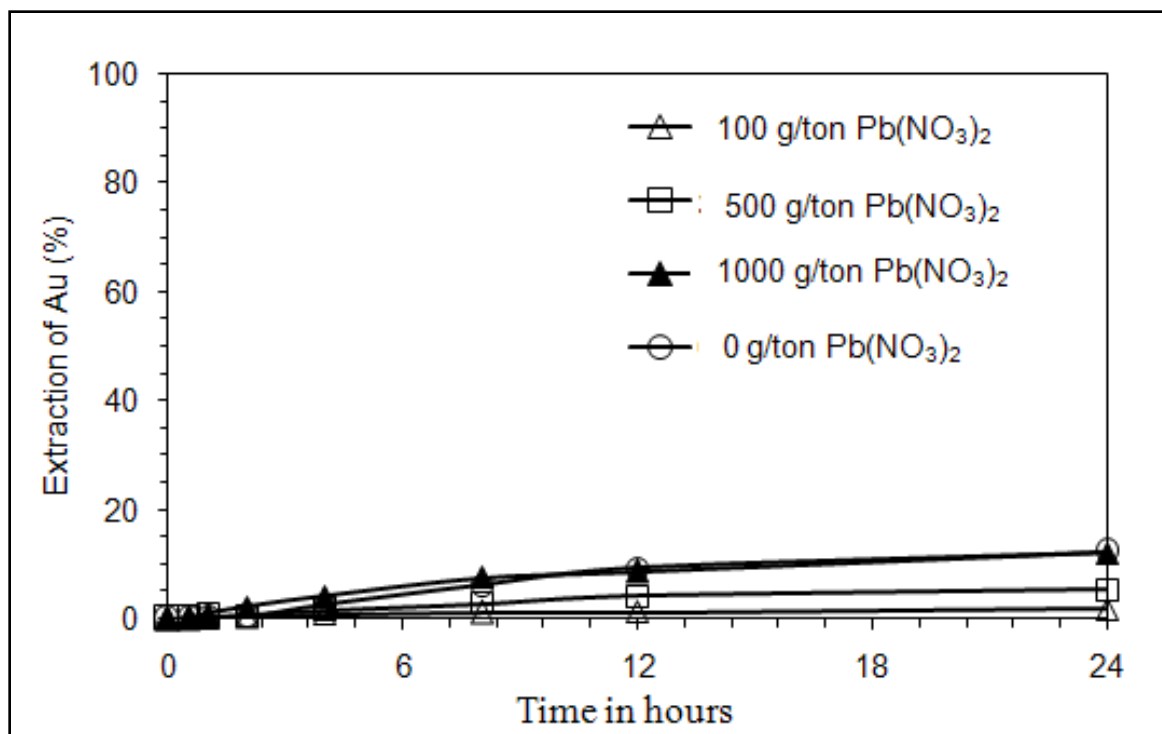
## RESULTS AND DISCUSSION

### Cyanide Leaching and Ammonia Pre-treatment

Figure 3 illustrates that conventional cyanidation of the ore results in unacceptable low extraction of gold. An increase in the concentration of NaCN from 1.5 g/L to 3 g/L improved, the extraction of gold only to a limited extent i.e. from 12.3% to 18.3%. Furthermore, the addition of lead nitrate (refer Figure 4) had no positive influence on the cyanide leaching of gold although it reduced the consumption of cyanide by 9.3-19%. These findings suggest that the ore is refractory in character, which could be associated partially with the presence of copper sulphides.



