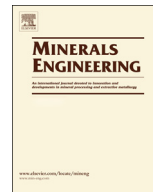




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Optimizing the SART process: A critical assessment of its design criteria

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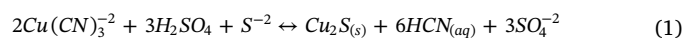
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ABSTRACT

The SART (Sulfidization, Acidification, Recycling and Thickening) process has been successfully installed to recover cyanide and copper in seven worldwide gold cyanidation plants in the last 15 years. This technology has allowed the extraction of gold ores containing high grades of cyanide-soluble copper. However, this process has high capital costs and requires rigorous operational control, which have limited the installation of this process in the last 5 years. These drawbacks have not been overcome despite the successful operation of the SART process worldwide, limiting the interest of gold mining in performing new studies to support new developments in order to optimize plant design. In this framework, this study attempts to give a critical assessment of the design criteria of the SART process, based on experimental work focused on optimizing the SART process, challenging some conventional criteria typically considered in the design of SART plants. Thus, this study involves (i) a kinetic characterization, which allows determining the optimal residence time in the sulfidization reactor to be determined, (ii) oxidation/reduction potential (ORP) measurements with respect to the conversion, which suggest an adequate control logic that maximizes metal recovery in the sulfidization reactor, and finally (iii) settling tests to propose a correct criterion for recycling the settled slurry into the sulfidization reactor. These results show that it is possible to reduce the residence time in the sulfidization reactor by up to 1 min. Furthermore, it was established that the precipitation performance depends on the ORP value. Therefore, a control logic as a function of this parameter could be implemented. Finally, the settling results pave the way for establishing a new criterion for recycling the underflow slurry from the thickener to the sulfidization reactor, based on the copper concentration in the feed solution. Hence, this study proposes new design criteria for future SART plants, saving capital costs and optimizing the metal recovery control.

1. Introduction

The SART technology (Sulfidization, Acidification, Recycling and Thickening) has become the most widely used process for cyanide recovery in gold cyanidation plants. In fact, in the last 15 years 7 SART plants have been successfully commissioned and operated in different gold mines (Guzman et al., 2010; Botz et al., 2011; Dai et al., 2012; Estay et al., 2012; Simons and Breuer, 2013; Hedjazi and Monhemius, 2014; Botz et al., 2015; Fleming, 2016; Baker et al., 2017; Kratochvil et al., 2018; Estay, 2018). This process recovers cyanide and copper from cyanide solutions based on a sulfidization reaction as shown in the following equation (MacPhail et al., 1998):



This reaction must be carried out at a pH level below 5.5. The precipitates generated are recovered using sequential stages of thickener and filter press. The complete typical block diagram of the SART process is shown in Fig. 1, where the sulfidization reactor feeds the precipitation slurry generated into a thickener. This recirculates part of the underflow in the same reactor. The overflow is treated in a neutralization reactor, where the pH increases to 10.5, in order to return the cyanide solution to the gold cyanidation plant. The SART process also includes thickening and filtration steps to remove the gypsum generated in the neutralization unit. All equipment must be connected to a scrubbing system to avoid emanations of HCN and/or H₂S to the

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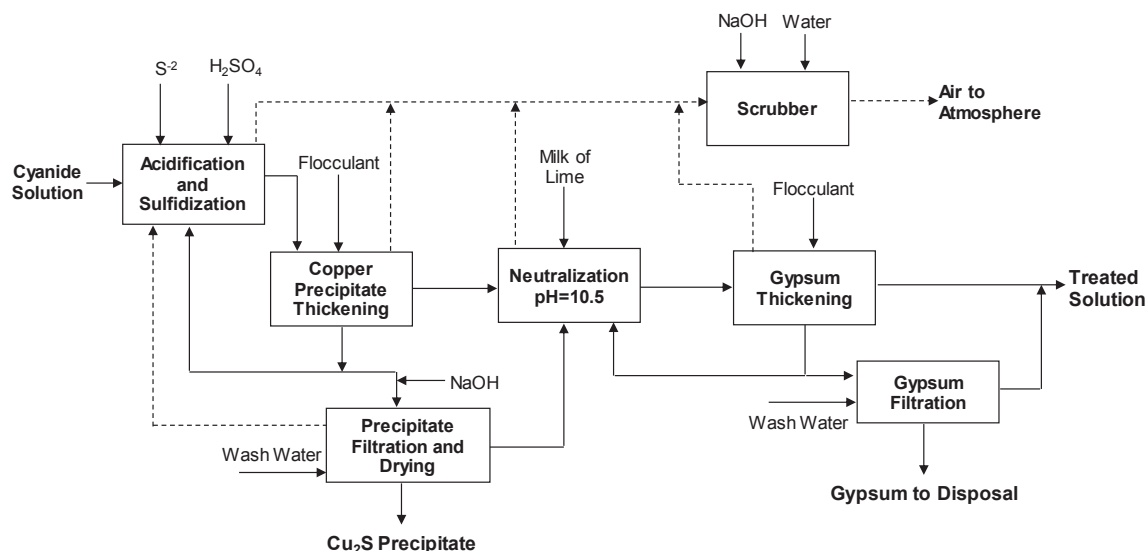


Fig. 1. Typical block diagram of the SART process (after Estay, 2018).

environment.

The flowsheet and equipment of the SART process have in fact remained practically unchanged since the first study published in literature (MacPhail et al., 1998). However, the design criteria of the SART process have been slightly modified since that study. Parameters such as sulfide dosage, pH and residence time in the sulfidization reactor, have each kept their values in similar ranges in the later studies. A brief revision of the main design criteria used in industrial application and some studies are presented in the following sub-sections.

1.1. Sulfidization reactor parameters

The sulfidization reaction presented in Eq. (1) is achieved at pH below 5.5 (depending on the CN/Cu molar ratio presents in the cyanide solution) and using stoichiometric sulfide dosage. The first study of the SART process (MacPhail et al., 1998) was carried out with different sulfide dosages (80–120% stoichiometric), at pH 3.0, assessing the copper recovery obtained for each condition. The sulfide dosage recommended in this study was 105%, in order to avoid H₂S generation and to reduce sulfide consumption. The study developed by Barter et al. (2001) recommended a set pH ranging from 4.5 to 5.0, to reduce acid and lime consumption, and a sulfide dosage of 95% stoichiometric, to avoid the generation of CNS⁻. Later studies (Ford et al., 2008; Dreisinger et al., 2008; Botz et al., 2011; Simons and Breuer, 2011; Lopez et al., 2014) maintained the operational pH range between 4.0 and 5.0, in order to reduce reagent consumption. However, the sulfide dosage was increased by over 100% stoichiometric in order to increase copper recovery to over 90%. This criterion has been taken into account by industrial plants, which currently operate in these pH and sulfides dosage ranges, as shown in Table 1. However, a recent study (Fleming and Melashvili, 2016) proposed to return to using a sulfide dosage criteria closer to 100%, since the excess of sulfide can promote the oxidation of Cu₂S to CuS, or the oxidation of H₂S to S⁰, according to the following reactions:



The Cu₂S oxidation to assess the effect of residence time on SART process performance was firstly proposed by Simons and Breuer (2013). Then, Fleming and Melashvili (2016) argued that the oxidation of sulfides – in the form of H₂S at low pH – to S⁰ is thermodynamically more favorable than the oxidation of Cu₂S, based on the K_{sp} values of CuS and S⁰ (160–180 at 0 °C for S⁰ respect to 70 at 0 °C for CuS).

