Kinetic gold leach monitoring including cyanide speciation

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Synopsis

Traditionally, bottle roll tests have been used to optimize the extraction process for best gold extraction and recovery. Such tests typically involve exposing the ore to defined reagent concentrations (lime, cyanide and sufficient oxygen) and balance the gold input with recoveries and losses. With mounting pressures to accommodate sustainability issues during development work, it became apparent that much more information would be required on the interactions and kinetic behaviour of solid and solution species during the entire leach process. This information is vital to enable proactive management of critical issues such as cyanide, arsenic, water and tailings management. Inadequate management of these aspects has led to temporary closures and, in cases of non-compliance, to the dynamically changing regulations.

MINTEK's advanced leach facility (ALF) is being developed with the aim of bridging the knowledge gap between the gold leach process and the predictable environmental impacts upon discharge. The facility aims to monitor all parameters of relevance such as pH, Eh, dissolved oxygen, metals, cyanide species, and viscosity during the entire process to enable more informed decisions on practical interventions.

The presented set of data reflects first experiences gained from processing a refractory gold ore concentrate. Attempts at optimizing the process were limited due to the developmental nature of the work. Data relating to leaches with differing preoxidation conditions and cyanide staging is presented.

Introduction

Due to the depletion of oxidized, free milling gold reserves that are relatively easily mined and managed, more challenging technologies have needed to be applied to liberate gold from sulphidic and, often, refractory ores[1,2]. Apart from the ever-present requirement of maximizing gold recoveries, the needs associated with sustainability issues have added additional objectives to process route development. Topics such as cyanide management, water balance optimization, arsenic fate and salt load minimization in discharges to the aquatic environment have become issues that require nearly as much attention as conventional process optimization targets.

Rising public pressure led to several initiatives supported by the mining industry that formulated the overall objectives seen as necessary to minimize risks to people and environment.

The Global Mining Initiative (1999 to 2002), the International Council on Mining and Metals (2002) and the International Cyanide Management Code (2002) were established as a result of this awareness. The Cyanide Code was developed by a non-profit organization, the International Cyanide Management Institute under the United Nations Environment Programme and the International Council on Metals and the Environment. All major gold producers (that use cyanide) were encouraged to become signatories to this code in the drive to better control the management of this hazardous reagent. Aspects of the code deal with the treatment of tailings and effluents[3] referring to specific numerical targets which require sound knowledge of the preceding leach chemistry.

As mentioned, the majority of newly developed gold reserves contain high levels of sulphide minerals, of which pyrite and pyrrhotite are some of the most common. The first cyanidation plant in the world was established close to Waihi, at the Crown Mine Karangahake in 1889. Pyrite leaching behaviour and general gold leach optimization has been a well studied field ever since[4-9].

Gold leach plant flow sheets of big scale operations are often extremely complex, combining old operating plants with newly designed parts of the operation. One of the biggest challenges in operations is achieving unremitting gold output whilst maintaining low reagent consumptions and positive

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compliance levels to all Safety & Health as well as environmental criteria. If monitored, the indicator species signalling potential difficulties in maintaining these standards (such as cyanide species, arsenic, certain metals and sulphur species) often display significant variability. In many cases, this would ask for specific interventions or reviewed process management strategies.

There are numerous factors that contribute to the difficulty of plant control, including differing mineralogy of ores from different sources, for example, and freshly crushed ores versus old stock piles. Often, not all the input parameters are well characterized. For example, blending is based on a restricted amount of set specifications such as head grades and comminution properties, focussing only on the valuable mineral, without taking further objectives into consideration. These could include highly fluctuating reagent addition, reagent consumption, discharge control and amelioration-specific measures. Practically, it would be unrealistic to affect characterization of all conceivable input parameters, but adding one or two key parameters to the decision criteria could strongly support the decision process by forcing a holistic approach.

The work presented in this paper focuses on cyanide addition management, although other parameters will be included in future. In recent years, the measurement and control of cyanide addition is regarded as critical and is preferably automated. Different cyanide detection and controlling devices are available, for example Kayton, Cascon T, Process Analytical Systems (TAC 1000) and MINTEK CYNOPROBE®, all with various advantages and disadvantages[10]. There are, however, limitations to the published data regarding the actual cyanide speciation during the first 48 hours of a typical gold leach. More work has been conducted focusing on final discharges. For example, a study undertaken by Johnson[11] *et al.* in 2008 aimed at determining the most dominant cyanide species present during the gold leach, by doing comprehensive sampling from four different operations found that the cyanide was mostly present as SAD. In their case the iron concentrations were too low to implicate $Fe(CN)_6^{4-}$ but at "normal" operating conditions significant amounts of cobalt cyanocomplexes were identified.

