Automating cyanide measurement & control in highly variable complex copper gold ores by applying a modified potentiometric titration determination

Brindel Barzola[2], Gilmar Guzman[3], Germán Chen[4], Egonk Arriagada[5], Peter Leckie[6] and Greg Zwolak[1]

[1] Senior Specialist Engineer - Cyanide, Orica, Sydney, Australia, (greg.zwolak@orica.com)
[2] Technical Specialist Peru, Orica, Lima, Peru, (brindel.barzola@orica.com)
[3] Superintendent of Metallurgical Services, Newmont Yanacocha, Peru, (Gilmar.GUZMAN@newmont.com)
[4] Senior Manager - Marketing (Cyanide), Orica, Lima, Peru, (german.chen@orica.com)
[5] Lead Process Plant Specialist, Blasting Services, Orica, Santiago, Chile (egonk.arriagada@orica.com)
[6] Senior Manager - Commercial, Digital Solutions, Orica, Melbourne, Australia (peter.leckie@orica.com)

SUMMARY

Online cyanide analyzers are an established tool for the measurement & optimization of cyanide-leach systems yet have well-known measurement & operational challenges in complex ores, namely:

- Inconsistent exclusion of interferences due to varying Cu & S feed mineralogy. This is especially true in conditions, where the Cu &S mineralogy and concentrations are variable.

- Subsequent overestimation of 'Free Cyanide' results by inclusion of slow-leaching $Cu(CN)_3^{2-}$ complex. $Cu(CN)_3^{2-}$ leaches gold about 4 times slower than free cyanide.

- Correct measurement more sensitive to correct configuration, often requiring specialized knowledge to troubleshoot.

- Difficulties in confirming analyzer results with operator performed titration techniques with conventional silver nitrate titration.

- Reduction of signal to noise ratio due to interferences from other species

- Increased maintenance due to fouling & scaling caused by solution chemistry

Newmont's Yanacocha operation in Peru presented an especially challenging environment for reliable cyanide measurement and control, processing 3 semi-distinct complex ore types with feed Cu ranging from below 250ppm (as CuCN) to more than 5000ppm, and feed S ranging from low to 5%, resulting in cyanide consumption from as low as 1.5 kg/t to as high as 3.1 kg/t, and gold recovery ranging from approximately 57% to about 78 % (average plant performance based on the type of ore).

A literature search by the authors to identify a method for accurate cyanide determination that was also suitable for automation settled on the work of Breuer et al (2011) as a basis. Early challenges in adapting the laboratory technique for the 'real solutions' and the range of variability experienced in the plant are discussed, as are other operational challenges due to the complex and changing solution chemistry.

Despite the challenging environment, the new automated analysis technique was able to enable introduction of automated cyanide control on site, resulting in an instant change in cyanide control and consumption. Cyanide consumption fell by about 30%, saving about $3.6M per annum. Despite lower cyanide consumption, gold recovery increased on average by about 2-2.5% due to reduction in periods of cyanide underdosing. Subsequently, low and steady concentration of cyanide in plant tails enabled the site to lower their peroxide usage in the detox system by an average of 70%, saving $3.0M per annum.

Longer term process economic impacts on plant performance are also reviewed, with an accompanying discussion on opportunities to further enhance process control via integrating the extra information offered from this modified determination.

1. Introduction

Yanacocha is the biggest gold mine in South America. Initially all ore was processed using heap leach. The Yanacocha Gold Mill was constructed in 2009 to process higher grade ore that wasn't porous enough to be processed in a heap leach process. It has the capacity to process about 5M tonnes per annum. The gold mill consists of a crusher, SAG mill, 6-tank leaching process, with zinc precipitation (Merrill-Crowe) to precipitate gold and silver, SART and cyanide detox using peroxide.

The ore can vary significantly with respect to mineralogy, lime and cyanide consumption, and gold and silver recoveries. For production purposes, the ore is divided into 3 categories: oxides, intermediate and deep sulphide ores (DEEP) (see figure below).