Nonetheless, elemental sulfur can precipitate with Cu₂S to form an equimolar mixture of Cu₂S·S, which is indistinguishable from CuS. Even though the oxidation reaction of the excess sulfide is not well determined, in both cases the copper grade will decrease. Furthermore, the generation of CuS or S⁰ is not desirable in a SART process, due to the increase of sulfide consumption with no additional increase in copper recovery. For this reason, Fleming and Melashvili (2016) proposed that the pH value should be decreased to between 3.5 and 4.0, in order to ensure high copper recovery. Unfortunately, this study did not show characterizations of precipitates or chemical measurements to support the possible generation of CuS under excess sulfide conditions.

Moreover, the correct way to control the sulfide dosage in the sulfidization reactor has not been reported in detail or with sufficient support. There are SART plants (e.g., Gedabek, Yanacocha, and Maricunga) which set the sulfide addition according to the copper concentration measured in the feed cyanide solution and the stoichiometric dosage defined. For heap leaching plants, where the variability of solution characterization is lower than that the one found in agitation leaching plants, this control criterion is satisfactory. However, lack of rigor might inhibit in-line control, which can change the exact sulfide addition required. In addition, when the variability of the copper concentration is high, e.g., in agitation leaching plants, a more sophisticated and in-line control system must be installed. In this regard, some authors (Lawrence and Lopez, 2011; Kratochvil et al., 2013; Lopez et al., 2014) have proposed the use of a controller, based on the oxide-reduction potential (ORP) value. Nevertheless, they do not give details of the supporting bases of its control philosophy, because the sulfidization reaction (Eq. (1)) is not a reduction-oxidation reaction, and the ORP value depends on the activities of the species contained in the solution. Therefore, it is not possible to obtain an exact ORP value though it is required to keep an optimal sulfide dosage maximizing the copper recovery. In answer to these problems, this work presents a methodology for identifying the utility of an ORP-controller for the sulfide dosage.

The residence time in the sulfidization reactor can fluctuate between 10 and 20 min (Table 1) according to the tests conducted by MacPhail et al. (1998), even when their study recommended that 5 min was enough residence time to complete the reaction. A study developed by Barter et al. (2001) assessed the effect of residence time on the copper conversion. They recommend at least 15 min of residence time, because at 10 min the conversion remains incomplete. Unfortunately, this study only tested three conditions of residence time: fixing pH, sulfide dosage, and cyanide and copper concentration. Therefore, these

Table 1
Recommended design criteria from experimental studies and typical operational conditions in industrial SART plants in operation.

SART experience	[Cu] in the feed, mg/L	pH	S ²⁻ stoichiometric dosage, %	Residence time, min	Copper recovery, %	References
Lobo-Marte tests	250–258	3.0	105	15	> 95	MacPhail et al. (1998)
Telfer tests	100–2,000	4.5–5.0	95	15	> 90	Barter et al. (2001)
Maricunga tests	220–290 (tested), 453 (design)	5.0	95–120	10	80–95	Ford et al. (2008)
Carmacks tests	321–426	4.0–5.0	100–120	15	> 95	Dreisinger et al. (2008)
Copler tests	301–831	4.5	110–115	10	~100	Botz et al. (2011)
Experimental study	1,250–2,000	4.0	112	NA	> 95	Simons and Breuer (2011)
Tests of Kazakhstan's project	95.4	3.9–4.25	120	10	99	Lopez et al. (2014)
Experimental study	523–5,000	3.5–4.0	100	~0	> 95	Fleming and Melashvili (2016)
Telfer plant	1,000–1,500	4.5	116–138	NA	90	Simons and Breuer (2013)
Yanacocha plant	90–740	4.0–4.5	120–140	10	80–99	Guzman and Acosta (2009), Guzman et al. (2010), Botz et al. (2015)
Gedabek plant	600–1,800	5.5	120	20	90–95	Estay et al. (2012), Hedjazi and Monhemius (2014)
Mastra plant	150–1,000	4.0–5.0	115	NA	90	Lawrence and Lopez (2011), Kratochvil et al. (2013)

NA: Not available.

results are not representative of all the SART plant conditions. This fact was not questioned later, and SART plants were installed using a residence time criterion that ranged between 10 and 20 min (Table 1). Likewise, all studies of the SART process have been carried out using residence time values over 10 min. There are only two studies (Stewart and Kappes, 2012; Fleming and Melashvili, 2016) which propose a minimum residence time in the sulfidization reactor, and recommend an in-line reagent dosage avoiding the installation of reactor. However, these studies did not publish experimental results to support these statements.

1.2. Thickening and recycling criteria

The sizing of thickeners in the SART process has been generally performed by consultants or suppliers. Therefore, the values of design criteria for settling rate or underflow recycling percentage are rarely published. A recent review of this technology (Estay, 2018) presents some operational values for these parameters, in which the rise rate has been ranged between 0.42 to 3.7 m²/m³h since rise rate must be lower than settling rate. Besides the underflow recycling percentage can achieve values from 3 to 100%. Since, in this case, the underflow bleeding is semi-continuous. Furthermore, there is no criterion reported to establish the base of recycling flow (e.g., solid content in the sulfidization reactor, solid content in the underflow, and recycling fixed value). In this regard, Fleming and Melashvili (2016) propose the possibility that the underflow recycling of the SART process can be eliminated, due to the behavior of the copper precipitates which it tends to aggregate (Wrighton-Araneda et al., 2019; Gim-Krumm et al., 2019). Hence, the original reason to recycle the underflow – to promote nucleation seeds for the new precipitates in order to improve the settling rate – has been faced according to this background. However, the impact of the aggregation behavior of copper sulfide precipitates in cyanide media in settling performance or recycling criteria have not been assessed.

Although there are a few studies that propose better operational conditions in the sulfidization reactor (e.g., pH, residence time and sulfide addition) and the thickening process, these studies lack on experimental support. Hence, this work aims to provide a critical assessment of the current design criteria used in the SART process by the sulfidization reactor and copper precipitate thickening, based on specific experimental tests.

2. Methodology

2.1. Reagents and equipment

Sulfidization tests were carried out using demineralized water (< 1μS) and reagents supplied by Merck-Sigma (NaCN, CuCN, NaHS·1.5H₂O, H₂SO₄, NaOH) with purities above 98%. Synthetic copper-cyanide solutions were generated by mixing NaCN and CuCN with water at pH 12, adjusted with NaOH. The weak acid dissociable (WAD) cyanide concentration was obtained as a result of copper concentration and free cyanide concentration, fixed at 100 mg/L. This value is based on typical conditions used in gold cyanidation plants to ensure gold dissolution (Marsden and House, 2006; Walton, 2016). The thermodynamic speciation of free cyanide and copper-cyanide complexes was estimated using the software Hydra/Medusa (Puigdomenech, 2004), according to the copper concentration defined. This procedure allowed the WAD cyanide concentration required to obtain 100 mg/L of free cyanide to be estimated.

