Pergamon

0892–6875(98)00035–1

Minerals Engineering, Vol. 11, No. 6, pp. 535–543, 1998

0892–6875/98 $19.00+0.00

REMOVAL OF Hg, As AND Se IONS FROM GOLD CYANIDE LEACH SOLUTIONS BY DISSOLVED AIR FLOTATION

F. TESSELE[§], M. MISRA[†] and J. RUBIO[§*]

§ Universidade Federal do Rio Grande do Sul-PPGEM,
Departamento de Engenharia de Minas, Porto Alegre, RS-Brazil.
† University of Nevada, Department of Chemical and Metallurgical Engineering, Reno, NV, USA
* Author for correspondence. E-mail: jrubio@vortex.ufrgs.br
(Received 8 September 1997; accepted 3 January 1998)

ABSTRACT

The removal of Hg, As and Se ions from processing streams of gold cyanidation circuits was studied by dissolved air flotation (DAF) at laboratory scale. Two different methods were applied. The first was based on the separation by flotation of the aggregates (AF) formed between the ions and NaDTC (precipitant), $LaCl_3$ or $FeCl_3$ (coagulants) and Bufloc (a flocculant). The second was adsorptive particulate flotation (APF), using solid sorbing materials for the ions (chabazite and La_2O_3) and microbubbles in the solid/liquid separation stage. Results showed that removal was efficient in both cases and followed the order : (AF) >APF-chabazite >APF-La_2O_3. Almost complete removal (>98 %) of the metal ions from solution was obtained. Process efficiency depended on the system solution and interfacial chemistry, aggregation phenomena and DAF operating parameters. © 1998 Elsevier Science Ltd. All rights reserved

Keywords
Environmental; gold ores; froth flotation

INTRODUCTION

Large volumes of aqueous effluents (process waters) from gold hydrometallurgy operations are commonly contaminated with heavy metal ions such as mercury, arsenic and selenium. Recycling of these streams of gold cyanidation circuits usually becomes a requirement and the task always requires an effective removal of the metal ions. These ions interfere in the gold leaching process causing economical (often water availability is a problem) and environmental problems.

Several methods to recover or separate these elements has been suggested, namely precipitation-flocculation [1-3], solvent extraction [4], filtration using microemulsion liquid membranes [5] and sorption by activated carbon [6] or ion exchange resins [7].

Flotation using microbubbles has been used for Hg and As precipitates, using Na2S, sodium oleate or KI for Hg and by adsorbing colloidal flotation using ferric hydroxide as the sorbing solid [8,9].

Presented at *Minerals Engineering* '97, Santiago, Chile, July–August 1997

The removal of mercury from gold cyanidation circuit streams, this has been a subject of recent research because mercury forms very stable complexes with cyanide ions and most common processes are not applicable. In some instances, the mercury cyanide complexes are precipitated using Na_2S, CaS and other inorganic sulphides and polysulphides. Recently, precipitation with sodium diethyl dithiocarbamate has been suggested [1,3,10,11]. Following precipitation, mercury dithiocarbamates were aggregated with the addition of coagulants and flocculants. The removal of the "aggregates" was then possible by settling [1,10,11] or by flotation [3,12].

With respect to As and Se, the situation is rather similar and their separations have been mostly accomplished by precipitation with ferric or aluminium hydroxides and sulphide ions. However, no work appears to have been done on the coprecipitation of the trilogy Hg, As and Se. This constitutes one of the aims of the present work.

Various technologies have been developed aimed at remediating the problems associated with the significant amount of arsenic released into the environment as a result of mining activities. Precipitation of metal arsenates has been studied extensively [13-15] and sorption of As species by various solid materials, namely pyrite [16], manganese oxides [17], activated carbon and alumina [18], several ion exchange resins and clay [19,20].

Treatment methods for arsenic include also sulphide precipitation (sulphide or ferrisulphide), or complexation with polyvalent heavy metals such as ferric iron and coprecipitation with the metal hydroxide [21]. This second process is typical of the traditional coagulation process used in the water treatment industry. For gold ore extraction plant effluent sulphide precipitation has been found partially effective for arsenate, but ineffective for arsenite, and no precipitate resulted from sulphide treatment of arsenite wastewater. Thus, arsenic is one of the most difficult elements to remove from aqueous solutions, especially to the low levels required by drinking water standards.

