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Gold-PM Keynote

FIXING THE CYANIDE ISSUE - ALLEVIATION OR REPLACEMENT?

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ABSTRACT

Cyanide processing has been the mainstay of hydrometallurgical gold recovery for over a century. The perception of a cyanide issue in relation to gold recovery seems to take little account of the number of people who have been harmed by it over the past century, or that gold recovery only consumes around 66,000 t/y out of the 1-2 Mt/y of global HCN production. A couple of key differences are that most of the current non-gold applications involve no off-site transport of the HCN and convert it into products with little potential for HCN release unless they are combusted.

Despite decades of research there is still no clear universal replacement in sight. Perhaps one has to remember that the initial driving force for application of cyanide was the high cost and low recovery for chlorine processing of 'lower grade' 'less oxidized' ores. This led to its use before its almost universal applicability was recognised, while the potential to dissolve gold in cyanide had been identified by researchers a century earlier. Our current understanding of thermodynamics and electrochemistry suggests there is little prospect of identifying a universal challenger to cyanide. However, as the remaining gold ores become more complex, more areas are identified where there are issues with the application of cyanide. Hence it is quite likely that some of the possible cyanide replacements can be developed to commercialisation for niche applications, as has been the case for thiosulfate at Barrick Goldstrike.

This paper reviews the current status of potential replacements for cyanide as well as the issues and the possible drivers for various niche applications.

In the absence of a cost effective replacement for cyanide, fixing the cyanide issue requires industry wide commitment to consistently address the real and perceived issues. The development and implementation of the International Cyanide Management Code has been a good start. Unfortunately, it will not be the 99% of compliance that attracts public, but the issues that slip through the net. Transport to site will continue to be viewed with concern, but the more significant issues are likely to be cyanide containing tailings and best practice water treatment for off-site disposal of excess water.

Keywords: Cyanide, Alternative Lixiviants, Thiosulfate, Tailings, Management, Water Treatment

INTRODUCTION

The Cyanide Issue

Cyanide as hydrogen cyanide (HCN) is used as an intermediate in chemical manufacture. The Cyanide Code web site estimates total global HCN production at 1.1 Mt/y, of which around 66,000 t/y (6%) is used in the gold mining industry[1]. Other sources estimate the gold mining proportion of cyanide use as high as 13%[2]. Evonik, who supply HCN production technology claim global production is over 2 Mt/y[3]. Whatever the precise figures, it is clear that the bulk of cyanide production attracts much less notice than the small proportion used by the gold industry. Figure 1 shows an estimated breakdown of uses of hydrogen cyanide in 2001[4].
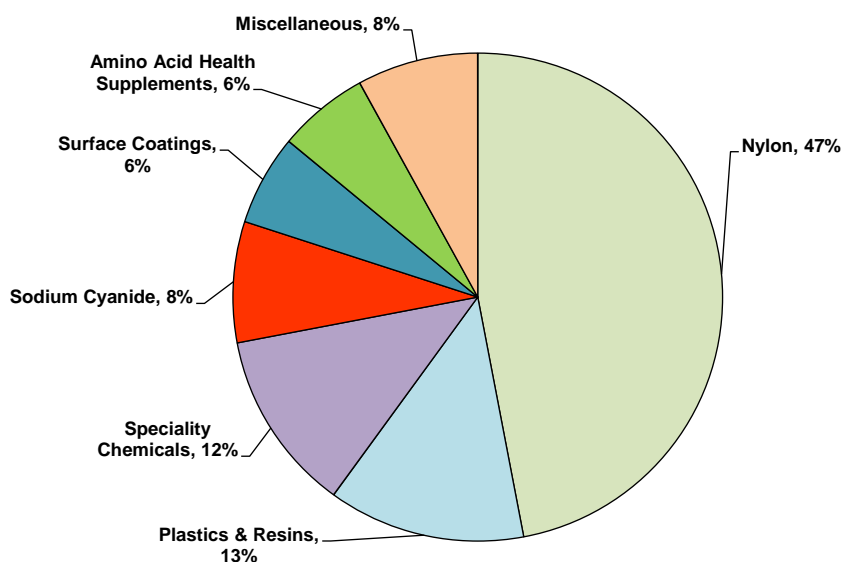

Figure 1: Estimated breakdown in hydrogen cyanide use in 2001 after Infomine[4]

When the word cyanide is mentioned many people immediately think of gold processing and mining disasters, but hospital emergency departments are much more familiar with people suffering cyanide effects from smoke inhalation. The link between cyanide and death has been reinforced by things like the cyanide suicide capsules in spy novels or wartime use in gas chambers. The hype can often lead to cyanide and related chemicals being portrayed as the principal villain in situations when they are only one of multiple factors, such as the HCN content in cigarette smoke, or the possible role of HCN in the deaths associated with the Bophal disaster.

These well-established perceptions of the hazards associated with gold recovery by cyanide are readily reinforced by pictures of tonnes of dead fish along rivers downstream of the Baia Mare tailings dam failure 17 years ago[5]. The Baia Mare tailings dam breach is often cited as a prime example that proves that the use of cyanide should be banned. It is not much of a defence to suggest that the heavily publicised downstream fish deaths in Yugoslavia may have been exacerbated by hypochlorite clean-up measures and dissolved heavy metals in leaked tailings solution, rather than just cyanide. The incident was certainly a wake-up call to the gold industry. One of the good things to come out of it was the development and implementation of the International Cyanide Code[6] to demonstrate a commitment to responsible practice. The incident highlighted the need for better water and tailings management. When the Baia Mare tailings treatment plant returned to operation five months after the spill, the new plant management added a cyanide destruction stage to the flow sheet. Often forgotten is the fact that the people involved in the Baia Mare disaster were extracting value from historic base metal tailings to aid in reducing the cost of their relocation away from city centre and possible groundwater pollution[7]. Baia Mare appears to now be back on the Rumanian tourist map and people can again eat fish caught in the Danube.

Cyanide does not accumulate or biomagnify, so chronic exposure to sub-lethal concentrations of cyanide do not appear to result in acute toxicity. No evidence exists of chronic exposure having teratogenic, mutagenic or carcinogenic effects[8]. Cyanide in wastewater is biodegradable under aerobic conditions at concentrations up to 200 mg/L but only up to around 2 mg/L under anaerobic conditions[9].

Both acute health issues from the high toxicity of cyanide and longer term health issues from tailings

containing heavy metals and their cyanide complexes can arise from exposure to gold plant tailings slurries. At the same time, low exposure to cyanide is non-cumulative. There have been no documented accidental human deaths due to cyanide poisoning in the Australian or North American mining industries over the past one hundred years[2], however the same cannot be said for wildlife[10] with multiple incidents on record.

We have to be careful with the suggestion that all the gold industry needs is a solution to the cyanide issue. By itself, removing cyanide from the equation will not create a social licence to operate, that remains the main challenge for the mining industry. A work injury to a single miner is often seen as motivation to question whether mining should be allowed to continue, while there are no suggestions to ban motor vehicles despite multiple deaths in road accidents. The fact that many people are ready to accept the 'necessary' risks of private vehicles, while entertaining thoughts of mining bans, demonstrates the slope on the playing field on which the mining industry operates. Solving the 'cyanide issue' will not level the playing field but it is a necessary part of earning the licence to operate.

PHYSICAL PROCESSING ALTERNATIVES

The simplest and most cost effective approach to operating without cyanide is to rely on gravity and flotation to produce concentrates that can be sold for processing elsewhere. These would account for most of the gold that is recovered as a by-product without the use of cyanide. It helps if the other minerals in the concentrate at least pay for the transport cost, if not cover the total cost of processing, as occurs with clean copper concentrates. Gold deportment determines potential gravity recovery and whether it is possible to generate a 'throw away' flotation tailing. For deposits where gravity and flotation can produce a cost effective solution there is no cyanide issue, as these approaches are always the first options to be considered in the development process. Things get more complicated with complex copper ores with higher penalty element content and worse for concentrates that cannot achieve an 'acceptable' copper grade or achieve gold grades of over 30 g/t. There are only a few mines that have been able to cost effectively sell gold concentrates without payable base metals.

ALTERNATIVE LIXIVIANTS

Alternative complexing agents, such as chloride, bromide, thiourea, and thiosulfate form less stable complexes than cyanide. Hence they require more aggressive leaching conditions, i.e. higher concentrations and stronger oxidants, to dissolve gold and silver and keep them in solution (see **Figure 2**)[11]. These reagents present their own risks to health and the environment. People make much of the lower acute toxicity of alternatives to cyanide without taking into account differences in reagent concentrations or even reagent consumptions. Thiosulfate has around 1/250 of the acute toxicity of cyanide, but its concentration in the tails solution at the end of the leach is at least 100 times that of cyanide, so there is not as much difference in acute toxicity of practical leach slurries than people might expect. In addition, while in some cases the unit costs of the reagents are lower than cyanide, a real comparison needs to take into account the concentration and consumption differences. In most cases the overall process is more expensive to operate. This helps to explain the ongoing dominance of cyanide as the primary reagent for the leaching of gold and silver from ores. Cyanide has become so fundamental to gold recovery that ores are defined as refractory on the basis of their response to leaching with cyanide.

There is no shortage of research on potential alternatives to cyanide, but it is a different story when it comes to demonstrating or even identifying commercially viable alternatives. The general dearth of commercial applications is evidence of incomplete development, demonstration of flowsheets and cost issues on top of reluctance for banks to lend money on unproven processes. Several phases can typically be identified in the search for alternatives lixiviants:

1) Initial research focuses on gold dissolution. If this seems promising then more systematic test work usually looks at extraction from some suitable ore types. Once this step has been repeated by several groups, the publicity machines start proclaiming that their researchers have demonstrated a new alternative to cyanide.

2) Months or years down the track other researches may get around to looking at how gold might be recovered from the solution complex identified in step (1), leading to claims of a viable alternative process for gold recovery. Step (2) May or may not include looking at how to strip the gold from the recovery step and produce gold metal!

3) Assuming steps (1) and (2) look promising, the process may be promoted as the solution to the cyanide issue, despite the parts in the process jigsaw puzzle that are still missing.