Then, precipitation assays (Eq. (1)) were performed in a batch reactor (stirred, jacketed and sealed) of 2 L capacity, operated at 15 °C. Reagent addition and sampling methods were specific for each analysis. The addition of acid and sulfide was carried out using solutions at 4 M and 5% w/w, respectively.

For all tests, the sampling was performed using a syringe filter (pore size = 0.22 μm) where a 2 mL sample was taken, which was then poured into Falcon tubes containing solution at pH 12. The copper concentration was analyzed by atomic absorption spectroscopy (AAS, GBC model SensAA dual).

2.2. Conversion and Eh of the sulfidization reaction

Copper precipitation tests were performed by fixing the required pH and adding 4 M sulfuric acid solution. The pH was measured by a pH-meter (Hanna HI61018). When the required pH was reached, an addition of ~20% stoichiometric NaHS solution was injected into the reactor. The volume of this last solution tends to increase the pH, then the pH value was adjusted with acid dosage. When the Eh value (measured by a Hanna oxide-reduction potential electrode, HI62004) was stable, a sample of slurry from the reactor was taken, filtered, its pH raised to later apply AAS analysis. Additionally, Eh value was registered. This procedure was repeated until reaching 200% sulfide stoichiometric dosage. Copper conversion was estimated using the analyzed copper concentration at each sulfide stoichiometric dosage and the initial copper concentration ($Cu\ Conv = 1 - [Cu]_{sample} / [Cu]_{initial}$). Copper concentrations and sulfide additions were corrected

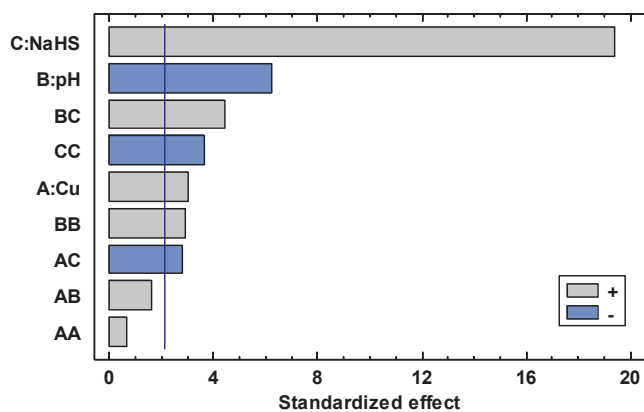


Fig. 2. Standard Pareto chart for copper conversion, resulting from the statistical assessment under the following operational conditions: pH: 3.5–5.0; [Cu]: 500–1,800 mg/L; NaHS stoichiometric addition: 80–120%.

according to the volume extracted by sampling and volume added by reagents for each point.

The range for each studied factor on the copper conversion and E_h of the sulfidization reaction was chosen within the following range: Copper concentration 500–1,800 mg/L, and pH 3.5–5.0. Experiments were performed according to a multilevel factorial design comprising 27 runs completely randomized with 17 degrees of freedom for the error. The main effect analysis for each factor was determined by using the analysis of variance (ANOVA). All the computations were done using Statgraphics Centurion XVIII (Statgraphics Technologies, Inc. USA, 2018).

2.3. Residence time of the sulfidization reaction

Copper sulfidization tests were used to assess the conversion of the precipitation reaction (Eq. (1)) according to the residence time. These tests were performed by adding 4 M sulfuric acid solution into the cyanide solution until reaching the required pH. Then, a NaHS solution was dosed until the defined sulfide stoichiometric addition was reached. During each test, the pH was controlled by a Hanna pH-controller (HI-504224-2) connected to a dosage pump. Samples were taken between 15 sec and 10 min of reaction time, in order to analyze the copper concentration according to the same procedure explained in sections 2.1 and 2.2. Likewise, the copper conversion for each time fraction was estimated as mentioned in Section 2.2. Copper concentration values were 500, 950 and 1,800 mg/L at pH ranges of between 3.5 and 5.0, and sulfide stoichiometric dosages of 100 and 120%.

2.4. Settling performance of copper precipitate

Settling tests of copper precipitate slurry generated in the sulfidization reactor were carried out with the purpose of quantifying the effect of underflow recycling in the reactor on settling performance. The sulfidization reaction was performed during 10 min of residence time, according to the typical industrial practice (Estay, 2018). The suspension generated in the sulfidization reactor was gravitationally discharged into a 1 L graduated cylinder, mixed with a 0.1 g/L solution of flocculant (FL2030, supplied by SNF) dosed at 2 mg of flocculant per liter of slurry, a typical dosage criterion used industrially (Estay, 2018). The slurry-flocculant mixture was manually agitated in the graduated cylinder for 10 s, and then allowed to settle. The slurry-supernatant interface level was measured with respect to the time. After 30 min, a sample of supernatant was taken. This sample was analyzed in terms of turbidity (NTU) using a turbidimeter (Hanna Instruments, model HI88703). After 24 h the supernatant was carefully extracted from the cylinder to collect the settled slurry, where a sample was taken, washed

and filtered to measure the solids content. This was achieved using a moisture balance (Boeco, Model BMA 150, Germany). The total settled slurry (2 L of initial slurry) was divided into two samples, one of 1/5 and other of 4/5. Both samples were used to perform a new sulfidization reaction, adding the fraction of settled slurry into the reactor. After 10 min, the procedure was repeated. Settling rates for each test were obtained from the curve of interface level with respect to the time, using the slope of the part when settling curve is a straight line.

For the settling analysis the ranges for the three studied factors were: (i) Copper concentration 500–1800 mg/L, (ii) pH 3.5–5.0, and (iii) NaHS dosage of 100–120% (stoichiometric dosage). A box-Behnken design with 15 experimental runs (completely randomized) including 3 central points and 5 degrees of freedom for the error was used to analyze the effect of each factor and the interaction effect between them on the settling performance of copper precipitate. The significance of the studied factors was carried out by ANOVA routine using the Statgraphics Centurion XVIII software (Statgraphics Technologies, Inc. USA, 2018).

Additional tests with no flocculant addition were performed at pH = 4.25 and 110% sulfide stoichiometric dosage, using the same range of copper concentration and methodology detailed earlier in this section. The aim of these is to confirm the effect of flocculant addition on the settling performance of the process.

3. Results and discussion

3.1. Conversion and E_h of the sulfidization reaction

Among the aims of this work was to estimate the optimal dosage of sulfide that maximizes the copper conversion. Additionally, ORP measurements were obtained and analyzed to identify the behavior that can support a control criterion of sulfide dosage using an ORP sensor. Results of the experimental design for copper conversion are shown as a standard Pareto chart (Fig. 2). This plot shows the comparative effect of sulfide dosage (NaHS), pH and the initial copper concentration (Cu) according to the resulting conversion. The Pareto chart shows the standardized effect of each studied parameter ([Cu], pH and NaHS) as well as the interaction effect between them on the copper conversion, in the range assessed (in this case pH: 3.5–5.0; [Cu]: 500–1,800 mg/L; NaHS: 80–120% stoichiometric dosage). The straight line crossing the bars indicate the significant effect on copper conversion, of NaHS, pH and Cu (in this order of importance). According to the results, the sulfide dosage is the most significant factor in copper conversion, producing an increase in the conversion as sulfide dosage was increased. In particular, NaHS dosage is around 3 times more incident in the copper conversion than pH. On the contrary, pH showed a significant effect on the copper conversion, but this effect is contrary to that observed in the NaHS dosage. This means that decreasing the pH values implies increasing the copper conversion. This fact is determined by the CN/Cu molar ratio and the stability of $\text{Cu}(\text{CN})_2^-$ at pH values ranging between 4.0 and 5.0. The same reason explains the effect of initial copper concentration on copper conversion, where the increase of copper concentration increases copper conversion. This is due to the fact that the CN/Cu molar ratio decreases when copper concentration is increase, in turn because the free cyanide concentration has been fixed. The results of the interaction effect are particularly interesting. They showed a significant effect on the copper conversion. That is also the case for the interaction between pH and NaHS dosage, as well as Cu concentration and NaHS dosage (Fig. 2). The above confirms that the reaction has several factors influencing the conversion, therefore the main and the interaction effects must be considered in the design and control system.