[figure 1]

It was previously established by Yanacocha that the various mineralogy requires different cyanide set-points for optimum recovery. The set-points were mainly dependent on the ore type, but also on the levels of reactive copper in the ore. Usually, most of the cyanide during oxide ore campaigns, was added to the milling circuit and controlled to a set-point in the first leaching tank. For intermediate and DEEP sulfide ores, first tank was used as a pre-ox/conditioning tank, while cyanide was added and controlled in tank 2. To further complicate matters, ore is sometimes stockpiled for extended periods of time before processing which also affected levels of reactive copper due to weathering. The levels of reactive copper affect the cyanide consumption, which in turn govern the dosage of cyanide needed to sustain optimum cyanide levels in the whole leaching circuit. Historically this was controlled by keeping free cyanide concentration above 150ppm (based on [CN-]) in the last leaching tank. Hence the optimum levels were the lowest for oxides (about 500-600ppm), higher for transition ore (600-800ppm) and highest for deep sulphide ore at around 800ppm. The set-points were controlled manually by operators.

Cyanide results were based on potentiometric titrations performed every two hours by trained operators using a Metrohm potentiometric titrator. The potentiometric titrator lacked the software required to identify the free cyanide peak, so it was decided that the end-point was equivalent to solution potential of -117 mV.

The level of cyanide in the feed and the tail were also analysed by the on-site laboratory using a Metrohm potentiometric titrator. In this case the software was used to identify the free cyanide peak. However, there were issues with both methods which are discussed later in the paper.

Orica's OCM5500 On-line Free Cyanide Analyser was installed late in 2017. It was initially sampling tanks 2, 3 and 6, however it was recognised that due to Yanacocha strategy with dealing with various ore types, analyser will be best utilised by temporarily testing solutions from tanks 1, 2 and 6 for majority oxide feed, and 1,2 and 3 once other ore types than oxides are processed in larger amounts. Following is a description of the challenges and ultimately successes of using this on-line titrator in a gold-copper process.

2. Use of online cyanide and copper analysis – early challenges

As reported previously by Breuer and Rumball (Breuer & Rumball, 2007), potentiometric titration with silver nitrate is an excellent method to detect free cyanide in gold bearing CIP/CIL solutions. It is reportedly the best method to detect cyanide-limited conditions during leaching of complex gold-copper ores. Other methods, especially indicator-based titrations, include part of the slower leaching Cu(CN)32- complex (Breuer, Sutcliffe, & Meakin, 2011). This can inflate perceived free cyanide concentrations and lead to lower than optimum cyanide levels, which in turn can lead to lower gold recoveries.

Potentiometric titration can also be used to detect sulfide in solution, which can interfere with indicator-based methods (positive interference due to reaction with silver ion) and other automated methods as well. It can also be used for indicative detection of copper in solution – copper produces the third "peak" in the first derivative of the potential curve (equivalent to the highest slope of the potential curve vs silver nitrate volume), however it can be affected by other species like thiosulfate (Breuer et al., 2011).

However, when used in plant solutions, there are a number of challenges that can affect quality of the results:

- Usual detection of cyanide and copper peaks can be challenging because:

  - o Cyanide and copper peaks positions vary with respect to potential depending on many factors:

    - Concentration of copper in solution – the higher the copper concentration in solution, the more negative the potential at which the free cyanide peak will occur (Breuer et al., 2011)

    - Fouling of the silver electrode by silver salt deposits – fouling can lower sensitivity and also will affect the position of the peaks (Breuer & Rumball, 2007)

    - Potential drift caused by reference electrode's fouling/leaking out of the reference electrolyte which changes positions of the peaks, while also reducing sensitivity

  - o Peaks can be much lower than in laboratory-prepared solutions, especially copper peak can be very low and not much higher than the background

  - o Peaks can be numerous, but very hard to detect, depending on number of species present (Breuer et al., 2011)

- Other challenges – filtration and scale formation, although not affecting the analysis directly, have to be accounted for in the analyzer software, so that lower solution flows don't affect the results due to low sample volumes during titration.