With respect to selenium ions, a level of 0.7 mg/l has been reported in wastewaters from copper smelting and electrolytic refining operations. Selenite appears to be the most common form of selenium in wastewater except for pigment and dye wastes, which contain the selenide (e.g., yellow cadmium selenide). A tertiary treatment reported in the literature included lime treatment to pH 11, sedimentation, mixed media filtration, activated carbon adsorption and chlorination [22]. Selenite removal also has been studied using ferric sulfate and or alum coagulation. These treatment technologies were not very effective. Treatment improved for both coagulants with increasing coagulant dosage and decreasing pH [23]. Other commonly employed industrial metal treatment processes (e.g., lime coagulation, settling, and sand filtration) were ineffective in recovering selenium, at least as the negatively charged anion. Thus, ion exchange appears to be the most effective technique for which actual results have been reported.

The removal of metal ions, from liquid systems (solid/liquid separation), by flotation is possible through various methods and techniques, [24-26]. Ion flotation and adsorbing colloid flotation have been studied recently for the removal of molybdenum (VI) and arsenic (V) from dilute aqueous solutions [9]. The ion flotation process used a cationic surfactant (dodecylamine) as collector. In the adsorbing colloid flotation ferric hydroxide was utilized as the coprecipitant (or sorbent) and sodium dodecylsulphate was used as the collector.

The second objective of this work is to extend the method of precipitation coagulation and flocculation to the removal of Hg, As and Se present together in an actual process water from a gold cyanidation circuit and to characterize on a laboratory scale the separation of the metal bearing aggregates by dissolved air flotation (DAF). Two different methods were applied: separation by flotation of the aggregates (AF) formed between the ions and Nadtc, $LaCl_3$ and Bufloc (anionic flocculant) and by adsorptive particulate flotation (APF), using solid sorbing materials (chabazite and La_20_3) for the ions and daf for the loaded carrier. The basis of the adsorptive particulate (or carrier) flotation is the cation or anion uptake by readily floatable particles and it resembles oxide flotation activation by metal ions or sulphide depression by anions [13,27].

EXPERIMENTAL

Materials and reagents

Sorbent materials. Lumps of a natural chabazite (Nevada-USA) were sampled and ground in a Tema mill to 100 % < 74 microns, and used as the metal ion sorbent -and-carrier. La_2O_3, a powdered commercial reagent, was used as the second metal sorbent.

Reagents. NaDTC, sodium dithiocarbamate, from Buckman Laboratories was used for the precipitation of the metal cyanide complexes; $LaCl_3$ analytical grade from Unocal 76-Molycorp and $FeCl_3$, p.a. from Spectrum Chem. MFG Corp. were used as coagulants and Bufloc 606 from Buckman as the flocculant.

In the preparation of the metal complexes NaCN 98.7% (Spectrum Chem. MFG Corp.) and standard solutions of the three metals in HNO_3 1.8% (Fisher Scientific) were used.

Methods

Dissolved air flotation, DAF

In the DAF process, microbubbles (about 0.01-0.1 mm) are formed by pressure reduction of a water stream saturated with air at a high pressure (saturator of 4 L capacity). Batch, bench scale, DAF tests were carried out using a 1.5 L flotation cell (Figure 1).