4) It is not until a mining company with a definite need for the process commits to trying to commercialise the new technology that the viability of the alternative can actually be determined. This step requires considerable determination and financial commitment. The different steps in the process need to be tested together and all the gaps in the earlier testwork such as reagent recycle investigated. It probably requires running a demonstration plant, but even that may not adequately close out longer term water recycle and tailings dam issues with the new technology. This step needs to gather the required data on which to engineer the process including:

- Reagent issues – concentration, leach recovery, consumption, recyclability, tailings facility issues

- Operating conditions – reagent concentrations, pH, Eh, temperature

- Constructability – residence time, pulp density, solid liquid separation, materials of construction

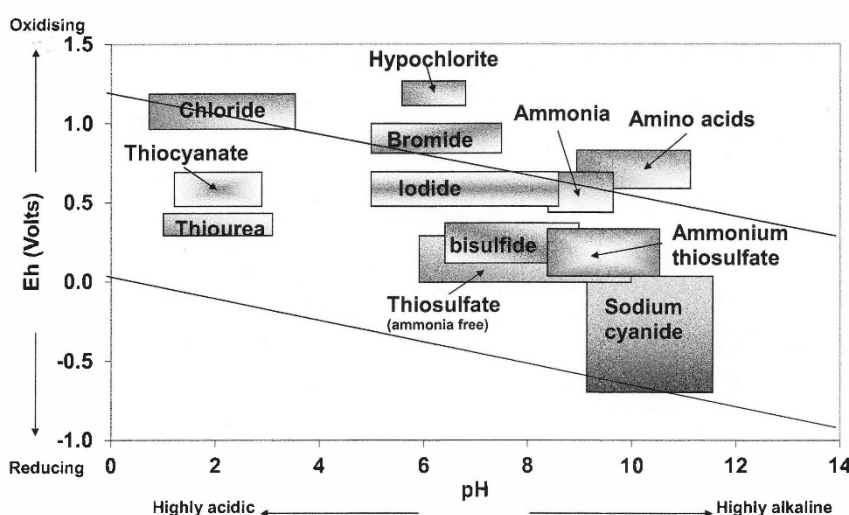- Gold recovery – adsorbent, elution, electrowinning and smelting to doré.

Figure 2 : Eh-pH operating conditions windows after Aylmore[11]

The ultimate step of demonstrating a viable alternative requires a full scale operating plant to prove that the technology is cost effective and free from hidden flaws, before there is any chance of less motivated (less desperate) companies considering adoption of the technology. Barrick has operated a full scale thiosulfate RIL process at Goldstrike for over two years to demonstrate its viability for a niche application on highly preg-robbing ore.

Thiosulfate, thiourea, chloride, thiocyanate and glycine are the better known alternatives to cyanide, but there are also a number of undefined options such as the Haber process, 'gold dressing agent' and EarthGold leaching reagent.

Commercialised Alternatives and Related Processes

Before cyanidation was developed, gravity and amalgamation were the main routes to gold recovery. However, by the mid-1880s many mines were getting into primary ore that responded poorly to amalgamation. Various experimenters discovered that hypochlorite, thiosulfate, bromine and chlorine could be used as gold leaching agents[12] so that these were in limited commercial use before cyanidation. The Platner process, with elemental chlorine dissolved in water, was one of the processing options used in Australia and North America to dissolve gold from ores and concentrates[13][14].

Amalgamation is still used by artisanal miners, but is generally accepted to be even worse than cyanide for the environment and for the miners. Thus it has no place in trying to solve the cyanide issue! Cyanidation replaced chlorine/chloride processing except in gold and platinum group metal (PGM) refining, where it is still the default process. Thiosulfate is commercially applied by Barrick at Goldstrike[15]. Thiourea was used by New England Antimony to recover gold from an antimony concentrate in the 1980s[16] and is currently used to strip gold from 'gold selective' resins, accompanied by metal recovery by electrowinning. Newmont also tested thiosulfate and thiocyanate leach systems on demonstration heap leach systems, without any subsequent commercial applications. Where alternative lixiviants have made it into commercial operations they are essentially for niche applications, rather than universal replacements for cyanide.

Chlorine and Chloride Systems

The reaction of chlorine with gold is as follows:

$$2Au + 3Cl_2 + 2Cl^- = 2[AuCl_4]^-$$
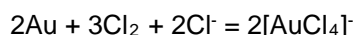
Under the highly oxidising conditions required for chlorination, sulfides are oxidised leading to high chlorine consumption or precipitation of gold from solution, if there is not enough oxidant to destroy the sulfides. Hence chlorination was usually preceded by roasting or base metals could be removed by acid pre-treatment. Silver may also need to be extracted by pre-treatment due to the low solubility of silver chloride, though its solubility is improved at high chloride concentrations. Another issue with the original Platner process was that gold extractions could be as low as 50%, with recovery by amalgam or cementation onto copper or iron giving an impure product[17]. Hence, it was easily displaced by cyanidation that offered lower cost, higher recoveries and avoided the hazards of working with chlorine gas. However, modern chlorination processes can offer faster leaching rates than can be achieved with cyanide or thiourea[18]. Chlorine / hydrochloric acid mixtures are still the basis for most gold and platinum group metal (PGM) refining processes and gold chloride baths are used in electroplating.

Chlorine has been commercially used to passivate preg-robbing natural carbonaceous matter in Carlin ores ahead of cyanidation and was also tested by the United States Bureau of Mines (USBM) to leach the gold, with recovery on activated carbon (Carbon-in-Chlorine Leaching – CICL). However, they provided no information on gold loadings on the carbon or how the gold might be recovered from the carbon[19].

More recently the Platsol process has been developed[20] as a single step autoclave process to oxidise sulfides and get gold and base metals into solution. It was originally developed for Cu-Ni concentrates containing PGMs and gold from the Northmet deposit, but has been proposed as an option for gold recovery from non preg-robbing refractory gold concentrates. It builds on previous work[21][22] on pressure oxidation in chloride solutions (6 g/L sodium chloride (NaCl) at 210-230°C), with sulfide oxidation and gold dissolution in a single step. The gold stays in solution in the autoclave discharge through flashing and solid liquid separation in the presence of 5-10 g/L NaCl and thanks to the use of ceramic grinding media in regrinding to a P_{80} around 15 µm, so that there is no iron present to cement out the gold. The gold can be recovered onto activated carbon. In tests, total gold + platinum + palladium loadings of around 650 g/t were achieved on the carbon, but the gold contribution was only around 90 g/t with significant base metal loadings of 4.2 kg/t iron, 2.2 kg/t copper and 0.96 kg/t nickel. The gold and PGMs could be eluted by a pressure Zadra caustic cyanide elution, but the iron was not stripped by acid washing and the carbon activity could not be restored by thermal regeneration, so precipitation with sodium hydrosulfide (NaSH) was also investigated for gold recovery. It is possible that the carbon poisoning was due to the Northmet liquor composition.

Intec has developed an at atmospheric pressure single stage chloride leaching process[23], , to treat dirty low grade copper concentrates and dissolve gold as gold chloride. The process has been adapted to treat gold concentrates ground to a P_{80} of <40 µm. It is carried out at around 75-100°C in concentrated sodium/calcium chloride brine with some sodium bromide; at a total halide concentration of 6-8 molar (mol/L). Leaching is carried out in closed circuit with electrowinning. Halex a mixed sodium bromide-chloride complex ($NaBrCl_2$), that is a strong oxidant is generated at the titanium anodes and recycled to the leach to supplement oxidation from air addition. Sulfide sulfur is oxidised to elemental sulfur. The gold process is run with 60-80 g/L copper in the leach solution to act as a catalyst. Dendritic copper is recovered at the cathode as the cells operate at three times the current density and half the cell potential, of normal sulfate electrowinning. The highly corrosive acidic conditions (pH 1-2) require the use of high performance plastics, fibreglass or titanium for wetted parts. After solid liquid separation, the gold is recovered in packed beds of activated carbon

or ion exchange resin, with silver recovery by silver selective resin after the gold recovery. Carbon can be stripped and reused without thermal regeneration for at least five cycles, or loaded to higher levels and smelted. While the process deals with sulfides it is not suitable for carbonaceous ores that would result in preg-robbing during the leach. Arsenic is precipitated as scorodite and iron as haematite.

JX Nippon Mining & Metals has developed the Nikko chloride process for gold containing low grade copper concentrates[24]. It has some similarities to the Intec process, but bromide is only used in the second stage of gold extraction, with all the copper, silver and 70-85% of the gold leached in 4 mol/L NaCl. After solid liquid separation iron is precipitated as goethite ahead of copper solvent extraction (SX). The hydrochloric acid raffinate after copper SX is returned to the leach and air sparged in to the tanks to give around 20 g/L cupric chloride and 5 g/L ferric chloride as oxidants. Silver is extracted by SX after the copper, while gold is extracted with activated carbon. The process was able to extract >90% of the gold and >98% copper from Newcrest concentrates from Telfer and Cadia.