**Figure 3.** Gold extraction from the ore in cyanide leaching

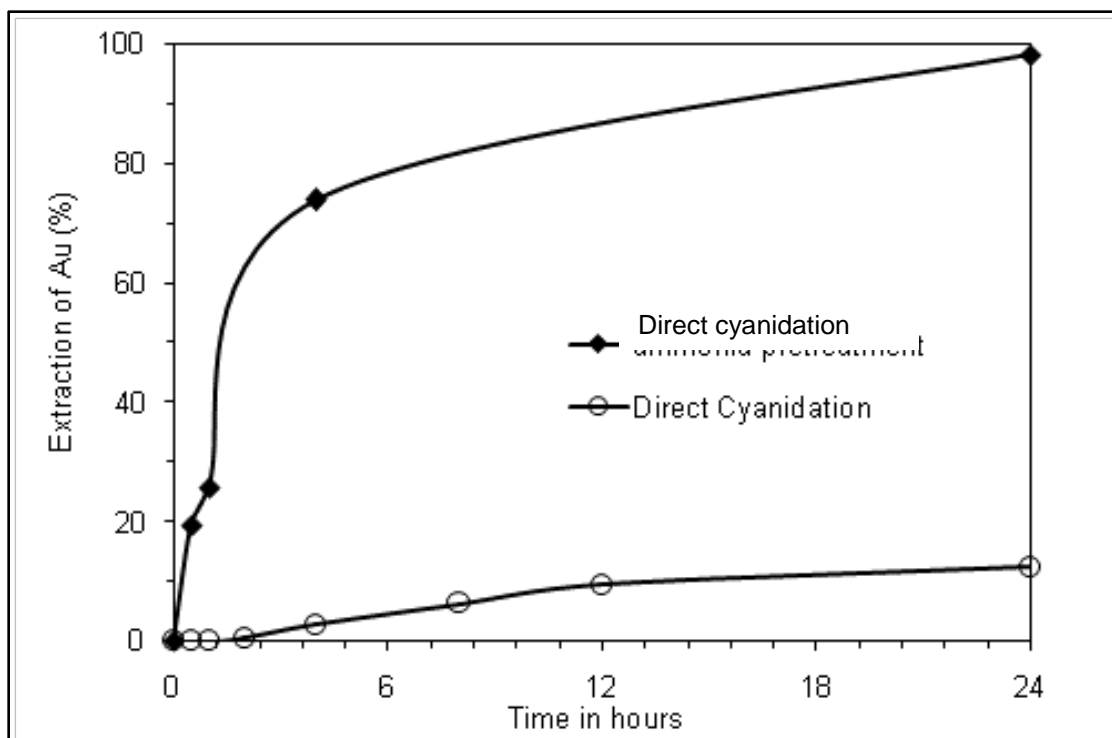


**Figure 4.** Effect of Pb(NO<sub>3</sub>)<sub>2</sub> on the extraction of gold (NaCN: 1.5 g/L)

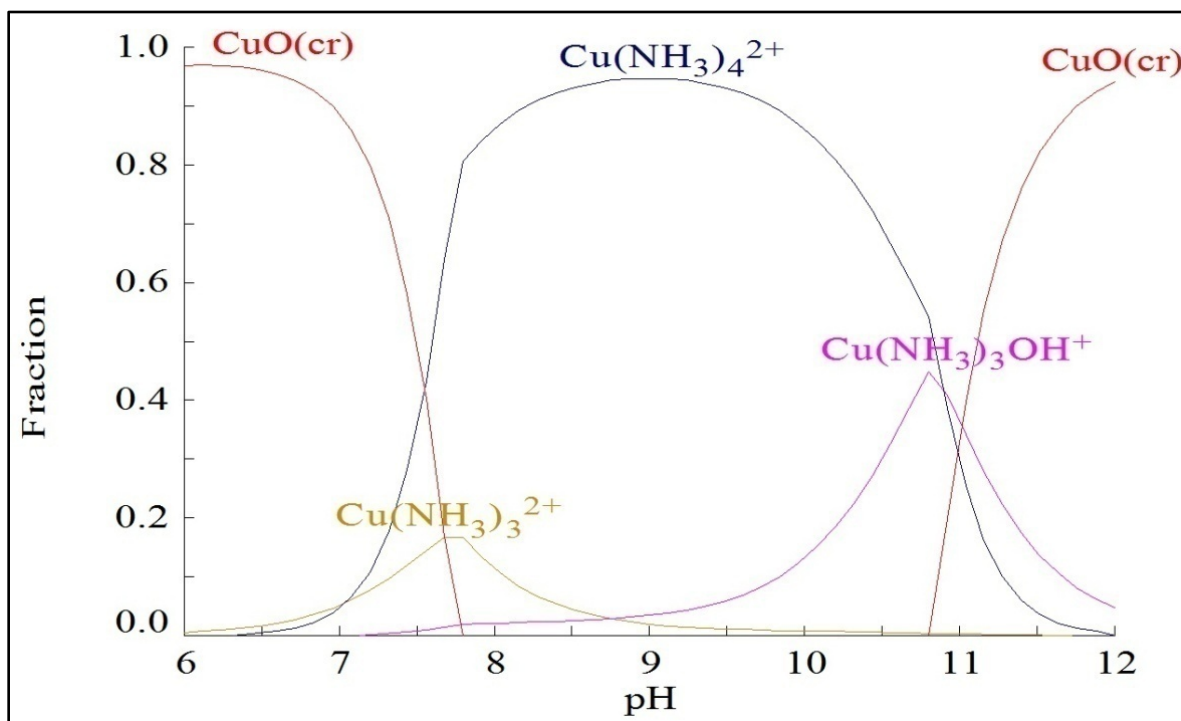
The pretreatment of the ore by ammonia (1 M) was therefore, investigated in an attempt to remove easily solubilised copper ahead of cyanidation. Ammonia pretreatment allowed to eliminate the refractoriness of the ore with a substantial improvement in the gold extraction from 12.3 to 98.2% (refer Figure 5). This improvement appeared to be concomitant with the removal of copper in the pretreatment stage where 58% of copper was dissolved. The remaining copper that appeared to be not particularly amenable to leaching by ammonia could be associated with chalcopyrite present in the ore. In the ammonia system (NH<sub>3</sub>+O<sub>2</sub>), the dissolution of copper from sulphide ores Eq. (4) is slow with relatively low copper extractions at low temperatures (Muir *et al.* 1991). pH and free NH<sub>3</sub> are important parameters controlling the dissolution process in which Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> is stable at pH 8.0-10.5 under the conditions tested in the current study (refer Figure 6). Considering the dependence of leaching of sulphides on free NH<sub>3</sub>, pH should be also controlled at high levels e.g. pH 9-10.5 to maintain high concentrations of free NH<sub>3</sub> in solution.