Moreover, the comparative tendency of the effect of each variable in the copper conversion is shown in the Fig. 3. These results were obtained by using the software Statgraphics Centurion XVIII. The lines (curves) in this figure indicate the estimated change in the copper conversion for each factor when it was moved from the minimum to the

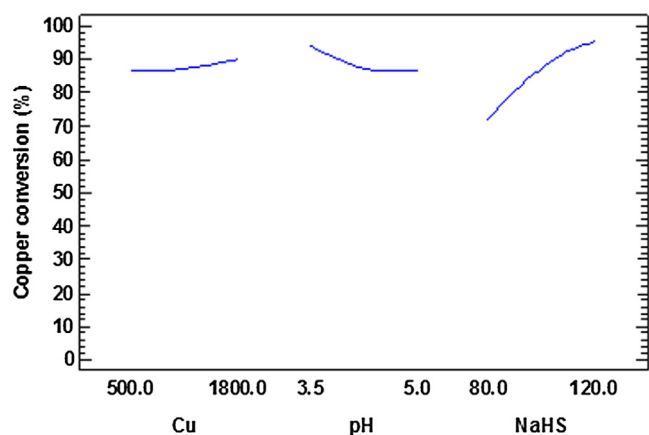


Fig. 3. Comparative analysis of the main effects for each factor on the copper conversion. Each factor ranged from the minimum to the maximum values studied when the others factors were kept at their average (in this case 950 mg/L of [Cu], 100% sulfide stoichiometric dosage and pH 4.25).

maximum values studied when the others factors were kept at their average (in this case 950 mg/L of [Cu], 100% sulfide stoichiometric dosage and pH 4.25). Results shown in Fig. 3 are in agreement with those observed in Fig. 2. This means that the increase in sulfide dosage is the more relevant effect in the copper conversion, although the pH

and initial copper concentration must also be considered in the definition of design criteria of the SART process, in order to ensure an optimal recovery. As mentioned above, the impact of pH and copper concentration on copper conversion is determined by the CN/Cu molar ratio contained in the cyanide solution that is fed into a SART process. In this study the CN/Cu molar ratio ranged between 2.0 (for [Cu] = 500 mg/L) and 1.86 ([Cu] = 1,800 mg/L), indicating a difference of almost 5 points in the conversion (Fig. 3). In this sense, the CN/Cu molar ratio of a cyanidation plant must be considered for a SART process design in terms of metal conversion. This is especially important because the free cyanide content is defined to ensure the gold recovery in leaching, thereby the CN/Cu molar ratio value cannot be regulated for a SART plant.

The Eh values measured by an ORP sensor are shown in Fig. 4 for [Cu] at 500 mg/L and 1,800 mg/L, where copper conversion curves have been included for each pH assessed. The conversion results demonstrate the direct effect of the sulfide dosage given by Equation (1), where the maximum values are reached for sulfide addition above 100% stoichiometric. At 100% stoichiometric sulfide dosage, the copper conversion is higher at pH 3.5. Over 120% stoichiometric, the copper conversion is close to 100% for each pH. These results are consistent with those shown in Figs. 2 and 3 described earlier. However, the Eh values decreased when the sulfide dosage was increased for all pH values, up to 100% stoichiometric. At this value, the Eh drops drastically and reaches a constant value for sulfide dosages over 120%

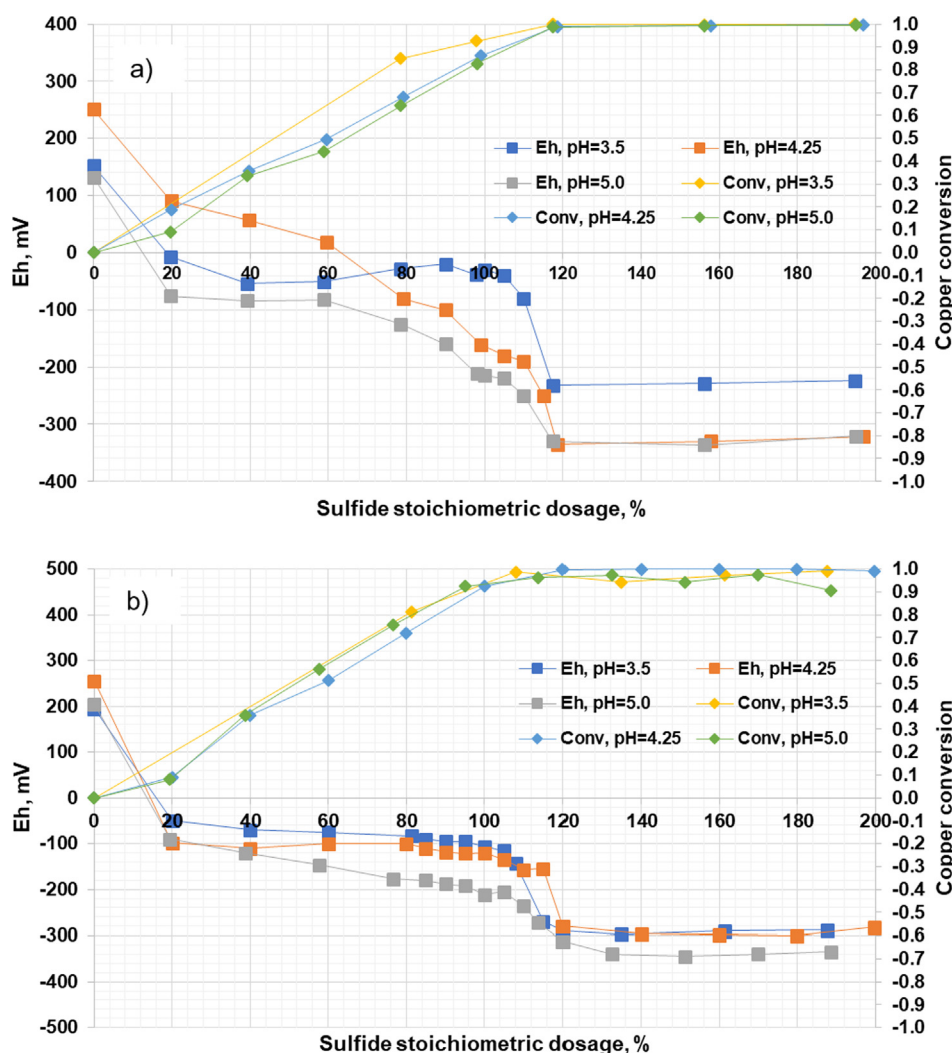


Fig. 4. Results of Eh and copper conversion for an initial copper concentration of (a) 500 mg/L, and (b) 1,800 mg/L.

