Pergamon

Minerals Engineering, Vol. 10, No. 8, pp. 803–811, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0892-6875/97 $17.00+0.00

0892-6875(97)00058-7

REMOVAL OF MERCURY FROM GOLD CYANIDE SOLUTION BY DISSOLVED AIR FLOTATION

F. TASSEL§, J. RUBIO§, M. MISRA† and B.C. JENA†

§ On leave of absence from Universidade Federal do Rio Grande do Sul,
Departamento de Engenharia de Minas, Porto Alegre, RS-Brazil
† University of Nevada, Department of Chemical and Metallurgical Engineering,
Reno, NV 89557, USA. E-mail: misra@equinox.unr.edu

(Received 13 March 1997; accepted 25 April 1997)

ABSTRACT

The removal of mercury from mercury cyanide complexes from the processing streams of gold cyanidation circuits was studied by dissolved air flotation (DAF) at laboratory scale. Selective aggregation of mercury was carried out after precipitation of the complexes with sodium dimethyl dithiocarbamate (NaDTC), coagulation with colloidal hydroxides of La and Fe, and flocculation with a polymer (Bufloc 606). Removal of the mercury was achieved by dissolved air flotation of the aggregates formed. Results showed almost complete removal (>98%) of Hg from dilute solution and the process efficiency was dependent on system solution and interfacial chemistry, overall aggregation phenomena and operating parameters. © 1997 Elsevier Science Ltd

Keywords
Flocculation; environmental; mineral processing; gold ores

INTRODUCTION

The removal of mercury from the processing streams of gold cyanidation circuits has become increasingly important, mainly because it creates environmental and economical problems at each stage of the gold concentration and refining processes, i.e., leaching, carbon adsorption and desorption [1], electrowinning or zinc precipitation, and smelting. Since mercury forms very stable complexes with cyanide ions, most of the common removal processes cannot be applied. Currently, the only widely practiced mercury removal process involves retorting of the electrowon cathodes in an evacuated and heated retort. The vaporized elemental mercury is then condensed and set aside. In some instances, the mercury cyanide complexes are precipitated using Na_2S, CaS and other inorganic sulfides and polysulfides. These compounds have proven to be noneffective in forming a stable mercury precipitate.

A recent study at University of Nevada, Reno has shown that mercury complexes from gold cyanide solution can be efficiently precipitated using dimethyl dithiocarbamate (DTC) [2]. Another interesting aspect of this finding is that, while these dithiocarbamates react with mercury to form insoluble complexes, they do not interfere with the processing of gold either during leaching or activated carbon absorption. DTCs have been used for the precipitation of most heavy metal ions from aqueous solution [3, 4, 5].

The present study was undertaken in order to examine the suitability of dissolved air flotation (DAF) for the removal of mercury dimethyl dithiocarbamate precipitates from the aqueous solution. Mercury cyanide complex was precipitated by sodium dimethyl thiocarbamate (NaDTC) addition and aggregated by adding suitable coagulants and flocculants.

"Aggregates" will be used in this paper as a generic term for the agglomerates formed after the coagulation-flocculation of the precipitates. The aggregates were then separated by applying the DAF technique and the separation efficiency was compared with that of the conventional settling-filtration process.

EXPERIMENTAL PROCEDURE

Materials

Reagents: Sodium dimethyl dithiocarbamate, NaDTC, from Buckman Laboratories was used for precipitation of mercury cyanide complexes; analytical grade $LaCl_3$ from Unocal 76-Molycorp and $FeCl_3$ p.a. from Spectrum Chem MFG Corp were employed as coagulating agents and Bufloc-606 from Buckman Laboratory was used as a flocculant. Synthetic mercury complexes were prepared by using 98.7% NaCN from Spectrum Chem MFG Corp and standard solution of mercury in 1.8% HNO_3 supplied by Fisher Scientific.

