

Processes for the regeneration of cyanide from thiocyanate

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Abstract

Cyanidation processes for the extraction of gold or silver frequently involve the processing of sulfur-containing solids that react with cyanide to form thiocyanate. The formation of thiocyanate is an undesired side reaction, and in many cases thiocyanate formation results in a prohibitively high cyanide consumption. With the increasing number of gold and silver mining projects that involve the processing of sulfide ores or concentrates or that utilize a biological sulfur oxidation process, more attention is being focused on minimizing thiocyanate formation and in treating solutions to eliminate toxicity associated with thiocyanate. Though not yet commercially applied, there are several processes available to recover cyanide from thiocyanate to reduce tailings toxicity and to allow the reuse of cyanide otherwise lost to thiocyanate formation. This paper presents an overview of processes available for recovering cyanide from thiocyanate along with estimated operating costs for the processes. Pilot testing data suggests that in some cases cyanide can be recovered from thiocyanate for approximately the same cost as newly purchased cyanide.

Key words: Cyanide regeneration, Cyanidation processes, Thiocyanate

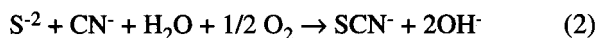
Introduction

It is generally believed that thiocyanate (SCN^-) is formed during cyanide leaching operations as a result of reactions between cyanide (CN^-) and sulfur species, including solid or dissolved sulfur. Examples of these reactions include the following:

Elemental sulfur



Sulfide



Thiosulfate



Depending on the sulfur content of the solids in contact with the cyanide, resultant concentrations of thiocyanate in solution may range from a few mg/L to well over 1,000 mg/L in some cases. In an extreme case it was found that cyanidation circuits following biological sulfur-oxidation processes may contain in excess of 5,000 mg/L of thiocyanate because of cyanide interactions with oxidized and partially oxidized sulfur species. High thiocyanate concentrations are also commonly found in cyanidation circuits processing high-sulfide ores or concentrates.

Process and environmental impacts associated with thiocyanate formation in a metallurgical circuit include the following:

- It is becoming increasingly common to utilize bacterial oxidation circuits for the pretreatment of sulfide-containing ores and concentrates to liberate gold for subsequent cyanide leaching operations. The bacteria used in these oxidation circuits are sensitive to cyanide and thiocyanate. Concentrations of these species in excess of approximately 10 mg/L are toxic. Therefore, it is important in these circuits that cyanide- and thiocyanate-containing solutions be segregated from bacterial oxidation circuits. This is accomplished by maintaining separate solution circuits for bacterial oxidation and cyanide leaching or by treating excess cyanidation solutions for cyanide and thiocyanate removal.
- While not commonly regulated in water discharges, thiocyanate may be toxic to aquatic species. If a water discharge is subject to compliance with a toxicity test, such as the US EPA's Whole Effluent Toxicity (WET) test, thiocyanate may be of concern. Because thiocyanate is not destroyed in most cyanide detoxification processes, an additional treatment technology may be required if thiocyanate removal is necessary.
- If it is assumed that sodium cyanide is purchased for \$1.30/kg, then each kilogram of thiocyanate formed in

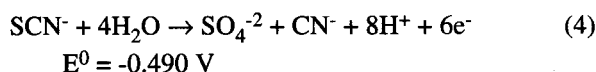
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a leaching circuit indirectly costs about \$1.10 because of increased cyanide consumption. Referencing Table 1, this could translate into an operating cost well in excess of \$1.0 million/year for a thiocyanate concentration greater than 1,000 mg/L in a cyanide leaching circuit.

As noted in the following sections, the cost of cyanide regeneration may be less than that associated with thiocyanate destruction due to the chemical behavior of thiocyanate in low pH systems.

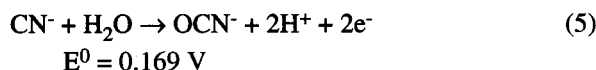
Thiocyanate chemistry

Regeneration of cyanide from thiocyanate requires the simultaneous chemical reduction of carbon and the oxidation of sulfur in the SCN complex to yield free cyanide and sulfate. This process is illustrated in the following half-reaction for the oxidation of thiocyanate to cyanide (all potentials are relative to the standard hydrogen electrode)



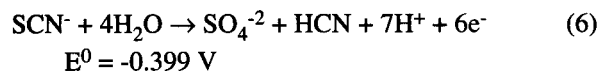
Referencing Table 2, in this reaction carbon is reduced from C(IV) to C(II) while sulfur is oxidized from S(-II) to S(VI). This reaction has been investigated with chemical oxidants and electrolytically. However, to date there have been no full-scale applications of such a process.

