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Leaching of Sludge from the AVR Process with Ammonium Thiosulfate: Alternative Technology to the Cyanidation

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***Abstract*— Nowadays there exists a growing trend to take advantage of mining products in the best way, and if possible, to give them an added value. Residues of the neutralization process AVR are a specific example of such materials. In this paper, waste from the AVR process of a mining company in the state of Sonora, México, were leached using $(NH_4)_2S_2O_3$ and NH_4OH. The initial sample was 10 kg of dry sludge, passing by 100% -150 mesh. Prior to leaching, the sample was analyzed by fire assay, atomic absorption, X-ray Powder Diffraction, and Scanning Electron Microscopy. The results showed the presence of copper thiocyanate, covellite, copper sulfate, and silver thiocyanate. The dissolution of the values were carried out using variable liquid-solid ratios going from 1:1, 2:1, 3:1, 4:1, 6:1, 8:1 up to 10:1, while maintaining constant the concentrations of both ammonium thiosulfate (60 gL^{-1}) and ammonium hydroxide, and by controlling the pH with $Ca(OH)_2$. Best extractions were achieved with liquid-solid ratio of 10:1, which provided an extraction of 86 % gold, 90.1 % silver, and 88.4 % copper. NH_4OH was used for complexation of copper and controlling the pH above 10. Consumption of $(NH_4)_2S_2O_3$ was 20 g/L, which makes it technically feasible for industrial scale process option and might have better results than conventional processes with cyanide.**

Keywords—AVR, ammonium thiosulfate, leaching

I. INTRODUCTION

The recycling of cyanide in the leaching circuit has great potential for economic and environmental benefits purposes [1],[2]. Over the years there has been developed and proposed a variety of processes for the recovery of cyanide, including those based on acidification such as Acidify, Volatilize and Reneutralize (AVR) and Sulphidize, Acidification, Recycling and Thickening (SART) process, direct electro taking, activated carbon, ion exchange resins, solvent extraction technologies among others[3]. It is common in sludge AVR process to find high percentages of copper, ranging from 13 to 20%, silver from 3.4 to 10 kg/T and gold 1.3 to 3.1 g/T. The ultimate goals is financial gain and not rely heavily on refineries and smelters as these are hampered by penalties, due to the presence of contaminants in the material. For over 100 years, cyanide has been the reagent of choice in the mining of gold and silver due to the high recoveries, selectivity and low costs. However, the damage from mishandling have initiated extensive research focused on identifying and developing less toxic leaching agents [4]. Currently there exist investigation in the optimal conditions in the processes necessary to implement the leaching flotation concentrates without pressure leaching, and for materials with high values of copper (usually 5 to 20 %) which are not suitable for cyanidation, for which it is studied stabilized ammonium thiosulfate as a substitute for cyanide [5]. There exist encapsulated materials and gold present in microscopic pyrites and arsenopyrites. Some of these materials are shipped to smelters and other overseas to be exploited. In these materials is often impossible to extract values for the traditional method of cyanidation. This has resulted in finding useful extractants for refractory mineral type. Studies have been reported leaching with ammonium thiosulfate values of some minerals of this class [6],[7]. In this work, a product of the neutralization process AVR material, also known as acidification, volatilization and neutralization was studied. The aim of this work is to retrieve the values of gold, silver, and copper in sludge produced in the recovery by the AVR cyanide process. The material was characterized by scanning electron microscopy and X-ray diffraction also chemical analysis was carried out by atomic absorption by varying the liquid-solid ratio.

Modified The problems presented materials containing high levels of copper, such as sludge obtained as a byproduct in the AVR process cyanide where cyanidation does not apply because the presence of the main cianicida which is copper, followed by lead and zinc in sludge, where high consumption of cyanide is present, which may be greater than 20 kg/T solutions and extractions under 3% silver and 10% gold [8]. Because copper consume very quickly to cyanide, we chose to use ammonium thiosulfate stabilized with ammonium hydroxide and calcium hydroxide for the recovery of gold, silver and copper, varying the liquid-solid for 1: 1 ratio, 2: 1, 3: 1, 4: 1, 6: 1 8: 1 and 10: 1; keeping constant the concentration of ammonium thiosulfate in 60 g/L and adding all the liquid-solid ratios a constant volume of 40 g/L of ammonium hydroxide and controlling the pH with 0.2 g of $Ca(OH)_2$ when necessary , to keep it in the range of 10.2-10.5.