Aggregation Studies

Aggregation tests were carried out in a 1.2 liter beaker containing 1 L Hollister water obtained from Newmont Mining Co. The physico-chemical properties of Hollister water are given in Table 1. The required amounts of NaDTC from a 24% (by weight) stock solution were added to the beaker and the pH was regulated by the addition of either NaOH or HCl. Three minutes after the precipitation had started, 2ml of 25 gpl coagulant ($LaCl_3$ or $FeCl_3$) was added.

TABLE 1 Chemical and physicochemical parameters in the Hollister water (approximate values).

PH	Alkalinity, ppm	Solids, total, ppm	Solids, dissolved, ppm
9.5-9.7	53-55	1.45-1.64	1446-1511

Ion $^{(+n)}$	Hg	Se	As	CN	Cu	Co	Fe	Ca	Mg
Concentration, ppm	0.20-0.98	0.82-0.84	0.22-0.25	3.00-3.70	0.03-0.04	1.00-1.20	0.16-0.20	236-269	0.73-1.22

The finely dispersed colloidal precipitates heterocoagulated with La or Fe hydroxide to form large aggregates of 1–3 mm size. Finally 1 ml of Bufloc-606 polymer from a 320 ppm stock solution was slowly added under vigorous stirring conditions for 30 s to obtain uniform flocculant distribution. The solution was further stirred gently for another 30 s and then settling or flotation tests were carried out. By this time the average aggregate had grown to a size larger than 10 mm. Figure 1 shows the progressive growth of the colloidal precipitates into large size aggregates with coagulant and flocculant addition.

The effect of molar ratios of NaDTC:Hg on the aggregation process was studied by varying the molar ratios between 1 and 4. The pH for the present study was maintained at 10.6 following the optimized process data reported elsewhere [6].

Settling Studies

The solution containing the aggregates was allowed to settle for 30 minutes and then the semi clear decanted liquid was filtered by using 0.2 µm polymeric filters from non sterile Acro-disc, lot 2837.

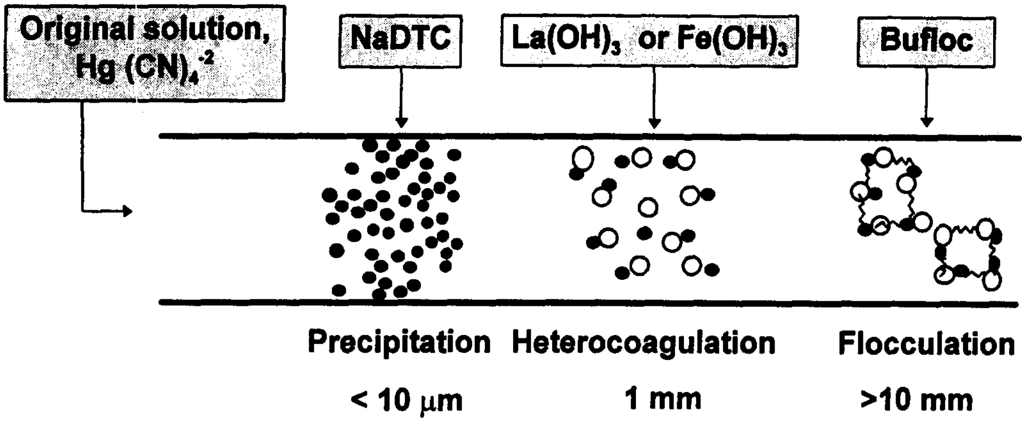

Fig.1 The schematic representation of aggregation of mercury ions from mercury cyano complexes with NaDTC, $La(OH)_3$ or $Fe(OH)_3$ and Bufloc-606 addition.