A significant difficulty encountered with thiocyanate oxidation to cyanide is the tendency to fully oxidize thiocyanate to cyanate then to cyanate:



If this reaction occurs, the first step via Reaction (4) would result in the regeneration of free cyanide. However, this cyanide would subsequently be destroyed via Reaction (5) by further oxidation to cyanate. Therefore, to affect the regeneration of cyanide from thiocyanate, it is necessary to promote the completion of Reaction (4) while minimizing the extent of Reaction (5).

Several researchers have noted that Reaction (4) will take place at acidic pH, and in this case aqueous hydrogen cyanide is formed in lieu of the free cyanide anion



Under acidic conditions, it was found that Reaction (5) does not occur to a significant extent and that cyanide regeneration via Reaction (6) may proceed to near completion. Note that Reaction (6) is acid generating. Therefore, there is a tendency for the reaction to naturally lower the solution pH, thereby preventing cyanide oxidation via Reaction (5). This behavior is advantageous in a cyanide regeneration system, as described below.

Regeneration chemistry

Thermodynamics suggest that cyanide regeneration via Reaction (6) is possible provided that the reaction environment has an oxidation potential greater than approximately -0.4 V. This potential could be provided as an induced voltage, or in reference to Table 3, by a suitable chemical oxidant. Note that, although thermodynamic data in Table 3 suggest that several oxidants would be suitable to affect cyanide regeneration

Table 1 — Operating cost associated with thiocyanate formation.

Thiocyanate concentration, mg/L	Annual NaCN cost due to thiocyanate formation
500	\$0.8 million
1,000	\$1.5 million
5,000	\$7.0 million

Note: Calculated for a solution flow of 150 m³/hr and a NaCN purchase price of \$1.30/kg.

Table 2 — Oxidation states of thiocyanate-related compounds.

Compound	Formula	Element oxidation state			
		C	N	S	O
Cyanide	CN ⁻	+2	-3	-	-
Thiocyanate	SCN ⁻	+4	-3	-2	-
Cyanate	OCN ⁻	+4	-3	-	-2
Thiosulfate	S ₂ O ₃ ⁻²	-	-	+2	-2
Sulfite	SO ₃ ⁻²	-	-	+4	-2
Sulfate	SO ₄ ⁻²	-	-	+6	-2

Table 3 — Half-reactions for oxidants (relative to the standard hydrogen electrode).

Oxidant	Oxidant half-reaction	E ⁰ (V)
Oxygen	O _{2(g)} + 4H ⁺ + 4e ⁻ → 2H ₂ O	
Chlorine	Cl _{2(g)} + 2e ⁻ → 2Cl ⁻	
Hydrogen peroxide	H ₂ O ₂ + 2H ⁺ + 2e ⁻ → 2H ₂ O	
Caro's acid	H ₂ SO ₅ + 2e ⁻ → SO ₄ ⁻² + H ₂ O	
Sulfur dioxide	SO _{2(g)} + O _{2(g)} + 2e ⁻ → SO ₄ ⁻²	
Ozone	O _{3(g)} + 6H ⁺ + 6e ⁻ → 3H ₂ O	

from thiocyanate, including oxygen, only a few have been demonstrated to affect this reaction at an appreciable rate. A summary of the chemistry associated with the oxidants listed in Table 3 is presented in the following sections.

Oxygen. The obvious advantage of utilizing oxygen for cyanide regeneration from thiocyanate would be its relatively inexpensive availability in atmospheric air. However, work of the author's suggests that, if the regeneration reaction does take place with oxygen, it is prohibitively slow for practical application. Therefore, additional information is not presented here relative to oxygen. At this time, work is being conducted by the authors to evaluate the possibility of using oxygen for this reaction in the presence of solid and aqueous catalysts.

Chlorine. Chlorine has been widely used for cyanide destruction, though this process typically takes place at a pH above about 10.0 and results in the complete oxidation of thiocyanate and/or cyanide to form cyanate. At a low pH, chlorine may partially oxidize thiocyanate to yield cyanide (Flynn and McGill, 1995), as illustrated in the following reaction

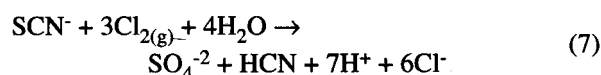


Table 4—Stoichiometric reagent demands for thiocyanate and cyanide oxidation with chlorine.