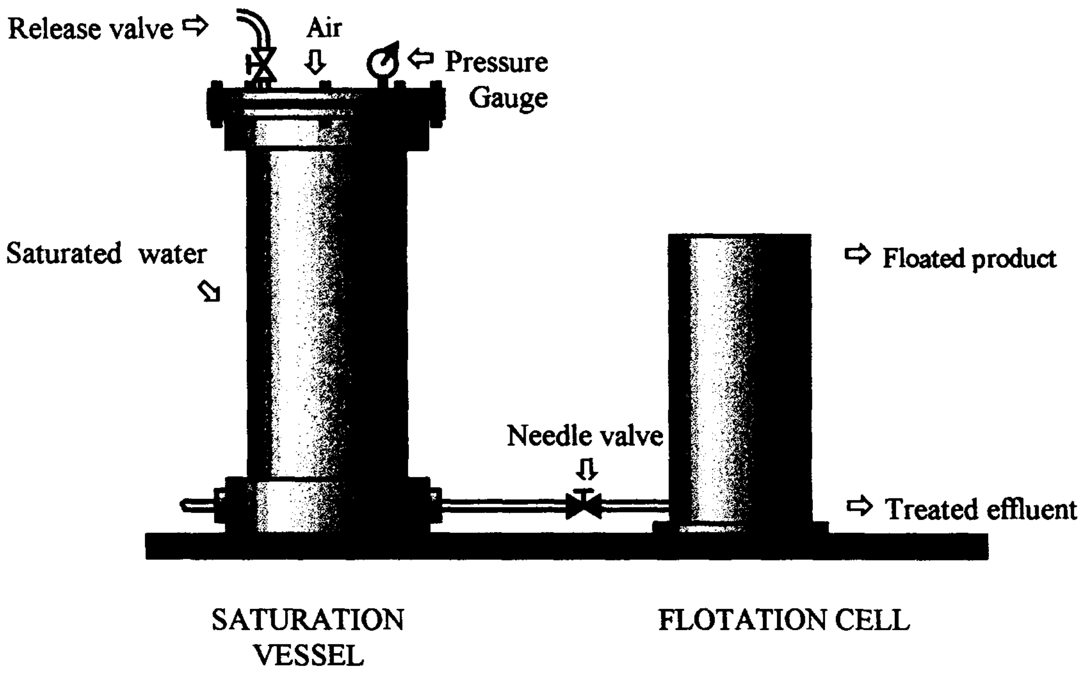

Fig.1 Dissolved air flotation (DAF) laboratory unit.

Synthetic metal bearing solutions were prepared using the water from the Newmont Mining Co., Hollister operation, as the matrix, and standard solutions As and Se (Fisher). Hg was already present in the Hollister water (about 120 ppb).

Process efficiency was evaluated by measuring residual content of metals and turbidity (NTU units) in the supernatants and by the rate of displacement of the solid/solution interface. Supernatant solutions after flotation and 5 min standing were analyzed for Hg, Se and As, using atomic absorption (spectrometer from Varian model Spectraa 200).

For the turbidity measurements, a nephelometer from HF Instruments (DRT-100B), was used. The time of flotation, unless otherwise noted, was 1 min. After flotation, an aliquot of the supernatant was sampled through a side outlet.

Before each test, 20 mL of solution was taken as a blank, leaving 980 mL as the final feed volume for the DAF tests. Using this general procedure, two different separation methods for the dissolved metals were conducted. Additional conditions are described in Table 1.

TABLE 1 **Removal of Hg, As and Se ions by DAF; Experimental conditions: saturation pressure, 5.5 atm.**

Test	Conditions	pH	Recycle ratio, %
1	30 ppm NaDTC, 50 ppm $LaCl_3$ and 0.3 ppm Bufloc 606	10.5	25
2	30 ppm NaDTC, 50 ppm $LaCl_3$ and 0.3 ppm Bufloc 606	8.1	25
3	0.5 g/L of chabazite, 15 ppm Fe^{+3} ($FeCl_3$) and 0.06 ppm of Bufloc 606	9.9	50
4	0.5 g/L of chabazite, 15 ppm Fe^{+3} ($FeCl_3$), $6x10^{-4}$ M of sodium oleate, and 0.15 ppm of Bufloc 606	7.3	10
5	0.5 g/L of chabazite, 15 ppm Fe^{+3} ($FeCl_3$), 0.3 ppm of Bufloc 606, and $6x10^{-4}$ M of sodium oleate	7.5	30
6	0.5 g/L of La_2O_3, 0.3 ppm of Bufloc 606 and $1.2 x10^{-4}$ M of sodium oleate	10.1	30

Aggregation-DAF (AF, method 1)

The experiments (1, 2 in Table 1) were performed in the flotation cell with 30 ppm of NaDTC and pH was regulated with NaOH or HCl. After a precipitation time of 3 min, 2 ml of a 25 gpL LaC13 (or $FeCl_3$) stock solution was added. Finally, after conditioning for 5 min, variable volumes of the Bufloc 606 polymer from a 320 ppm solution, were slowly placed under high stirring (for a good flocculant distribution) for 30 s. Then, the system was stirred gently for another 30 s, using a magnetic stirrer, for floc-formation before flotation (Figure 2).