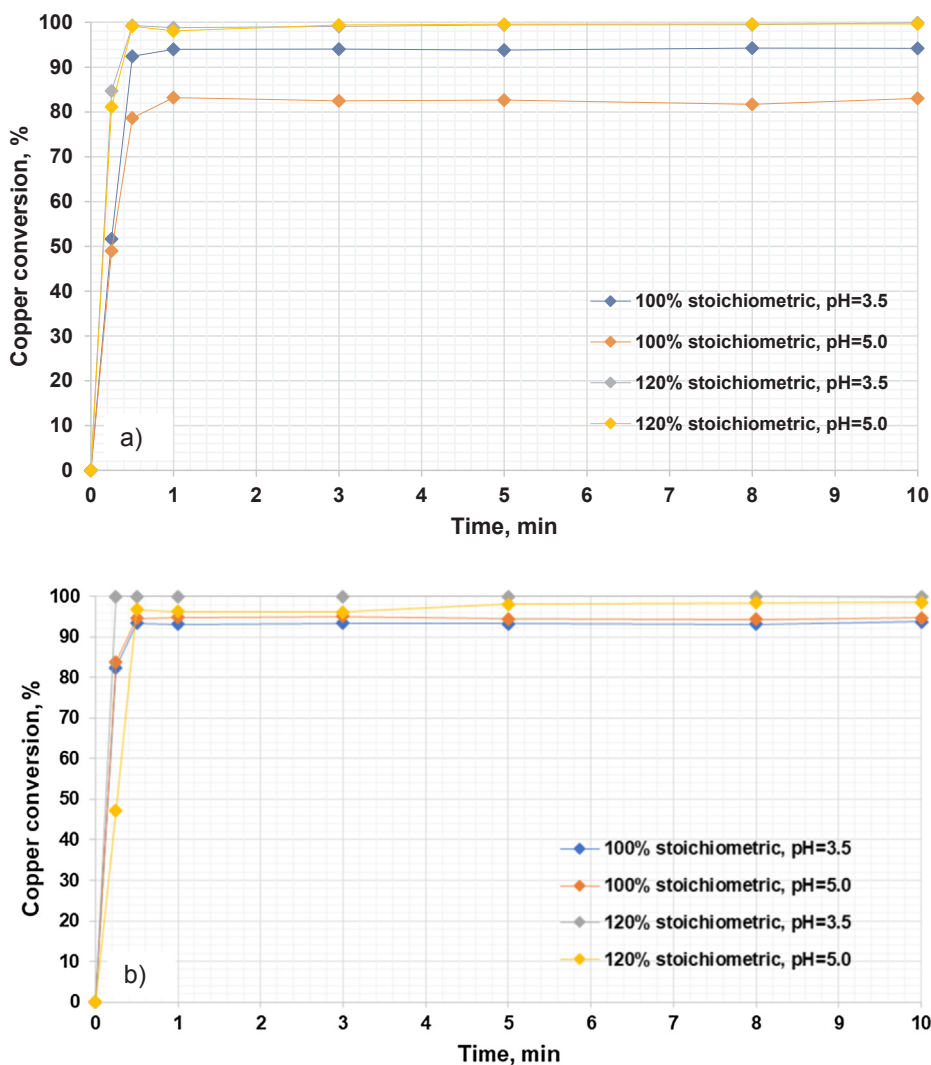


Fig. 5. Results of copper conversion respect to time reaction for an initial copper concentration for (a) 500 mg/L, and (b) 1,800 mg/L.

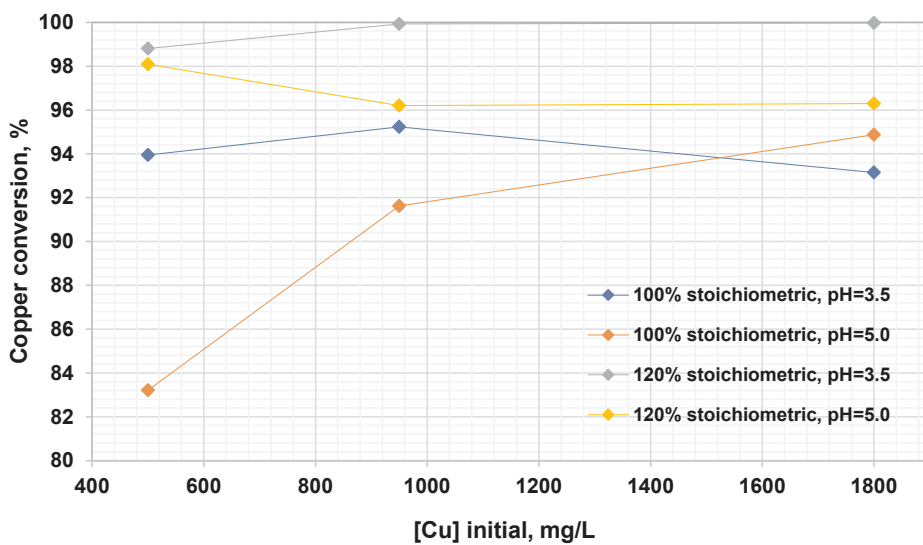


Fig. 6. Copper conversion at 1 min of time reaction with respect to the initial copper concentration for different pH values and sulfide stoichiometric dosages.