II. CHEMISTRY OF THE AVR PROCESS

The chemistry of this and other cyanide recovery processes is well known [9]. When H_2SO_4 is added to a sodium cyanide solution to be acidified, most cyanide compounds decompose and form hydrogen cyanide. In this case a sterile solution to be treated with electroplating sulfuric acid and reacting the hydrogen cyanide (HCN) is obtained at a pH of 2, the free cyanide becomes cyanide HCN and this can be separated from the solution by passing a stream of air, where this is absorbed in an alkaline solution of 50% NaOH and NaCN regenerating again acidified sterile low cyanide solution is sent to a neutralization tank where the pH 2 solution rises to pH 8, in this solution which precipitates is sent to filtration to remove solids (sludge) are produced. The formed reaction of HCN is:

$$2NaCN + H_2SO_4 = 2HCN+2Na_2SO_4 \qquad (1)$$

In this reaction the formation of hydrogen cyanide over sodium sulfate occurs. In reaction (2), sodium cyanide H_2SO_4 reacts with silver to form silver cyanide more hydrocyanic acid with the formation of sodium bisulfate,

$$Na[Ag(CN)_2] + H_2SO_4 = AgCN +HCN + NaHSO \qquad (2)$$

With copper is taken for reaction (3), forming copper cyanide, hydrogen cyanide, sodium bisulfate,

$$Na_2[Cu(CN)_3] + H_2SO_4 = CuCN + 2HCN + 2NaH \qquad (3)$$

In the AVR cyanide recovery process becomes 93.6% and sulfuric acid consumption is 9.1 kg/T. The AVR process is designed not only for the destruction of cyanide in effluents and sludge formation, but rather for recovering and recycling the same. Another objective in this process is the removal of the metal complexes in pulp cyanidation, to then obtain a solution which can be treated by the AVR process, separating and recovering metal cyanide cyanide dissolved for future recovery or disposal.

The AVR process develops in three stages. The clarified first solution is acidified, transforming hydrocyanic gas CN, HCN, which is exemplified by reaction 4.

$$2CN^- + H_2SO_4 = 2HCN + SO_4^{-2} \qquad (4)$$

The volatilization step shown in reaction 5, occurring by air stripping gas to form hydrogen cyanide,

$$2HCN_{(aq)} = \text{arrastre con aire} = 2HCN_{(g}. \qquad (5)$$

The third stage is neutralization, which occurs by the reaction (6), passing the gas over a gas absorption tower and is passed to form aqueous sodium hydroxide 50 % recovery of NaCN in aqueous medium.

$$2HCN_{(g)} + 2NaOH_{(aq)} = 2NaCN_{(aq)} + 2 \qquad (6)$$

The metals present in the solution, such as copper, silver and gold are exemplified in reactions 2 and 3 once conducted a three-stage process of AVR and passed by the absorption of gases and to contact the NaOH solution NaCN regeneration cycle being returned allowed cyanidation.

III. CHEMISTRY OF THE AMMONIUM THIOSULPHATE

The high copper content of the sludge is beneficial in the complexation of gold and silver with ammonium thiosulfate. In leaching solutions implemented with different liquid-solid ratios with ammonium thiosulfate are the cuprammonium complex of Cu^{+2} and $Cu(NH_3)_4^{+2}$ is beneficial to thiosulfate because acts as oxidant according to the reaction (7), it is seen that increasing velocity ammonia concentration and degree of oxidation of thiosulphate decrease,

$$Cu(NH_3)_4^{+2} + 4S_2O_3^{-2} = Cu(S_2O_3)_3^{-5} + 1/2S_4O_6^{2-} + 4NH_3. \qquad (7)$$

The Cu^{+2} as $Cu(NH_3)_4^{+2}$ thiosulfate oxidizes to form Cu^{+1} as $Cu(S_2O_3)_3^{-5}$. The latter in turn is re-oxidized to form Cu^{+2} as $Cu(NH_3)_4^{+2}$ by effect of dissolved oxygen in solution[10.] However, there are other factors to the oxidation of thiosulfate; ammonia helps to limit the oxidation of thiosulphate as shown in reaction (7), the pH is other important factor upon reaction (8):

$$2S_4O_6^{-2} + 3OH^- = 5/2S_2O_3^{-2} + S_3O_6^{-2} + 3/2H_2O \qquad (8)$$

In reactions (9) and (10) shows how copper reacts with gold and silver,

$$Au^o + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Au(S_2O_3)_2^{-3} + 4NH_3 + Cu(S_2O_3)_3^{5-} \qquad (9)$$

$$Ag^o + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+} = Ag(S_2O_3)_2^{-3} + 4NH_3 + Cu(S_2O_3)_3^{5} \qquad (10)$$

But the OH^- ions in solution give us a partial conversion of tetrathionate to thiosulfate as shown you in reaction (8), however when there is a loss of OH we recommend adding $Ca(OH)_2$.

