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Sulfide precipitation of copper from alkaline glycine-cyanide solutions: Precipitate characterisation

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ABSTRACT

A synergistic leaching system using glycine containing starvation levels of cyanide as lixiviants has been shown to be an effective approach to leach gold-copper ores, allowing the consumption of cyanide to be reduced significantly while glycine is recycled. Sulfide precipitation to remove the bulk of the copper was studied. The previous study on the precipitation behaviour of Cu and Au from the alkaline glycine-cyanide solution shows that the cupric (Cu^{2+}) glycinate can be easily precipitated, while the gold and cuprous (Cu^{+}) cyanide species remain stable in the solution. Due to the sparingly soluble nature of metal sulfides, colloidal and poorly settling particles are usually formed without control methods, which create challenges for solid-liquid separation processes such as thickening and filtration. This study investigated the effects of chemical and operational conditions on particle characteristics particularly particle size distributions (PSD). Settling characteristics, particle morphologies and particle structure were also studied. In the presence of divalent cations such as Ca^{2+} and Mg^{2+}, particularly Ca^{2+}, large and fast settling particle agglomerates were generated. Increasing ionic strength of the solution was also noted to enlarge the particles. The high supersaturation level has insignificant effects on the PSD as long as Ca^{2+} is present. A relatively large particle size is generated at a medium stirring speed with fast addition rate. There are no significant effects of aging, heating, and seeding on the PSD, but these factors profoundly influenced the morphologies of the individual particles according to the SEM results. SEM and XRD analysis illustrate that a more mature and crystalline copper sulfide precipitates were produced after aging, heating, or seeding.

1. Introduction

A synergistic glycine-cyanide leaching system has been studied and reported by numerous authors Oraby & Eksteen (2015) and Oraby et al. (2017) indicating that it is a possible alternative leaching process to conventional cyanidation for processing gold-copper ores, which are normally excessive cyanide consuming ores. In the presence of glycine, the cyanide consumption can be significantly reduced, e.g. by at least 75% (and often > 90%) compared to conventional cyanidation whilst allowing glycine recycle. In this leaching system, the pregnant leach solutions contain Au and Cu which mostly presents as cupric glycinate and a small portion of cuprous cyanide species. In a synthetic glycine-cyanide solution, the Cu^{2+}/Cu^{+} ratios are controlled by the $[Cu_T]:[Gly]:[CN^{-}]$ ratio in the system by adding CuCN, glycine and NaCN accordingly (Deng et al., 2019; Tauetsile et al., 2019a,b). The carbon adsorption tests specific to the glycine-cyanide system in the presence of gold and copper carried out by Tauetsile et al. (2019a,b) elaborate that gold can effectively adsorb onto activated carbon. However, it was also illustrated that the competing adsorption of copper onto activated carbon cannot be avoided and the cuprous cyanide species in solutions have higher affinity onto the activated carbon than their cupric glycinate counterparts.

In order to explore the feasibility of other downstream processes for the novel glycine-cyanide leaching system, a conventional sulfide precipitation for the recovery of Cu was studied (Deng et al., 2019). The authors found that the cupric glycinate in the system can be easily precipitated in 5 min by adding concentrated NaHS solutions. The copper recovery was found to be dominated by the Cu^{2+}/Cu^{+} ratio, as the cuprous cyanide species cannot be precipitated under alkaline conditions. Pre-oxidation tests of Cu^{+} to Cu^{2+} using hydrogen peroxide was conducted; with basically all cupric glycinate in solutions, a high copper removal (~96.5%) was achieved with a $[HS^{-}]:[Cu_T]$ ratio of

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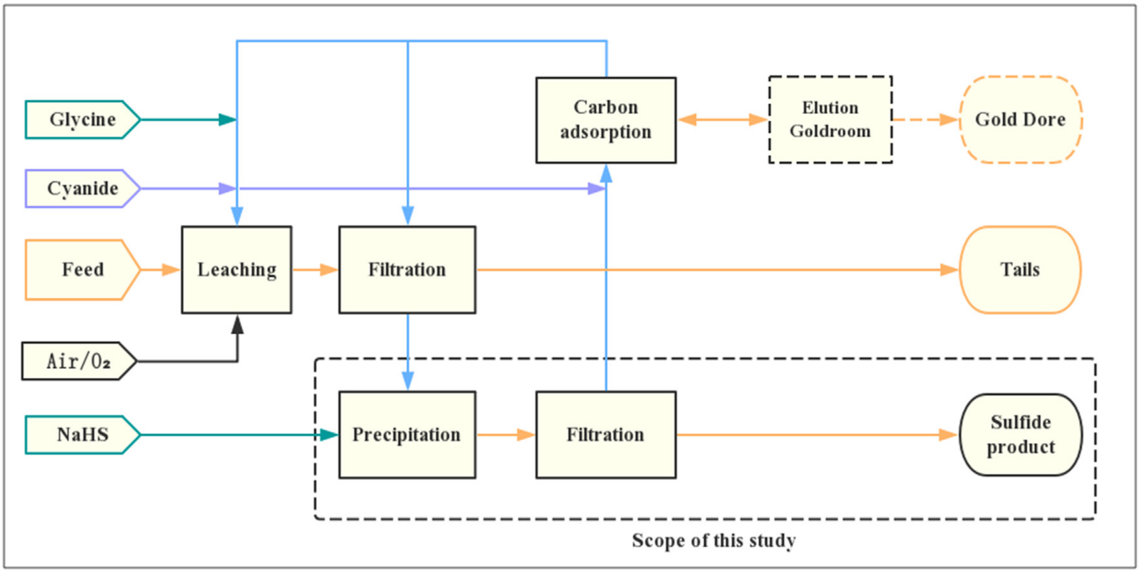

Fig. 1. Block diagram flowsheet of glycine leaching process utilising cyanide at starvation levels with copper removal by sulfide precipitation and carbon adsorption (Seaman et al., 2019).

