Electrochemical behavior of gold cyanidation in the presence of a sulfide-rich industrial ore versus its major constitutive sulfide minerals

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ABSTRACT

A detailed study on the relative importance of passivation phenomena and galvanic interactions during gold cyanidation was carried out. Mineral disc electrodes consisting of a sulfide-rich industrial ore and major sulfide components were prepared along with an Au electrode (gold/silver alloy) in use for gold leaching rate tests. These leaching tests that were conducted by hyphenating gold and mineral disc electrodes conjointly in one electrochemical cell or in two separate electrochemical cells objectified both passivation-induced setbacks as well as boosts by Au/mineral galvanic interactions on gold dissolution. To decipher the role of sulfide ores on gold cyanidation, a systematic study was performed by monitoring the leaching behavior of an Au disc electrode successively immersed in slurries of industrial ore and its major sulfide constituents, i.e., pyrite, sphalerite and chalcopyrite. The tested mineral constituents and ore exhibited an inhibiting effect on gold leaching, decreasing in the following order: chalcopyrite>sphalerite>industrial ore>pyrite. Pre-oxidation of the industrial sulfide ore prior to cyanidation improved the gold leaching rate. However, in spite of noticeable reductions in cyanide consumption, no beneficial effect of pre-oxidation on gold leaching was observed for the major sulfide (ore) constituents when tested separately. Although cooperating permanent galvanic interactions between gold and main constitutive minerals in the industrial ore prompted higher gold leaching rates, predictability of the latter from lab-controlled leach tests of the nearly pure constitutive sulfide minerals still remain premature.

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1. Introduction

Since the discovery of gold dissolution in cyanide solutions in 1783 by Carl Wilhelm Scheele (Marsden and House, 2006), myriad studies followed to elucidate the mechanisms in play during this reaction. Elsner (1846) was the first to shed light on the mechanism of gold dissolution in aerated cyanide solutions while cyanidation evolved coevally into a commercial process after a patent filed by MacArthur et al. (1887). Nowadays, with virtually depleted gold-bearing oxide deposits around the globe, gold extraction from less friendly sulfide deposits is stretching the limits of cyanidation into uncharted territories. Unlike oxides, which divert marginal quantities of cyanide and have generally minor impact on gold leaching (Marsden and House, 2006), most of the corresponding metal sulfides display a range of reactivity in alkaline gold leaching cyanidation (Marsden and House, 1992, 2006). Due to poor cyanide selectivity for gold over the enclosing sulfide mineral matrix, such parasitic reactions inflict utility extra costs and profit losses resulting from high levels of cyanide consumption and/or some side-reaction

products which can directly reduce the gold leaching rate. Consequently, gold processing has become more complex and early mechanisms, as described by Elsner in simple cyanide solutions, cannot be relied upon to anticipate the behavior of gold dissolution in the presence of metal sulfides.

Since most of the sulfide minerals are endowed with significant electric conductivity allowing charge transfer at their surface, galvanic interactions, by virtue of gold–sulfide contacts, could substantially increase or decrease the leaching of gold in aerated cyanide solutions. In principle when gold open circuit potential is lesser than that of sulfides, gold anodic dissolution can be prompted (Aghamirian and Yen, 2005). Conversely, galvanic phenomena can also impede gold dissolution when the adjoining sulfide mineral acquires anodic potential prompting on gold surfaces oxygen reduction rather than gold dissolution (Aghamirian and Yen, 2005). However, there is still some controversy regarding the role of galvanic interactions on gold dissolution. Filmer (1982), Paul (1984) and Lorenzen and van Deventer (1992) postulated that the presence of pyrite and pyrrhotite substantially decreases gold leaching rate that they ascribed to galvanic effects. Aghamirian and Yen, (2005) and Dai and Jeffrey (2006) interrogated systematically the interrelation between galvanic effects by some sulfides (i.e., pyrite, chalcopyrite, pyrrhotite, galena, chalcocite) and the kinetics of gold leaching. Their findings concluded

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that pyrite, pyrrhotite and galena induce positive galvanic interactions promoting gold dissolution when a gold electrode was paired with one of those sulfides; unlike chalcopyrite and chalcocite for which contradictory results were reported in the literature.

Meaningful comparisons of the findings among above studies are difficult to establish since various experimental strategies were used by different authors. For example, Lorenzen and van Deventer (1992) used a high-purity gold electrode that is now accepted to be highly vulnerable to passivation (Jeffrey and Ritchie, 2000) and not representative of the naturally-occurring gold/silver alloys. In the same study, while a correct approach was devised to study macroscopic galvanic couples by pairing the gold and mineral electrodes first in one cell and then in two separate cells, in contrast, the galvanic current and potential as a function of time were not reported. In addition, no anodic and/or cathodic behaviors of minerals were considered. In Aghamirian and Yen's (2005) study, galvanic couples were tested only in one single electrochemical cell unveiling only global outcomes on gold leaching from combined galvanic interactions and surface passivation. In Dai and Jeffrey's work (2006), the galvanic current/potential conditions relating to the Au-minerals contacts were barely detailed. In addition, in the majority of the relevant studies, indications about the mineralogy of the studied minerals were seldom provided. For example, pyrite often occurs naturally in association with other minor sulfides which, even if present in minute quantities, tend to play an important role in shaping pyrite reactivity (Cruz et al., 2001) and as a consequence in affecting the extent of galvanic interactions on gold leaching.

