Effects of the seeding phenomenon in the scorodite precipitation process

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ABSTRACT: In the copper mining industry, the impurity of the highest concentration is arsenic, with ore grades of up to 0.3% in mine minerals. During the copper production process via sulphide, arsenic is concentrated simultaneously with the copper closing the treatment cycle in copper smelting. Because of its toxic, mutagenic and carcinogenic characteristics, it should precipitate and be disposed of as a stable residue, in order to prevent it from infiltrating into the soil, and thus into the ground water. Ecometales has designed a process at industrial scale to stabilize arsenic from flue dust into the form of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), a highly stable compound. This process comprises the stages of primary leaching, oxidation and precipitation of arsenic in the form of scorodite. The present study aims at evaluating an optimization of the scorodite precipitation stage by using seeds in the primary precipitation stage. In this sense, laboratory tests were carried out simulating the industrial circuit. Parameters such as the precipitation kinetics and arsenic grade in the precipitated residue were verified. By using the seeds, a substantial improvement was obtained in: the precipitation kinetics (from 24 to 16 h) and in the arsenic grade in the obtained residue from 9 to 13%. The percentage of scorodite in the residue grew from 30 to 41%.

1 INTRODUCTION

In the copper mining industry, the impurity of the highest concentration is arsenic, with ore grades of up to 0.3% in mine minerals (Filippou *et al.*, 2007). During the copper production process via sulphide, arsenic (As) is concentrated simultaneously with the copper closing the treatment cycle in copper smelting. Because of its toxic, mutagenic and carcinogenic characteristics, it should precipitate and be disposed of as a stable residue, in order to prevent it from infiltrating into the soil, and thus into the groundwater.

Ecometales has designed a process, which is unique at industrial scale, to stabilize arsenic from flue dust into the form of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), a highly stable compound (Demopoulos, 1995). The residues treated correspond to flue dust, refinery effluents and effluents from the acid plant. The process comprises the stages of primary leaching, oxidation of Pregnant Leaching Solution (PLS) and precipitation of arsenic in the form of scorodite.

Currently the plant processes around 155 tons d^{-1} of flue dust and 500 m^3/d^{-1} of refinery effluent, generating 130 tons d^{-1} of solid waste of which only 30% represents scorodite and 70% gypsum, residues which are disposed of in a deposit of hazardous industrial waste (Kruusn & Errrr, 1988).

The low scorodite concentration in the precipitated residue is a problem since it reduces the storage capacity of the deposit. Therefore, an increase in scorodite grade in the precipitate is required.

The present study aims at optimizing the primary scorodite precipitation stage by using seeds. In this

sense, precipitation tests were carried out in a laboratory simulating the industrial circuit. Finally, parameters such as the precipitation kinetics and arsenic grade in the precipitated residue were verified.

2 METOHODS/EXPERIMENTAL

Precipitation kinetics tests were performed in 130 L reactors in batch mode, simulating an industrial process of two stages: a primary and a secondary.

The materials used for the tests such as scorodite (to be used as seeds), oxidized PLS, solution of ferric sulphate, limestone slurry, neutral water and acidified water, were sampled from the industrial plant and previously characterized.

2.1 Primary precipitation tests

Oxidized PLS was poured into an agitated 130 L reactor and the temperature was established at 80°C. The ferric solution was added adjusting the $\text{Fe}^{+3}/\text{As}^{+5}$ ratio to 1. Three tests were carried out: one without adding seeds and with an initial solid concentration of 1% p/p (PP1), one with addition of seeds (initial solid concentration of 5% p/p) of a scorodite sample obtained from the previous test (PP2) and one with addition of seeds (initial solid concentration of 5% p/p) of a scorodite sample obtained from the industrial plant.

The oxidized PLS slurry was left to react for a period of 24 h and every 4 h samples were taken from the pulp. They were filtered and sent to be analyzed for As_T , As^{+5} , Fe_T , Fe^{+3} , H^+ both in solid and liquid phases.

Figure 1. Concentration of As^{5+} in the final PLS versus time for tests PP-1, PP-2 and PP-3.

Figure 2. Percentage of precipitation accumulated As^{5+} versus time for tests PP-1, PP-2 and PP-3.

2.2 Secondary precipitation tests

The test was continued in the same reactor with the same parameters of the primary leaching test. However, the acid concentration was adjusted to 20 g L^{-1} , by adding limestone slurry. The initial solid concentration varied from 5 to 3 and 8% (PS-1, PS-2 and PS-3, respectively). Then, the oxidized PLS slurry was left to react from a period of 16 h and every 4 h samples were taken from the pulp. They were filtered and sent to be analyzed for As_T , As^{5+} , Fe_T , Fe^{+3} , H^+ both in solid and liquid phases.

3 RESULTS

3.1 Primary precipitation tests

Figure 1 shows that for PP-1 a value of 0.931 g L^{-1} was achieved, PP-2 a value of 1.459 g L^{-1} and for PP-3 0.98 g L^{-1} . Taking into consideration this variable, the best results were obtained in tests PP-1 and PP-3.

This may be due to the fact that in SC-3, industrial plant scorodite was used, which could contain small amounts of unreacted limestone, which would enhance the precipitation of As^{5+} , which did not happen in the case of PP-2, where the seed generated from PP-1 (without addition of limestone) was used.

Figure 2 shows that the kinetics for the tests with seeding (PP-2 and PP-3) is much faster than for the test without seeding (PP-1), mainly due to the phenomenon of heterogeneous nucleation (contribution of surface), which facilitates the precipitation.

When reaching 24 h residence time, precipitations of 93% are reached for the test without seeding (PP-1), 89% for the test with seeds of the laboratory test (PP-2) and 92% for the test with seeds of the industrial

Table 1. Summary of results obtained in tests PS-1, PS-2 and PS-3.

Nº	Precipitation As^{5+} (%)		As^{5+} in PLS (g L^{-1})		As_T in pptate (%)	Scorodite in pptate (%)
	t = 16 h	t = 32 h	t = 16 h	t = 32 h	t = 32 h	t = 32 h
PS-1	93.0	99.0	1.74	0.11	13.17	41
PS-2	96.0	99.5	0.53	0.05	13.16	41
PS-3	96.0	99.5	0.57	0.20	13.4	41

plant (PP-3). It can be observed that the flat line of the curves (maximum precipitation) is reached after 16 h.

3.2 Secondary precipitation tests

Table 1 shows that the PLS in the PS-1 test has a final concentration of As^{5+} of 0.11 g L^{-1} which means that 99% of the As^{5+} managed to be precipitated. This condition generates a precipitate with an As_T concentration of 13.17, equivalent to a scorodite concentration in the precipitate of 41%. This presents an improvement to the plant condition (without seed-ing) of only 30%.

For all tests an As^{5+} precipitation of close to 99% is achieved, which thus confirms that the initial solid concentration does not affect the As^{5+} precipitation percentage.

In the secondary stage there is no large degree of progress in the precipitation reaction due to the fact that everything precipitates that had not precipitated in the first stage, which represents a small portion. However, the last stage is necessary for compliance with the process parameters ($[\text{As}_T] \leq 1 \text{ g L}^{-1}$ in final PLS).

4 CONCLUSIONS

- (1) When incorporating the seeding, the As^{5+} precipitation kinetics in the first stage improved from 24 to 16 h, thus achieving an average As^{5+} precipitation of 90%.
- (2) At the end of the second precipitation stage, an As^{5+} precipitation of 99% was received, with a scorodite concentration in the precipitate of 41%.
- (3) For both stages, the initial solid concentration does not affect the arsenic degree or the As^{5+} precipitation percentage As^{5+} .

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