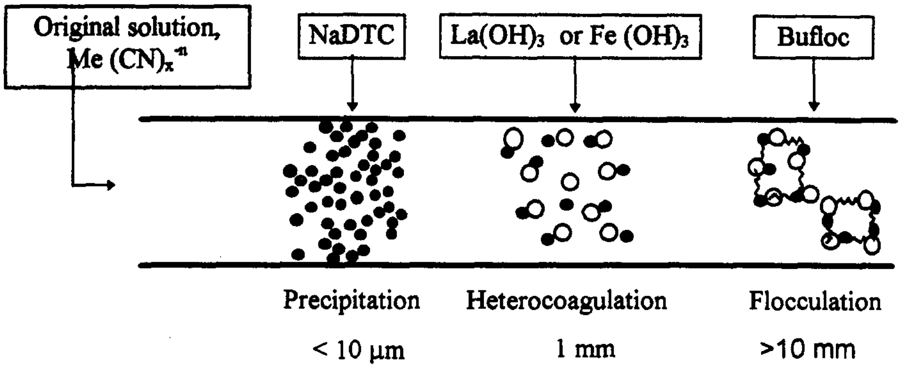

Fig.2 The "aggregation" process of ions from cyano-complexes with NaDTC, La $(OH)_3$ or Fe $(OH)_3$ and Bufloc (polymer flocculant).

Adsorptive particulate flotation-APF (method 2)

In tests 3 - 5, 0.5 g of chabazite (< 74 (m) was added to the solution containing the target ions. The conditioning time was 1 hour before $FeCl_3$ (coagulant) was added at different concentrations and pH values.

After conditioning to form the $Fe(OH)_3$ precipitates, 0.06 ppm of Bufloc 606 was added during stirring (test 3). In test 4, sodium oleate (6×10^{-4} M) was added before the flocculant to make the hydroxides more hydrophobic. In test 5, the order was altered with the flocculant added prior to the sodium oleate.

Finally, in test 6, 0.5 g/L of La2O3 was utilized as the sorbent material, keeping all other conditions established in test 5.

RESULTS AND DISCUSSION

Results obtained are shown in Tables 2, 3 and Figures 3-6. Table 2 and Figure 3 show comparative results between the two methods; Figure 4 shows flotation rates (also Table 3) and Figure 5 the corresponding solution turbidities after DAF (values in Table 3). Finally Figure 6 shows comparative results between DAF-aggregates and DAF-ions bearing chabazite. This Figure 6 compares the quality of the treated water (after flotation), by measuring the residual amount of each ion.

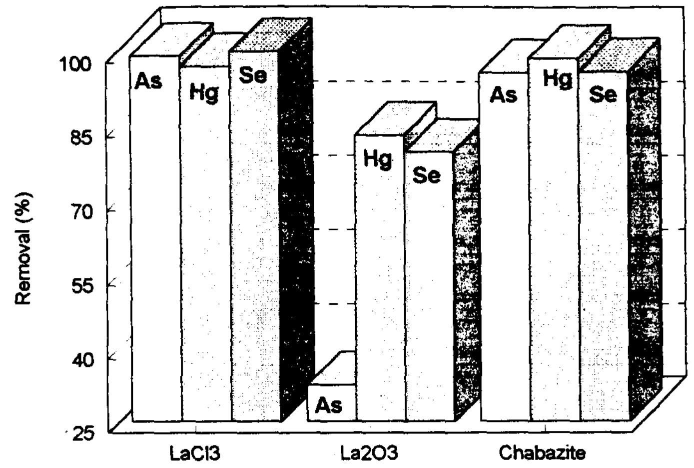

Fig.3 Removal of Hg, As and Se ions by DAF. Comparison between DAF-aggregates with $LaCl_3$ (test 1) and with DAF of sorbent materials (test 6-La_20_3 and 3-chabazite). Experimental conditions, in Table 1.