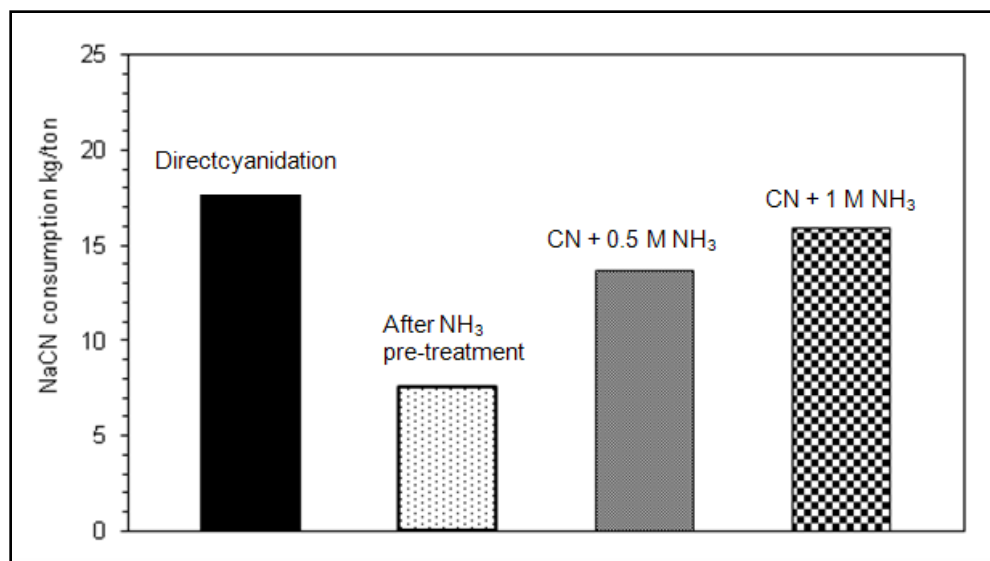
Ammonia pretreatment also lead to a significant reduction (by 42%) in the consumption of cyanide was recorded after the ammonial pretreatment (refer Figure 7). Muir *et al.* (1991) reported, excessively high consumption of cyanide (i.e. 30 kg/ton) required for the extraction of gold (90% Au) from a copper-bearing tailing sample. They demonstrated that ammonia pretreatment considerably reduced the cyanide consumption in that 83% of gold was extracted at a NaCN consumption of only 2 kg/ton. These findings suggest that ammonia pretreatment prior to cyanidation of gold can be suitably used for copper-bearing refractory gold ores as also noted by others (Tran *et al.*, 1997, Muir, 2011).