Reaction	Reagent demand
Cyanide regeneration	3.67 g Cl ₂ /g SCN regenerated
	3.86 g CaO/g SCN regenerated
Complete thiocyanate destruction	4.90 g Cl ₂ /g SCN destroyed
	4.83 g CaO/g SCN destroyed

Table 5—Stoichiometric reagent demands for thiocyanate and cyanide oxidation with hydrogen peroxide.

Reaction	Reagent demand
Cyanide regeneration	1.76 g H ₂ O ₂ /g SCN regenerated
	0.97 g CaO/g SCN regenerated
Complete thiocyanate destruction	2.35 g H ₂ O ₂ /g SCN destroyed
	0.97 g CaO/g SCN destroyed

Table 6—Stoichiometric reagent demands for thiocyanate and cyanide oxidation with Caro's acid.

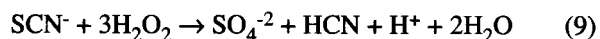
Reaction	Reagent demand
Cyanide regeneration	5.90 g H ₂ SO ₅ /g SCN regenerated
	3.86 g CaO/g SCN regenerated
Complete thiocyanate destruction	7.86 g H ₂ SO ₅ /g SCN
	4.83 g CaO/g SCN destroyed

In addition, chlorine is known to oxidize cyanide to cyanate via the reaction



Reagent demands associated with cyanide regeneration by Reaction (7) and complete thiocyanate destruction by Reaction (7) plus Reaction (8) with chlorine are summarized in Table 4. Note that the estimated lime demands (i.e., the lime needed to neutralize the acid generated in the reactions) are shown in Table 4.

Hydrogen peroxide. Similar to chlorine, hydrogen peroxide has been widely used for cyanide destruction and has been demonstrated to affect the regeneration of cyanide from thiocyanate at a low pH (Wilson and Harris, 1960a and 1960b). The reaction of thiocyanate with hydrogen peroxide to yield free cyanide is



In addition, hydrogen peroxide is known to oxidize cyanide to cyanate in the presence of a soluble copper catalyst via the following reaction



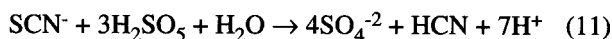
Reagent demands associated with cyanide regeneration and complete thiocyanate destruction with hydrogen peroxide are summarized in Table 5.

Although Soto et al. (1995) indicate that hydrogen peroxide is not a sufficiently strong oxidant to affect the oxidation of thiocyanate to cyanide, it is well established that this can be done (Wilson and Harris, 1960a, 1960b; Orbán, 1986). Wil-

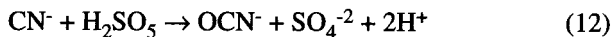
son and Harris (1960b) focused on determining the reaction sequence and stoichiometry for complete thiocyanate oxidation with hydrogen peroxide. However, experimental data showing the formation of free cyanide as an intermediate were also presented. In one of the experiments, a less than stoichiometric dosage of hydrogen peroxide partially oxidized thiocyanate, with 75% of the reaction products being free cyanide and 25% being other cyanide-related compounds. It was also noted that the presence of dissolved copper resulted in the rapid catalytic oxidation of cyanide to cyanate, even at a low pH, thereby destroying any regenerated cyanide.

Therefore, with this reaction it is critical to ensure that the dissolved copper concentration is sufficiently low to minimize the catalytic oxidation of cyanide to cyanate.

Caro's acid. Caro's acid, also known as peroxymonosulfuric acid, has the chemical formula H₂SO₅ and is generated through the reaction of sulfuric acid with hydrogen peroxide. Caro's acid is a relatively strong oxidant and is increasingly being used for the destruction of cyanide in the mining industry. At low pH, Caro's acid is capable of regenerating cyanide from thiocyanate (Smith and Wilson, 1966), as illustrated in the reaction

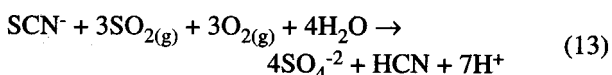


In addition, Caro's acid is known to oxidize cyanide to cyanate via the reaction

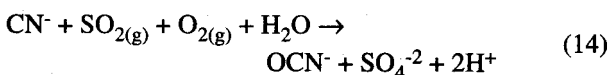


Reagent demands associated with cyanide regeneration and complete thiocyanate destruction with Caro's acid are summarized in Table 6.