TABLE 2 Removal of Hg, As and Se ions by DAF. Experimental conditions, in Table 1. Concentrations in ppb, i = initial, f = final; % R = removal percent

Test	[Hg]i	[Hg]f	Hg %R	[Se]i	[Se]f	Se %R	[As]i	[As]f	As %R
1	148	4.6	96.9	1830	2.0	99.9	1161	10.4	99.1
2	152	4.1	97.3	1053	58.0	94.4	1216	17.0	98.6
3	106	1.4	98.7	1230	49.0	96.0	1033	43.2	95.8
4	121	33.5	72.3	1105	33.0	97.0	1005	9.9	99.0
5	132	37.0	72.0	830	44.9	94.9	1097	92.0	91.6
6	196	34.0	83.0	1431	291	79.7	1039	702	32.4

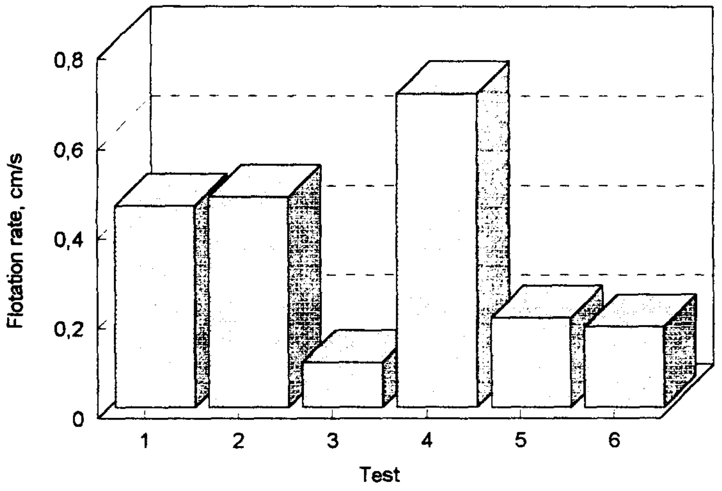

Fig.4 Removal of Hg, As and Se ions by DAF: Flotation rates of different tests (see Table 1 and 3).

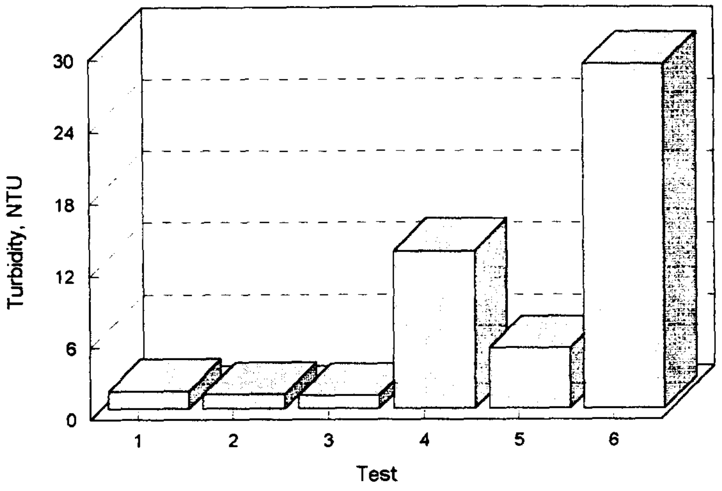

Fig.5 Removal of Hg, As and Se ions by DAF (see also Table 3). Solution turbidity. Experimental conditions, in Table 1.

TABLE 3 **Removal of Hg, As and Se ions by DAF. Solution turbidity and flotation rates. For experimental conditions, see Table 1**

Test	Turbidity, NTU	Flotation rate, cm/s
1	1.5	0.45
2	1.2	0.47
3	1.1	<0.1
4	13.2	0.70
5	5.05	0.20
6	28.8	0.18

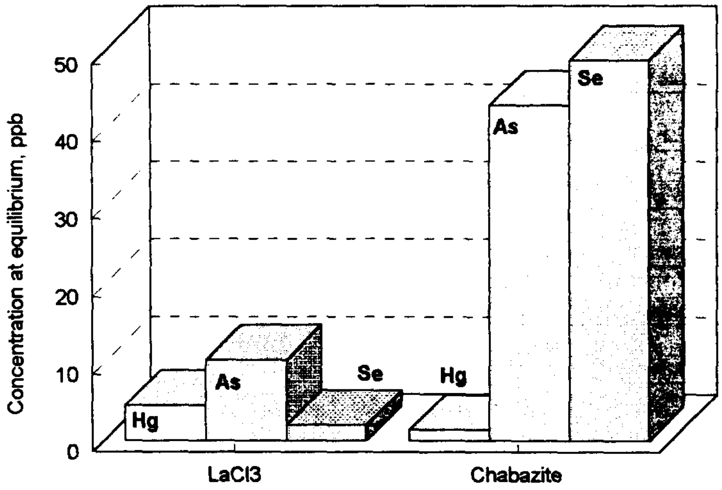

Fig.6 Removal of Hg, As and Se ions by DAF: Comparative results for the final equilibrium concentration of metals. Experimental conditions, in Table 1 (see also Table 2). Tests 1 and 3.