IV. EXPERIMENTAL

The sample was 10 kg received from the AVR process, namely dry sludge, which was grounded and passed by 100% -150 mesh. For leaching, the chemical reagent used was industrial grade ammonium thiosulfate concentration 60 % for pH control and concentrated ammonium hydroxide was used. The mineral species were determined by X-ray powder diffraction (XRD) using a Bruker make, model D8, with Cu Ka radiation = 1.5406 and a secondary monochromator (nickel filter) that eliminated kβ radiation. The intensity of the X-ray tube generator was adjusted in all measured at 20 mA and 40 kV. The samples were mounted on an aluminum support. The recording was performed using an interval 2 theta 5 to 80 °, with a scan rate of 0.02 °/min. The interpretation was made by Eva software. The micro analysis was carried out in a scanning electron microscope (SEM) Jeol JSM6300 mark Armed with a device for elemental chemical analysis with energy dispersive spectroscopy

(EDS). A team of atomic absorption Perkin Elmer, model 200 Analyst to analyze the solutions of gold, silver and copper are also used. Analyses of mineral feed and tail were made by fire essays. Thiosulfate concentration was determined by titration using a yodimétric method as methyl orange indicator. 1:1, 2:1, 3:1, 4:1, 6:1, 8:1 and 10:1, the liquid-solid ratio was varied from 1 to give a contact time of 24 hours with the extraction fluid. The solids were washed twice with 10 g/L ammonium thiosulphate and 5 ml of concentrated ammonium hydroxide.

V. RESULTS AND DISCUSSION

The results of the chemical analysis of the sludge are given in Table I. It can be seen the high copper and sulfur. The gold and silver values were obtained by analyzing the fire. In Figure 1 and 2 shows the micrograph of a SEM image and EDS spectrum appreciated respectively.

Table 1: Chemical analysis by MEB, EDS and fire assay of the sludge sample from AVR process.

g/T	g/T	%	%	%	%	%	%	%
Au	Ag	C	N	Na	Al	Si	S	K
1.3	2334	9.04	5.87	1.57	0.13	2.11	5	0.14

The Figure 3 shows the diffraction pattern of the sample identified sludge characterized rays. According to these results, the mineral phases present in the sample treated mineral species are mainly copper thiocyanate, cristobalite, covellite, silver cyanamide, dolerofanita, among others. The results of these techniques (SEM, EDS and XRD) corroborate the presence of mineral phases and microstructural characteristics.

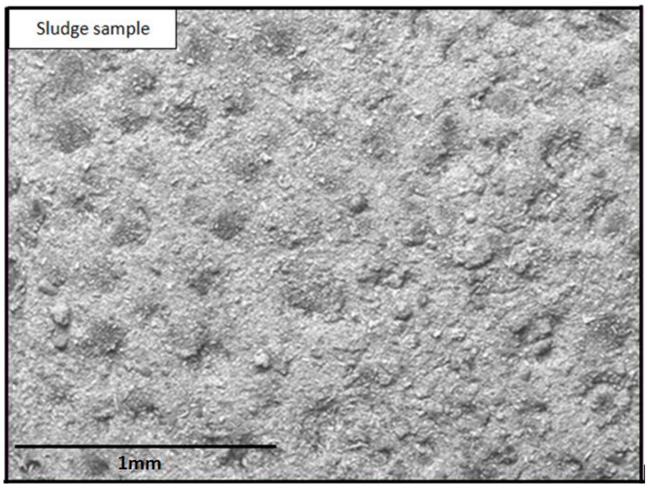

Fig 1: SEM image from the sludge sample from AVR process.

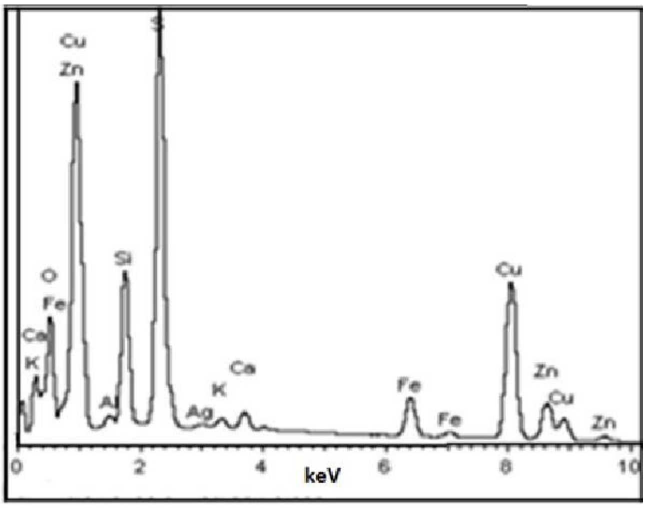

Fig 2: EDS spectrum from the sludge sample from AVR process.