Cyanide is renowned for its poisonous properties; cyanide binds to the iron carried in the red blood cells responsible for oxygen transfer, preventing oxygen transfer to the cells, and so becomes a deadly poison. The cyanide chemistry is quite complex due to the high reactivity of cyanide and its ability to form cyano-complexes with most metals. The allowable potable water standards for cyanide (free cyanide) are 0.2 ppm (United States Environmental Protection Agency), 0.07 ppm (World Health Organisation), 0.05 ppm (European Union), 0.5 ppm (World Bank), 0.05 ppm (The Netherlands) and 0.05 ppm (South African National Drinking Water Standard)

Using the ASTM international standard (D 6696-01) as a reference document[12], the main cyanide species could be defined in broad terms as follows:

➤ *Free cyanide*—refers to either ionic cyanide (CN^-) or molecular hydrogen cyanide (HCN) which is usually present as HCN (aq) at >pH 11 or as HCN (g) at <pH 7

➤ *Simple cyanide*—cyanide bound to an alkali metal, alkaline earth metal or ammonium cation for example Sodium cyanide

➤ *Metal cyanide complex*—usually, several cyanide ions bound to a single metal cation, for example $Au(CN_4)^{3-}$

➤ *Titratable cyanide*—includes the free cyanide as well as the Zn, Cd and Cu metal cyanide complexes

➤ *Weak acid dissociable (WAD) cyanide*—this defined group of cyanide species includes the free cyanide, titratable cyanide, as well as the Ni and Ag complexes. These species dissociate and liberate measurable free cyanide when refluxed under weakly acidic conditions (pH 4.5–6) therefore named WAD

➤ *Total cyanide*—This refers to the sum total of all the inorganic chemical forms of cyanide that dissociate to give free cyanide when refluxed under strongly acidic conditions and includes the free cyanide, titratable cyanide, WAD cyanide as well as the Fe, Co, Au, and Pt complexes

➤ *Strong acid dissociable (SAD) cyanide*—This group of cyanide species refers to the difference between the total cyanide and the WAD cyanide which, basically, includes Fe, Co, Au and Pt cyanide complexes

➤ *Cyanide based degeneration products*—SCN- (thiocyanate) and CNO- (cyanate).

For mass balancing reasons, the determination of direct degeneration products can be very important. At MINTEK, HPLC/IC is used to quantify these compounds. In this paper, only the cyanide part of thiocyanate is used in graphs and discussions to allow for direct comparisons.

It is obvious that the cyanide chemistry is very complex, but linking speciation with leach kinetics does give a good indication regarding the leach behaviour of major metals and related species such as sulphur.

The motivation to construct the ALF (Advanced Leach Facility) was based on the following reasoning. It is still common to observe that environmental problems emerging as a function of changing ore composition are dealt with in a reactive fashion through ad-hoc application of amelioration steps. The ALF was designed to augment the old bottle roll technique by following the leach reaction kinetics of the target metal and the environmental parameters in relation to the process conditions applied. It should be possible to modify and evaluate those parameters of a process that a mine site can realistically change, such as:

➤ pH, Eh, oxidants, viscosity, varying cyanide concentrations

➤ effectiveness of staged addition of cyanide

➤ pre-oxidation (with detailed DO measurements)

➤ the effect of adding supporting reagents such as lead nitrate.

Investigations, hence, try to focus on the fate and mass balancing of cyanide and other solution parameters in relation to prevailing leach conditions while simultaneously monitoring the kinetics of the gold dissolution and adsorption.

This study focussed on basic leach optimization of a gold float concentrate to establish reasonable leach parameters regarding effluent control versus gold recovery. Detailed

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cyanide speciation was performed throughout the 48 hour leach time, as well as intensive monitoring of most leach parameters including base metal analysis.

Materials and methods

The sulphide float concentrate (80% passing 106 μm) was supplied by TEAL mining. The head grade analysis of the sample indicated that it contained 13 g/t gold, 48.8% Iron and 37.7% Sulphur. The leach was performed in a small scale, 3L, reactor fitted with an overhead stirrer and compressed air/pure oxygen (Afrox 99%) sparger.