Outotec have proposed several chloride based processes utilising their processing equipment and capable of dissolving gold. HydroCopper[25][26] was targeted at the same low grade/dirty copper concentrate market as Intec and Nikko and has similarities to both the other processes. Gold in the copper concentrate is leached as the gold chloride complex and can be recovered on activated carbon. The process was also capable of leaching gold bearing pyrite by adjustment of the redox potential. HydroCopper proposed leaching at atmospheric pressure in concentrated chloride (near saturated 250-280 g/L NaCl) solution with cupric ions (40-60 g/L) as oxidant. Chlor-alkali electrolysis of NaCl was proposed to generate chlorine to supplement air for oxidation to increase gold dissolution, with the hydrogen from chlor-alkali used to reduce the copper oxide precipitated with NaOH from chlor-alkali cell, to copper metal. It was noted that arsenopyrite can be oxidised under the same conditions as copper concentrates with air as oxidant to get to an Eh of 800 mV, but chlorine addition was required for pyrite oxidation to get the Eh to 850-950 mV. In the absence of gold containing pyrite the process Eh can be fine-tuned to minimise pyrite oxidation but keep gold in solution. The multi-stage leach used intermediate thickeners to recover solubilised copper as in the Nikko process. It was noted that the more oxidizing conditions required for pyrite oxidation put arsenic and iron in solution and oxidised sulfur to sulfate requiring lime addition. While the process could operate as a single step process for gold dissolution from pyrite the chlorine requirements made it uneconomic.
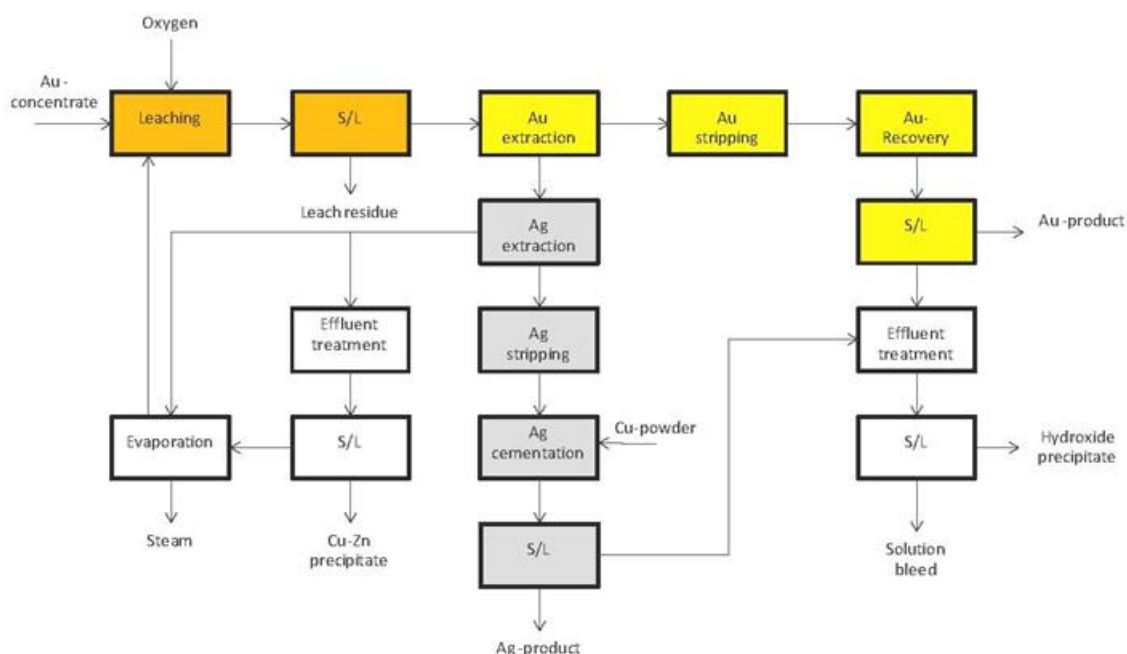

Figure 3: Outotec gold chloride process after[27].

More recently Outotec[27] has proposed a fast acidic (pH ~1.7) gold chloride/bromide leach process as shown in **Figure 3**. However, the process is only suitable for oxidised ores or materials that have already been pre-treated by roasting or pressure oxidation, to avoid the cost of chlorine for oxidation of sulfides. The ore is leached at 80-90°C in the presence of around 100-225 g/L chloride and 40-80 g/L bromide. The main advantages are that it does not use cyanide and offers much faster leach

kinetics with similar or slightly better recovery of the gold as metallic gold on activated carbon. However, high reagent concentrations and the need for efficient liquid/solid separation and washing to retain reagents in the circuit present operating challenges.

Dundee Sustainable Technologies[17][28] have also proposed a chloride (sodium hypochlorite and sulfuric acid) based gold recovery processes that may be applicable to high grade ores and flotation concentrates, where cyanide is banned. The hypochlorite is produced by electrolysis of a brine with 300 g/L NaCl and 1-3 g/L NaBr. They provided an estimated operating cost for the chlorination loop part of the process (see **Figure 4**) of US$ 156/oz on 4.3 g/t feed ($21/t) for 91-97% extraction from oxidised ore. However, they did not provide an indication of the overall cost including the more ore specific sulfide oxidation (roasting) and base metal leach pre-treatment steps that would be required ahead of chlorination to process sulfide ore.

There are several chloride based processes on offer from technology vendors but to date none have been commercialised. The strongest potential driver would appear to be treatment of high value concentrates, at sites where the use of cyanide is prohibited, as targeted by the Dundee and Outotec chloride gold processes. Both of their flowsheets incorporate stages such as solid-liquid separation / filtration and evaporation to manage the water balance and recycle chemicals. These aspects add capital cost, but are required to make the flowsheet operate. They could well increase the appeal for an environmentally sensitive location and may just stack up if the feed grade is high enough.
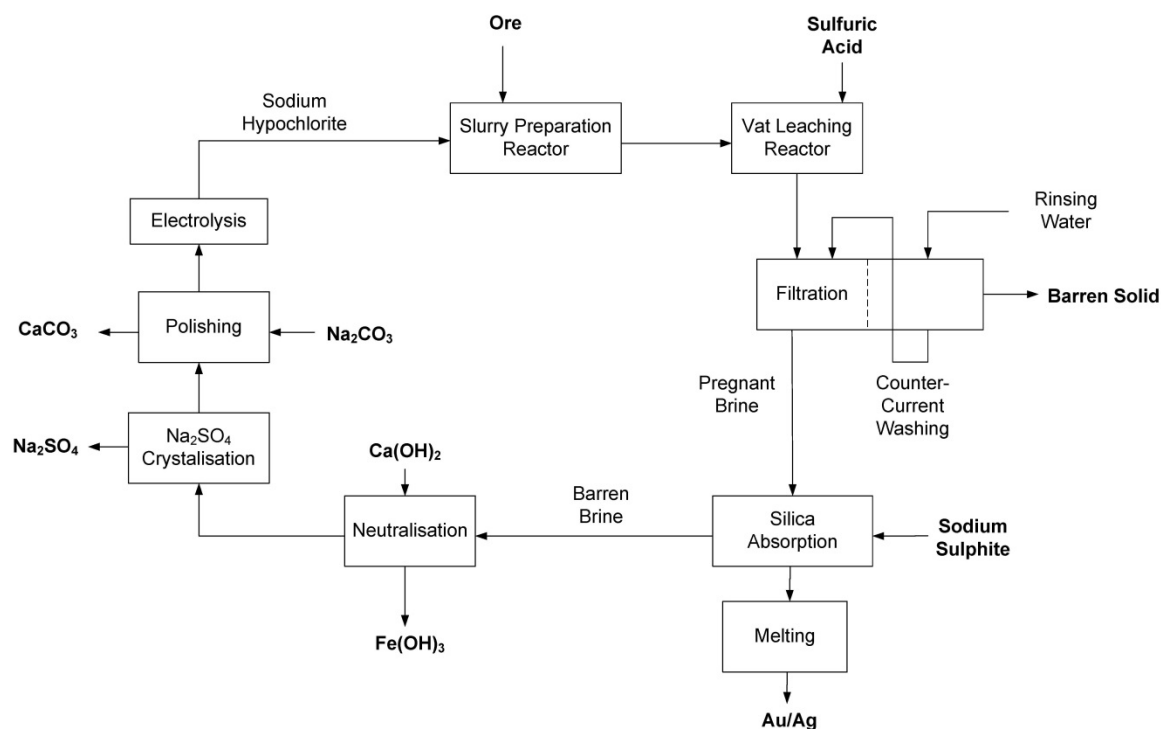

Figure 4 : Dundee Sustainable technologies gold process after[28]

Thiosulfate

More research has gone into the application of thiosulfate than any other alternative options. Most of the work has been focused on the use of the ammonium thiosulfate (ATS) system, as it offers the highest leaching rates with copper(II) as oxidant. As seen from the operating windows shown in **Figure 2** non-ammonium (calcium thiosulfate (CaTS) and sodium thiosulfate (NaTS)) systems can be used over a wider pH range from at least 7-10, but require slightly more oxidising conditions than cyanide[11].

$$4Au + 8[S_2O_3]^{2-} + 2O_2 + 2H_2O = 4[Au(S_2O_3)_2]^{3-} + 4OH^-$$
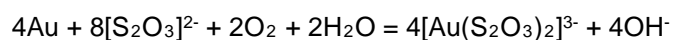
The chemistry of the thiosulfate leach system is complicated by the fact that oxidation of thiosulfate occurs at a lower potential, than that required to form the gold thiosulfate complex. Hence thiosulfate degradation to polythionates, $(S_nO_6)^{2-}$ and sulfate occurs in parallel to gold leaching. Polythionates can hinder the gold leaching process, as well as contributing to thiosulfate consumption.

Multiple reviews of the work on thiosulfate have been published over the past 15 years including recent comprehensive reviews by Aylmore[11][29]. Unlike many of the other alternative lixiviants, where almost all the work has been done by university researchers or technology developers, there has also been significant work by potential users. Technology developed by someone who needs it is more likely to end up being applied, than something developed by researches that becomes just another potential solution looking for an application. Newmont, Barrick and Placer Dome have all carried out work at up to large pilot plant scale. The motivation has been to identify alternative treatment options for their carbonaceous Nevada ores that cannot be treated by cyanidation, unless they are first roasted. This work resulted in all three companies taking out patents for different aspects of thiosulfate processing.

Newmont[30][31][32] tested out ATS heap leaching following bio-oxidation on 'low grade' (1-5 g/t Au) double refractory Carlin carbonaceous sulfidic ore. Leach solutions ran at 10-40 g/L ATS (7-30 g/L thiosulfate, S_2O_3 - TS) with 2-5 g/L free ammonia and up to 60 mg/L Cu at pH ~9, for reagent consumptions up to 7.3 kg/t TS. Between 1995 and 1999 they processed 1.24 Mt of ore in four ~300,000 t heaps, with ore crushed to -19 mm and a cycle time of 90-176 days. Two campaigns looked at direct ATS leaching and two at ATS leaching after heap bio-oxidation. When bio-oxidation was used the heaps were reclaimed and neutralised with lime before ATS leaching. Gold was recovery by cementation onto copper powder, with the barren solution recycled to the heap. Gold recoveries ranged from 51-70%, compared with less than 20% by cyanidation on the same ores.