3. Results

As mentioned previously, the number and variety of ores processed at Yanacocha makes it difficult to compare the circuit performance after a change has been implemented. The choice of the baseline is a complex problem, which can only be solved by the site personnel, who know the plant and the ore processed the best. The baseline choice was influenced by the following factors:

- Type of ore being processed before and after automation of cyanide dosing – most of the ore processed after automation was oxide ore

- Number of tanks on-line – any periods of tank maintenance were excluded

- Performance of the grinding and leaching circuits

As mentioned above, most of the ore processed after installation of the Orica OCM5500 analyzer, was oxide, so all the results presented below are based on that ore type only. Based on these factors, Newmont Yanacocha decided that the best period to use for the baseline was Sep – Mar 2018. This long baseline should average out all factors which are not currently measured in detail required for analysis – impact of different ores and their mineralogy, concentrations of reactive copper and sulfides, DO profiles, and some others. The effects were also studied for a long time to take into account the same variables that impact cyanide consumption and gold recovery during the baseline period.

To account for different performance of the various ore types in regard to cyanide consumption and gold recovery, it was decided to exclude from analysis 4 days of results after a change of processed ore type. This should ensure that all results are not affected by the transition periods when the results of the current ore type are affected to some degree by the previous ore type.

The impact on cyanide concentration control is illustrated by Figures 1-3 below. We can see that during the baseline, the spread of the actual concentrations is much larger than during the period with automatic control. It is also clearly visible that the automatic control reduced the time the leaching system is under dosed with cyanide, defined here as period of time, where actual cyanide concentration is below 80% of the setpoint – from 39% of the total time during the baseline period to about 14% (see Figure 3). This suggests that the automatic control should increase gold recovery, unless the cyanide concentrations experienced (including the low concentrations) are sufficient to provide optimum leaching conditions throughout the circuit. In that case, the site would be able to reduce the cyanide setpoint, which should result in cyanide savings.

[figure 2]
[figure 3
[figure 4]

Initially, use of the analyzer coupled with automatic control increased cyanide consumption from 1.42 kg/t during the baseline period, to 1.55 kg/t of ore (a 9% increase). This increase was influenced by the decision to increase the setpoint from 500ppm [CN-] to 600ppm [CN-] to offset any unforeseen reductions in cyanide dosing, when using the new and untested system. Actual average concentrations for these two periods gave even larger difference – 385 ppm for the baseline vs 654 ppm for the period after automatic control (based on operator titration results, not the analyzer results, as analyzer wasn't available during most of the baseline period). Given that the set-point during the auto control period was increased by 20% from the base, while actual results increased by close to 70% on average, and cyanide consumption due to copper and other minerals increases with increasing concentration of cyanide, with the average concentration remaining the same, the automatic control would result in cyanide consumption of about 0.91 kg/t – a reduction of about 35% from the baseline. However, this cyanide loss was more than made up by the increase in gold recovery from 78.45% to 83.01%. This is in line with reduction of the time the leaching system spends below the optimum cyanide concentration not just in the first tank, but also in the later tanks.

Table 1: Cyanide consumption and gold recovery results Sep 2017 - Dec 2018. Results in brackets for Jun – Aug 2018 are adjusted for increase in actual [CN-] from the [CN-] during baseline period.

Time period	NaCN Consumption (kg/t)	Au Recovery (%)	Reduction in NaCN use (%)	Increase in Au recovery
Sep 2017 – Mar 2018 (Baseline)	1.42	78.5	-	-
Jun – Aug 2018	1.55 (0.91)	83.0	-9 (35)	4.5
Sep 2018	0.86	82.3	39.4	3.8
Oct 2018	0.94	83.5	33.8	5.0
Nov 2018	0.65	81.6	54.2	3.1
Dec 2018	0.74	84.1	47.9	5.6
Jan 2019	1.25	80.0	12.0	1.5
Feb 2019	1.22	81.7	14.1	3.2

Subsequently, the site was able to experiment with lower cyanide setpoints and studying their impact on gold recovery. It's apparent that with further improvements in cyanide dosing control and reductions in cyanide setpoint during times of low consumption, as indicated by the cyanide concentration in the last leaching tank, the site was able to significantly reduce cyanide consumption without too much impact on the gold recovery. It is also apparent that the various subtypes of oxide ore can produce variable results with respect to gold recovery and cyanide consumption, which further justifies using a long baseline and testing periods. Results of cyanide consumption and gold recovery are presented in Table 1.