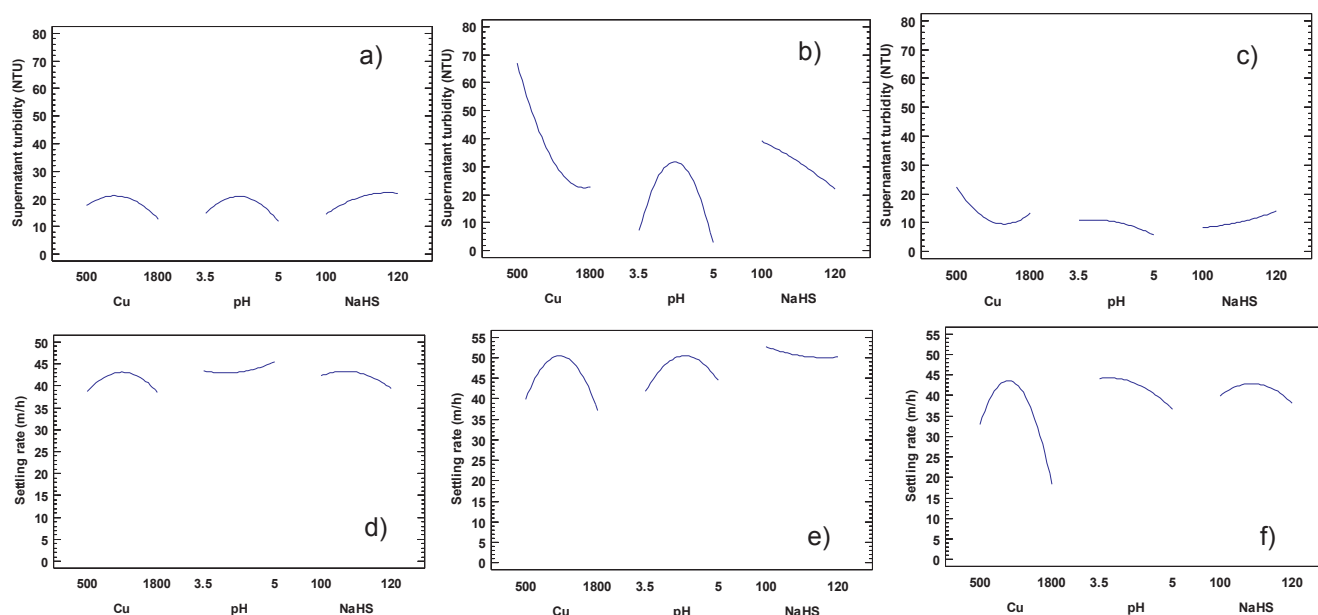


Fig. 7. Individual effects of pH, sulfide addition and initial copper concentration in turbidity and settling rate. The values reported are based on the central condition of the others variables. (a) Turbidity of supernatant with 0% recycling; (b) Turbidity of supernatant with 20% recycling; (c) Turbidity of supernatant with 80% recycling; (d) Settling rate with 0% recycling; (e) Settling rate with 20% recycling; and (f) Settling rate with 80% recycling.

stoichiometric. This change in tendency matches with the maximum copper conversion obtained for different pH conditions. Therefore, the control of sulfide addition in the sulfidization reactor of the SART process can be regulated by using an ORP sensor operating with a control philosophy that uses the changes in the Eh curves as a control mechanism. It must be noted copper concentrations of 950 mg/L (data not shown) behave very similarly. The main difference is the value of Eh reached (slightly lower for higher copper concentrations).

According to the copper conversion ($\sim 100\%$), further sulfide addition over the stoichiometric dosage should decrease the Eh value. Nevertheless, the results shown in Fig. 4 present a constant value of Eh for sulfide dosages higher than 100%. This unexpected behavior can be explained by the presence of a reduction–oxidation reaction in the system, in this case, the oxidation of Cu_2S or H_2S when sulfide is in excess ($> 100\%$ stoichiometric), according to the Eqs. (2) and (3). As mentioned earlier, these reactions are undesirable because the copper grade decreases in the final precipitate. Moreover, the CuS could redissolve to $\text{Cu}(\text{CN})_2$, decreasing the whole copper recovery of the process (Simons and Breuer, 2013). Hence, the sulfide dosage must be slightly defined higher than 100% stoichiometric, in order to reach copper conversions close to 100%. That said the final definition must consider the further sulfide consumption given by the presence of others metals which can precipitate. Furthermore, the sulfide addition must be defined together with pH definition which in turn depends on the CN/Cu molar ratio. Today, industrial SART plants in operation (Table 1) are processed with a sulfide excess criterion, promoting the oxidation of precipitate. This is a detrimental condition for the sale price.

The highest copper conversion is obtained at pH 3.5 (Fig. 4). Therefore, a sulfide stoichiometric dosage slightly higher than 100% at pH 3.5 can ensure copper conversion of over 95%. However, the operation at low pH not only increases the acid consumption – and consequently the lime consumption –, but could also decrease the copper grade in the precipitate. This is due to the generation of copper sulfide species with a theoretical weight percentage lower than chalcocite (Cu_2S), such as anilite ($\text{Cu}_{1.75}\text{S}$), roxbyte ($\text{Cu}_{1.8}\text{S}$), digenite ($\text{Cu}_{1.8}\text{S}$) or covellite (CuS). The presence of these species has been predicted by Eh-pH diagrams, which show a stability zone of sulfide copper species in cyanide media, where chalcocite (Cu_2S), djurleite ($\text{Cu}_{1.934}\text{S}$), anilite

($\text{Cu}_{1.75}\text{S}$), roxbyte ($\text{Cu}_{1.8}\text{S}$) and/or covellite (CuS) can be found. According to Marsden and House (2006), Cu_2S and CuS will be present in a cyanide-sulfide-copper system. However, a simulation in Hydra/Medusa software predicts the presence of Cu_2S , $\text{Cu}_{1.934}\text{S}$ and $\text{Cu}_{1.75}\text{S}$. In both cases, the decrease of pH increases the stability zone of CuS or $\text{Cu}_{1.75}\text{S}$, the species with lowest copper content: 66.4% for CuS , 77.6% for $\text{Cu}_{1.75}\text{S}$ with respect to 79.9% for Cu_2S . Therefore, the operation at pH below 4.0 could promote the formation of covellite or anilite, thereby decreasing the copper grade in the precipitate produced and increasing the sulfide consumption. Further studies which focus on the characterization of copper precipitates at different conditions should be conducted, which might consider the amorphous nature and oxidation tendency of precipitates. Furthermore, in SART plants and future studies, the oxygen content in the sulfidization reactor should be measured and related to the ORP behavior and copper conversion.

3.2. Residence time of the sulfidization reaction

Results of copper conversion with respect to considerations of time show a rapid increase in copper conversion in the first minute, reaching the maximum value at this time, and then this conversion kept a stable value up to 10 min. Fig. 5 shows the results for an initial copper concentration of 500 and 1,800 mg/L. The behavior for concentration of 950 mg/L (data not shown) was very similar in terms of the tendency and time reaction where the maximum recovery is obtained, although the conversion values are higher, as it was mentioned above. In this regard, Fig. 6 shows the copper conversion for different initial copper concentration achieved at 1 min of reaction time (where maximum conversion has been reached). The lowest copper recovery was obtained by 500 mg/L, 100% stoichiometric addition and pH 5.0, whereas the highest conversion was reached for 1,800 mg/L, 120% stoichiometric dosage and pH 3.5. In terms of values and tendency, these results are similar to those discussed earlier, demonstrating that conversion is highly dependent on copper concentration (i.e., CN/Cu molar ratio) for pH of 5.0 and 100% sulfide stoichiometric addition. For a higher sulfide addition, the copper conversion differs within a range of less than 2 points for all copper concentrations. Taking into account the discussion above and the results shown in Fig. 6, the operational conditions recommended to reach copper recoveries around 95% (maximizing the