Thiosulfate is the only one of the alternative lixiviants with a current full scale operating plant treating autoclaved sulfidic carbonaceous ore using CaTS with gold recovery by RIL (see **Figure 5**). The challenges of commercialisation of alternative lixiviant technology can be seen in that it took almost two decades of research and development by Barrick[33][34][35][36] and other groups before the commercial plant at Goldstrike, Nevada was commissioned at the end of 2014.
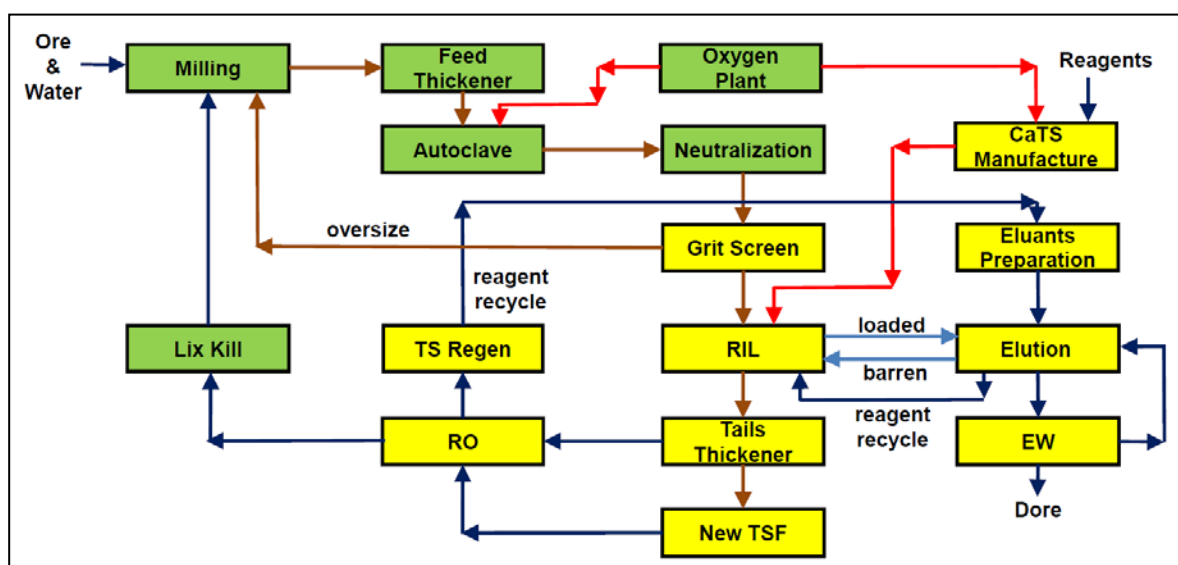

Figure 5 : Simplified Barrick Goldstrike flowsheet after[35]

CaTS leaches gold more slowly than copper catalysed ATS, as it relies on oxygen for oxidation rather than the copper(II) ammonia complex in the ATS system. The disadvantage of the slower leaching rate is balanced by lower thiosulfate consumption. In addition, the use of CaTS avoids ammonia emission issues and reduces build-up of dissolved solids in in the leach liquor, as the solution concentrations of calcium and sulfate from CaTS oxidation are stabilised by gypsum precipitation. The slower CaTS leaching rate is adequate for the pressure oxidised Goldstrike ore as the solid solution gold within sulfides in the ore is converted to ionic gold during pressure oxidation[29]. The process was tested on a 5 t/d demonstration plant at Goldstrike to provide data for detailed engineering of the full size plant. Gold recovery averaged 75-80% over the 16 months of operation on mainly acid autoclaved material. Using RIL in thiosulfate processing of highly preg-robbing carbonaceous materials more or less doubles the gold recovery[35]. Not only does the resin remove gold from solution to prevent it been preg-robbed onto carbonaceous matter, but it also adsorbs polythionates from solution preventing passivation of the leaching process.

The commercial driver for the application of CaTS at Goldstrike was a search for technology that could use the existing autoclave mill, to extract gold from the remaining high carbonate high preg-

robbing ores, more cheaply than building a second roaster[15] At the time these ores could only be treated by cyanide after roasting. The solution that was identified was parallel trains of acid and alkaline pressure oxidation in the five larger autoclaves. Autoclave discharges from the acid and alkaline streams were combined, neutralised and sent to two parallel RIL trains[37]. CaTS and copper sulfate are added to first tank to achieve a target ~0.1 mol/L (11.2 g/L TS) concentration in the leach in each train. Resin flow is co-current in the first two tanks and counter current in the rest of the circuit, to maximise gold recovery and minimise the effect of polythionates competing with gold on the resin.

The elution procedure is similar to the process described by Jeffrey[38] but uses a sulfite-trithionate mixture rather than the sulfite-chloride system originally proposed by CSIRO[39] (see **Figure 6**). Identification of the benefits of the addition of sulfite to the eluant was the major CSIRO contribution to the process. As shown in[38][39] sulfite addition generates a mixed gold sulfite-thiosulfate complex that is more easily stripped from the resin. It also enables the gold to be electrowon without cathode passivation by gold sulfide[38], after which the sludge is retorted and smelted.
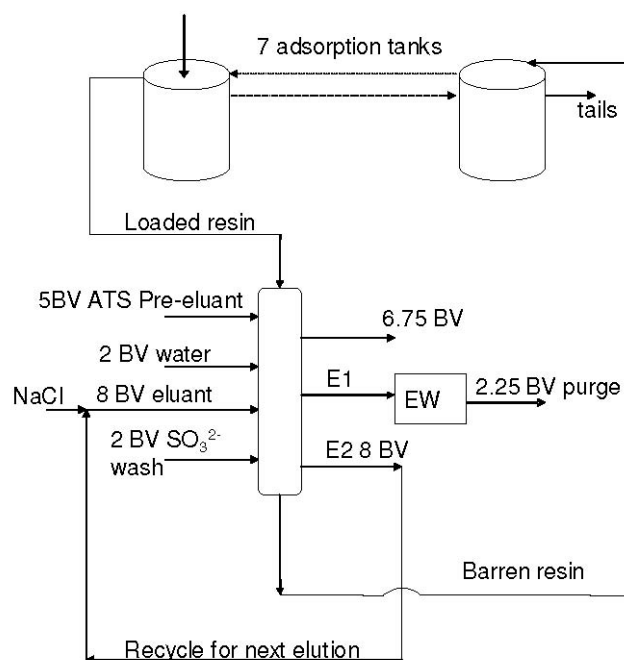

Figure 6 : CSIRO developed chloride/sulfite elution circuit after[39]

The higher reagent concentrations required for alternative reagents means that as much as possible of the reagent needs to be recycled. A further complication in the treatment of preg-robbing ores is that no lixiviant can be tolerated in the comminution circuit. Hence the recycle loop needs to be able to generate clean water and concentrated reagent to be recycled to the leach. To achieve this the circuit includes a tails thickener[40][41], with the overflow sent to membrane treatment (see **Figure 5**). The reverse osmosis (RO) stage provides a pure water permeate stream that is the main water source for comminution, while the concentrate stream recycles thiosulfate back to leach circuit via a regeneration circuit to control the concentration of polythionates ($S_nO_6^{2-}$).

Even though the process operates at pH values only slightly lower than cyanidation, the corrosivity of thiosulfate necessitates the use of stainless steels, plastics or nitrile rubber. In particular, the use of both copper and carbon steel has to be avoided as both are rapidly corroded and precipitate gold from solution.

The Goldstrike plant has demonstrated a niche application for thiosulfate RIL processing for autoclave treated highly preg-robbing carbonaceous ores. Barrick has carried out further testwork to potentially extend the application of their thiosulfate technology to oxide ores that have not been autoclave treated[42]. However, capital, operating and recovery issues show that the current technology does not offer a general replacement for cyanide beyond carbonaceous ores.

Thiourea

Acid Thiourea

The cyanide process was already fairly well established by the time Moir suggested the use of thiourea as an alternative lixiviant for gold processing in 1906[43]. Despite a few publications in the 1940s nothing much more was heard about thiourea until the 1970s when researchers at the South African Chamber of Mines Research Organisation (later to become Mintek) looked at it for possible leaching of both gold and uranium in a single process or making use of its lower toxicity for in-stope leaching[44][45]. As a result of the South African work thiourea became flavour of the month in the 1980s attracting research in USA[46], Australia[47] and Canada[48]. The level of interest was reduced when it was reported that some tests suggested that thiourea might have carcinogenic properties. Nevertheless researchers continue to work on application of thiourea for gold processing[11].

$$Au + 2NH_2CSNH_2 + Fe^{3+} = [Au(NH_2CSNH_2)_2]^+ + Fe^{2+}$$
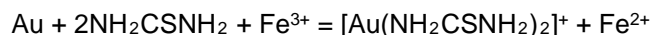
As shown in **Figure 2** thiourea requires slightly more oxidizing conditions than thiosulfate (around 400-450 mV Eh, using oxidants such as iron(III), peroxide or manganese dioxide. Unlike cyanide and most of the other alternate lixiviants, the gold thiourea complex is cationic, so it can be preg-robbed onto materials with cation exchange capacity, such as clays containing montmorillonite. Although the region of stability extends to around pH 3, highest gold recoveries are achieved around pH 1[47] at a thiourea concentration of at least 10 g/L. Thiourea itself is oxidised to formamidine disulfide at a slightly higher potential than that required for formation of the gold thiourea complex, or can be hydrolysed to urea and hydrogen sulfide. Formamidine disulfide is itself unstable, decomposing to give thiourea, cyanimide and elemental sulfur. Thus, thiourea decomposition products can accumulate with solution recycle and may affect gold recovery[49][50]. Hence application of thiourea leaching requires good control of pH and Eh. Failure to appreciate these issues with all reagents added at the beginning of a test may account for the fact that different researchers have reported thiourea consumptions of up to 47 kg/t[11]. Some research has investigated the use of thiourea stabilisers[51] (such as sulfite) or ferric complexing agents[52] to reduce the issues from thiourea decomposition.

Gold can be recovered from solution onto activated carbon. Unlike the chloride system where most of the gold is present on the carbon in the form of metallic gold, most of the gold remains as the gold thiourea complex, though some metallic gold can also be detected[53]. For some ores silver recovery can be significantly less than gold recovery[47][49].