3.2. On-line analyzer OCM5500 copper results

Understandably, most of the effort initially was directed at steadying the process using the cyanide analysis and dosing control. However, use of the potentiometric method can be extended to analysis of sulfides and copper (Breuer & Rumball, 2007). Concentration of sulfides in leaching systems is usually low due to dissolved oxygen in the slurry, so analysis of sulfides is usually not of great benefit, unless it can indicate serious issues with earlier process stages, e.g. POX. In this case sulfide detection was switched off after an extended period of very low results for sulfide concentration. However, copper analysis in copper gold solutions can be of major benefit, e.g. it can be used as a forward indicator of cyanide consumption due to copper, and be used as a forward indicator for cyanide detox systems. Breuer et al. however cautioned that the copper results from potentiometric titrations can be influenced by other species that exist in the complex solutions of real leaching processes, e.g. thiosulfate (Breuer et al., 2011). To establish how the potentiometric titration performs in actual copper-gold plant solutions, analyzer copper results were compared to results from the on-site laboratory. A sample of the results is presented in the table below:

Table 2: Results of the copper analysis - analyzer vs laboratory

Date	Ore type	Laboratory result $[Cu]_{aq}$	Analyzer result $[Cu]_{aq}$
13/01/2019	Oxide	11 ppm	23 ppm
7/12/2018	Oxide	89 ppm	137 ppm
9/12/2018	Oxide	185 ppm	189 ppm
18/12/2017	DEEP	556 ppm	523 ppm

It is clear, that although not perfectly in agreement with the laboratory results, the potentiometric method can be used as a good indicator of the concentration of cyanide bound copper in solution, as well as an indicator of the likely cyanide consumption due to copper minerals in the ore. This result can then be used to adjust the cyanide concentration setpoint to maintain optimum leaching conditions in the whole leaching circuit. Orica's LeachIT software was designed to optimize cyanide concentration set-points based on reactive copper levels, amongst other variables, and could be used for that purpose (Zwolak & Leckie, 2016).

However, the results of the copper analysis overall were not reliable enough for control purposes. Due to the issues indicated previously, e.g. electrode fouling and deterioration or changes to copper peak position and size, the software was sometimes "looking" for the copper peak in the wrong section of the potential curve. Also, the copper peak tends to be much smaller, when testing real leach tank solutions, than what can be expected in clean laboratory-prepared solutions. These effects are illustrated below in Figures 4-6. All these effects combined to make the results too unreliable with the current software. Subsequently the copper analysis logarithm was changed to take account of all these effects. Results of the copper concentration using this new version of software will be presented at a later date.

[figure 5]
[figure 6]
[figure 7]

3.3. Flow-on effects

One of the consequences of lower cyanide additions was a significant reduction in peroxide usage in the cyanide detox process. Histogram of the peroxide consumption in total and as ratio of peroxide to cyanide is shown below.

[figure 8]
[figure 9]

It is clear from the above graphs that, although for some reason the ratio of peroxide to cyanide was at a yearly high during the baseline period, it fell to yearly lows during October to December 2018 period, with respect to overall usage of peroxide, and also as a ratio of peroxide to cyanide used in that period. This is clearly a result of reduced free and copper cyanide concentrations in the leach tail, as a result of lower cyanide additions at the front of the leaching circuit.