1.4:1. The authors showed that a high level of gold and copper separation can be achieved by H_2O_2 oxidation followed by sulfide precipitation where no gold precipitation was observed. By this means, copper can be effectively removed under alkaline conditions without intensive pH modification before traditional carbon adsorption for gold recovery, minimizing the competitive effects of copper onto the activated carbon.

A recent pilot plant campaign (Seaman et al., 2019) was conducted to demonstrate the metallurgical performance of the alkaline glycine leaching system under starved cyanide conditions in a continuous, closed-circuit operation, as applied to low-grade copper-gold flotation (rougher) concentrates. A flowsheet including copper recovery by sulfide precipitation and gold recovery by carbon adsorption is illustrated in Fig. 1 (Seaman et al., 2019). The results demonstrated that almost all Cu^{2+} was successfully removed as covellite with no Cu^{+} and Au precipitation.

However, metal sulfide precipitation reactions are usually difficult to control due to the sparingly soluble nature of sulfide precipitates (very low solubilities) and high supersaturation levels (up to 10^{35} and higher) (Lewis & van Hille, 2006; Mokone et al., 2010), which lead to very fine and highly dispersed particles usually being generated. This can result in significant technical difficulties regarding solid-liquid separation and the downstream recovery processes. Therefore, the PSD should be optimized to an acceptable level for solid-liquid separation processes.

Similar difficulty was noted by the authors that extremely fine precipitates (highly dispersed particles) were generated after adding NaHS solutions at the preliminary stage of a previous study focusing on sulfide precipitation chemistry, where the pH of the synthetic solutions was only adjusted by NaOH (Deng et al., 2019). It was observed that the particles were very fine and a large portion of fines cannot be filtered by the 0.45 μm membrane filter paper. It was found that if the pH of the synthetic solutions were adjusted by NaOH and $Ca(OH)_2$, large and filterable precipitates were generated. This phenomenon implied that the addition of Ca^{2+} or other cations can be a critical factor for the formation of large precipitates (Deng et al., 2019).

There are many studies which addressed the issues of the formation of fines through controlling the chemical conditions such as sulfide and initial metal concentrations (Al-Tarazi et al., 2005; Farahani et al., 2014; Lewis & van Hille, 2006; Sampaio et al., 2010) and operational conditions such as stirring speed (Eksteen et al., 2008; Farahani et al., 2014; Houcine et al., 1997; Marcant & David, 1991; Torbacke & Rasmuson, 2001), aging time (Eksteen et al., 2008; Söhnel & Garside, 1992), temperature (Roy & Srivastava, 2007) and adding seed materials (Agrawal et al., 2018; Donnet et al., 2005). However, few of them have investigated the copper sulfide precipitation under alkaline conditions since $Cu(OH)_2$ precipitation will be the dominant species in the precursor aqueous system. None of the studies have investigated the sulfide precipitate characteristics from an alkaline glycine-cyanide solution in the presence of Cu and Au which is mainly a mixture of cupric glycinate, cuprous dicyanide, gold cyanide and free glycine.

To minimise the production of very fine precipitates, a more detailed investigation on the effects of different processing conditions on the copper sulfide precipitates characteristics from the glycine-cyanide solutions was conducted. The main objective of the current study is to investigate the effects of different chemical conditions (i.e. addition of cations, dosage of cations, sulfide concentrations, copper concentrations and ionic strength) and operational conditions (i.e. stirring speed, sulfide addition rate, aging time, temperature, and addition of seeds) on particle characteristics. The settling performance of the precipitates were also investigated as the supplementary evidence for the PSD results. The morphologies of individual particles which may be influenced by aging, heating, or seeding was visualised by Scanning Electron Microscope (SEM). The phase and crystal structure of the precipitated product was identified by means of X-ray Powder Diffraction (XRD). Fig. 2 shows a typical precipitation process with the potential impact factors on each step based on the literatures (Agrawal et al., 2018; Al-Tarazi et al., 2005; Donnet et al., 2005; Eksteen et al., 2008; Farahani et al., 2014; Houcine et al., 1997; Lewis & van Hille, 2006; Marcant & David, 1991; Sampaio et al., 2010; Söhnel & Garside, 1992; Torbacke & Rasmuson, 2001).

2. Experimental design

2.1. NaHS solutions

A 50 g of NaHS solid (Sigma-Aldrich) was dissolved in 100 ml deionised water to make a very concentrated NaHS stock solutions. The sulfide concentration of the stock solution was 5 M which was determined by the concentration of Na and S measured by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). This ICP-OES confirmation is important due to the hygroscopic nature of the