A number of sulfide minerals readily dissolve in aerated cyanide solutions making gold cyanidation a process difficult to optimize. Hence, numerous investigations were carried out to understand how the resulting dissolution products would interfere with gold leaching (Hedley and Tabachnick, 1968; Liu and Yen, 1995; Deschenes et al., 1998; Guo et al., 2005; Dai and Jeffrey, 2006; Breuer et al., 2008). It is generally accepted that sulfides interfere with gold dissolution through: (1) excess cyanide and oxygen consumptions as a result of transition metals (such as Cu, Fe and Zn) dissolution (Habashi, 1967), (2) gold surface passivation by some reaction products such as Fe (OH)$_3$ (Guo et al., 2005) or sulfur (Lorenzen and van Deventer, 1992; Dai and Jeffrey, 2006), which are suspected to form a passivating layer on the surface of gold, (3) detrimental effects by sulfide ions on gold leaching rate as pointed out by several authors (Weichselbaum et al., 1989; Jeffrey and Breuer, 2000).

Atmospheric pre-oxidation was shown to be an effective tool to knock-down the undesirable reactivity of certain sulfide minerals such as marcasite and pyrrhotite (Marsden and House, 2006). Ore pre-oxidation strategies are thus investigated as preventive measures to turn their sulfide cyanicides into barren entities vis-à-vis cyanide consumption. However, pre-oxidation mitigation measures were often tested on individual sulfide minerals. Multi-factorial galvanic interactions stemming from the different mineralogical phases present in the ore during pre-oxidation were disregarded which may give rise to totally different subsequent cyanidation responses. In addition, the effect of these interactions on the speciation of the reaction products was only poorly addressed in the open literature. Thus, developing pre-oxidation strategies that will consider the mineralogical specifications of the industrial gold ore still remains an opportunity where a contribution could be made.

In consideration of above interrogations, this work aims at several targets:

1. to investigate the effects of sulfide ores and minerals on gold leaching during cyanidation;
2. to attempt sorting out the individual contributions during cyanidation as effected by galvanic interactions between gold and sulfide minerals and by the formation of passivating layers on gold surface; and

3. to investigate the effects on gold leaching rate of pre-oxidation of sulfide ore and its sulfide minerals components prior to cyanidation.

2. Experimental

2.1. Reagents

Distilled water was used for all our cyanidation/pre-oxidation experiments. Sodium cyanide, NaCN (98%, Sigma-Aldrich Canada), sodium hydroxide, NaOH (Fisher Scientific Canada), calcium hydroxide Ca(OH)$_2$ (95%, Sigma-Aldrich Canada), boric acid H$_3$BO$_3$ (99.5%, Sigma-Aldrich Canada), and KAu(CN)$_2$ (98%, Sigma-Aldrich Canada) used in this study were all certified analytical grade.

2.2. Materials

Four sulfide-rich ore samples were used in the present work. One sample (MRI-1) came from a mine in the northwest of Québec province, Canada, while the other three samples were provided by Ward's Natural Science and referred to as pyrite (MRI-2), chalcopyrite (MRI-3) and sphalerite (MRI-4) by virtue of the dominant proportion of the named sulfide mineral therein (see Table 1). The samples had a controlled particle size distribution and were stored in the freezer to minimize surface alterations.

Tables 1 and 2 describe, respectively, the mineralogical composition and the elemental analysis of each mineral. All minerals were characterized using a combination of atomic absorption spectrometry, scanning electron microscopy (SEM) and X-ray diffraction patterns (XRD). The first mineral (MRI-1) is clearly more complex than the others, having more metallo-species and also a more complicated mineralogy. The mineralogical weight distribution of sulfides for MRI-1 ore was 44.15% pyrite, 0.11% chalcopyrite, 0.31% sphalerite and some traces of galena and arsenopyrite (Table 1). Fig. 1a and b shows the mineralogical associations of the main sulfide phases for MRI-1; as will be shown later, these associations are believed to have a direct influence on the behavior of the ore during cyanidation.

2.3. Electrochemical campaign

2.3.1. Preparation of disc electrodes

The experiments were carried out using a Rotating Disk Electrode (RDE) system, as this technique was shown to ensure reproducible experimental conditions (Churchill and Laxen, 1966). The electrochemical behavior of gold was studied using a gold/silver alloy (96%–4% by weight) disc, mimicking industrial situations where gold usually occurs alloyed with silver. The active surface area of the Au/Ag disc, in contact with the cyanidation medium, was 1.09 cm^2 and was embedded in a Teflon disc holder so only its lower surface was exposed to the solution. This disc holder was then threaded and attached to a Teflon rod itself threaded and attached to the main steel

Table 1
Mineralogical composition of the four sulfide ore samples.

Ore/Phase	Pyrite (FeS$_2$)	Chalcopyrite (CuFeS)	Sphalerite (ZnFeS$_2$)	Galena (PbS)	Arsenopyrite (FeAsS)	Gangue
	% w	% w	% w	% w	% w	% w
MRI-1 (industrial ore)	44.15	0.11	0.31	0.05	0.08	55.3
MRI-2 (pyrite)	96.6	tr.	tr.	tr.	tr.	3.4
MRI-3 (chalcopyrite)	0.8	63.2	18.3	tr.	tr.	17.7
MRI-4 (sphalerite)	4.7	tr.	90	tr.	tr.	5.3

tr.: trace (<0.05%w); Gangue: SiO$_2$ (maj.), Al$_2$O$_3$, CaO, MgO.