Results obtained show that removal of Hg, As and Se ions by DAF is feasible by both methods. However, the separation of the ions bearing aggregates by DAF was more efficient under the experimental conditions tested, mainly because of the low flotation efficiency of the loaded chabazite. Main features found may be summarized as follows:

1. Ion removal (Hg, As, Se) by DAF was almost complete using the concept of precipitation with NaDTC followed by coagulation with $LaCl_3$ and flocculation with Bufloc (see Table 1 and Figures 3 and 6). The separation was more effective at pH 10.5 than at pH 8.1.

2. Chabazite was found to be a good sorbent for all ions studied and best performance was found to occur at pH 9.9 (compared to pH 7.3-7.5). Another interesting feature was that sodium oleate, added before the flocculant Bufloc, enhanced flotation rate by about three times (compare tests 4 and 5). This was due to the hydrophobization of the surface of $Fe(OH)_3$ used to aggregate the chabazite sorbent, and allowed the use of a small recycle ratio (Rubio and Tessele, 1997). Moreover, if Fe(OH)3 was not added, the DAF rate was very low (test 3).

3. La_20_3 was not found to be a good ion sorbent at pH 10.1 when compared to chabazite and yields high residual turbidities.

4. Dissolved air flotation, DAF, was found to be very efficient in ion removal (Hg, As, Se) using precipitation with NaDTC, followed by coagulation with $LaCl_3$ (or $FeCl_3$) and by polymer flocculation. When compared to aggregation-settling, DAF was a faster separation process always yielding clear supernatants.

DAF is, among the bubble adsorptive techniques, by far the most well known method in the treatment of industrial effluents. Further, DAF has several advantages compared to other solid/liquid separation processes: high overflow rates and low detention periods, thicker scum and sludge. The authors believe that the process will be used in mining and metallurgical in the near future.

ACKNOWLEDGEMENTS

Jorge Rubio thanks to Universidade Federal do Rio Grande do Sul and CNPq-Brazil for the leave of absence and support. Authors acknowledge Newmont Mining Co. and Newmont Exploration Limited and USBM Generic Center for Waste Treatment & Recovery, for financial support and to Prof. Ross Smith (UNR-Reno) for the English revision.

