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AN EXPERIMENTAL SCREENING OF METHODS FOR WASTE THIOSULFATE-LEACHATE SOLUTION TREATMENT

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Introduction

The use of thiosulfate as a replacement for cyanide lixiviant for gold recovery has shown some promise, the complexation of gold being facilitated in the presence of ammonia and copper. Thiosulfate is potentially a less toxic alternative to cyanide, however the available data on excess process water polluting matrix and detoxification methods are scarce. Additionally, access to real wastewater for testing is currently unavailable. There is a need for viable technical and economic solutions to manage these waste streams. This study investigates detoxification of process wastewater resulted from thiosulfate-based gold recovery focussing on treatment methods involving oxidation and de-complexation followed by heavy metals removal.

Materials and methods

The process water was obtained by contacting (4h) a gold ore concentrate (roasted pyrite, 2 kg per batch) with $Na_2S_2O_3$ solution (25 g/L), adding ammonia (0.09 mol/L solution), $CuSO_4$ (0.002 mol/L), dosed in the form of cuprammonium complex for a mass ratio [*ore: leaching solution*] of 1:2 kg/kg. Mixing was done with a pitch blade turbine under which process air was sparged (80NL/min). Process temperature was 20±2°C. The resulting solution after leaching and thickening (24h) had *p*H = 9.90, total reducing substances (thiosulfate + sulfites) = 155 mEq/L (referenced to iodine) and COD-Cr = 10830 mg O_2/L, high concentrations of Cr, Fe, Cu, Zn, Mo, Pb, which were present in a dissolved state (complexation). The removal of metals from the system through precipitation of metals from complexes could be difficult, as the destruction of the thiol ligand is necessary before precipitation. For the excess water that is to be treated for discharging into receiving rivers, a dilution is to be considered relative to the concentration of the leach solution. For the processing of thickened solids and hydro-transport, they are mixed with the process water from the tailings settling pond facility, where other water flows are entering and some natural attenuation occurs. For this laboratory level work, a 10-fold dilution of the thiosulfate leachate solution was considered, thus resulting the thiosulfate effluent that must be treated by oxidation. Treatment alternatives for the thiosulfate effluent were: Alternative 1: *Oxidation with air*, sparging under the mixing turbine for 6 to

24h. Alternative 2: *Oxidation with air, with UV-C irradiation*. Tested with air feed similar to Alternative 1, with irradiation using a medium pressure lamp TQ150Z1 (150W) with a radiation power of 47 W (200-600 nm range) and 14 W (200-300 nm). It was studied at *p*H = 5, 8.5 and 10.2, using adjustments with $Ca(OH)_2$. Alternative 3: *Bio-oxidation* using water percolating bio-filter with expanded clay filling (fraction 4-10 mm: 80%, fraction 2-5 mm: 20%), with forced-pulsed aeration and recirculation. Maximum load was 0.2 $kg/(m^3{\bullet}day)$ equivalent $S_2O_3^{2-}$. Alternative 4: *Oxidation with* H_2O_2 *and* H_2O_2 / Cu^{2+} *or* Fe^{2+} *catalyst*.

The treatment goal was to maximize the transformation of thiosulfate and intermediaries of polythionate type to sulfate. The progress of the oxidation reaction was monitored in relation to the variation in sulfate ion concentration, total reducing substances versus iodine, chemical oxygen demand COD-Cr, and also residual active oxygen versus iodide (for Alternative 4).

Results and conclusions

Although thiosulfate is oxidizable with air, the process of treating the thiol effluent by oxidation under mild air conditions (pressure and temperature) is too slow and cannot be considered a useful technological option.

Oxidation in the UV/Air system proceeds well at pH = 8.5 or 10.2, however energy figures-of-merit were not favourable. The reducing character towards iodine decreases, simultaneously with COD-Cr (confirms the total oxidation to sulfate, which is the final oxidation product). After 120 min, 92% of the theoretically possible maximum amount of sulfate is produced. The character of the aqueous system changes from one containing metals in the soluble phase in the form of complexes, soluble at basic pH, to a system with stable metals in ionic form at acidic *p*H. Precipitation of metals with calcium hydroxide occurs simultaneously with oxidation and ensures compliance with the limits for these species.

Regarding *bio-oxidation*, the following technical issues are of particular relevance: The overall chemical oxidizability of the process wastewater can only be partially reduced by biological treatment. In addition to sulfate, the process also generates colloidal sulfur and likely polythionates, which are not oxidizable by iodine, but possess reducing properties that can affect natural receptors. The biological process produces the acidification of the effluent (down to *p*H = 3.20). The phenomenon will also occur naturally, if the process wastewater is discharged without adequate treatment. Therefore, the technology must also include *p*H correction phases, destabilization of the colloidal sulphur system (sulfur is also produced during alkalinisation) and separation.

Chemical oxidation can be very efficient: hydrogen peroxide oxidizes thiol compounds in the process wastewater to sulfate, but the introduction of a catalyst is necessary, the most efficient reaction system being H_2O_2/ Fe^{2+} (pH<3). A *p*H control is not necessary at the reaction phase; the *p*H is produced by the in-situ generation of H_2SO_4. A post-treatment of the effluent after oxidation is necessary, for *p*H correction and removal of heavy metals.

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