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Preg-robbing verification and prevention in gold chloride-bromide leaching

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ABSTRACT

The use of cyanide is becoming more challenging due to the related environmental risks, increasing the interest in cyanide-free gold leaching. Chloride-bromide leaching is one of the widely investigated alternative lixiviants for gold recovery. However, gold is known to adsorb or precipitate readily on the carbonaceous matter present in the ore, being one of the challenges in chloride process development.

The current study presents an equation indicating gold loss due to preg-robbing into solids in chloride-bromide media. The equation was verified using a naturally preg-robbing gold concentrate. It was shown that the graphite naturally present in gold ore can be an equally active preg-robbing agent for gold chloride complex as industrially manufactured and commercially available activated carbon. In order to study preg-robbing prevention during gold leaching in chloride-bromide media, carbon blinding, and Cl_2-pretreatment were applied. Blinding with ShellSol D70 was shown to improve gold recovery only slightly whereas Cl_2-pretreatment was shown to increase gold recovery from 2% to 45% for a naturally preg-robbing gold concentrate.

1. Introduction

The preg-robbing phenomenon, i.e., gold precipitation back onto the gold ore or concentrate during gold leaching, in chloride as well as in cyanide media, has been known for decades (Aylmore, 2005). Almost all gold lixiviants are known to suffer from preg-robbing. However, the nature and the extent of preg-robbing and gold complex stability vary. (Aylmore, 2005; Miller et al., 2005) Gold cyanide complexes are the most stable gold complexes, followed by thiosulfates. Gold chloride complexes are not as stable as cyanide complexes and are also less stable than other halide (Br, I) complexes. (Aylmore, 2005) This indicates that the tendency for preg-robbing can be higher in gold chloride leaching compared to thiosulfate and cyanide leaching.

The tendency of gold to precipitate on various (organic) substances was well known as early as the 1800s (Rose, 1896) and the major issue in the development of gold chlorine/chloride leaching technology has been the tendency of gold to precipitate onto the ore, wood, or other organic material or construction material that is in contact with a gold-containing solution.

Preg-robbing is mostly associated with carbonaceous matter, such as hydrocarbons, organic acids, or natural carbon, the latter being the most important species for preg-robbing (Adams and Burger, 1998). The preg-robbing effect of carbonaceous matter for gold cyanide complex is substantially stronger than any of the other minerals present. In addition, carbons differ in their preg-robbing activities; amorphous carbon (free reactive carbon without a crystalline structure) has been identified as the main carbon form causing preg-robbing. In contrast, a shale ore with graphitic material has been found to have a lower degree of preg-robbing. In addition, hydrocarbons have been found to have only a minor effect on preg-robbing (Adams and Burger, 1998).

Other minerals can also cause preg-robbing. Silica, in the forms of quartz (Baghalha, 2007; Mohammadnejad et al., 2014a), pyrophyllite (Mohammadnejad et al., 2014b), feldspar, kaolinite, and mechanically activated silica, has been found to reduce gold complexes from chloride solutions. Mechanical activation of silica can break the covalent ≡Si−O bonds and create reactive sites (free radicals of ions) where the gold chloride complex can first adsorb and then precipitate (Mohammadnejad et al., 2012). However, for cyanide solutions it has been reported that the effect of mica (phyllosilicate) on preg-robbing is negligible compared to that of carbonaceous matter (Adams and Burger, 1998).

It is also known that gold present in chloride solutions precipitates on sulfide surfaces at lower redox potentials. Mikhlin and Romanchenko (2007) found that the gold uptake for different sulfide minerals changed in the order $CuFeS_2$ > ZnS > PbS > FeAsS > FeS_2 > Fe_7S_8 for polished mineral surfaces with 10^{-4} M $[AuCl_4]^-$ at pH 1.5. However, compared to carbonaceous matter, the preg-robbing effect of pyrite and other sulfide minerals is minor for gold cyanide solutions (Adams and

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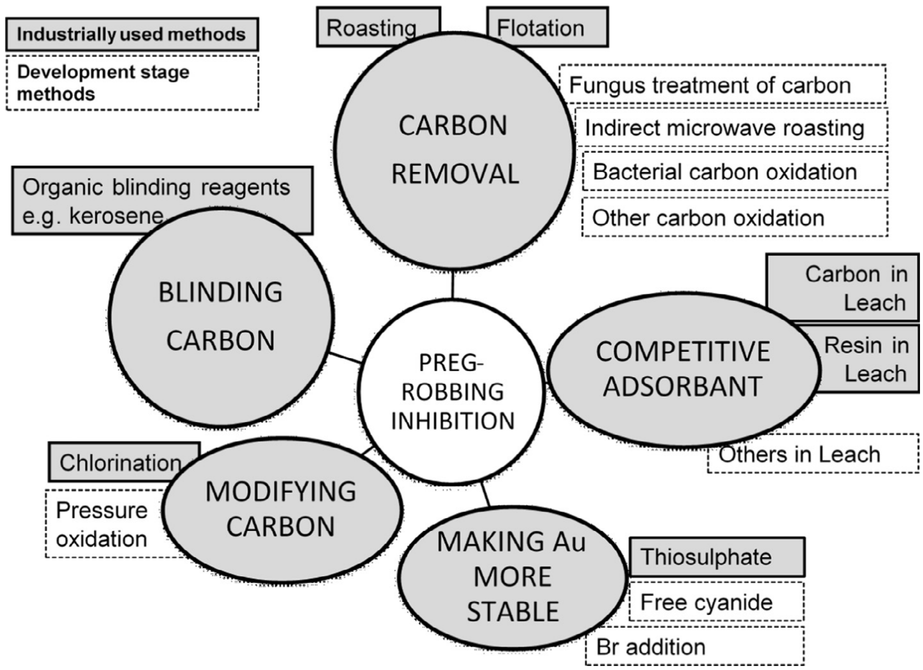

Fig. 1. Classification of industrially used (gray) and development stage (dashed lines) preg-robbing inhibition methods for dealing with preg-robbing by carbonaceous materials in hydrometallurgical gold production.