4. Conclusions

Potentiometric titration, as applied using Orica's OCM5500 Free Cyanide Analyzer, was proven to significantly increase gold recovery, while significantly decreasing cyanide consumption in a complex gold-copper ore process at Yanacocha Gold Mine. This was despite various challenges experienced in this highly complex environment. Consumption of peroxide in the cyanide detox process was also significantly reduced. All these results can be attributed to a much tighter control of cyanide concentration in the leaching tanks, which results in lower incidence of cyanide underdosing (loss of gold) and overdosing (loss of cyanide). Copper results were also validated versus the on-site laboratory and will be used in the future to adjust free cyanide setpoints, to ensure optimum leaching conditions throughout the leaching circuit. The copper concentration results were initially not reliable enough for process control, however the causes of the errors were analyzed, and the copper analysis algorithm was adapted to allow for effects experienced in on-line analysis in a copper-gold process.

Thanks

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Illustrations

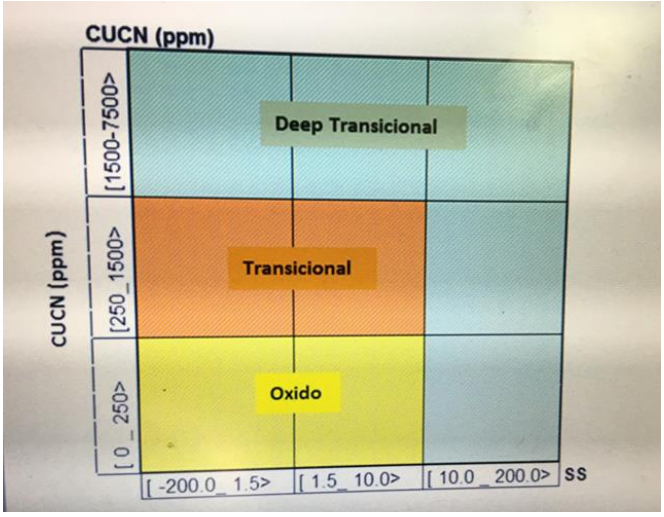

Figure 1: Various types of ore processed in Yanacocha gold mill.

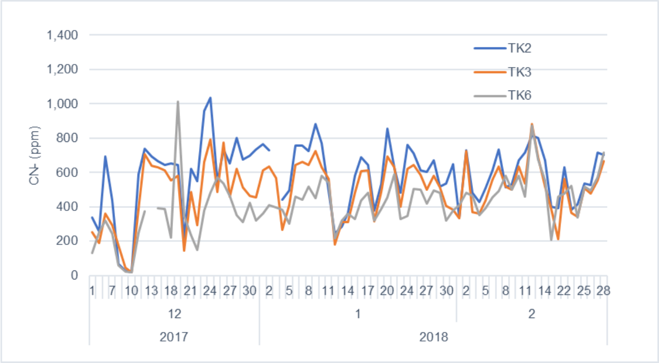

Figure 1: Typical profile of cyanide concentrations in the leach tanks with manual control at Yanacocha. Points indicate average daily cyanide concentration.

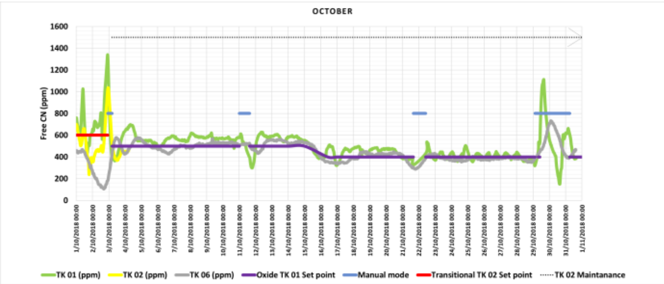

Figure 3: Effect of automatic control on cyanide concentration variability in Tank 1, 2 and 6.