The leach was carried out by using 1:1 concentrate: water ratio. Analytical grade sodium cyanide (Analytical Chemical Enterprises (PTY)) 20g/kg and 7g/kg was used for cyanidation. 1.25g/kg lead nitrate (Analytical Chemical Enterprises PTY) was used for leach optimization of the 7kg/t NaCN leach test. Leach parameter monitoring was carried out using a METROHM 704 pH and redox meter. Do (dissolved oxygen) measurements were performed using a WTW Oxi 330 fitted with a WTW CellOx 325 probe.

25 mL samples were extracted using a 50 mL glass pipette at the following time intervals 0, 1, 2, 3, 4, 5, 6, 11, 24 and 30/48 hours. The samples were centrifuged for 5 minutes at 7000 rpm using a HNS-ii centrifuge supplied by International Equipment Company USA. The supernatant was used for gold analysis by AA and metal ICP analysis.

The cyanide analysis was performed as follows: CNWAD and CNTotal and CNSCN by means of SFIA, segmented flow injection analysis. This method is an analogue to ASTM D 4374–93 or ISO 14403-2002. All SFIA analysis has a lower detection limit of 2 ppb, and the quantification limit is currently set to <10 ppb for both parameters. The standard uncertainty of the analytical results, from statistical analysis, based on a standard deviation of 1 sigma, approximately 68% confidence, is 2.9% for the WAD cyanide channel and 3.1% for the Total cyanide channel using a segmented flow injection analyser. The CNfree was analysed using a Ion selective electrode (ISE) fitted to a METROHM 704 meter. At the end of each leach the residue was filtered and rinsed with 1 volume of distilled water before drying at 70°C overnight. 200 g of the dried residue was submitted for total gold analysis by Fire Assay.

Results and discussion

It is known that the rate of gold leaching in air saturated water increases with increasing cyanide concentration, but the rate becomes independent of cyanide when it exceeds approximately 0.05% cyanide and the diffusion of oxygen becomes the rate controlling step[9]. There are numerous other factors that contribute to the gold dissolution chemistry including temperature, pH, particle size, presence of preg-robbing materials etc.

General consensus favours the opinion that the more difficult to leach ores require higher cyanide additions to ensure complete dissolution. This study tried to verify some of the underlying assumptions as shown in Table I, by tests in which the same float concentrate was leached under three different leach conditions:

a) No preoxidation with 20 kg/tonne sodium cyanide
b) Leach after 4 hour intensive preoxidation using 20 kg/ton sodium cyanide
c) No preoxidation with 7 kg/ton sodium cyanide added in three stages (plus the addition of 0.125 kg/tonne lead nitrate).

Analysing the obtained data yielded some surprising observations. Firstly, it was noted that the 4 hour intensive preoxidation (using pure oxygen at an average DO of 30.5 ppm) did not dramatically improve the gold dissolution kinetics as could be expected from published data[2,9]. The usually desired effect of surface passivation as a function of the preoxidation might also have inhibited the gold dissolution. It should be remembered that the ore is essentially refractory in nature.

In contrast, it was found that when using almost three times less sodium cyanide, added in three additions (in conjunction with using 0.125 kg/t PbNO3) 88.8% of the gold was leached within 48 hours. The noticeable loss in gold dissolution was, however, accompanied by strongly reduced leaching of sulphide minerals as evident by the much lower iron and sulphur values in solution compared to the leaches done using 20 kg/ton sodium cyanide. See Figures 1 and 2.

Figure 1 compares the iron concentrations as monitored during the leach tests. It is important to note that the analytical detection limit of this specific method was maximum 1000 ppm total iron. The plateau effect in Figures 1 and 2 is, hence, an apparent one; much higher values for iron and sulphur might be masked behind these figures.

It was found that the test using only 7 kg/t NaCN showed significantly lower amounts of iron leached, 88 ppm, compared to the 20 kg/t NaCN tests both reaching more than 1000 ppm total iron. These results suggest that raising cyanide addition to the leach system enhances not only gold dissolution, but also that of the cyanicides. The resulting

Table I

Comparing overall gold leach results

	No pre-ox + 20 kg/ton NaCN	Pre-ox + 20 kg/ton NaCN	No pre-ox + staged add 7 kg/ton NaCN + lead nitrate
Actual head grade	13 g/ton		
Residual gold after leach (g/ton)	0.3 g/ton	0.4 g/ton	1.5 g/ton
Percentage leached	97.8%	97.3%	88.8%