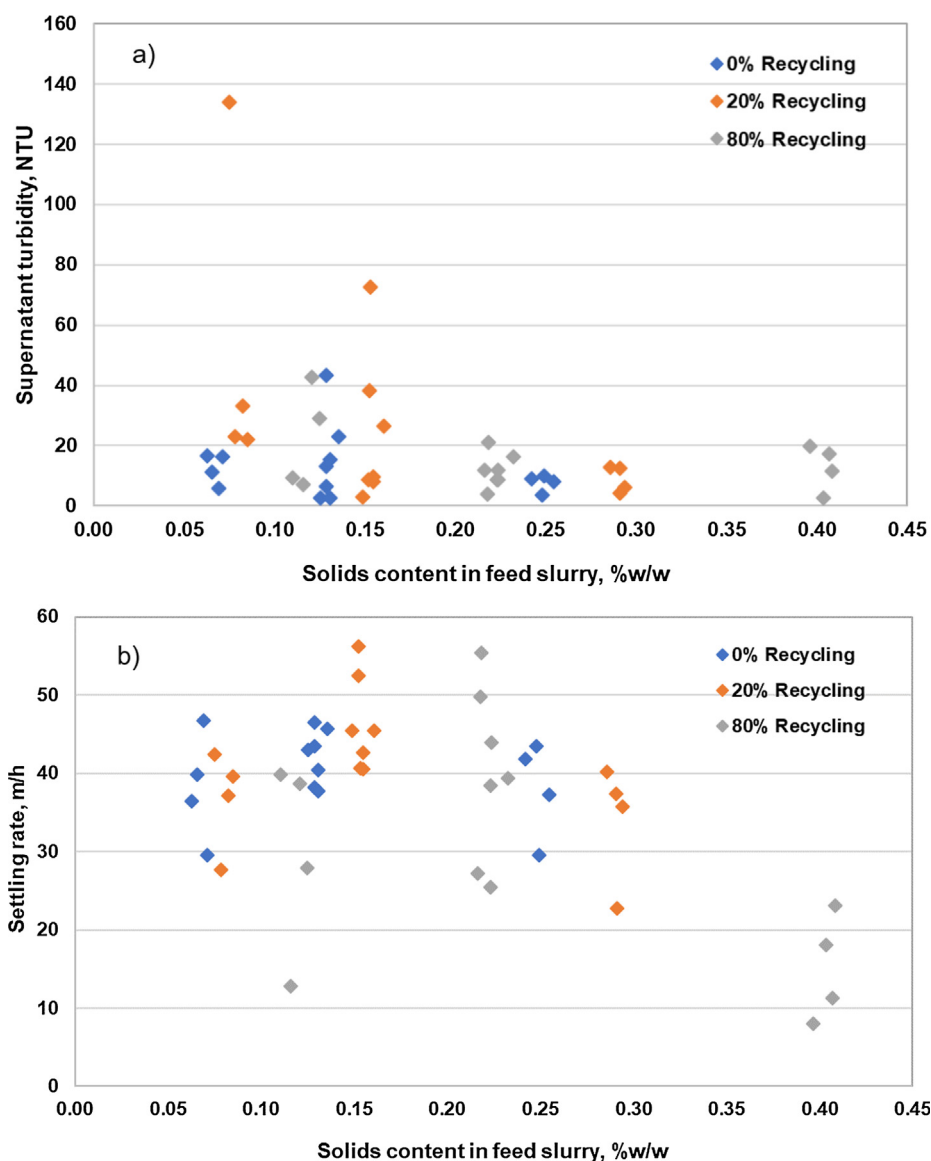


Fig. 8. Results of supernatant turbidity (a) and settling rate (b) with respect to the solids content in the slurry fed into the graduated cylinder of the settling tests, using 2 mg/L flocculant dosage.

copper grade and avoiding the precipitate oxidation), should be around the yellow and blue lines of Fig. 6. That implies a pH value ranging from 4.0 to 4.3, and sulfide stoichiometric dosages around 105%-110%. Nevertheless, this recommendation must be reviewed case by case, where the cyanide solution composition and the CN/Cu molar ratio must be taken into account in the final definition.

The residence time used by the current industrial SART plants is over 10 min, an excessive design criterion according to the results obtained in this study. Hence, the future SART plants can be designed using a residence time around 1 min. Although the results shown in Fig. 6 do not show a detrimental effect of the reaction time in the copper conversion, according to Simons and Breuer (2013), if CuS has been formed by precipitation or oxidation, it could re-dissolve to $\text{Cu}(\text{CN})_2^-$. This phenomenon could be caused by excessive contact time of the precipitate with the cyanide solution. Therefore, the reduction of residence time in the sulfidization reactor could also avoid the re-dissolution of the copper precipitate.

The copper conversion and residence time results are consistent with the recommendations given previously by some authors (Stewart and Kappes, 2012; Fleming and Melashvili, 2016) about the elimination of the sulfidization reactor, changing by the addition of a reagent in the

pipe. These suggestions were based on the very low solubility of the Cu_2S ($\text{pK}_{\text{sp}} = 47.3$), which determines a high level of supersaturation. In this context, the residence time obtained (1 min) can be attributed to the mixing and homogenization required in the stirred reactor in order to put together reagents with copper-cyanide complexes. In this sense, a different type of reactor, for example, a plug flow reactor (the pipe), could improve the time for mixing and homogenization, thereby decreasing the residence time required. However, the pH control in a pipe could be complex, and inasmuch as pH is crucial to achieve the copper conversion expected, the resolution to install the reactor in a pipe section must be proven by specific tests and a rigorous control philosophy.

The residence time results were obtained in a batch reactor, therefore the effect of a continuous flow fed into the reactor has not been assessed. This could increase the residence time in a steady state condition. Likewise, the reduction of the residence time in the reactor and its impact on the settling rate of copper precipitates in the thickening stage must be taken into account for further studies.