Dissolved Air Flotation (DAF) Studies

In the dissolved air flotation (DAF) process, microbubbles are formed by decreasing the pressure of an air saturated pressurized water stream. The size of the air bubbles range from 0.01 to 0.1 mm in diameter [7, 8]. DAF tests were carried out in a laboratory scale apparatus consisting of a 4 L pressure vessel used for saturating water with air, which was connected to a 1.5 L flotation cell via a needle valve. A schematic of the DAF apparatus is shown in Figure 2. About 980 ml of the solution, containing the aggregates, was placed in the pressure vessel and saturated with air by passage of air under desired pressure. The solution was then allowed to flow to the flotation cell by releasing the needle valve, thereby releasing the air pressure. The reduction of air pressure resulted in the formation of air bubbles which floated the aggregates. Flotation was usually carried out for 1 minute duration. After the completion of the flotation test, an aliquot of the supernatant solution was collected through a side outlet as sample.

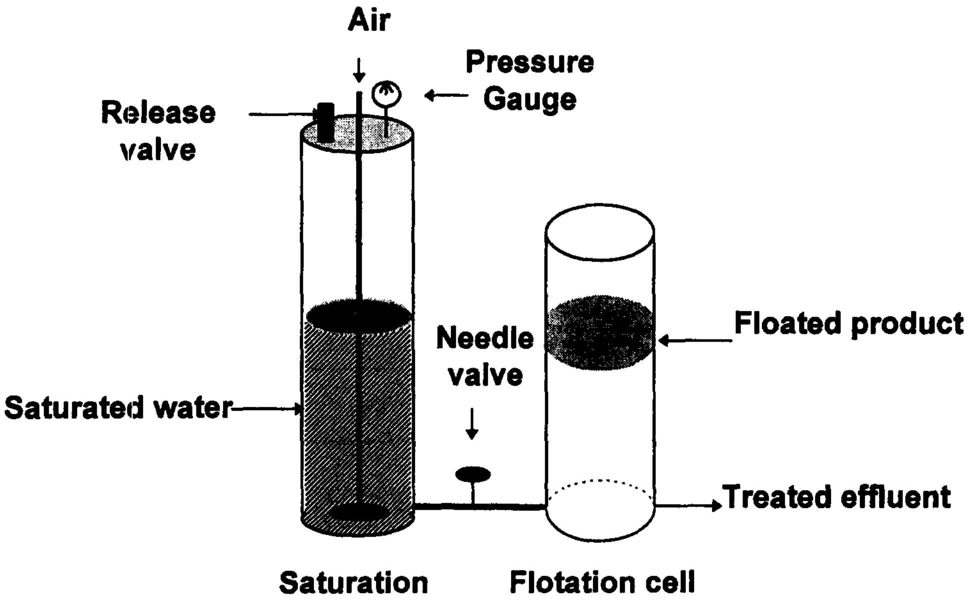

Fig.2 Schematic diagram of dissolved air flotation laboratory unit.

The following parameters were studied: the effect of coagulating agents and flocculants, initial mercury concentration, recycle ratio and saturation pressure.

The process efficiency of each process i.e; the settling-filtration and DAF, was evaluated by analyzing the initial and final concentration of mercury in the solution, level of turbidity and rate of displacement of solid/liquid interface. Mercury concentration was determined by using a cold vapor atomic absorption spectrophotometer (Varian model SpectrAA 200). The turbidity measurement was carried out by a nephleometer from HF instruments (DRT-100B).

RESULTS AND DISCUSSION

Aggregation-Settling Studies

Most of the aggregates formed with the addition of coagulants and flocculants were very large, the average size being 10 mm, well structured and with good settling properties. However, a small amount of fragile and small size aggregates were also formed which did not settle after 30 min settling time and an additional filtration stage was necessary to separate those aggregates.