Sulfur dioxide. Sulfur dioxide-based processes may be the most widely used for cyanide destruction in the mining industry, though thiocyanate destruction with this process is typically less than 10% at reaction conditions required for efficient cyanide destruction. The use of sulfur dioxide and oxygen for thiocyanate oxidation to regenerate cyanide has not been thoroughly investigated, though the following reaction may occur at an acidic pH



In addition, sulfur dioxide and air are known to oxidize cyanide to cyanate in the presence of a soluble copper catalyst and oxygen via the reaction



Reagent demands associated with cyanide regeneration and complete thiocyanate destruction with sulfur dioxide are summarized in Table 7.

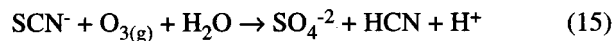
Ozone. Ozone is a strong oxidant and widely used for water and wastewater treatment for the oxidation of contaminants. Relative to cyanide destruction, ozone use is typically limited to small-volume and low-concentration systems due to its relatively high cost compared to other oxidants such as chlorine, hydrogen peroxide and sulfur dioxide. However, it has been well documented that ozone is efficient at regenerating cyanide from thiocyanate (Layne et al., 1984; Jara et al., 1996). The thiocyanate and cyanide oxidation reactions that occur with ozone are

Table 7— Stoichiometric reagent demands for thiocyanate and cyanide oxidation with sulfur dioxide and air.

Reaction	Reagent demand
Cyanide regeneration	3.31 g SO ₂ /g SCN regenerated 3.86 g CaO/g SCN regenerated
Complete thiocyanate destruction	4.41 g SO ₂ /g SCN 4.83 g CaO/g SCN destroyed

Table 8— Stoichiometric reagent demands for thiocyanate and cyanide oxidation with ozone.

Reaction	Reagent demand
Cyanide regeneration	0.83 g O ₃ /g SCN regenerated 0.97 g CaO/g SCN regenerated
Complete thiocyanate destruction	1.10 g O ₃ /g SCN destroyed 0.97 g CaO/g SCN destroyed



and



Reagent demands associated with cyanide regeneration and complete thiocyanate destruction with ozone are summarized in Table 8. Note that the redox reaction for ozone listed in Table 3 is not the reaction typically listed in published compilations of redox potentials. However, as described in a following section, the experimentally observed stoichiometry for ozone oxidation of thiocyanate to regenerate cyanide is approximately one mole of ozone per mole of thiocyanate oxidized. This indicates that the reaction as listed in Table 3 applies to the ozone-thiocyanate oxidation system at an acidic pH.

To date, the majority of experimental work conducted using chemical oxidants to regenerate cyanide from thiocyanate has been performed using ozone. Representative results are presented in Fig. 1, which shows the concentration of cyanide-related compounds as a function of time in an ozonation reactor (Layne et al., 1984). Referencing Fig. 1, during the first 20 min of the reaction there is a rapid decrease in the thiocyanate concentration that corresponds to a rapid increase in the cyanide concentration. Beyond 20 min of reaction time, the cyanide concentration begins to decrease, and, at 40 min, the cyanide concentration approaches zero. Through most of the reaction there is a gradual increase in the concentration of cyanate (OCN⁻), indicating that the oxidation of cyanide to cyanate competes with thiocyanate oxidation, though this reaction rate is relatively slow. At approximately 20 min of reaction time, the cyanide concentration is a maximum and cyanide regeneration is approximately 75%. These results parallel those presented by Kemker et al. (1980), in which a maximum cyanide regeneration of approximately 80% to 85% was observed at a pH of 10.0.

