THE INFLUENCE OF WATER QUALITY ON THE FLOTATION OF THE ROSH PINAH COMPLEX LEAD-ZINC SULFIDES.

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Abstract
The flotation separation of the Rosh Pinah ore into lead and zinc concentrates are based on the selective flotation of the lead containing minerals followed by the activation and recovery of the zinc sulfides. In the present work the influence of the composition of the water on the selective flotation of the lead containing minerals is reviewed and the results given of the laboratory investigation of the influence of activating species such as silver, lead and copper, on the selective recovery of lead minerals from the Rosh Pinah ore. It was found that it was difficult to prevent the activation of the sphalerite by the metal species in solution in the absence of cyanide, and that colloidal precipitates most probably also serves as a significant carrier of these activators in the flotation circuit. Removal of heavy metal species from the solution by means of an adsorbent is possible, but most probably not practical.

Introduction
The complex sulphides ore mined at Rosh Pinah typically contains 5 to 9% zinc, as sphalerite, 1 to 3 % lead, as galena, 6 to 8% iron, mainly as pyrite, 0.2% copper, as chalcopyrite, small quantities of silver and gold, and dolomite and quartz as the main gangue minerals (Reyneke, 2000). Separation of the ore into lead and zinc concentrates are achieved by first depressing the sphalerite and floating the galena to obtain a lead concentrate containing 55 to 60% lead, 200 to 500 g/t silver and 5 to 7% zinc, at lead recoveries ranging from 70 to 75%, and then activating the sphalerite with copper sulfate and floating it to obtain a zinc concentrate containing 52 to 55% zinc, 1 to 2% lead, at zinc recoveries ranging from 80 to 85% (Rosh Pinah, 2002). The quest is to optimize the separation between the lead and zinc, with maximum recoveries and grades, and to limit the use of cyanide as depressant for the sphalerite during the galena flotation. Although sphalerite does not interact strongly with xanthate collectors, and typically has to be activated for good recoveries to be obtained (Chen and Yoon, 2000), the sphalerite present in the Rosh Pinha ore does float to a significant extent during the galena flotation and has to be suppressed, by typically using cyanide and dextrin additions.

It is generally accepted that the activation of sphalerite occurs by a metathesis reaction in which the more labile zinc sulfide is exchanged for more stable sulfides such as copper, lead and silver (Finkelstein, 1997), as indicated in table 1. In the case of the Rosh Pinah ore the activation of the sphalerite is probably due to some dissolution of copper, silver and lead minerals during storage and minerals processing, and the exchange of these metal ions with the zinc on the surface of the sphalerite. The advantage of minerals processing at higher pH values are illustrated by the reduction of the activities of the metal species as a function of pH, as indicated in figures 1 to 3. However, the formation of the metal sulfides will still be thermodynamically possible due to their high stabilities, although the rate of activation of the sphalerite will be slower due to mass transfer limitations, as has been found by Popov, et al (1989) for the activation of sphalerite by lead, and by Chen and Yoon (2000) for copper. The effect of cyanide on the concentration of the copper and silver in solution is illustrated in figures 4 and 5, and it follows that high concentrations of cyanide will be required to significantly lower the metal ion concentrations, and that even in that case, the activation of sphalerite would rather be mass transfer than thermodynamically limited. Cyanide is not an effective depressant for lead as it is not significantly complexed by cyanide.

An alternative method to reduce the activity of activating metal ions from solution is to adsorb them on a solid that may be removed from the circuit with the residues. Hydroxyapatite is such an absorbent that is readily available and is often used to remove lead from water (Takeuchi and Arai, 1990; Rashchi and Finch, 2000).

Although cyanide is a very effective depressant for sphalerite, its use is problematic due to its toxicity and potential environmental problems. In this work potential causes for the strong floatability of sphalerite in the Rosh Pinah circuit will be investigated by following the changes in water composition with successive contacts with fresh ore. The use of natural hydroxyapatite as an absorbent for metal cations in solution to reduce the activation of the sphalerite will also be investigated.

Experimental

Pure mineral samples of sphalerite, from Elmwood Mine, were obtained from Ward's. These samples were ground in an agate pestle and mortar and screened to -180 + 150 µm for the adsorption tests. Ore samples originating from the Eastern Ore Field at Rosh Pinah were crushed to less than 3.35 mm and packed in 20 kg batches at the plant. The ore was further crushed to minus 2 mm and stored in plastic bags at the laboratory. 1 kg of ore was wet ground in a ball mill just prior to the flotation experiments using a solid to liquid ratio of 2:1 to a fineness of ≈ 75% -75µm. The flotation experiments for the water recycling experiments were done in a 2L Denver flotation cell at the natural pH of the pulp that ranged from 7.8 to 8.2, with 1×10^{-4} M sodium normal propyl xanthate as collector, and 15mg/L of Senfroth 6005. The pulp from both flotation products was filtered and the water returned to the mill to be used in the next cycle. About 85% of the water was recycled and the balance was made up using tap water. The water samples were analysed used ICP. The adsorbent evaluated was a natural hydroxyapatite (NHAp) from Yichang, China, and was milled to 90% -90µm just prior to use. The effect of the absorbent on the floatability of the sphalerite mineral was evaluated using microflotation tests on the sphalerite mineral, prepared as described above. The H-type Hallimond tube used for these experiments had an effective volume of 100 mL, fitted with a magnetic stirrer. The 1 g mineral sample was washed in aqueous hydrochloric acid with a pH of 2, followed by rinsing in distilled water just prior to the experiments. The flotation was done in distilled water with borax as buffer to control the pH at 9.18. The collector used was sodium normal propyl xanthate at a concentration of 1 x 10^{-4} M. Flotation was done by introducing air through a frit at the bottom of the cell at a rate of 50 mL/minute for 5 minutes, after which the flotation product was collected, dried and weighed. The adsorption of the copper and lead by the natural hydroxyl apatite was measured by first introducing 200 mg natural hydroxyl apatite to 100 mL pulp containing 4 g sphalerite mineral with a size range of -180 + 150 µm, and then adding 10 mg/L of lead (II). 40 mg/L of cyanide was added for the cyanide depression experiment. An adsorption time of 10 minutes was used.