Removal of mercury cyanide complexes by aggregation and settling-filtration was found to be a function of NaDTC:Hg molar ratio as shown in Table 2. The precipitation of mercury complexes from the solution takes place according to the following reaction:

$$2(CH_3)NCS_2Na + Hg(CN)_4^{-2}/Hg(CN)_2^{-1} = Hg[(CH_3)_2NCS_2]_2 + 2CN^{-1}/4CN^{-1} + 2Na^{+1} \qquad (1)$$

Ibrado [1,9] has identified the tetracyano complexe ($Hg(CN)_4^{-2}$) to be the most prevailing mercury complex species at the operating pH of 10.6 . According to reaction (1), a minimum NaDTC:Hg molar ratio of 2 is required for complete removal of mercury. However, the actual reagent consumption is usually higher than the stoichiometric amount due to the presence of other cations present in Hollister water, which also react with NaDTC [10]. A 99.7% mercury removal could be achieved at a NaDTC:Hg molar ratio of 4:1, as the Hg concentration decreased from 6360 ppb in the original solution to 20 ppb in the supernatant solution.

TABLE 2 Effect of molar ratio NaDTC/[Hg] on the removal of Hg by aggregation-settling-filtration processes. Solution pH = 10.6; 50 ppm $LaCl_3$ and 0.3 ppm Bufloc.

Molar ratio	[Hg] initial, ppb	[Hg] final, ppb	% Removal
1:1	6750	3104	54.07
2:1	6620	201	96.98
3:1	6490	57	99.12
4:1	6360	20	99.67

DAF studies

Effect of Reagents

The feed for the DAF studies was prepared by maintaining an optimum NaDTC:Hg molar ratio of 4:1. The effect of $LaCl_3$ and $FeCl_3$ as coagulants and Bufloc-606 as flocculant on the extent of mercury removal by DAF is shown in Table 3. In the absence of a flocculant the coagulants were not efficient in removing mercury from the solution, as the aggregates formed were weak and offered little resistance to shearing forces during flotation. As a result, these aggregates broke down and redispersed in the solution resulting in a turbid supernatant solution. Mercury removal was improved, and residual turbidity was reduced, by addition of the flocculant, Bufloc-606. Addition of flocculant consolidated these weak aggregates in to larger ones thereby increasing the air to solid ratio and the resistance to shear. The bubble-aggregate adhesion was also improved, due to better hydrophobicity of these aggregates [11] leading to better floatability.

TABLE 3 Dissolved air flotation (DAF) of mercury bearing aggregates: Effect of reagents. Hollister water with NaDTC:Hg=4:1 (molar ratio); pH 10.6; saturation pressure, 4.5 atm and 30 % recycle ratio.

Test	Other conditions	[Hg] initial, ppb	[Hg] final, ppb	Removal, %	Turbidity, NTU
1	50 ppm $LaCl_3$	8050	470	94.2	18.03
2	10.3 ppm of Fe^{+3} ($FeCl_3$)	8050	300	96.3	12.54
3	50 ppm $LaCl_3$ + 0.3 ppm Bufloc 606	8400	80	99.0	8.83
4	10.3 ppm Fe^{+3} ($FeCl_3$) + 0.3 ppm Bufloc 606	8400	130	98.4	3.22
5	-	8400	4440	47.1	70.50

$FeCl_3$ appears to be a better coagulant than $LaCl_3$, as a lower residual turbidity value was obtained by the addition of the former, which may be attributed to heavier aggregates formed with $Fe(OH)_3$. Mercury removal with no coagulant and flocculant addition was poor, as only 47% mercury could be removed and the supernatant turbidity was higher than 70 NTU. This shows that the colloidal suspensions formed by NaDTC addition do not possess good floating properties. It should be noted that the turbidity values of the Hollister water before precipitation and the distilled water are 2.96 and 0.65 NTU, respectively.

Effect of Initial Mercury Concentration

The effect of initial mercury concentration on mercury removal, residual turbidity and flotation rate is shown in Table 4. Figure 3 is a plot of mercury removal as a function of initial concentration. As shown in the Figure, the extent of mercury removal is low at low initial concentrations, increasing with increasing initial concentration and reaches a maximum value at high concentrations. The flotation rate also followed a similar trend, as seen in Table 4. At low initial Hg levels, little precipitation of Hg-DTC occurred, therefore fewer floatable aggregates were formed. With increasing Hg concentration, more precipitates were formed, which in turn grew into larger aggregates which floated easily. It should be emphasized that flocs as large as 1 cm can be removed efficiently by DAF due to the low density of these aggregates, which is not possible for mineral particles of identical size.