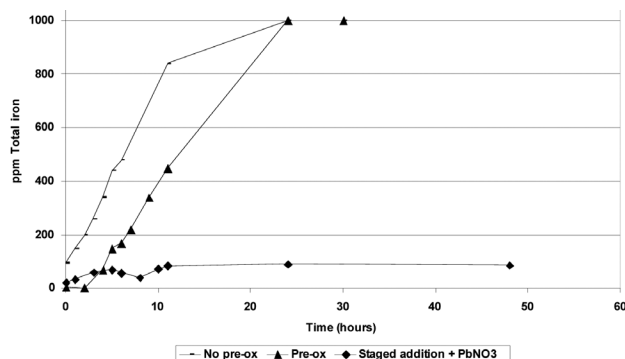# Kinetic gold leach monitoring including cyanide speciation

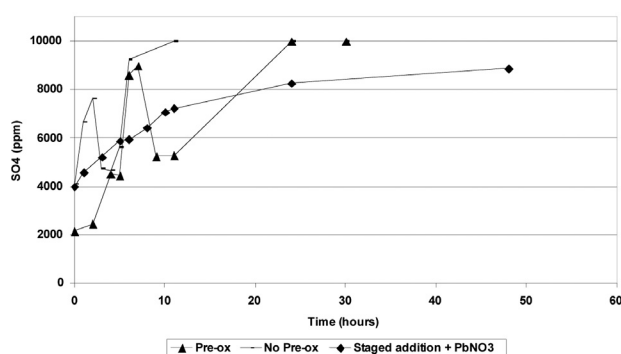**Figure 1—Comparing total iron in solution for three different leach tests**

Figure 2—Comparing the sulphate in solution for three different leach tests

levels of ferrocyanide in solution as well as increased salt loads could have fairly serious impacts on environmental compliance at discharge level.

Similar observations made for iron could be obtained for total sulphur in solution (expressed as sulphate). The leach test using 7 kg/t NaCN did not reach 10 000 ppm during 48 hours compared to the No pre-ox test reaching 10 000 ppm SO_4 within 11 hours of operation. The lower concentrations of sulphate in the solution consequently also led to a lower concentration of thiocyanate in the leach system as shown in Figure 2. In certain instances, where discharge water is recycled to a biological oxidation plant, for example, this could have important consequences for the water reusability.

The cyanide results are displayed as the total cyanide value comprising: Free CN, WAD cyanide (WAD minus the free CN), SAD cyanide (Total minus WAD), and the cyanide bound to thiocyanate (SCN). This allows for cyanide species comparison in an accumulative fashion. Figure 3 shows the evolving cyanide species during the leach using 20 kg/t NaCN. While the total cyanide was maintained at levels around 9000 ppm, it is the species shift that is of particular interest. The relatively stable total cyanide results indicated that only minimal amounts of cyanide were lost to volatilization or precipitation. WAD cyanide decreased from 2820 ppm down to 875 ppm WAD cyanide largely as a function of rapidly reducing free cyanide (confirmed by ISE

measurements). The SAD cyanide increased as the WAD cyanide and 'free' cyanide decreased, suggesting a shift in speciation. Considering the available data on iron in solution, the only likely species which could account for the SAD cyanide contingent is ferro-cyanide.

Figure 4 gives the cyanide results of leach test with pre-ox. The total cyanide only decreased slightly from 11900 ppm to 9390 ppm during the 30 hours. This decrease could be due to volatilization (sparging dry, neat oxygen directly from the Afrox oxygen cylinder) or a function of precipitation. The WAD cyanide as well as the 'free' cyanide decreased drastically until low concentrations of 362 ppm and 363 ppm remained after 30 hours. The pre-oxidation did not greatly improve the cyanide consumption rate as was expected.

Figure 5 displays the cyanide speciation of the staged addition leach test. At time zero, 5 g/t NaCN was added, and a further 1 g/t NaCN was added after 5 hours and 11 hours, respectively. It was found that the total cyanide did slightly decrease after each cyanide addition but, overall, had an average of 1760 ppm (Min= 1180 ppm Max= 2210). The free cyanide and WAD cyanide decreased after each NaCN addition, while the SAD cyanide increased inversely. The 'free' cyanide showed an average of 1040 ppm with a minimum of 312 ppm and a maximum of 1660 ppm. The red triangles represent the gold in solution as detected by AAS-
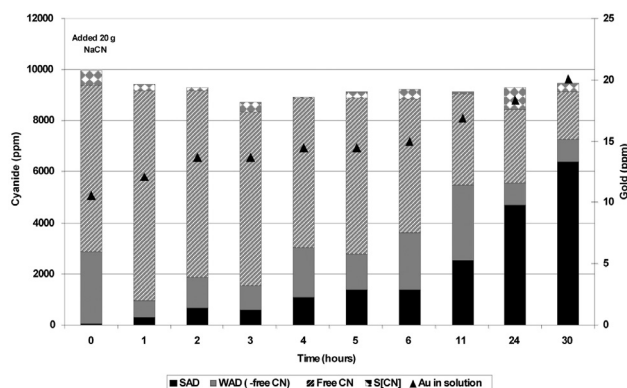