The first and probably the only commercial application of thiourea in the western world was commissioned in 1982 and ran for at least 2 years[16]. New England Antimony used acid thiourea leaching with ferric iron as oxidant, to recover gold from an antimony concentrate (68% Sb with 40-50 g/t Au), before it was sent for smelting. Unlike copper concentrates where smelters pay for most of the gold value, no credit is provided for gold in an antimony concentrate. The leach process gave 50-80% gold recovery, depending on gold liberation (pyrite encapsulation) and antimony concentration[16]. It was run as an 8 t batch process, with a gold leach time of around 15 minutes within the 8 hour process cycle. After solid/liquid separation the gold was recovered onto powdered activated carbon. This was filtered off and sold for smelting at a gold loading of 6-8 kg/t. Thiourea consumption was up to 2 kg/t.

Newmont tested thiourea leaching following heap bio-oxidation of a carbonaceous sulfidic Nevada ore on a 495 t heap[50]. Laboratory tests showed that although the sulfides had been partially (~40%) oxidised, the carbonaceous matter remained preg-robbing with virtually zero recovery achievable by direct cyanidation. A laboratory column test was able to give 44% gold extraction after 41 days with a thiourea consumption of 5.4 kg/t. However, only 29% of the gold was extracted from the 495 t heap over 110 days, so the test was terminated before it was complete. During the test gold recovery by both strong base cation resin and activated carbon were investigated. Neither was particularly successful with all gold loadings below 190 g/t. Gold loading on the resin was limited by high loadings of iron and other base metals present in the acidic solution. Both resin and carbon were affected by elemental sulfur coatings (that may also have limited gold leaching!). The heap had been drained after bio-oxidation and washed with water, before application of the acidic 10 g/L thiourea solution. However, it would appear that this might have been less successful than in the laboratory column, leading to higher concentrations of iron in solution that swamped the resin loading capacity. The pregnant liquor typically only assayed 1 g/L thiourea so that there was plenty of scope for elemental sulfur generation from thiourea degradation. Given the fact that the gold thiourea complex can be recovered onto activated carbon, it is surprising that anyone would test thiourea leaching on preg-

robbing carbonaceous ore, apart from the attraction that an acid lixiviant avoided the need to reclaim the heap and neutralise the ore ahead of gold leaching. The point is also well made by the researchers[50] that there had been very little previous work with recycled thiourea solution[49]. (The New England Antimony plant used a batch process with a 15 minute leach that neatly avoided most of the detrimental effects of thiourea decomposition products[16].) Perhaps the most surprising result of the Newmont test was that they did actually recover 29% of the gold.

Thiourea is in commercial use for stripping gold from strong base gold selective resins such as the Russian AM-2B resin[54] or Dow Amberplex 91419. Thiourea is used as the gold thiourea complex is a cation. Hence once it is formed the gold is no longer held on the anion exchange resin. Stripping is typically carried out at 50-60°C with a solution containing around 76 g/L thiourea in 50-60 g/L sulfuric acid[55][56]. Gold is recovered by electrowinning in a Zadra type process with the column in closed circuit with electrowinning.

Alkaline Thiourea

As previously noted the acid thiourea system is only used below pH 3, especially if iron(III) is used as oxidant. However, researchers have shown that thiourea can be used in alkaline solution with appropriate choice of stabilisers and oxidant. Zheng et al.[57] tested alkaline thiourea leaching on several ores. In all tests they observed lower recoveries than could be achieved with acid thiourea and almost all tests resulted in lower recoveries than could be obtained with cyanide. However, somewhat lower recovery is not necessarily the end of the story if environmental regulations prohibit the use of cyanide.

Jin Chan[58] offer an 'environmentally friendly gold dressing' agent, also known as 'golden cicada'. They claim it can be used as a direct cyanide substitute, with gold recovery onto activated carbon. According to Chinese patent application 201510900415, the product manufactured by Guangxi Senhe High Technologies has a composition of: 40-60 parts thiourea, 20-40 parts potassium ferrocyanide, 10-15 parts sodium tripolyphosphate, 8-15 parts ammonium iodide, 10-15 parts ammonium persulfate, 8-12 parts sodium peroxide, 20-40 parts sodium carbonate, 5-10 parts sodium hydroxide and 4-8 parts sodium dodecyl sulfate. According to the Senhe High Technologies internet site[58] the product is used on an oxidised ore at the 1,000 t/d Gansu Xihe County Zhongbao Mining Co., Shandong Gold group processing plant to give >88% gold recovery by CIP. They claim it is also used at the 500 t/d Gansu Hongyuan Mining Co., National Green Mine Pilot Organisation plant to give ~91.3% gold recovery in an 18-22 h leach at pH 11-12, at a reagent consumption of 0.2-0.3 kg/t. So perhaps alkaline thiourea leaching may have reached small commercial scale. However, while their process is claimed not use cyanide the patent abstract suggests the lixiviant contains 'cyanide' in the form of potassium ferrocyanide.

Thiocyanate

Thiocyanate was first suggested as a gold lixiviant in the early 1900s however, it escaped further attention for gold recovery for almost 80 years[59] until picked up in South African research in the 1980s as a possible single step leach for gold and uranium[60].

$$Au + 2SCN^- + Fe^{3+} = [Au(SCN)_2]^- + Fe^{2+}$$
$$Au + 4SCN^- + 3Fe^{3+} = [Au(SCN)_4]^- + 3Fe^{2+}$$
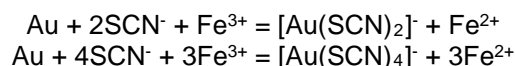
While thiocyanate was slightly more successful than thiourea in achieving the goal of a single lixiviant for both metals, thiocyanate consumption was too high under conditions that maximised gold extraction, while the pH was too high for effective uranium extraction under conditions that minimised thiocyanate consumption. Optimum conditions for gold leaching were ~10 g/L thiocyanate with ~2.5 g/L iron(III) at pH ~1.5 (to give >650 mV Eh) at 22°C. While these conditions favoured gold dissolution they resulted in ~50% thiocyanate decomposition over 24 h. Although >650 mV is well above the theoretical decomposition potential for thiocyanate, it is partly stabilised by formation of ferric thiocyanate complexes, $[Fe(SCN)_n]^{(3-n)-}$. These are less stable than the gold thiocyanate complexes so can release lixiviant and oxidant for gold leaching. If the leach potential was not controlled a fall to 560 mV could result in all the gold precipitating as metallic gold[60].

During the 1990s Newmont evaluated the use of thiocyanate for gold extraction after bio-oxidation in bottle roll and laboratory column tests[61] in comparison to cyanide. Twenty-four hour bottle roll tests with 2.9 g/L thiocyanate and 5-10 g/L iron(III), achieved 64% gold extraction with thiocyanate, compared to 69% with cyanide. In column tests thiocyanate achieved 52% gold extraction at a reagent consumption of 0.6-0.8 kg/t over 16 days, while slower leaching cyanide only gave 40.6%

extraction after 16 days, but cyanide consumption was only 0.33 kg/t. Gold was recovered from the thiocyanate heap leach solution by cementation onto iron. The leach tests showed that thiocyanate was nearer to cyanide in performance than thiourea and still able to save the cost of heap reclamation and lime neutralisation after bio-oxidation. Newmont has continued investigations of gold recovery using thiocyanate in conjunction with researchers at the University of Utah[59][61] and taken out patents on the processing[62].

The gold thiocyanate complex can be recovered onto activated carbon or anion exchange resin[60][63], but carbon catalyses decomposition of around half the iron(III) in the solution[60]. Gold can be eluted from the resin by an alkaline thiocyanate-cyanide mixture or acid thiourea. Newmont has also investigated gold recovery by solvent extraction[62] as they claimed the upgrade from solution to adsorbent on resin was not as high as with carbon in the cyanide system. Results in their patent[62] show equilibrium gold loadings on standard strong base resin of 13.7 kg/t at 1 mg/L gold in 1.2 g/L thiocyanate solution, falling to 4.8 kg/t at 1 mg/L gold in 2.9 g/L thiocyanate.
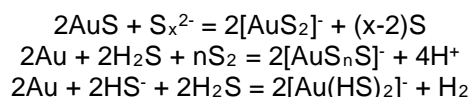
While the performance of thiocyanate seems to be nearer to that of cyanide and is certainly less toxic, it is not as readily available as a bulk chemical[11]. Despite the lower toxicity its concentration in tailings is regulated in countries such as Russia. The standard copper catalysed Inco SO_2/air destruction process used for cyanide hardly affects thiocyanate. The need to use reagents like ozone or Caro's acid for thiocyanate destruction, plus higher reagent concentrations would further increase the cost of application of thiocyanate. Given that one of the objectives of looking at alternatives was to get away from cyanide, using a chemical that sounds as though it still contains the cyanide, and in theory can be oxidised to HCN as one of its potential intermediate decomposition under leaching conditions[59], may not be the most robust solution.

Sulfide / Polysulfide / Bisulfide / Sulfite

Various sulfide / bisulfide / polysulfide systems have been proposed for gold recovery and gold dissolution by sulfide and polysulfide has been trialled commercially. The original elution process for activated carbon developed by Zadra at the USBM, that was piloted at the Getchell mine, used caustic sodium sulfide solution to strip the gold from the carbon[64] before it was electrowon. The caustic cyanide Zadra process, for which the man is rather better known was the second iteration developed a couple of years later[65]. In testwork Zadra showed that carbon could be eluted at 25°C in 4 hours using the sodium sulfide system. However, the process did not elute silver and base metals, plus the gold could be readsorbed onto the carbon[66] if the sulfide concentration got too low, as carbon catalyses reactions of sulfide to polysulfide and elemental sulfur.

Gold dissolution by polysulfide was used in a demonstration scale process developed for Consolidate Murchison to extract gold and antimony from a high arsenic (~4.5% As) waste stream[67]. The material had too much arsenic to sell as an antimony concentrate, but contained ~31.5% antimony and 60 g/t gold. The 150 t/month demonstration plant leached the material in 40% ammonium polysulfide solution at 25°C to give ~80% gold dissolution. The leach slurry was centrifuged and gold was recovered from the clarified solution with activated carbon, before allowing the leach solution to proceed to antimony recovery. Given the work by Zadra on stripping gold from activated carbon using polysulfides, the choice to go with activated carbon for gold recovery may seem a bit strange, but probably offered lower technical risk than use of ion exchange. They were able to achieve gold loadings on the carbon of 1.5 kg/t, but the gold could not be stripped from the carbon, so it had to be incinerated to recover the gold. While alkaline sulfide processing is now well established for antimony production, application to gold recovery has not developed[68].