TABLE 4 **Effect of initial mercury concentration on Hg bearing aggregates removal by DAF. Conditions: 4:1 NaDTC: Hg molar ratio, 50 ppm $LaCl_3$, 0.3 ppm of Bufloc 606 and 30% recycle ratio.**

[Hg] initial, ppb	[Hg] final, ppb	Removal, %	Turbidity, NTU	Flotation rate, cm/s
30	28	6.7	1.12	0.12
105	12	87.6	1.08	0.18
345	15	95.7	1.25	0.26
585	6,5	98.9	1.29	0.29
967	27	97.2	1.36	0.30
2165	65	97.0	-	0.27
4300	53	98.8	1.94	-
6800	96	98.6	2.08	0.28
9600	120	98.8	2.56	0.35

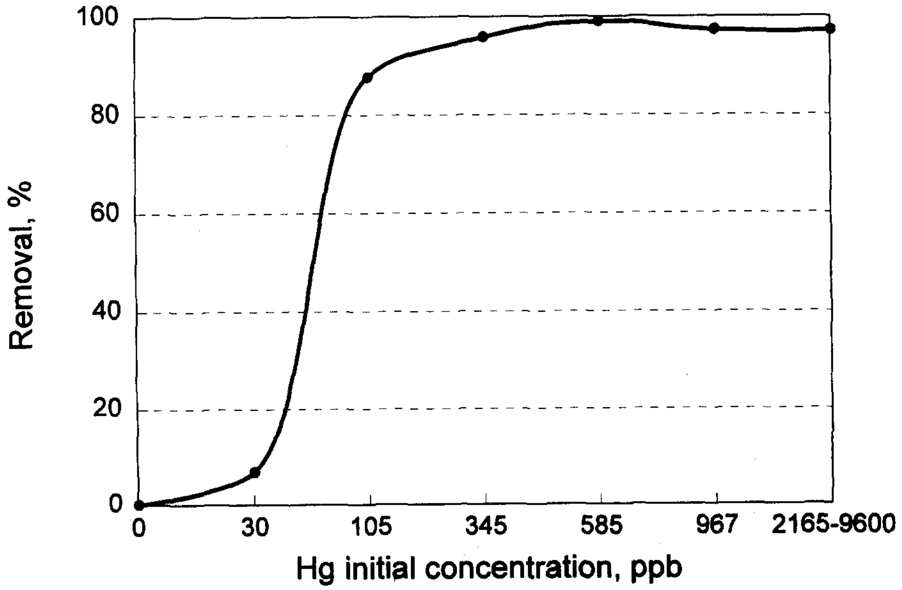

Fig.3 Removal of mercury bearing aggregates as a function of the initial Hg concentration during dissolved air flotation under experimental conditions as described in Table 4.

Figure 4 shows that a linear relationship can be obtained by plotting the amount of mercury removed as a function of initial mercury concentration. The relationship is given by the following equations:

$$(C_{i,\,Hg,} - C_{f,\,Hg}) = 0.97\ Ci._{\,Hg} \qquad (2)$$

or

$$C_{f\,,\,Hg} = (1-0.97)\ C_{i.,\ Hg} \qquad (3)$$

Where

$C_{i,\ Hg}$ = Initial mercury concentration

$C_{f,\ Hg}$ = Final mercury concentration

Equation (3) allows prediction of the final mercury concentration from knowledge of initial concentrate, with an experimental error of 9.5%.