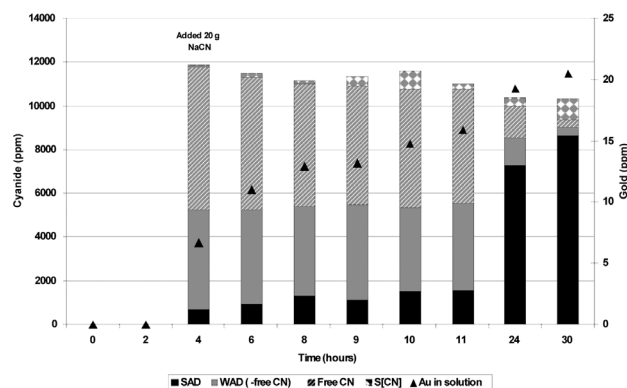**Figure 3—Cyanide speciation of leach test with No pre-ox and 20 kg/t NaCN**

Figure 4—Cyanide speciation of leach test with pre-ox and 20 kg/t NaCN

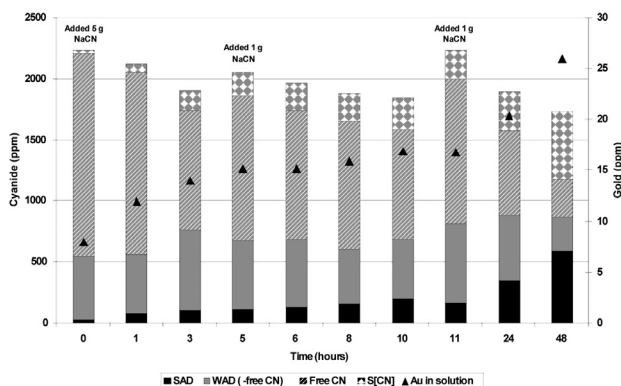# Kinetic gold leach monitoring including cyanide speciation

Figure 5—Cyanide speciation of leach test with no pre-ox and 7 kg/t NaCN

ETA; this shows the gradual increase of the gold in solution during the leach. Of particular interest was the fairly pronounced elevation after the last addition; decoating of gold particles, previously passivated might serve as a partial explanation.

It should be remembered, that these tests represent scouting experiments and not optimization tests (notwithstanding the difference in gold dissolution). The different cyanide management during the leach led to different end products.

An overall lower total cyanide residual content could be expected as a function of the addition rate. However, it is important to note that all experiments displayed sufficient free cyanide residuals to support further gold dissolution. This suggests that the leach system was not restricted by cyanide availability even though only 7 kg/ton sodium cyanide was used in the one case. This suggests that with careful optimization, a gold dissolution of the benchmark 97% might be obtainable without necessarily sacrificing the achievements made towards sustainability goals in the form of less cyanide addition, reduced salt loads and reduced tailings related liabilities and risks.

Conclusions and future work:

These preliminary results indicate that a good technique for 'real time' comprehensive gold leach monitoring has been established. It could be demonstrated that by monitoring more parameters during a leach than just the target metal in solution, more holistic information is obtained and secondary objectives related to sustainability issues can be addressed. This technique could now be used for specific leach optimization and process control as well as better waste management. Parameters such as arsenic speciation, more detailed sulphur speciation, as well as additional process control indicators (Eh, DO, viscosity etc) will in future be co-monitored in order to assess issues from a more fundamental base.

Optimal results would be achievable when integrating advanced leach work with the preceding steps such as gravity separation, optical sorting and other systems leading to fractionating of ores and, therefore, potentially isolating problems. For maximum returns, this approach should be adopted during the exploration phase as it would retain the freedom to choose optimal process designs unrestrained by existing infrastructure.

With more and more deposits and projects being based on sulphide ores, often of a refractory nature, a holistic approach to leach process investigations should be considered indispensable.

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