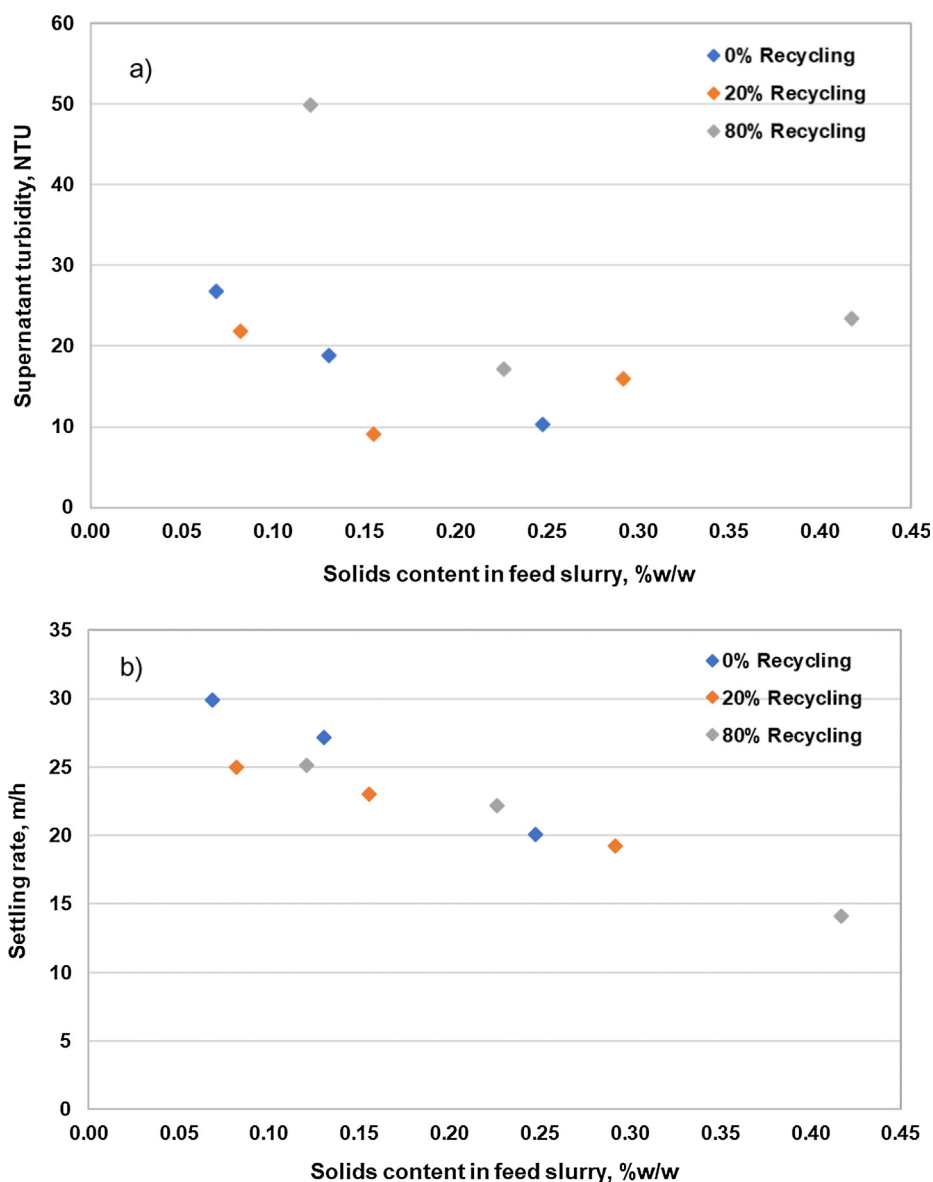


Fig. 9. Results of supernatant turbidity (a) and settling rate (b) with respect to the solids content in the slurry fed into the graduated cylinder of the settling tests with no flocculant addition at pH = 4.25 and 110% stoichiometric sulfide dosage.

3.3. Settling tests of copper precipitate

The settling performance of the copper precipitates was influenced by the pH, sulfide dosage and initial copper concentration, as shown in Fig. 7. This figure shows the individual effects of each assessed variable in the results of turbidity and settling rate for 0, 20 and 80% of underflow recycled. Settling rate values (Fig. 7d, e and f) ranged from 10 to 55 m/h, where the highest values are reached for 0% and 80% of settled slurry recycled, although the effect of pH, sulfide addition, and copper concentration is higher in the tests with recycled slurry. This is probably due to the change in the interface properties of the new precipitates. Consequently, the colloidal characteristics of the sulfide copper precipitates are affected by the contact of solids with different characteristics, disputing the benefits of recycling. This fact can be complemented by the high settling rates achieved with no recycling, which were at least 3 times higher than those achieved in industrial plants (Estay, 2018). However, there are some conditions in Fig. 7e that indicate maximum settling rates results when 20% of slurry is recycled. Hence, these results cannot be conclusive with respect to the recycling criterion.

However, the supernatant turbidity (Fig. 7a, b and c) showed high variability for the values reached, ranging between 3 and 65 NTU for the central conditions evaluated. The lowest values of turbidity were achieved for higher copper concentrations, considering the recycling of the settled slurry. Although the results presented in Fig. 7 provide interesting information regarding the settling rate, turbidity magnitudes, and the effect of the main variables involved in the process, it is complicated to establish a recycling criterion. Nevertheless, when the operational conditions are used to estimate the solids content in the slurry, which fed into the graduated cylinder, the turbidity and settling rate can be assessed as a function of the solids content in the feed slurry (Fig. 8). These results show high uncertainty, due to the different factors affecting the settling process (e.g., temperature, pH, sulfide content, chemical characterization of slurry, and particle size), although the variability decreases for the turbidity results (Fig. 8a) when the solids content in the feed slurry increased over 0.25 w/w for each recycling criterion. These results could imply that recycling can be eliminated from the SART process, since the supernatant turbidity and settling rate values do not significantly improve when a part of the settled slurry is recycled into the reactor. Nonetheless, when the SART

process is fed with a cyanide solution containing a copper concentration below 1,000 mg/L, this implies a ~ 0.15% solids content in the sulfidization reactor, so that a recycling of the underflow is highly recommended. This reduces the uncertainty of the settling results, particularly the supernatant turbidity, which determines the overall copper recovery in the SART process. This behavior can be explained by the increase of the particle size promoted by the recycled slurry, since the characteristics of the precipitates tend to aggregate fine particles in pre-formed aggregates.

However, the settling rate results (Fig. 8b) decrease slightly the solids content increases, reaching values lower than 10 m/h at 0.4%w/w solids, reaching maximum values that ranged between 0.15 and 0.25 %w/w of solids content in the feed slurry. The settling rate decreased up to 4 times when solids content increased from 0.15%w/w to 0.4%w/w, the absolute magnitude (~10 m/h) indicates excellent settling properties, even suggesting an oversizing of the current thickeners installed in SART plants. These results must be revalidated with further studies using real cyanide solutions from a gold plant.

In turn, the supernatant turbidity values reached in the tests with no flocculant addition are similar to the tests with flocculant dosage, in terms of magnitude, below 30 NTU (Fig. 9), except for one condition. Likewise, the uncertainty decreases when the solids content increases, confirming a similar tendency with respect to the flocculant dosage tests. However, the settling rate values are lower in the tests with no flocculant addition (around 15–30 m/h), although the results reached are still higher than typical industrial design criterion used. Hence, these results demonstrate that the sulfide copper precipitates formed in the SART process could operate without flocculant dosage in a wide range of feed copper concentration.

Nevertheless, this study presents interesting results that pave the way to optimize the current SART process design and operational criteria, in order to reduce the size of thickeners, defining standardized recycling criterion as function of copper concentration, and minimizing or even eliminating the flocculant addition.

The results obtained in this work can be useful for others applications of sulfide precipitation processes, such as copper recovery from acid mine drainage (Fu and Wang, 2011), copper precipitation from glycinate-cyanide (Deng et al., 2019) or glycinate solutions (Eksteen et al., 2017), purification of Co and Ni in hydrometallurgical processes (Habashi, 1997), and finally, mercury and lead recovery from wastewaters (Li et al., 2015).

4. Conclusions

A critical assessment of the design criteria used in the SART process has been conducted, based on specific experimental methodologies. Our results demonstrate that it is possible to control the copper conversion by using ORP measurements and by adding more precise dosages of sulfide, thereby ensuring high copper conversions. Also, our results demonstrate that the pH, sulfide dosage, and CN/Cu molar ratio in the feed solution determine the maximum copper conversion and copper grade in the precipitate. In order to maximize the copper conversion, a pH value of 4.25–4.5 should be used, with sulfide dosages slightly higher than the stoichiometric (105–110%), although this value can be defined using a ORP control to reach the maximum copper conversion. Moreover, the residence time of the sulfidization reactor can be drastically reduced down to 1 min, keeping the maximum conversion reached at 10 min. Furthermore, the thickening stage can be optimized by fixing a recycling criterion, depending on the copper concentration in the feed solution of the SART process. Accordingly, it is possible to establish that there are promising results in reducing the thickeners size, due to the use of higher settling rate in the design, avoiding or reducing the flocculant dosage.

The experimental methodologies applied in this study can be used to conduct further studies that confirm these results using real solutions for specific plants or projects. Overall, these results can provide useful

input for decision-makers who are considering others applications of sulfide precipitation processes, such as copper recovery from acid mine drainage, copper precipitation from glycinate-cyanide or glycinate solutions, purification of Co and Ni, among others.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2019.106116>.

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