It can also be seen from Table 4 that there is a progressive increase in the residual turbidity level of the supernatant solution as the initial mercury concentration increases, and the extent of mercury removed does not increase beyond a maximum level of 98.6 to 98.85%. At high initial mercury concentrations, as the amount of colloidal dispersants increases, an increasing number of small aggregates are formed which are difficult to float.

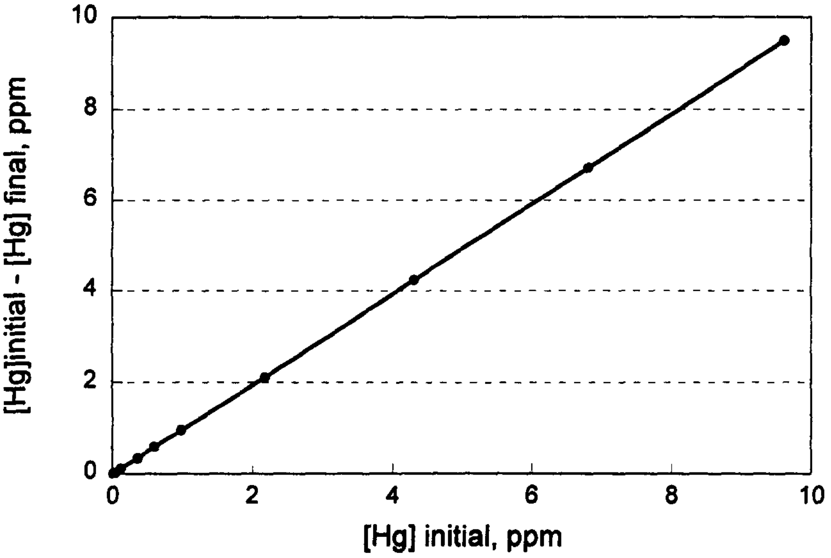

Fig.4 Amount of Hg (in ppm) removed as a function of the initial Hg concentration during DAF under experimental conditions as described in Table 4.

Effect of Recycle Ratio

The effect of recycle ratio on mercury removal by DAF was carried out with solutions containing a high initial mercury concentration of 10520 ppb, in order to study the process efficiency under extreme conditions. Tests were carried out at three recycle ratios of 17%, 25% and 30% and the results are shown in Table 5. The results show that the extent of mercury removal increases with increasing recycle ratio. At higher recycle rates more air bubbles are available due to the higher gas hold-up which enhances overall capture of aggregates.

TABLE 5 **DAF of mercury bearing aggregates: effect of recycle ratio. Initial [Hg] = 10520 ppb. Conditions: 4:1 NaDTC: Hg molar ratio**

Recycle ratio, %	[Hg] final, ppb	Removal, %	Turbidity, NTU	Flotation rate, cm/s
17	231.4	97.8	5.01	0.45
25	201.6	98.1	6.74	0.23
30	136.8	98.7	4.42	0.94

Effect of Saturation Pressure

Table 6 shows the effect of the saturation pressure on DAF of the mercury bearing aggregates. The saturation pressure was varied between 3.5 and 5.5 atm and the recycle ratio was maintained at 30%. The removal efficiency increases with increasing saturation pressure. Thus, for a constant recycle ratio, dissolved air increases (Henry's law), gas hold-up and the air-to-solids ratio are higher, and a larger amount of finer bubbles are available for aggregate capture.

TABLE 6 **DAF of Hg bearing aggregates: effect of saturation pressure on Hg removal, residual turbidity and process kinetics. Conditions: 4:1 NaDTC: Hg molar ratio, 50 ppm $LaCl_3$, 0.3 ppm of Bufloc 606 and 30% recycle ratio.**

Saturation pressure, atm	[Hg] initial, ppb	[Hg] final, ppb	Removal, %	Turbidity, NTU	Flotation rate, cm/s
3.5	10440	570.0	94.5	2.08	0.32
4.4	10520	136.8	98.7	4.42	0.94
5.5	10300	120.5	98.8	2.50	0.21

Comparison of aggregation-settling (AS) results with that of aggregation-DAF (A-DAF) shows that the latter process often yielded cleaner solutions with higher separation rates (usually two times faster). This may be attributed to the formation of small size aggregates which remained dispersed and contributed to high turbidity in the supernatant solution. These small aggregates had poor settling characteristics, therefore their separation was difficult. However, these aggregates could be readily floated by DAF, resulting in their efficient removal. Due to advantages such as high separation rates and good clarification, DAF competes well with other conventional separation processes.