Burger, 1998).

In cyanide media, preg-robbing prevention can be classified according to the phenomenon behind the method: carbon removal, carbon blinding, carbon modification, providing a competitive adsorbant, or increasing the gold complex stability in the solution (Fig. 1). Roasting is the oldest technique and for a long time it was the only commercial means for handling preg-robbing gold ore. However, environmental concerns may also favor the use of other sulfide decomposition/preg-robbing prevention methods. (Miller et al., 2005; Marsden and House, 2006; Chryssoulis and McMullen, 2005). In addition, carbon removal by flotation (Sibrell et al., 1990) has been industrially applied, e.g., at the Agnico Eagle Mines Kittilä mine, Finland, where graphite pre-flotation has been applied to decrease preg-robbing and increase gold recovery (Agnico Eagle Mines Limited, 2015).

Many blinding agents such as light petroleum oils, anionic and nonionic surfactants, and cationic surfactants have been tested and used to prevent preg-robbing to some extent in conventional cyanide leaching processes. Blinding chemicals can block the active sites of carbon, thus preventing preg-robbing. For instance, kerosene, fuel oil, and RV-2 (para nitro benzol azo salicylic acid) are known to be used for this purpose in gold cyanide leaching. (Afenya, 1991; Zhou et al., 2013).

Carbon modification by Cl_2-pretreatment was used for preg-robbing prevention industrially in the 1970s and 1980s in gold cyanide leaching plants (Sibrell et al., 1990; Anonymous, 1996). However, it is not currently applied industrially. It has been suggested that the mechanism of Cl_2-pretreatment is not the oxidation of carbon to carbon dioxide, but the modification of active sites of carbon forming chlorohydrocarbon or carbonyl structures of carboxyl groups (Adams and Burger, 1998). These groups with negative charge passivate or block the active sites of carbon, repelling gold complexes (Marsden and House, 2006). Cl_2-pretreatment was practiced industrially at least at Newmont in the 1970s and at Jerritt Canyon in the 1980s, for sulfide-carbon-rich and carbon-rich ores, respectively (Sibrell et al., 1990; Anonymous, 1996). These plants have been shut down due to the lack of carbonaceous oxide ore and the price of chloride gas. (Marsden and House, 2006; Miller et al., 2005).

In addition, there are several preg-robbing prevention methods in the development stage such as carbon removal by biodegradation (Ofori-Sarpong and Osseo-Asare, 2013: Liu et al., 2016). It is suggested that micro-organisms in leaching can simultaneously reduce the carbon content of the ore and improve gold recovery from a carbon-containing ore (Portier and Rouga, 1991). Carbon modification by long-term oxidation has also been investigated as a potential method for creating surface groups that repel preg-robbing (Marsden and House, 2006; Rose, 1896; Sibrell et al., 1990; Tuncuk et al., 2012). Also, the presence of free cyanide decreases the tendency for pre-robbing on sulfidic materials in cyanide solutions. (Rees and van Deventer, 2000).

The mechanism of preg-robbing differs in cyanide and chloride media. In cyanide media, the aurodicyanide complex is known to adsorb from solution to the carbonaceous ore. (Goodall et al., 2005) The mechanism in gold recovery onto activated carbon is also adsorption, the suggested theory of gold adsorption being physisorption of gold cyanide complex. (McDougall and Hancock, 1981; Pleysier et al., 2008;) In chloride media, the gold preg-robbing mechanism is suggested to be reduction of gold chloride complex by electrons donated by the carbonaceous matter. It has been observed that the content of gold on carbon after exposure in gold chloride solution is relative low. (McDougall and Hancock, 1981; Hughes and Linge, 1989; Sun and Yen, 1993) The carbonaceous material in ore is not the only cause of preg-robbing, but also iron sulfides (e.g. pyrite, arsenopyrite) and silicates may promote this reduction phenomenon in chloride media (Mycroft et al., 1995; Mikhlin et al., 2006; Mohammadnejad et al., 2011).

This paper focuses on studying the tendency of preg-robbing in cyanide-free chloride-bromide leaching. The experimentally demonstrated preg-robbing phenomenon is verified using a naturally preg-robbing concentrate. In addition, two different methods for reducing preg-robbing are investigated in chloride-bromide media: blinding and Cl_2-pretreatment.

2. Materials and methods

2.1. Solution and solid analysis

The solids analysis for base metals were conducted using total dissolution and solution analysis by Inductive Coupled Plasma Optical Emission Spectrometry (Thermo Scientific iCAP 6000). Nitric acid,