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Impact of recycling cyanide and its reaction products on upstream unit operations

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ABSTRACT

A typical operations outcome to dealing with the environmental and economic issues associated with cyanide in gold plant tailings streams involves the recycle of cyanide and its associated reaction products. This recycle stream may take the form of return dam water or tailings thickener overflow to the mill, or a cyanide recovery stream to the leach from a SART (sulphidization–acidification–recycling–thickening) or AVR (acidification–volatilization–reneutralization) circuit. The chemical composition and cyanide speciation of these solutions may be relatively complex, containing various metal cyanide species, thiocyanate, cyanate and other breakdown products.

Several of these species are reported to have a deleterious effect on upstream unit operations. For example, while cyanide is in common use as a depressant for pyrite in mineral flotation, ferrocyanide and thiocyanate ions have also been shown to exhibit a depressant action in some cases. Primary flotation recovery of gold can thus be compromised and may be responsible for significant lost revenue, particularly from high-grade refractory gold operations. Bioleaching plants tend to separate cyanide circuits to an independent water balance to ensure that no cyanide or thiocyanate returns to inflict dire consequences on the bacterial population. Tolerable levels of these ions are exceedingly low, creating a risk factor and constraining water balance flexibility. Milling-in-cyanide has been periodically mooted as a beneficial circuit modification, particularly in operations that have tailings thickening, SART or dolomitic ore from which significant levels of free and complexed cyanides and thiocyanates are present. Potential consequences include unwanted side reactions with freshly activated mineral surfaces within mills operating at elevated temperatures and significant cyanide losses under these conditions.

The evidence for the effects of recycled cyanides and associated species on upstream gold processing circuits have to date not been assessed in a systematic fashion. This paper presents a review of the available literature and analysis of associated data in these areas. Common arguments from operators justifying certain process plant configurations, modifications and operating setpoints around recycle streams are examined. Impacts of cyanide recycle on milling, flotation and bioleaching are quantified in the context of exemplary case studies. The various literature and case study flowsheets provide a useful analysis of the application of recycle streams to operating plant flowsheets, often requiring creative or inelegant solutions. In the current work, plant operating data is analyzed to quantify some of these effects; moreover, a simulation model has been developed to further quantify and explain some of these effects and provide insight into the decision-making process for plant designers and operators alike. Recycles without water treatment or other means may raise thiocyanate and cyanide levels above site-specific tolerances for operability.

1. Introduction

Gold plants are under increasing pressure to recycle water back to unit operations in the front end of their processes. Tightening restrictions on aqueous emissions discharging to tailings storage facilities (TSF) and to the environment are brought to bear on decisions to recycle. Operations in arid regions such as Australia, Africa and North America are particularly affected by water budget issues and the negative water balance and low or unassured availability of process water adds further incentive to minimize water losses.

The presence of cyanide in tailings water provides a compelling case in some instances for recovery or recycle of the reagent used to leach gold in the first place (Fleming, 2005). The economic benefit of supplementing make-up cyanide reagent with recovered cyanide from process streams is worthy of consideration, but offset by the capital and operating costs involved on a case by case basis. Industry initiatives such as the International Cyanide Management Code

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(Gibbons, 2005) as well as local or country discharge regulations for cyanide, metals and other chemicals found in these streams makes a case for minimizing mass flows at discharge points.

An important consideration in any recycle stream scenario is the impact of components of the stream on upstream unit process, as well as the buildup of aqueous concentrations in these streams. Of particular concern is cyanide and its reaction products, both from an economic aspect and potential impact on unit efficiencies. This paper addresses the question of whether cyanide in recycle streams is fully utilized or partly destroyed in milling and associated circuits. Also examined are the nature and potential impact of chemical species (Smith and Mudder, 1991; Adams, 2001) including cyanide, metallocyanide complexes, thiocyanate, cyanate and ammonia, on flotation and bioleaching circuits.

2. Cyanide and reaction products in gold plant streams

2.1. Cyanide

Only a tiny portion of the dosed cyanide in a leach circuit is utilized to solubilize gold as the aurocyanide complex $Au(CN)_2^-$. Excess free cyanide is required to provide the equilibrium driving force for the cyanide leach reaction typically depicted as Eq. (1), resulting in significant free cyanide concentrations in spigot discharge to TSF:

$$\text{Anodic}: Au + 2CN^- \rightleftharpoons Au(CN)_2^- + e \quad (1)$$

$$\text{Cathodic}: O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O \quad (2)$$

Free cyanide is present at equilibrium with dissolved HCN, with Reaction (3) having a pK_a of 9.2.