The gold bisulfide complex is less stable than gold cyanide but more stable than gold thiosulfate[69].

$$2AuS + S_x^{2-} = 2[AuS_2]^- + (x-2)S$$
$$2Au + 2H_2S + nS_2 = 2[AuS_nS]^- + 4H^+$$
$$2Au + 2HS^- + 2H_2S = 2[Au(HS)_2]^- + H_2$$

Heated (150°C) sulfate/sulfide solutions have been suggested for in-situ gold leaching under anaerobic conditions, with gold recovery by reducing the pressure and allowing H_2S disproportionation[70][71]. Yellowstone Environmental Science (YES) Inc proposed that the H_2S and bisulfide input could be provided by biological generation using sulfate reducing bacteria[72], to teat sulfates produced from bio-oxidation to liberate the gold from sulfide minerals. They proposed extending the use of bio-processing to a second stage of extraction followed by gold recovery either onto activated carbon, by zinc cementation, or precipitation by adjusting pH or solution composition.

The main attraction for sulfide/bisulfide/polysulfide system would appear to be that it should be able to cope with preg-robbing carbonaceous ores with relatively low reagent costs. It may also offer an alternative way to recover gold after sulfide pre-treatment processes such as medium temperature POX, where part of the sulfide is only oxidised to elemental sulfur[70]. However, the elevated temperatures and pressures required to get acceptable gold dissolution with the sulfide / bisulfide systems[69][71], will add to capital and operating costs. Also, given the presence of H_2S in the reactions it may just result in exchange of one toxic species for another[11].

Ammonia

The Merrill Company was reported[73] to have developed the earliest elution processes for recovering gold from activated carbon based on the use of ammonia. The equipment was installed at the Carlton Mill at Cripple Creek Colorado (first CIP plant in world). The carbon was placed in a column that was pressurised with ammonia to 150 psi (1034 kPa) and heated. The ammonia containing vapour was condensed at the top of the system and flowed back through the carbon column stripping gold (soxhlet type extraction with ammonia solution) and flowing back to the heated sump below the column. At the end of the process gold was recovered from the ammoniacal solution by zinc precipitation. The system ran into problems with sludge formation (species loaded onto the carbon but with limited solubility in ammonia solution) and was replaced by the Zadra process[73].

$$Au + (Cu(NH_3)_4)^{2+} = [Au(NH_3)_2]^+ + (Cu(NH_3)_2)^+$$
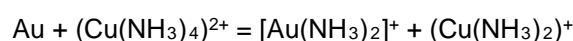
Gold can be leached in ammoniacal solutions at elevated temperatures and pressures to give the cationic gold amine complex. Tests carried out at 140-180°C with 50 g/L ammonia and 10 g/L copper(II) with 400 kPa oxygen overpressure, showed that copper(II) with oxygen was a more effective oxidant than hypochlorite[74]. Refractory ores with gold encapsulated in sulfides can be processed in the ammonia system to give sulfide oxidation and gold dissolution in one process, but the required residence time was around two hours at 180-200°C[75] for up to 95% extraction. Carbonaceous sulfidic ores could also be processed but required more oxygen than straight sulfide ores and careful attention had to be paid to leach conditions to prevent gold reprecipitation onto the carbonaceous matter after leaching. The gold amine complex can be recovered onto activated carbon with loadings up to 10 kg/t[76]. Like the sulfide system, the requirement for high temperatures and pressures result in higher capital and operating costs and the hazard of dealing with gaseous ammonia limit the applicability of the processing route.

Other Potential Alternatives

Glycine

The solubility of gold in amino acids was originally established in connection with medical research[77]. Researchers at Curtin University have shown that gold dissolution in glycine can occur over the pH range of 9-11 at 40-60°C[78]. It is fastest at pH 11 with a significant difference between pH 10 and pH 11. Glycine is a bulk chemical with ~0.5 Mt produced in 2010 and unit cost around $2,000/t. Potential oxidants are peroxide, oxygen or copper(II). The gold leaching rate is significantly slower than cyanide, so it may be better suited to heap or vat leaching, except that solutions probably need to be heated to speed up the process. Laboratory tests were run for up to 200 h with 37.5 g/L (0.5 mol/L) glycine and 10 g/L H_2O_2 at pH 11 and 60°C. Under identical conditions to cyanide, leach rates are 20-30 times slower.

$$2Au + 4NH_2CH_2COOH + 2OH^- + H_2O_2 = 2[Au(NH_2CH_2COO)_2]^- + 4H_2O$$
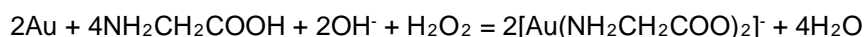
The best chance of the application of glycine would be in connection with copper-gold materials. Glycine can offer selective leaching of copper and gold, as many copper minerals are leached at ambient temperatures, whereas effective gold leaching requires elevated temperatures. It can also be used in conjunction with cyanide, under what would be cyanide starved conditions, as the glycine can react with weak acid dissociable (WAD) copper cyanide complexes, to release cyanide for gold dissolution. At low levels of copper, glycine catalysed cyanide enables 800 mg/L NaCN in presence of 5 g/L glycine at pH 11.5 to give 99% gold extraction in 30 h, compared to ~32% at 50 h with 800 mg/L NaCN by itself[79]. On oxide ore 5 g/L glycine with 300 mg/L NaCN gave greater gold recovery at 79 h than 1 g/L NaCN. A preliminary cost estimate simulation conducted by Dry[80] suggested the process may well have potential for copper-gold ores, but there were many assumptions that need to be clarified by testwork results.

For leaching copper sulfides the Curtin university researchers originally proposed a two stage

process with intermediate solid liquid separation and repulping in fresh solution (to overcome passivation?). Around 50% of chalcopyrite was leached in a single stage process or 80% in two stages, to give an overall 98% dissolution of copper from a gravity concentrate sample. Tests were run for 24-48 h at 16% solids with 22.5 g/L glycine, 10 g/L H_2O_2 at 22°C and pH 11[81]. It was proposed that copper could be recovered by electrowinning and barren solution recycled to leach, but no information was available on reagent consumption/losses and effects of impurity recycle. Leach solution assays show arsenic in solution at 25-30 mg/L after a single cycle. More recently[82] the Curtin researchers have proposed the flowsheet shown in **Figure 7** to treat copper sulfide concentrate for copper and gold recovery.
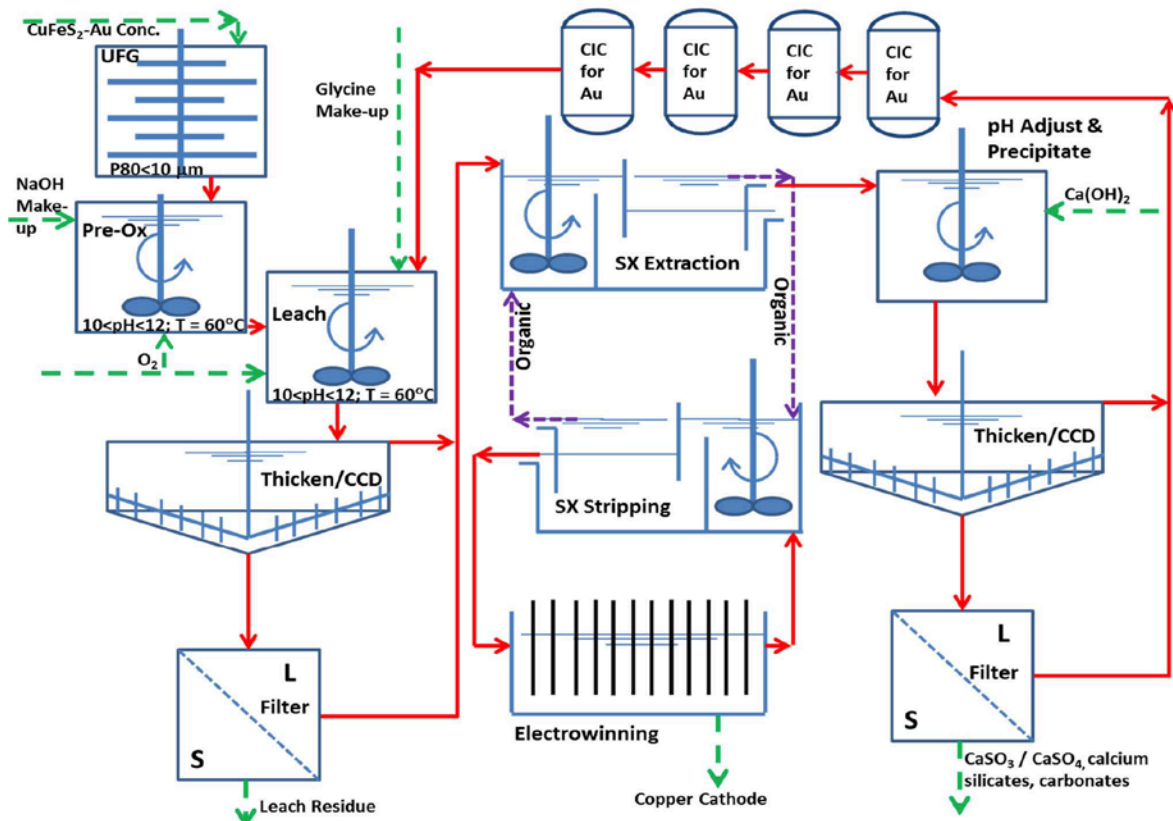

Figure 7 : Two stage flowsheet for copper and gold recovery from chalcopyrite concentrate[82]

The previous two-stage glycine leach has been replaced by ultra-fine grinding and caustic pre-oxidation to convert chalcopyrite to oxide that is more amenable to glycine leaching. The circuit is also more realistic with the inclusion of thickeners and filtration to recycle reagents and allow for dry stacking of tailings. Compared against the other alternative technologies alkaline glycine leaching probably offers the lowest toxicity option. However, the technology is still in its infancy[80] with no public domain information on reagent consumptions to compare with other options.