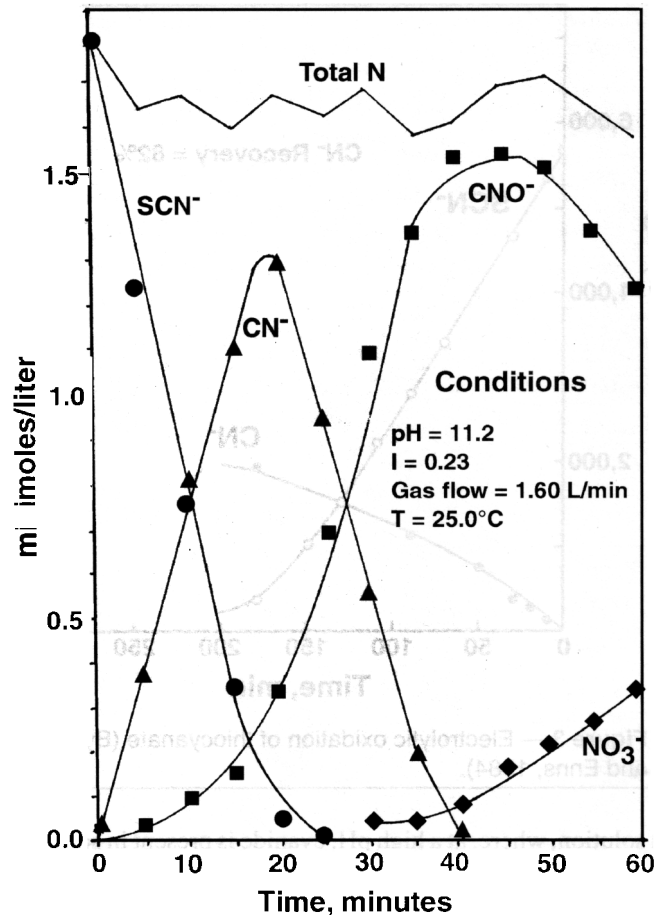


Figure 1 Ozone oxidation of thiocyanate (Layne et al. 1984).

Results presented in Fig. 1 were generated at a solution pH of 11.2. However, Soto et al. (1995) indicated that the ozonation reaction and subsequent regeneration of cyanide is pH dependent. Referencing Fig. 2, it appears that, above a pH of approximately 10.0, cyanide formed through the oxidation of thiocyanate is subsequently oxidized to cyanate. The rate of cyanide oxidation to cyanate decreases as the pH decreases, with negligible oxidation below a pH of approximately 4.0. This observation is explained by the pH behavior of cyanide

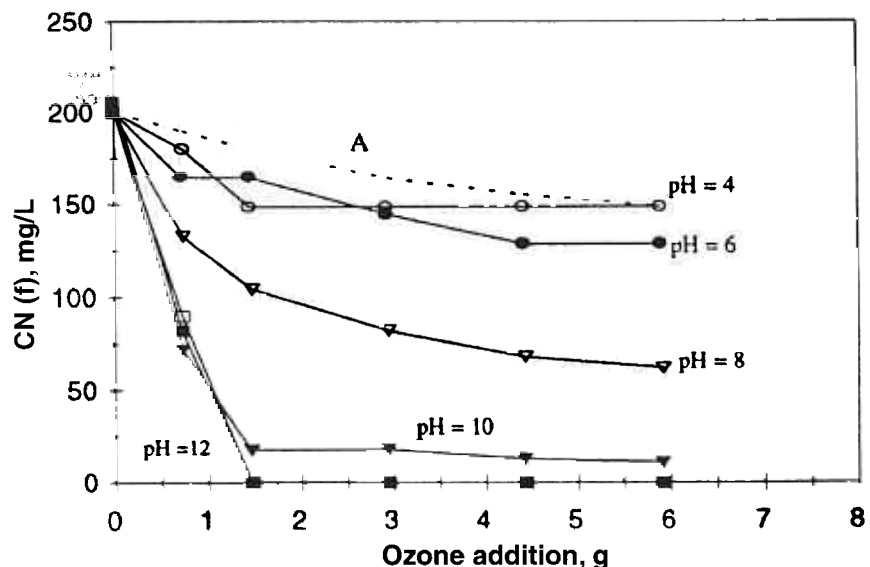


Figure 2 Effect of pH on ozone oxidation of thiocyanate (Soto et al., 1995).