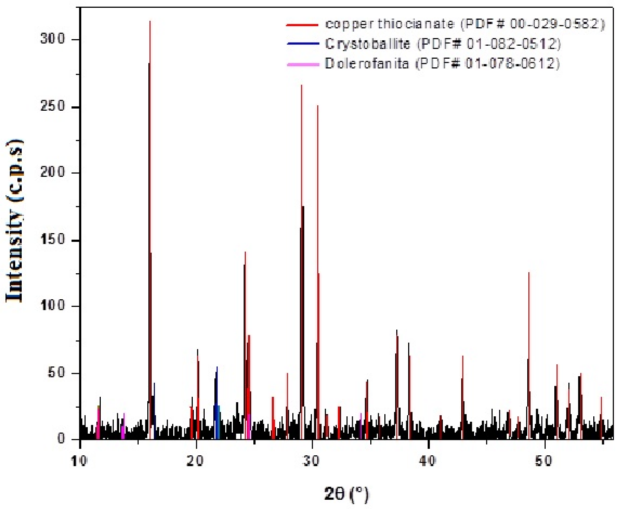

Fig 3: XRD from the sludge sample from AVR process.

A. *Leaching*

The dry sample was reground passed by 100% -150 mesh and into a beaker of 2 L of ammonium thiosulfate was added at a concentration of 60 g/L ammonium thiosulphate and 40 mL hydroxide ammonia to adjust the pH increased to 10 each sample was stirred at 250 rpm for 24 hours by varying the liquid-solid ratio and was found that the best value for extraction of copper, gold and silver are given in the ratio of 10:1, as shown in Figures 4, 5 and 6 respectively. Consumption of ammonium thiosulfate was 20 g/L as shown in Figure 7 and ammonium hydroxide was 30 g/L in the complexation of copper and having a control pH greater than 10 at the ratio 10:1 presented us with a gold extraction of 86% silver and 90.1 and 88.4% Cu. It is well known that the main challenge to develop substitutes for cyanide is to ensure that the particular selected metallurgical process for gold extraction work with ore characteristics (Gavin Hilson et al, 2006). Alternative leaching must also be cheap, recyclable, selective, non-toxic and compatible. . It can clearly be seen by the results of this investigation that ammonium thiosulfate meets some of these features making it a viable candidate for the process.

B. *Tails analysis*

The samples were washed three times with ammonium hydroxide and ammonium thiosulphate 10 g/L. The results are given in Table II.

TABLE 2: ANALYSIS OF SOLIDS SLUDGE SAMPLES OF AVR PROCESS FROM LEACHING WITH AMMONIUM THOSULPHATE

g/T	Au	Ag	% Cu
Feed	1.3	2334.30	13.5
Tails	0.15	160	1.56

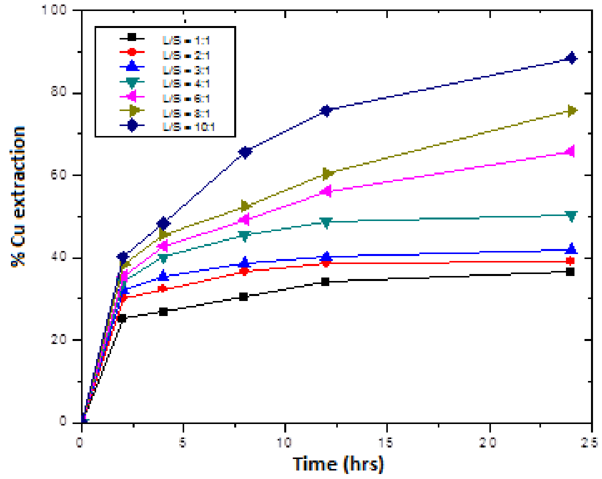

Fig 4: Copper extraction kinetics for liquid-solid ratios 1:1, 2:1, 3:1, 4:1, 6:1, 8:1 ó 10:1.