Undisclosed Processes

Aladdin (Haber) Process

The Aladdin (formerly Haber) process has remained the classic secret proprietary reagent process claimed to offer fast non-toxic gold dissolution. The safety of the reagent was 'demonstrated' on camera up by one of the company directors supposedly drinking a beaker of the lixiviant. It was proposed to recover the gold from solution following solid liquid separation, by precipitation with another proprietary reagent. Originally offered by Haber Corporation, more recently it was offered by Aladdin Separation Technologies, with more of a focus on offering African artisanal miners a safer small scale centralised alternative to do it yourself gold recovery by amalgamation[83].

EarthGold 200, 300, 500

EarthGold is claimed to be a direct replacement for sodium cyanide with low acute oral toxicity and higher leaching rates. It is recommended to operate at pH 10-12 at an addition rate of 0.5-1 kg/t[84]. It may be based on or contain cyanuric acid (1,3,5-triazine-2,4,6-triol $(CNOH)_3$) (commonly used as

chlorine stabiliser in swimming pools and spas[85]. It is described as a solid clathrate 'with some cyanide content' locked in the clathrate[84]. Analysis by the Western Australian Department of Mines and Petroleum[86] suggested that the EarthGold 200, 300 and 500 products actually contain 17-27% sodium cyanide. While organic nitriles have been investigated as gold lixiviants, e.g. acetonitrile (methyl cyanide) there is nothing in the literature to suggest cyanuric acid will dissolve gold. Acetonitrile has been used as an additive in atmospheric Zadra elution process to reduce the elution time as an alternative to operating at elevated temperatures.

Environmental Outcomes

If we are seeking to solve the cyanide issue by moving to an alternative lixiviant, then we need to ensure that we are not just exchanging one set of issues for another set. Most of the issues with cyanide arise from the tailings left after processing. Hence, it is important to look at what will be left after the use of alternative lixiviants. There has been little work investigating the environmental consequences of the application of alternative lixiviants. De Voto and McNulty[12] published one of the few parallel studies looking at the composition of leach solutions after treating McDonald (Montana) ore with different lixiviants as shown in **Table 1**.

Table 1 : Parallel leach solution chemistries for McDonald ore after[12]

Parameter	Units	CN	Thiourea	Ammonium Thiosulfate	Chlorine	Bromine
pH		11.0	1.6	9.1	5.9	2.4
Total Dissolved Solids (TDS)	mg/L	790	15,100	30,100	107,000	15,500
Sodium	mg/L	234	40	2,160	36,900	2,120
Calcium	mg/L	64.5	534	53	910	816
Chloride	mg/L	430	1,500	10,400	66,000	5,700
Sulfate	mg/L	10	11,400	600	260	3,460
Ammonia	mg/L as N	3.41	9.31	5,060	<0.05	1.72
Cyanide, Total	mg/L as CN	280	<0.01	<0.01	<0.01	<0.01
Chlorine, Free as Cl,	mg/L	-	-		424	-
Bromine, Free as Br,	mg/L	-	-	-	-	1,100
Bromide	mg/L	-	-	-	-	8,830
Thiourea	mg/L	-	2,000	-	-	-
Thiosulfate	mg/L	-	-	10,859	-	-
Aluminium	mg/L	0.290	230	<0.2	<3	161
Arsenic	mg/L	0.048	11.0	0.605	1.4	18.1
Cobalt	mg/L	0.05	3.1	0.11	<1	0.5
Copper	mg/L	0.29	2.1	47.3	0.6	0.9
Iron	mg/L	0.68	1,390	0.13	<1	154
Manganese	mg/L	<0.005	88.5	0.40	<0.5	32.7
Nickel	mg/L	0.52	12.7	2.77	16	6.6
Thallium	mg/L	0.0004	0.31	0.218	0.09	0.058
Zinc	mg/L	0.74	3.1	0.28	33	4.5

De Voto and McNulty's conclusion for the McDonald project was that the alternative lixiviant solutions posed as much if not more environmental risk than a properly managed cyanide solution. The total dissolved solids (TDS) concentrations in the alternative lixiviant solutions are already 20-130 times higher than the cyanide system after the first cycle and will get higher with solution recycle. The table also shows that various heavy metals may show up as issues in different lixiviant systems. The use of lime for pH control in the cyanide system places some limit on how high the TDS can go in the presence of reactive sulfides, as sulfate will be precipitated as gypsum, as also occurs with sulfate from thiosulfate degradation in the alkaline calcium thiosulfate system.

People are quick to point out that the alternative lixiviants are less toxic than cyanide but that is too simplistic. All the alternatives are used at higher concentrations than cyanide, so there can be less overall difference in toxicity than people might expect. People also like to point out that many of the alternative lixiviants are biodegradable, but they forget to take account of the reagent concentrations that bacteria can cope with. Thiourea and thiosulfate can be used as fertilisers, but uncontrolled

release into the environment at typical lixiviant concentrations is likely to have consequences. For instance, bacterial degradation of thiosulfate can produce acid and consume oxygen in the process. Hence, it is likely that the alternative lixiviant may need to be recovered as part of the closure process, while maximising recycle in the meantime, to minimise reagent cost. In fact it is likely that application of most of the alternatives discussed above will need to incorporate at least thickening / filtration to recover solution and probably membrane treatment[40][41][80] and/or evaporation / crystallisation[27][28] to close the water balance. These requirements might be seen to add to capital and operating cost, but may be a necessary part of the licence to operate.

At low residual reagent concentrations, as in most cases with cyanide, it is cost effective to destroy the residual reagent, but this is not the case for the higher reagent concentrations required with the alternative lixiviants. To use the application of thiosulfate at Goldstrike as an example the operating cost of destruction and supply of fresh reagent would have been prohibitive, so that the plant could not operate without the incorporation of membrane treatment for reagent recovery within the flowsheet[40][41]. Similarly, the choice to go with the more technically complicated trithionate-sulfite resin elution system, rather than the alternative chloride-sulfite system initially proposed by CSIRO was favoured as it avoided the need to also add evaporation/crystallisation to the flowsheet to deal with a chloride bleed stream.

Economic Issues

Most of the alternative lixiviant systems are more corrosive than cyanide. As previously noted alkaline thiosulfate requires the use of stainless steels, nitrile rubbers or plastics. The Intec chloride system requires fibreglass and high performance plastics. The acid thiourea leach system will at least require stainless steel, rubber linings and plastics. Stainless steel cannot be used with the higher acid and thiourea conditions for thiourea stripping of gold selective anion exchange resins, so that plastics, fibreglass, rubber lined steel or titanium have to be used. Many of these requirements increase the capital cost relative to cyanide, in addition to the need for some combination of filtration, membrane treatment and evaporation systems.

The cost of Reagent transport will be more significant with the higher reagent concentrations. Goldstrike has an on-site CaTS manufacture plant, for over the fence supply as it is the largest consumer of CaTS in North America.

Replacement Options

All the current commercial applications of alternative lixiviants discussed above are essentially niche applications. None of the alternatives has the potential to be as generally applicable as cyanide.

Potential Applications

Legislative Drivers

Locations where cyanide is banned might have been expected to be the most likely areas to have seen the first application of alternatives lixiviants, but this has not happened yet. It could be that the challenge of working with an unproven processing technology on top of location issues, has so far created too much risk. Locations where cyanide is banned may well also lack appropriate support infrastructure. It would appear to need a technology vendor with deep pockets to finance the first plant to get much chance of success with the me-second and me-third projects.

Jurisdictions that have banned export of mineral concentrates and where there are insufficient locally available concentrates to support smelting, may open the way to hydrometallurgical processing of copper-gold concentrates. This could open the door to wider consideration of alternative lixiviants for materials containing elemental sulfur that are not readily amenable to conventional cyanide processing.
Preg-robbing Ores

Treatment of highly preg-robbing ores, where existing support infrastructure is available has been the driver to get thiosulfate over the line for Barrick at Goldstrike. Preg-robbing sulfidic ores are also targeted by several the other technologies discussed above, so perhaps there is more action to be seen in this category.

High Antimony Ores

As discussed above both sulfide and thiourea have had limited application for gold recovery from

antimony concentrates with significant gold grades, as smelters do not pay for this gold content.

ALLEVIATION

The Cyanide Code was a good start but for the gold industry to reduce its cyanide profile further, the major areas that need to be tackled are tailings and transport to site.

Transport

The Australian Government review of sodium cyanide under the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) 2010 report on sodium cyanide[10] provides data on seven transported related incidents in Australia between 1992 and 2007 and seven overseas transport incidents between 1984 and 2004. While there are no recorded human casualties in any of these incidents, some of the incidents resulted in deaths of wildlife, birds and fish. Two of the Australian incidents resulted in spills of 40 t of cyanide pellets, but in the absence of rain the dry pellet spills were mostly recovered without significant environmental impact. Liquid cyanide spills of up to 6 m³ had more impact on wildlife. The quantities of cyanide involved in the overseas incidents ranged from 100 kg to 260 t. Chinese incidents involving 5-11 t that went into rivers had a more significant effect with a 5 t spill affecting at least 14 km of river. The 1984 PNG incident involved loss of a barge heading to the Ok Tedi mine and carrying 260 t of cyanide in 100 kg drums, of which only 10 t was ever recovered, while the fate of the other 250 t was unknown!

While safer transport options, such as the use of rail, are often proposed to reduce the issue, some of the Australian incidents have shown that rail transport does not remove the risk. On site manufacture would appear to be a more robust long term goal that could be part of the solution to alleviate the cyanide issue.