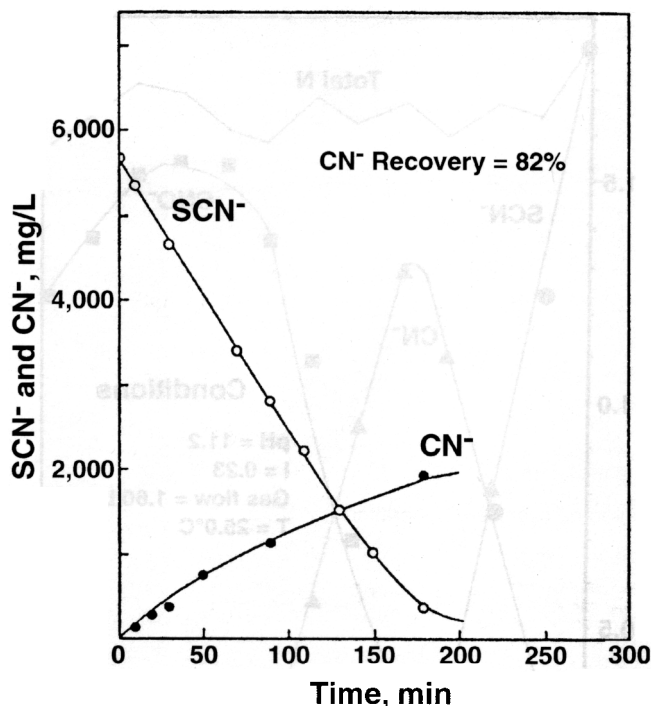


Figure 3 — Electrolytic oxidation of thiocyanate (Byerley and Enns, 1984).

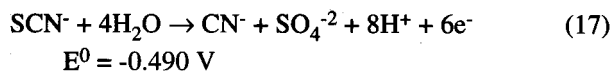
in solution, where, at a high pH, cyanide is present in solution as CN^- and is susceptible to attack by ozone. However, at a low pH, cyanide will be present primarily as HCN , which is less susceptible to attack by ozone.

The effect of dissolved copper on the oxidation rate of cyanide to cyanate by ozone is quite significant and a copper concentration in excess of approximately 10 to 50 mg/L results in significant oxidation of cyanide to cyanate at any pH. The catalytic action of copper to promote cyanide oxidation to cyanate has been observed by many others and forms a basis for several cyanide destruction patents (Mathre, 1971; Neville, 1980; Borbely et al., 1984). However, removal of copper from solution to less than approximately 10 mg/L reduces cyanide oxidation to a low level and accommodates the regeneration of cyanide from thiocyanate. Processes available for the removal of copper from cyanide leach solutions are discussed in Botz and Parodi (1997) and Botz (2001).

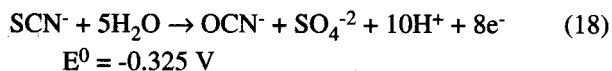
Electrolytic oxidation of thiocyanate

In addition to chemical oxidation of thiocyanate, an induced electric potential can also be used to provide the oxidizing environment to regenerate free cyanide. Electrolytic oxidation of thiocyanate to regenerate cyanide has been researched on a small-scale. However, to date, there have been no full-scale applications.

The reactions representing the electrolytic oxidation of thiocyanate to yield cyanide, cyanate and sulfate are (Byerley and Enns, 1984)



and



In addition to the above reactions, which occur at the anode

of an electrolytic cell, water is oxidized at the anode to yield oxygen gas according to



Occurring simultaneously at the cathode is the reduction of water to form hydrogen gas



Other reactions in addition to Reaction (20) will also occur at the cathode if suitable compounds are present in solution. For example, the copper-cyanide complexes will react at the cathode to give elemental copper, while, at the anode, thiocyanate will oxidize to yield free cyanide (Dickson, 1989). It has been experimentally observed that Reactions (17) through (20) occur simultaneously at the cathode and anode, respectively. However, reaction conditions can be controlled to maximize cyanide regeneration according to Reaction (17).

Byerley and Enns (1984) presented experimental data for electrolytic oxidation of thiocyanate using synthetic solutions at varying pH values. It was found that approximately 80% cyanide regeneration could be affected with a solution pH of approximately 2.0 to 2.5, with significantly lower regeneration efficiencies observed at neutral to alkaline pH values. This was explained by the pH behavior of cyanide solutions in which free cyanide is present primarily as the cyanide anion at high pH values and this complex is susceptible to oxidation to cyanate. At low pH values, cyanide is present primarily as undissociated hydrogen cyanide, which is less susceptible to electrolytic oxidation to cyanate.

Representative electrolytic cyanide regeneration data presented by Byerley and Enns (1984) is provided in Fig. 3. As indicated, after approximately 200 min of reaction time, the cyanide regeneration is about 82% at a final solution pH of 2.4. Similar experiments conducted at a pH of 10.7 gave a maximum cyanide regeneration of 13% after approximately 30 min of reaction time. However, beyond 30 min, the regeneration efficiency decreased and approached zero at 120 min. Byerley and Enns (1984) indicated that electrical power usage for the regeneration of cyanide from thiocyanate is approximately 0.03 kW-hr/g of thiocyanate oxidized.