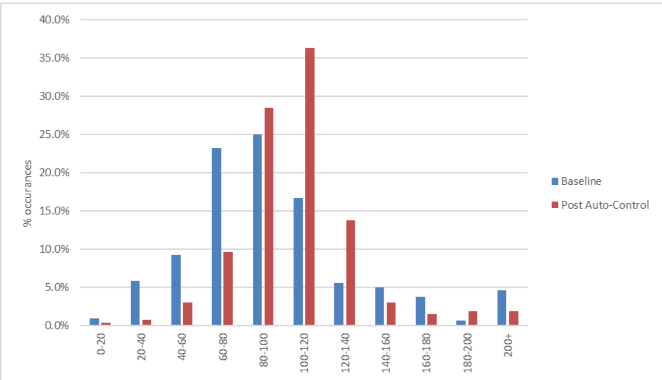

Figure 4: Impact of automatic control on actual cyanide concentration in tank 1. Oxide Ore: CN Control, Baseline 13/09/17-1/3/18. Post-auto control - 1/06/18 - 1/09/18.

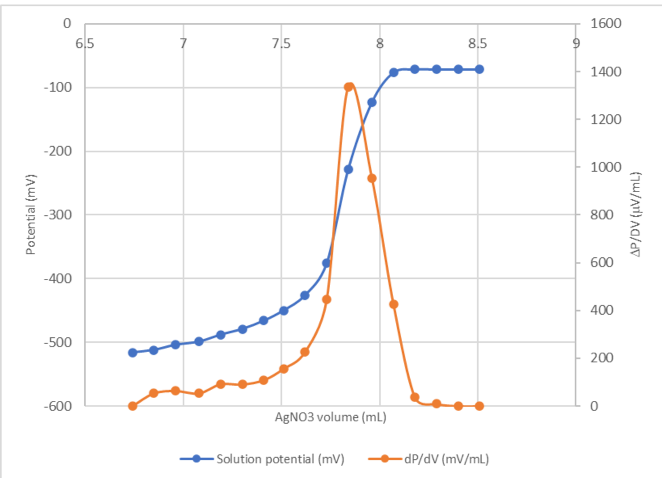

Figure 5: Cyanide-copper potentiometric titration (OCM5500) with no copper present. Large 1336 mV/mL cyanide peak at -228 mV.

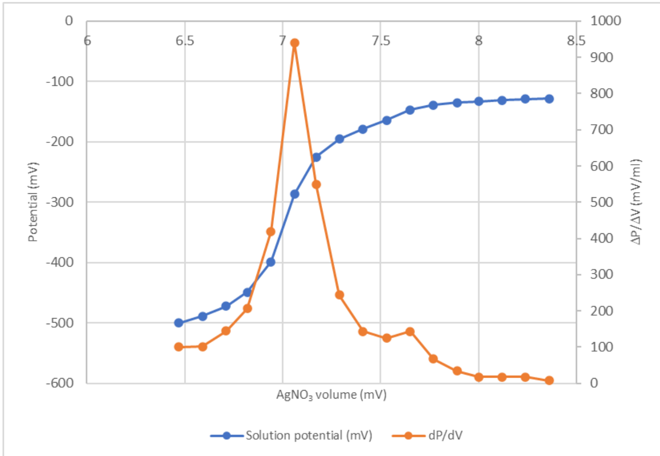

Figure 6: Cyanide-copper potentiometric titration (OCM5500) with shifted and reduced copper peak in oxide ore. Large 941mV/mL cyanide peak at -287 mV. Small 143mV/mL shifted copper peak at -147mV.

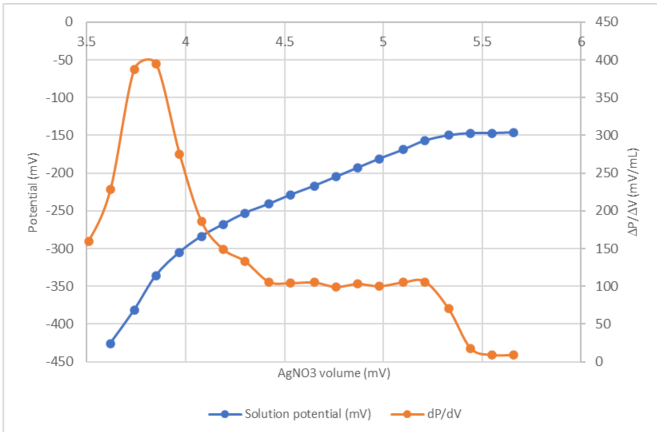

Figure 7: Cyanide-copper potentiometric titration (OCM5500) with shifted and reduced copper peak in sulphide (DEEP) ore. Copper peak is barely distinguishable from the background. Reduced 395mV/mL cyanide peak at -336 mV, Very small 106mV/mL and shifted copper peak at -157mV.