On-site Manufacture

Synergen Met[87] developed a 100 kW pilot scale on-site cyanide manufacture system in a 40 ft shipping container, that was tested in a 15 month trial at the Henty mine in Tasmania in 2014-2015. An electrically generated plasma was used to create the conditions for hydrogen cyanide formation from a hydrocarbon (natural gas, propane, butane, LPG, or, naphtha) and a nitrogen source (nitrogen from air or ammonia). The HCN was then dissolved in sodium hydroxide to produce 20-30% sodium cyanide solution.

$$2CH_4 + N_2 = 2HCN + 3H_2$$
$$HCN + NaOH = NaCN + H_2O$$
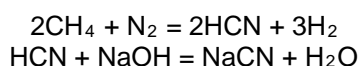
The Synergen team took out the top prize in the 2014 Institution of Chemical Engineers Global Awards in UK by winning the 2014 Award for Outstanding Achievement in Chemical and Process Engineering, as well as the Core Chemical Engineering categories. Since completing the testwork at Henty the focus has been on optimising the design to provide more certainty in the cost of NaCN production. Synergen Met is negotiating to sign its first contract for the supply of a full scale production unit that is proposed to be in operation in early 2019[88].

They are currently developing 400 t/y and 750 t/y units. The power requirement for the 400 t/y unit will be approximately 600 kW. A power input of 600 kW for 400 t/y (ie~8.76 MWh/t NaCN) is still a big improvement on the 60 t/y produced in the 100 kW pilot unit tested at Henty (i.e.~14.6 MWh/t). Given the power requirement for the plasma gun it is not surprising that Synergen Met explain that the cost of produced cyanide is sensitive to the cost of electricity and current units are not capable of cost effective cyanide production at Western Australian Goldfields electricity prices.
Additional costs to consider include the capital and operating cost of a PSA system to generate nitrogen for the feed to react with the natural gas, as well as cost of the natural gas. The Duckworth patent[89] suggests that the methane utilisation efficiency could be around 80%. Hence around 360 kg methane are required per tonne of NaCN. The patent also suggests with ammonia as nitrogen source, ammonia utilisation efficiency could be around 90% with lower processing energy requirement than if nitrogen is used.

The reaction also yields by-product hydrogen that could be burnt in a gas turbine. For a 400 t/y unit the total heat output from hydrogen combustion could be around 4,000 GJ/y. A significant amount of the electrical energy input into the plasma process (~18 MJ/kg HCN) is released to the cooling water

when the reaction gases are quenched. The heat energy released from the process is roughly equivalent to the energy required for the gold elution circuit. Synergen is investigating recovering the heat from their process for use in the elution circuit, to increase the overall energy efficiency.

Further cost savings may be possible by production of calcium cyanide rather than sodium cyanide, but cyanide recycle experience suggests that scale formation may be an issue. Calcium cyanide is not normally used due to a shorter shelf life. However, with on-site and on-demand cyanide production technology, Synergen's process can deliver liquid calcium cyanide as required, overcoming any long terms storage issues of liquid calcium cyanide.

Provided that there is no significant energy efficiency penalty for going with 400 t/y units, then a 1,000 t/y NaCN requirement could be met by 3 units to provide some redundancy, until a 1,000 t/y unit becomes available.

Tailings Issue

There are several aspects to the tailings issue:

- The quantity of cyanide containing water in the tails storage facility (TSF)

- The cyanide concentration in the water in the TSF

- Base metal cyanides

- Other solution species, e.g. Mn, sulfate, TDS.

The Australian Government NICNAS report on sodium cyanide[10] provides data on four Australian incidents involving cyanide in TSFs between 1995 and 2001, three of which involved dam overtopping. Fortunately, two of these were at mines that were no longer operating so that cyanide concentrations were low. However, the other incident in Tasmania involved release of 40,000 m³ of cyanide containing material that polluted streams and killed fish. In addition, there was the Northparkes incident in 1996 where 2,736 birds[10][90] were reported to have been killed by TSF cyanide concentrations over 50 mg/L (that were permitted by the operating licence at the time). In addition the NICNAS report provides data on 22 overseas unplanned cyanide releases, seven (~1/3) of which were associated with TSF issues. In addition to Baia Mare there were three other spills that contaminated 80 km stretches of rivers.

The severity of the cyanide TSF incidents could probably have been significantly reduced if cyanide concentrations were lower. For example, from the volume of slurry and quantity of cyanide released in the Baia Mare incident[5] it would appear that the cyanide concentration in the dam could have been of the order of 1,000-1,200 mg/L. Had the cyanide detox plant been in place before the incident, the peak cyanide concentration in the rivers might have been only around 1 mg/L.

International Cyanide Code signatory companies generally commit to TSF WAD cyanide levels of no more than 50 mg/L. Had the Northparkes TSF solution WAD cyanide concentration been below 50 mg/L in 1995, rather than ~350 mg/L[10], it might not have become infamous for killing birds. While there is general anecdotal evidence that 50 mg/L offers a safe limit for birds seeking water in non-saline dams, the NICNAS review did not find enough scientific evidence to totally affirm 50 mg/L WAD cyanide as a safe level. They accepted that Western Australian and Northern Territory research had established that significant wildlife mortalities are unlikely at WAD cyanide levels below 50 mg/L. However, they pointed out that safe limits for sensitive bird species could be below 1 mg/L to prevent delayed mortality by reduced flying ability of migratory birds or greater susceptibility to predators. Hence there is little room for complacency.

Cyanide Recovery / Destruction

After the leach process some cyanide is often recovered by using a tails thickener to recover cyanide containing solution to be recycled to the front of the process. Technology for further cyanide recovery[91][92] by acidification, volatilisation and reneutralisation (AVR) or sulfidization, acidification, reneutralisation and thickening (SART) is available but is not usually considered to be cost effective[93]. SART is used for some for high copper cyanide solutions and AVR after silver recovery at Cerro Vanguardia[94] and at Almo Dorado[95]. Cyanide recovery reduces the amount of cyanide that needs to be removed to comply with Cyanide Code target of <50 mg/L WAD cyanide in the TSF. Compliance is usually achieved by use of a cyanide destruction process such as with the Inco SO_2/air process. Destruction of the residual cyanide is usually the most cost effective option as the cyanide concentration at the end of the leach process is relatively low. (Destruction is not a cost

effective option for any of the alternative lixiviants as they are used at much higher concentrations[40]!)

Off-Site Disposal

The 1998 World Bank Pollution Prevention and Abatement Handbook[96] proposed discharge limits of 0.1 free cyanide, 0.5 mg/L WAD cyanide and 1 mg/L total cyanide, along with 0.5 mg/L copper for discharges from mining operations to surface waters. Standard cyanide destruction options go a long way towards meeting these guidelines and Cyanide Code signatories commit to achieving discharge standards of 0.5 mg/L WAD cyanide and 0.022 mg/L free cyanide within the receiving water (after mixing and dilution). However, if the World Bank standards are required to be met before dilution (as in countries such as Brazil), then membrane polishing treatment may be required for water positive sites to reliably achieve off-site discharge targets. In some cases additional gold recovery has helped pay for the cost of membrane treatment[40].

'Dry' Disposal of Tailings

Two high profile tailings dam failures in the last two years – Imperial Metals Mount Polley TSF in Canada[97] and Samarco Fundão TSF in Brazil[98] have highlighted the potential financial implications of dam failures with conventional tailings disposal.

One way to reduce the risk from conventional wet tailings disposal is to move to towards dry disposal, by use of paste backfill, surface paste disposal[99], co-disposal with waste rock[100] or so called 'dry stacking' systems[101]. Previously dry stacking was only an option for small scale operations as large scale filtration equipment was not available. Dry stacking has been recommended for mines with severe lack of water, or other environmental constraints (such as difficult topography and foundation conditions)[102] and where cheap energy is available[101]. Filtration systems[103] with capacities of up to 10,000 t/d (~3.6 Mt/y) have been installed at South American copper concentrators[104] and a recent Ausenco study for the Rosemont project[105] proposed dry stacking tailings disposal for the 90,000 t/d (~29.8 Mt/y) copper concentrator. FLSmidth are reported to be developing systems with capacities of more than 120,000 t/d[104]. Hence availability of filtration technology is not the issue it used to be. While most applications of dry stacking disposal of tailings to date have been at base metal concentrators, it has been used at a few gold plants: Santa Rosa (Columbia) 1,000 t/d[106], Almo Dorado Ag/Au Mexico 4,000t/d[95], El Sauzal Mexico 6,000 t/d[107] (now closed).

Dry tailings disposal makes good sense in arid environments where water is at a premium. However, if sulfides have not been completely oxidised they need to be kept completely dry, otherwise they have increased potential for generation of acid mine drainage, compared to tailings kept submerged under anaerobic conditions. Dry disposal also removes one of the process water impurity sinks, so that bleed streams may need to be treated by more expensive approaches such as evaporation and crystallisation to control build-up of impurities. Dry disposal would also make things worse in water positive sites, as there is more water to treat and it will contain higher levels of impurities. This will increase the cost of treatment to achieve the required effluent discharge guidelines. Nevertheless thickening/filtration followed by some form of 'semi-dry disposal', will reduce the tailings risk from cyanide and metal cyanide complexes. It also reduces what needs to be done at mine closure, enabling more rapid rehabilitation of the site.

CONCLUSIONS

There is very little prospect of any of the alternative lixiviants taking over from cyanide to provide a universal solution to the cyanide issue. Those that have been used still have tailings associated closure issues that have not been fully resolved and are may require reagent recovery via membrane treatment prior to full closure.

The lowest hanging alleviation fruit seem to be related to tailings storage and cyanide transport to site. The 50 mg/L WAD cyanide limit accepted by Cyanide Code signatories is certainly a good start to the process of defusing the tailings issue, but further measures are probably required to reduce risks further to stay ahead in maintaining a social licence to operate. Thickening and filtration with some form of dry stacking could well be a more robust solution to the tailings issue. Paste backfill is another approach to tap into the benefit of out of sight out of mind. Dry stacking comes with an operating cost penalty and brings increased requirements for water treatment for recycle and for off-site disposal, but offers benefits beyond the cyanide issue. Before Baia Mare (in Europe) and Northparkes (in Australia) cyanide destruction to <50 mg/L WAD cyanide was seen as an unnecessary expense. In the light of failures such as Imperial Metals Mount Polley dam[97] and Samarco's Fundão dam[98], perhaps it is time to start looking at the expense of minimising water storage in tailings dams in a similar way. Had cyanide been used for gold recovery at Mount Polley rather than just gold recovery into a copper flotation concentrate, cyanide regulation would possible already be more severe.

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