**Figure 5.** Effect of  $\text{NH}_3$  pre-treatment on cyanide leaching of gold ( $\text{NaCN}$ : 1.5 g/L,  $\text{NH}_3$ : 1 M)



**Figure 6.** pH-dependent stability of copper species in ammonia solution (MEDUSA, 2004.)



**Figure 7.** Effect of ammonia pretreatment (1 M NH<sub>3</sub>) and the addition of ammonia (0.5-1 M NH<sub>3</sub>) on the consumption of NaCN (NaCN: 1.5 g/L)

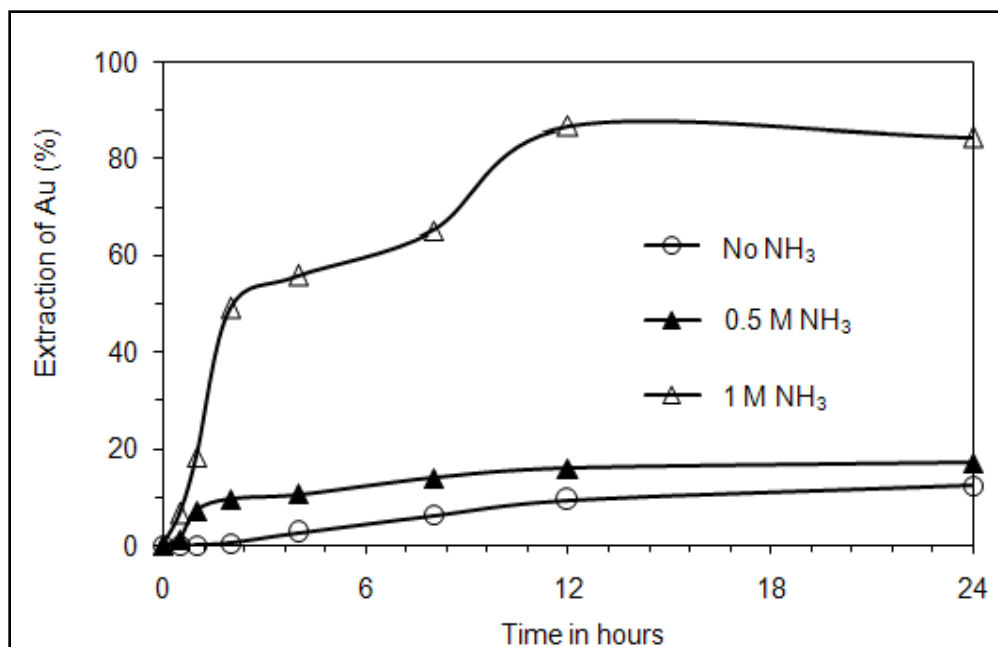
## Ammoniacal Cyanide Leaching

Ammoniacal cyanidation is one of the most promising alternative processes for copper-rich gold ores (Muir *et al*, 1991; Costello *et al*, 1992; Muir, 2011; Dai *et al*, 2012). Muir (2011) claimed that, with regard to reagent costs, ammoniacal cyanide leaching is more economic than ammonia pretreatment despite similar gold extractions. Therefore, the addition of ammonia (0.5-1 M NH<sub>3</sub>) into the cyanide solution (1.5 g/L NaCN) was tested in this study. Figure 8 illustrates the beneficial effect of addition of ammonia on the extraction of gold. At 0.5 M NH<sub>3</sub>, the extraction of gold enhanced only to a small extent. However, a significant improvement in the extraction of gold was achieved with a further increase in the ammonia concentration to 1 M NH<sub>3</sub>. This could be attributed to the complexation of copper by ammonia (refer Figure 5) thereby the activity of Cu<sup>2+</sup> is reduced, and its oxidation potential is minimized (Muir *et al*, 1991). In fact, up to 23.4% reduction in the cyanide consumption was observed with the addition of ammonia (refer Figure 7).