CONCLUSIONS

Removal of mercury dimethyl dithiocarbamate (Hg-DTC) precipitates from gold cyanide leach solutions by dissolved air flotation was studied. The colloidal dispersants were aggregated by the addition of $LaCl_3$ and $FeCl_3$ as coagulants and Bufloc-606 as flocculant. The results indicate that $FeCl_3$ is a better coagulant than $LaCl_3$ and best aggregation was obtained by the coagulant -flocculant combination. The aggregates were then separated by settling and dissolved air flotation (DAF) techniques. DAF was found to be more efficient than the settling technique for the removal of the aggregates, in terms of process kinetics, solution turbidity and cleaner solution product. Separation of the Hg depends mainly on initial mercury concentration, saturation pressure and recycle ratio.

ACKNOWLEDGMENTS

Jorge Rubio would like to thank Universidade Federal do Rio Grande do Sul and CNPq-Brazil for the leave of absence and support. The authors acknowledge Newmont Mining Co. and Newmont Exploration Limited and USBM Generic Center for Waste Treatment & Recovery, for financial support.

REFERENCES

1. Ibrado, A.S. & Fuerstenau, D.W., Adsorption of the cyano complexes of Ag (I), Cu (I). Hg (II), Cd (II) and Zn (II) on activated carbon. *Minerals and Metallurgical Processing*, **6** , No.1, 23–28 (1989).
2. Lorengo, J.A., The removal of mercury from cyanide leach solutions using dithiocarbamate. *M. Sc. Thesis*, University of Nevada, Reno, Department of Chemical and Metallurgical Engineering, (1996).
3. Leja, J., *Surface Chemistry of Froth Flotation.* (Plenum Press, New York), 258–259 (1982).
4. Wing, R.E. & Redford, W.E., Heavy metal removal using dithiocarbamate. *Plating and surface finishing*, **69**, No.1 , 67–71 (1982).
5. Sedwick, P., Shin, D. & Zeitlin, H., The separation of metals from treated deep-sea ferro manganese nodules by adsorptive bubble techniques using salicylaldoxime and sodium diethyl dithiocarbamate as organic precipitating reagents. *Separation Science and Technology*, **19**, No. 2–3, 183–190 (1984).
6. Sultan, B., Raichur, A. & Misra, M., Flocculation of Hg Bearing Aggregates, *SME Meeting*, Colorado, (1997).
7. Bratby, J. & Marais, G.V.R., Solid/liquid separation equipment scale-up, *Flotation,* ed. D.B. Purchas, (Upland Press), 155 (1977).
8. Lazaridis, N.K., Matis, K.A., Stalidis, G.A. & Mavros, P., Dissolved air flotation of metal ions. *Separation Sci. & Tech.*, **27**, No.13, 1743–1758 (1992).
9. Ibrado, A.S., *M. Sc. Thesis*, University of California, Berkeley, Dept. Mat. Sci. and Min. Eng., (1986).
10. Miller, E., Alfaro, M., Misra, M. & Lorengo, J., Mercury Control in the cyanidation of Gold Ores, *Proceedings of the Engineering Foundation, Technical Solutions for the Pollution Prevention in the Mining and Mineral Processing Industries*, (1995).
11. Solari, J. & Rubio, J., The effect of polymer flocculents on dissolved air flotation of heavy metals. *Proceedings, Reagents in Mineral Industry*, IMM, London, UK, 271–276 (1984).