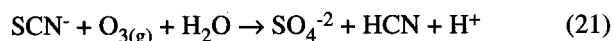
Pilot testing results

In 1998 and 1999, TVX Hellas investigated the possibility of regenerating cyanide from thiocyanate at its Olympias project in Greece. Gold and silver ore at the Olympias project is refractory and near complete oxidation of mineral sulfides is required to permit efficient extraction of gold and silver via cyanidation. In laboratory and pilot studies conducted with bacterially oxidized ore samples, it was observed that cyanide reactions with oxidized and partially oxidized sulfur species resulted in a significant generation of thiocyanate in the proposed leach process. Thiocyanate concentrations in the tailings ranged from a low of about 2.5 g/L to a high in excess of 12 g/L in the tests conducted. The high amount of thiocyanate formed in the process was responsible for approximately 90% of the total cyanide consumption in the circuit, and, therefore, options for recovering cyanide from thiocyanate were investigated.

Following a review of regeneration process options, TVX proceeded with small-scale pilot testing of ozone oxidation of thiocyanate to regenerate free cyanide. The following is a summary of this test work that was conducted using a syn-

thetic thiocyanate solution and samples of laboratory-generated tailings pulp.

Pilot tests. Pilot testing of the ozone regeneration of cyanide from thiocyanate was conducted by Ozonia at their laboratory in Bern, Switzerland, in 1998. Pilot testing involved the continuous pumping of pulp or solution through a bubble-column reactor, which was sparged with ozone-containing gas. During this time, ozone consumption and concentrations of thiocyanate, cyanide and cyanate were monitored, and the cyanide regeneration efficiency as a function of pH, ozone dosage and time was determined. For the first one to two hours of reaction time, the pulp or solution pH was allowed to decrease from an initial value of approximately 10.5 to less than 2.0 according to the acid-generating reaction



Results for one test conducted with a synthetic thiocyanate solution prepared with potassium thiocyanate are presented in Table 9. For this test, the reactor was operated for a total of nine hours, and the average cyanide regeneration efficiency was 85%. The overall cyanide balance calculated for this test with thiocyanate and total cyanide analyses closed to within 95% to 99%, indicating that oxidation of cyanide to cyanate was not significant. The consumption of ozone during this test was approximately 0.93 gram per gram of oxidized thiocyanate or about 1.12 moles of ozone per mole of oxidized thiocyanate. This is in close agreement with the stoichiometry of Reaction (21) and with data published by Palmer et al. (1988) and represents about 10% excess ozone consumed in the process.

Ozone was fed to the bubble column reactor as a gas mixture with oxygen, and, therefore, a portion of regenerated cyanide was volatilized from the reactor as hydrogen cyanide gas. On average, approximately 5% of the cyanide was volatilized as HCN, while the remaining 95% reported in the solution discharged from the reactor. Data in Table 9 for the treated solution include cyanide volatilized from the reactor, which was absorbed in an off-gas caustic scrubber.

A similar test was conducted with laboratory-generated tailings pulp to assess the impact of solids on the performance of the ozone reaction with thiocyanate. The test was conducted with pulp at approximately 40% solids, and the average cyanide regeneration efficiency during the test was about 50%. A summary of results from this test is presented in Table 10.

The cyanide regeneration efficiency for the test involving pulp was significantly less than that observed using clear solution. For the test with pulp, approximately 10% of the feed thiocyanate went unreacted, 50% was converted to free cyanide and 20% was converted to cyanate (OCN). Accordingly, approximately 80% of the feed thiocyanate was accounted for in thiocyanate, cyanide and cyanate analyses, while the remaining 20% was unaccounted for in the mass balance. It is anticipated that the unaccounted for thiocyanate in the mass balance may have been precipitated as a metal-cyanide and/or metal-thiocyanate complexes due to solution-solid reactions at the low pH conditions. In addition, the relatively high amount of thiocyanate converted to cyanate was likely due to the presence of copper in solution that acted to catalyze the oxidation of thiocyanate fully to cyanate. Test work at Ozonia is ongoing to further define reactions of ozone in a pulp system and to evaluate reaction conditions for optimal cyanide regeneration efficiency. As with the solution test, hydrogen cyanide gas from the bubble-column reactor was collected in a caustic

Table 9 — Cyanide regeneration pilot testing results for clear solution.