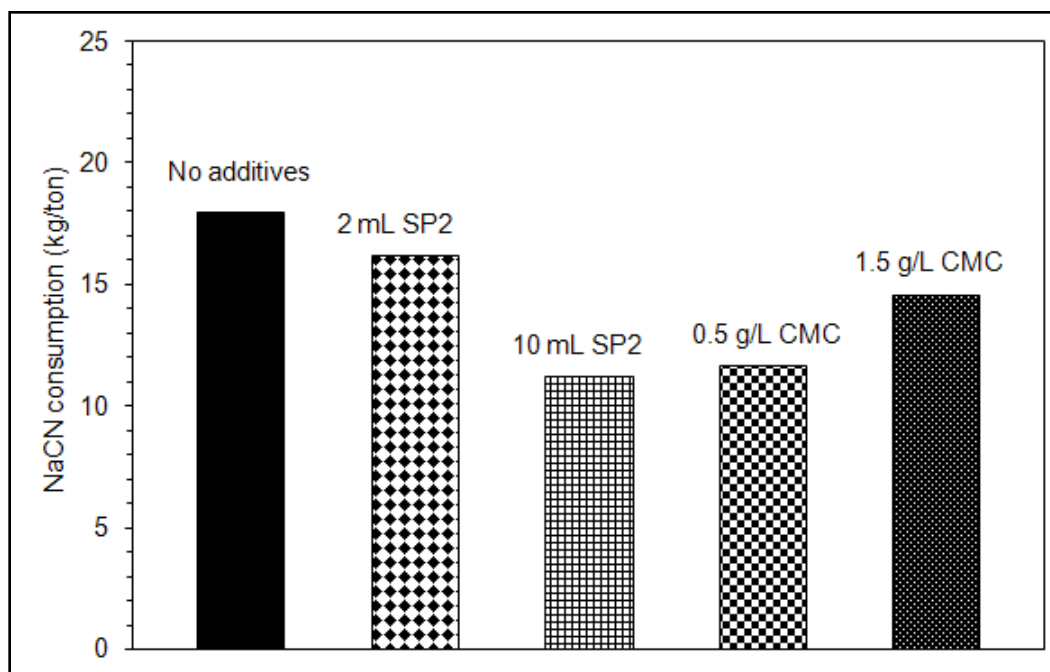
Previous studies (Muir *et al*, 1991; Muir *et al*, 1993; Muir, 2011) have confirmed, that pH is a significant parameter influencing the extraction of gold and copper. Gold extraction is enhanced at high pHs at which the concentration of free NH<sub>3</sub> and, concomitantly, the dissolution of copper also increase. Excess Cu<sup>2+</sup> (>5 mM) was reported to have a detrimental effect on the process leading to the degradation of copper(I) cyanide species (Muir, 2011). Optimization of leaching conditions appears to be required for high gold extractions with minimum dissolution of copper. Muir (2011) reported the optimum conditions for oxidized copper-gold ores to be 1-2 kg/ton NH<sub>3</sub> and 1-2 kg/ton NaCN at pH 10.5-11 and the adverse effect of increasing reagent concentrations on gold recovery and leaching selectivity over copper. Notwithstanding this, a high gold extraction was achieved only at 1M NH<sub>3</sub> and 1.5 g/L NaCN. Further studies may be required to optimize the reagent consumption.

## Effect of Additives

Feng and van Deventer (2011) reported the beneficial effect of the addition of carboxymethyl cellulose (CMC) at certain levels on the ammoniacal thiosulphate leaching of gold. They attributed this to the complexing effect of CMC on cupric ions thereby stabilising thiosulphate. In a similar manner, the addition of CMC and SP2 (polycarboxylate condensate) were also tested in this study. Although, no discernible effect on the extraction of gold was observed in the presence of these additives, they reduced the consumption of cyanide by 35-39% (refer Figure 9) presumably due to their complexing ability for copper.



**Figure 8.** Effect of NH<sub>3</sub> in ammoniacal cyanidation of gold (NaCN: 1.5 g/L)



**Figure 9.** Effect of additives on the consumption of cyanide (NaCN: 1.5 g/L)

## CONCLUSIONS

Copper-bearing gold ores prove difficult to treat due to the adverse effect of copper on cyanide leaching of gold. This study has shown ammonia pretreatment and ammonia assisted cyanide leaching of a copper-rich gold ore. Ammonia pretreatment prior to cyanide leaching, was found to be effective, with a significant improvement in the extraction of gold from 12.3% to 98.2%, apparently due to the removal of easily soluble copper present in the ore. It also allowed the reduction of cyanide consumption by 52%. Ammoniacal cyanide leaching was also observed to enhance the extraction of gold from the ore with concurrent reduction in cyanide consumption. This could be



attributed to the formation of copper amine complexes reducing the detrimental effect of cupric ions. The addition of lead nitrate had negligible effect on the extraction of gold. The additives including carboxymethyl cellulose (CMC) and polycarboxylate condensate (SP2) with their ability to bind copper ions reduced the consumption of cyanide, but, did not affect the leaching of gold from the ore. These findings suggest that the ammonia pretreatment and/or ammoniacal cyanide leaching can be effectively used for the treatment of refractory copper-bearing gold ores.

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