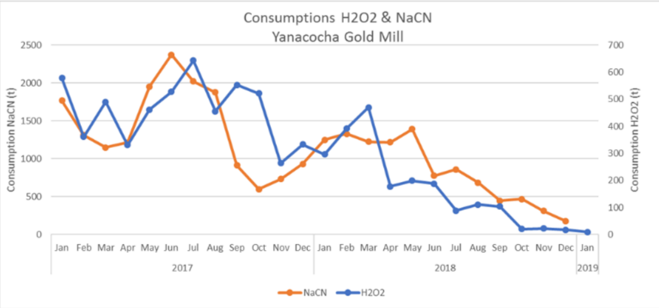

Figure 8: Consumption of H2O2 and NaCN in Yanacocha Gold Mill over time.

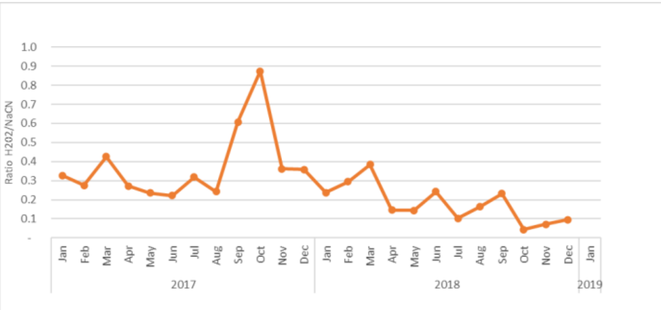

Figure 9: Ratio of H_2O_2 to NaCN in Yanacocha Gold Mill over time.

Professional profile

PhD in Chemical Engineering from UNSW (2009).
Bachelor in Chemical Engineering from UNSW (1998).
The lead cyanide leaching expert for Orica's global NaCN supply business which supplies almost 60 mines in 17 countries.
Author's name: Greg Zwolak
Charge: Senior Specialist Engineer - Cyanide
Enterprise: Orica Australia
Email: greg.zwolak@orica.com
Phone / Cell Phone: +61 419 803 016
Address: 16-20 Beauchamp Rd, Matraville, NSW 2170, Australia

Professional profile

Metallurgical Engineer from the Universidad Nacional Mayor de San Marcos.
Author's name: Brindel Barzola-Cruz
Charge: Technical Specialist Peru
Enterprise: Orica Peru
Email: brindel.barzola@orica.com
Phone / Cell Phone: +51 943 561 057

Professional profile

Metallurgical Engineer. Currently Superintendent of Metallurgical Services, Newmont Yanacocha, Peru.
Author's name: Gilmar Salvador Guzman
Charge: Superintendent of Metallurgical Services
Enterprise: Newmont Yanacocha
Email: gilmar.guzman@newmont.com
Phone / Cell Phone: +51 919 803 016

Professional profile

Industrial Engineer from the Catholic University of São Paulo, specialist in Applied Finance, Master in Business Administration and Advanced Project Management.
Author's name: German Chen-Diaz
Charge: Senior Manager - Marketing (Cyanide)
Enterprise: Orica Peru
Email: german.chen@orica.com
Phone / Cell Phone: +51 987 226 474

Professional profile

Chemical Engineer from Adelaide University
Author's name: Peter Leckie
Charge: Senior Manager – Commercial, Digital Solutions
Enterprise: Orica Australia
Email: peter.leckie@orica.com
Phone / Cell Phone: +61 423 290 363