Feed solution chemistry:	pH 10.5 0 mg/L total CN 2,580 mg/L SCN
Bubble column reactor residence time:	1.5 hours
Average ozone dosage:	14% (by weight) O ₃ in O ₂ 97% of stoichiometric requirement
Average treated solution chemistry:	pH 1.50 950 mg/L total CN 380 mg/L SCN
Average cyanide regeneration efficiency:	85%

Table 10 — Cyanide regeneration pilot testing results for pulp.

Feed pulp chemistry:	pH 10.4 60 mg/L total CN 5,300 mg/L SCN 0 mg/L OCN 170 mg/L Cu
Bubble column reactor residence time:	3.4 hours
Average ozone dosage:	14% by weight O ₃ in O ₂ 106% of stoichiometric requirement
Average treated pulp chemistry:	pH 1.80 1,230 mg/L Total CN 440 mg/L SCN 760 mg/L OCN
Average cyanide regeneration efficiency:	50%

scrubber, and, for this test, approximately 15% of cyanide reported to this scrubber.

In summary, this test work demonstrated that cyanide could be efficiently regenerated from thiocyanate in a clear solution system, while less efficient regeneration can be affected in a pulp system.

Estimated operating costs

Order-of-magnitude operating cost estimates were developed for the oxidation processes to allow a quantitative comparison of various oxidants. These costs are presented in US dollars and include only costs associated with oxidation reagents, lime for neutralization and power, as summarized in Table 11. Costs presented in Table 11 reflect stoichiometric reagent dosages, though in practice actual reagent dosages would likely be greater than stoichiometric. Construction costs are not presented as the processes require specialized equipment, the costs for which cannot be accurately defined at this time.

A summary of estimated operating costs for cyanide regeneration and for complete thiocyanate destruction to form cyanate is presented in Table 12. Note that the cost for thiocyanate destruction does not include the cost of lost sodium cyanide, which is approximately \$1.10/kg of thiocy-

Table 11 — Reagent purchase costs.

Reagent	Purchase cost
Ozone	\$0.90/kg
Chlorine	\$0.30/kg
Hydrogen peroxide	\$1.25/kg
Caro's acid	\$1.00/kg
Sulfur dioxide	\$0.25/kg
Lime (CaO)	\$0.08/kg
Power	\$0.05/kW-hr

Note: Ozone production cost assumes 18 kW-hr per kilogram of O₃, including the cost for purified O₂ production.

Table 12 — Approximate operating costs for thiocyanate oxidation processes.

Process	Cyanide regeneration,	Thiocyanate destruction,
	\$/kg regenerated NaCN	\$/kg destroyed SCN
Ozone	\$0.97	\$1.07
Sulfur dioxide	\$1.35	\$1.49
Chlorine	\$1.67	\$1.86
Electrolytic	\$1.78	—
Hydrogen peroxide	\$2.69	\$3.02
Caro's acid	\$7.34	\$8.25

anate destroyed. Therefore, the net total cost for thiocyanate destruction would be the costs indicated in Table 12 plus approximately \$1.10/kg of destroyed thiocyanate.

Overall, it appears that the ozone oxidation process would be the least expensive of the processes considered. However, within the accuracy of these estimates, the chlorine, sulfur dioxide and electrolytic processes would have similar operating costs. Note that the ozone, chlorine and sulfur dioxide processes appear to be capable of regenerating cyanide for less than the purchase cost of new sodium cyanide. Relative to the solution chemistry following treatment with each of the oxidants considered, it appears that all except the ozone, hydrogen peroxide and electrolytic processes would yield high total dissolved solids (TDS) concentrations.

Summary and conclusions

To date, there have been no full-scale operations in which cyanide has been regenerated from thiocyanate. However, in cyanidation operations where high cyanide consumption is attributed to thiocyanate formation, it appears that several

oxidation technologies would be suitable for the regeneration of cyanide from thiocyanate. Specifically, these regeneration technologies appear well suited to metallurgical operations where a bacterial sulfur-oxidation process is employed or where sulfide concentrates are leached. With a system involving the regeneration of cyanide in a clear solution, the cost of cyanide regeneration would approximately equal the value of recovered sodium cyanide, and it appears that cyanide regeneration would be less expensive than thiocyanate destruction.

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