$$CN^- + H^+ \rightleftharpoons HCN \quad (3)$$

2.2. Metallocyanide complexes

Additionally, gold ores and concentrates contain minerals and chemicals that are cyanide consumers (cyanicides) and allowance must be made for these side reactions to be satisfied in the leach by further overdosing of the cyanide lixiviant. There is a wide range of cyanide complexes of different stabilities that are formed with metals including Au, Ag, Cu, Ni, Fe, Zn, Co that are commonly found in these plant solutions (Eq. (4)):

$$M^{x+} + yCN^- \rightleftharpoons M(CN)_y^{x-y} \quad (4)$$

The stability constants of the most important metallocyanide complexes are listed in Table 1 in order of increasing stability and grouped into free, weak, moderately strong and strong complexes. Note that typical categorization of cyanides into weak acid dissociable (WAD), strong acid dissociable (SAD) and total cyanide (TCN) are analytical method-based, comprising the complete or partial dissociation of the complex species in Table 1 under different measurement conditions.

2.3. Reaction breakdown products

Thiocyanate is formed in gold plant cyanidation pulps by the reaction of cyanide with labile sulphur in the ore, which may be released by the action of oxygen, lime or cyanide on reactive sulphide minerals. Thiosulphate, polythionate, sulphide and polysulphide ions are variously produced during the oxidation of many sulphide minerals. While these ions are unstable to oxidation by dissolved oxygen, they can be present in solution for extended periods, available for reaction with cyanide and in some cases representing a substantial contribution to overall cyanide consumption:

$$S_2O_3^{2-} + CN^- \rightleftharpoons SCN^- + SO_3^{2-} \quad (5)$$

$$2S_2O_3^{2-} + O_2 + 2CN^- \rightarrow 2SCN^- + 2SO_4^{2-} \quad (6)$$

$$2S^{2-} + 2CN^- + O_2 + 2H_2O \rightarrow 2SCN^- + 4OH^- \quad (7)$$

$$S_2^{2-} + CN^- \rightleftharpoons SCN^- + S^{2-} \quad (8)$$

Table 1
Stability of important cyanide species in gold plant streams.

Category	Species	Log K_n
Free cyanide	CN^-	n.a.
	HCN	9.2
Weak complexes	$Cd(CN)_4^{2-}$	17.9
	$Zn(CN)_4^{3-}$	19.6
Moderately strong complexes	$Cu(CN)_2^-$	16.3
	$Cu(CN)_3^{2-}$	21.6
	$Cu(CN)_4^{3-}$	23.1
	$Ni(CN)_4^{2-}$	30.2
	$Ag(CN)_2^-$	20.5
Strong complexes	$Fe(CN)_6^{4-}$	35.4
	$Fe(CN)_6^{3-}$	43.6
	$Co(CN)_6^{3-}$	64.0
	$Hg(CN)_4^{2-}$	39.0
	$Au(CN)_2^-$	38.3

It may be necessary to remove thiocyanate from the tailings, depending on local legislation. While thiocyanate is not currently deemed significantly toxic to warrant consideration in most parts of the world, there are instances where this is not the case. The Russian Federation requires both cyanide and thiocyanate to be removed from cyanide tailings (Russian Federation Main State Sanitarian Doctor, 2003; Russian Federation State Fishery Committee, 1999).

Products from the oxidation of cyanide include cyanate (OCN^-), ammonia (NH_3) and carbonate (HCO_3^-, CO_3^{2-}) via some intermediate urea ($CO(NH_2)_2$):

$$2CN^- + O_2 \rightleftharpoons 2OCN^- \quad (9)$$

$$CNO^- + 2H_2O + H^+ \rightarrow NH_4^+ + HCO_3^- \quad (10)$$

$$CNO^- + NH_4^+ \rightarrow CO(NH_2)_2 \quad (11)$$

Ammonia in discharge streams is subject to regulation in some parts of the world. Cyanide in both bound and free states can be oxidized via the reactions presented in Eqs. (9)–(11) ultimately to carbon dioxide and nitrogen.

2.4. Cyanide destruction products

The oxidation reactions are constrained by their relatively slow rates as well as the low oxygen solubility in water. Modern cyanide detoxification circuits therefore typically employ chemical oxidation processes, such as the SO_2/Air process, the peroxide (H_2O_2) process, and the Caro's acid (H_2SO_5) process.

The SO_2/Air process, originally developed by DeVuyst et al. (1989) uses air or oxygen sparging along with either gaseous SO_2 sparging or addition of chemical forms of the active form, such as sodium meta-bisulphite ($Na_2S_2O_5$) or sodium sulphite (Na_2SO_3), along with copper (II) sulphate as catalyst if insufficient copper is present in solution. The reactions depicted in Eqs. (12) and (13) apply for reaction with cyanide and thiocyanate, respectively:

$$SO_2 + O_2 + H_2O + CN^- \rightarrow OCN^- + SO_4^{2-} + 2H^+ \quad (12)$$

$$SCN^- + 4SO_2 + 4O_2 + 5H_2O \rightarrow CNO^- + 5H_2SO_4 \quad (13)$$