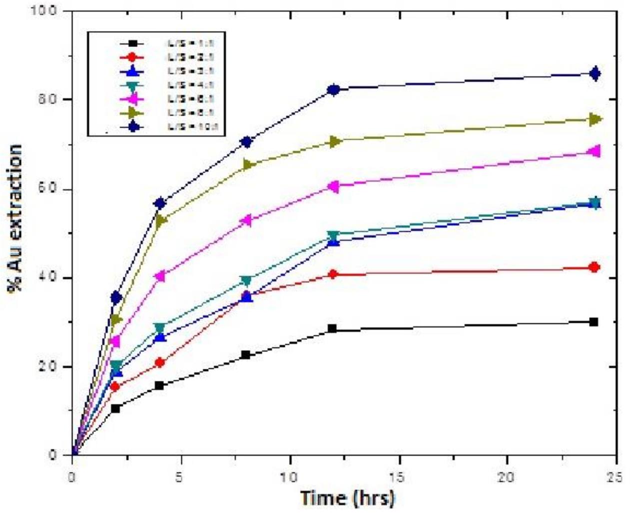

Fig 5: Gold kinetics extraction for liquid-solid ratios 1:1, 2:1, 3:1, 4:1, 6:1, 8:1 ó 10:1.

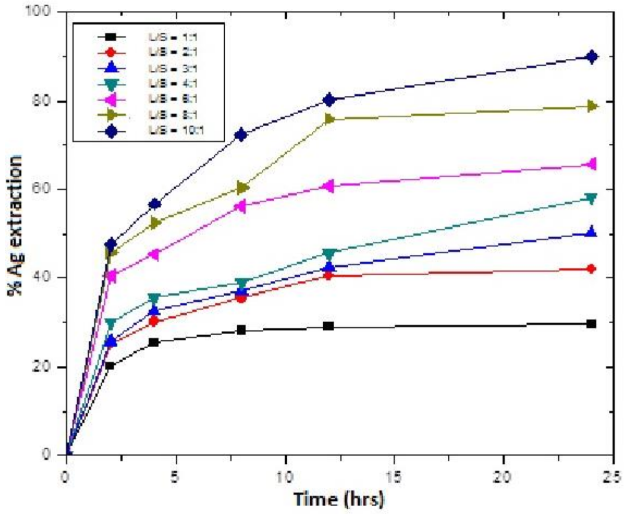

Fig 6: Silver kinetics extraction for liquid-solid ratios 1:1, 2:1, 3:1, 4:1, 6:1, 8:1 ó 10:1.

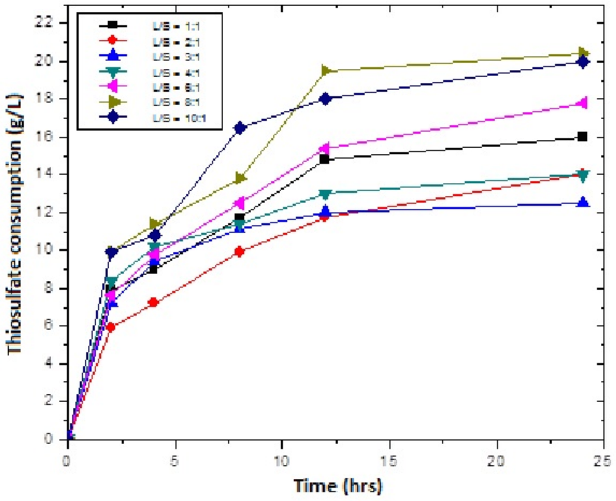

Fig 7: Ammonium thiosulfate consumption depending of time elapsed of contact sample-leaching for diferents liquid-solid ratios. Initial concentration was 20 g/L of ammonium thiosulfate and 30 g/L of ammonium hydroxide.

VI. CONCLUSIONS

The sludge from the neutralization process can be leached by AVR ammonium thiosulfate as an alternative to conventional cyanidation processes, where cyanide fails good extractions and further has high consumption thereof. With ammonium thiosulfate extractions may be economic to develop a process of this type are achieved. The solid-liquid best recovery results presented relationship was 10:1 displaying a gold extraction of 86%, 90.1% silver and 88.4% copper. Doing a cost-benefit analysis can be said that consumption of thiosulfate are not very high and the recovery values becomes feasible. As can be seen, based on the results obtained, it is possible that the sludge from the AVR process can be treated in the same processing plant without being shipped abroad, generating savings in transportation, labor and punishment in foundries by harmful elements. This process is environmentally friendly and sustainable.

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