REFERENCES

1. Misra, M. & Lorengo, J. *U.S Patent*, October 1996.
2. Manceau, A. & Gallup, D.L., Removal of selenocyanate in water by precipitation: characterization of copper-selenium precipitate by X-ray diffraction, infrared, and X-ray absorption spectroscopy. *Environmental Sci. & Technology*, 1997, **31** (Apr. '97) p. 968-76.
3. Tessele, F., Rubio, J., Jena, B.C. & Misra, M., Removal of mercury from gold cyanide leach solutions by dissolved air flotation. *Minerals Engineering*, 1997, **10**(8), p. 803-811.
4. Chapman, T., Extraction-metals processing, In: *Handbook of Separation Processes Technology*, R. Rousseua (ed.), J. Wiley and Sons, 1987, NY, Chapter 8.
5. Larson, K.A. & Wiencek, J.M., Mercury removal from aqueous streams utilizing microemulsion liquid membranes. *Environmental Progress*, 1994, **13**, p.253-262.
6. Huang, C.P. & Blankenship, D.W., The removal of mercury (II) from dilute aqueous solution by activated carbon. *Water Research*, 1984, **18**, p.37-43.
7. McGarvey, F.X., 1993. Mercury removal with IONAC ion exchange resins. In: *Mercury and Arsenic Wastes. Removal, Recovery, Treatment and Disposal.* U.S. EPA-Pollution Technology Review No. 214, p 36–38.
8. Kabil, M.A., Selective separation of Hg (II) from aqueous solutions by the precipitate flotation technique. Fresenius *J. Anal. Chem.*, 1994, **348**, p.246-247.
9. Zhao, Y., Zouboulis, A.I. & Matis, K.A., Removal of molybdate and arsenate from aqueous solutions by flotation. *Separation Sci. and Tech.*, 1996, **31**(6), p. 769-785.
10. Lorengo, J.A. The removal of mercury from cyanide leach solutions using dithiocarbamates. *MSc. Thesis*, University of Nevada, 1996.
11. Sultan, B., Raichur & Misra, M., Flocculation of Hg bearing aggregates, 1996. Submitted to *SME Meeting 1997.*
12. Rubio, J. &d Tessele, F., Removal of heavy metal ions by adsorptive particulate flotation. *Minerals Engineering*, 1997, **10**(7), p. 671-679.
13. Robins, R.G., The stabilities of arsenic (V) and arsenical compounds in aqueous metal extraction systems. *Hydrometallurgy, Research, Development and Plant Practice.* Osseo-Asare K. and Miller J. Eds AIME, Warrendale, 1982, 291-310.
14. Krause, E. & Ettel V.A., Solubilities and stabilities of ferric arsenate compound. *Hydrometallurgy*, 1989, **22**, p. 311-337.
15. Swash, P.M. & Monhemius, A.J., Hydrothermal precipitation from aqueous solutions containing iron(III), arsenate and sulphate. *Hydrometallurgy '94*, IMM, Chapman and Hall, 1994, p.177-190.
16. Zouboulis, A.I. & Kydros, K.A., Arsenic (Ill) and arsenic(V) removal from solutions by pyrite fines. *Separation Sci. and Tech.*, 1993, **28**, p. 2449-2463.
17. Nishimura, T. & Umetsu, Y., Removal of arsenical, arsenic(V) with manganese from aqueous solution by ozonation. *Internal. Symp. on Impurity Control and Disposal in Hydrometallurgical Processes.* Harris B. and Krause E. Eds, CIM, Canada, 1994, p. 91-100.
18. Mortazavi, S., Volchek, K. & Whittaker, H., The removal of arsenic from water by adsorption and microfiltration. *10th Technical Seminar on Chemical Spills*, St. John, New Brunswick, 1993.
19. Gardiner, W.G., and Munoz, F., 1971. Mercury removed from waste effluent via ion exchange. *Chem. Engineering*, **78**, 57–59.
20. Yadava, K.P., Tyagi, B.S. & Sing V.N. Removal of arsenical from aqueous solution by China clay. *Environmental Technology Letters*, 1988, **9**, p. 1233-1244.

21. Isaacson, A.E., Corwin, R.R. & Jeffers T.H., Arsenic removal using immobilized ferric oxyhydroxides. *Internal Symp. on Impurity Control and Disposal in Hydrometallurgical Processes.* Harris B. and Krause E. Eds, CIM, Canada, 1994, 47-55.
22. Patterson, J.W. Treatment technology for selenium. In *Water Treatment Technology*, 1985, Chapter 19, p.215. Ann Harbour Sci.

23. Linstedt, K.D., Houch, C.P. & O'Connor, J.T., Trace Element Removals in Advanced Wastewater Treatment Processes, *J. Water Poll.*, 1971, Cont. Fed. **43**, p. 1507-1513.
24. Zabel, T., Flotation in water treatment. In: Mavros, P., Matis, K.A. (Editors), *Innovations in Flotation Technology*. Kluver Academic Publishers, Dordrecht, 1992, p.431.
25. Rubio, J., Schneider, I.A.H. & Aliaga, W., New process for heavy metals separations from waste water streams in the mining industry. *Clean Technologies for the Mining Industry*. Proceedings Congress, Chile, 1996, April, p.1.
26. Matis, K.A., (Editor). *Flotation Science and Engineering*. Marcel Dekker, N.York, 1995, p.558.
27. Zouboulis, A.I., Matis, K.A, Lanara, B.G. & Loos-Neskovic, C., Removal of Cadmium from diluted solutions by hydroxyapatite. II. Flotation studies. *Separation Sci. and Tech.*, 1997, **32**, p. 1755-1767.

Correspondence on papers published in *Minerals Engineering* is invited, preferably by e-mail to min.eng@netmatters.co.uk, or by Fax to +44-(0)1326-318352