Results

Effect of recycling on water properties

The effect of recycling the water used for flotation on the water quality is summarised in figure 6. The results are rather disappointing in the sense that the hydrolysis of most of the metal cations at pH 9.18 caused their concentrations to be generally below the detection limit of typically 0.02 mg/L. This is unfortunate as a cation like the cuprous ion will certainly be capable of activating sphalerite at concentrations below this level. Furthermore, it is likely that the excess metal cations will precipitate out as colloids which may act as a reservoir for activating metal cations in the recirculating water. The increasing level of iron recorded must be due to this as the equilibrium concentration of even ferrous iron is lower than the approximately 1 mg/L measured. It is interesting the total dissolved solids was still increasing after 5 cycles of recycling while the metal cation values stayed below detection.

Effect of water recycling on flotation recoveries

The flotation recoveries obtained for the flotation of Rosh Pinah ore with increasing recycling of water, in the absence and presence of the natural hydroxyapatite absorbent, are summarised in figure 7. The natural floatability of the sphalerite, with a recovery of 40% without specific activation, indicates that better suppression than that offered by the absorbent would be required to prevent the flotation of the sphalerite during galena flotation. The initial increase in the flotation of the sphalerite with recirculation of the water indicates that some activating species are probably released into the water, although the poorer recovery for the more contaminated water is difficult to explain. The recovery of the galena increased slightly with one recycle of the water, but like the sphalerite again decreased slightly for more recycles. The presence of the hydroxyapatite did not significantly affect the recovery of the galena as would be expected.

Suppression of copper and lead adsorption on sphalerite by cyanide and natural hydroxyapatite

The results of copper and lead adsorption on pure sphalerite particles and the microflotation test results indicate that cyanide, at a cyanide to copper ratio larger than five, is very effective in preventing the adsorption of copper on sphalerite, but has no effect on the adsorption of lead. The fact that cyanide is effective as suppressant in the Rosh Pinah circuit indicates that activation of the sphalerite by lead is probably not a significant problem. The hydroxyapatite was effective in lowering, but not preventing the adsorption of lead on the sphalerite, and of decreasing the recovery of sphalerite from 86 to 30%, but only at 250 times the mass of lead added.

Conclusions

The concentration of metal cations such as copper, lead and silver, that may activate sphalerite for xanthate flotation, is relatively low at alkaline pH values due to the hydrolysis of the cations. However, even though these values are below the detection limits of typical water analyses done, they are probably still high enough to activate the sphalerite, though be it at a relatively slow rate. The recirculation of water used in flotation increased the total dissolved solids, but not that of the metal cations significantly, as these hydrolise significantly at alkaline pH values. Although the flotation of sphalerite is initially increased in low cycle recirculated water, it decreased again for higher cycle recirculated water, indicating that the relationship between recirculation and sphalerite flotation is not simple. Cyanide additions to water were very efficient in preventing the adsorption of copper, but not lead, on sphalerite. An absorbent such as natural hydroxyapatite reduced the adsorption of lead, but not copper, on sphalerite and also reduced the flotation of the sphalerite in the presence of lead cations, but only at relatively high addition rates. As copper activation is probably the more significant problem in the Rosh Pinah circuit the use of an absorbent such as hydroxyapatite would be of limited value.

Acknowledgements

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Table1. Solubility products at 25°C for some metal sulfides calculated using the free energy values listed in the MinteqA2 database.

Metal sulfide	**Ksp**
ZnS	2.81×10^{-25}
PbS	8.58×10^{-29}
Cu_2S	2.72×10^{-48}
Ag_2S	1.00×10^{-49}

Table 2. Copper and lead adsorption by sphalerite particles at pH 9.18, and in the presence of cyanide (CN^-/Cu^{2+}, Pb^{2+} = 5.18), or natural hydroxyapatite (NHAp/ ZnS = 1/20), as indicated. The flotation recoveries were determined using microflotation.

	Cu^{2+} adsorbed, µg/g	**Pb^{2+} adsorbed, µg/g**	**ZnS flotation recovery, Pb^{2+} activated, NHAp/Pb^{2+} = 250 g/g**
ZnS	50	155	86%
ZnS + CN^-	0	170	---
ZnS + NHAp	41	30	30%

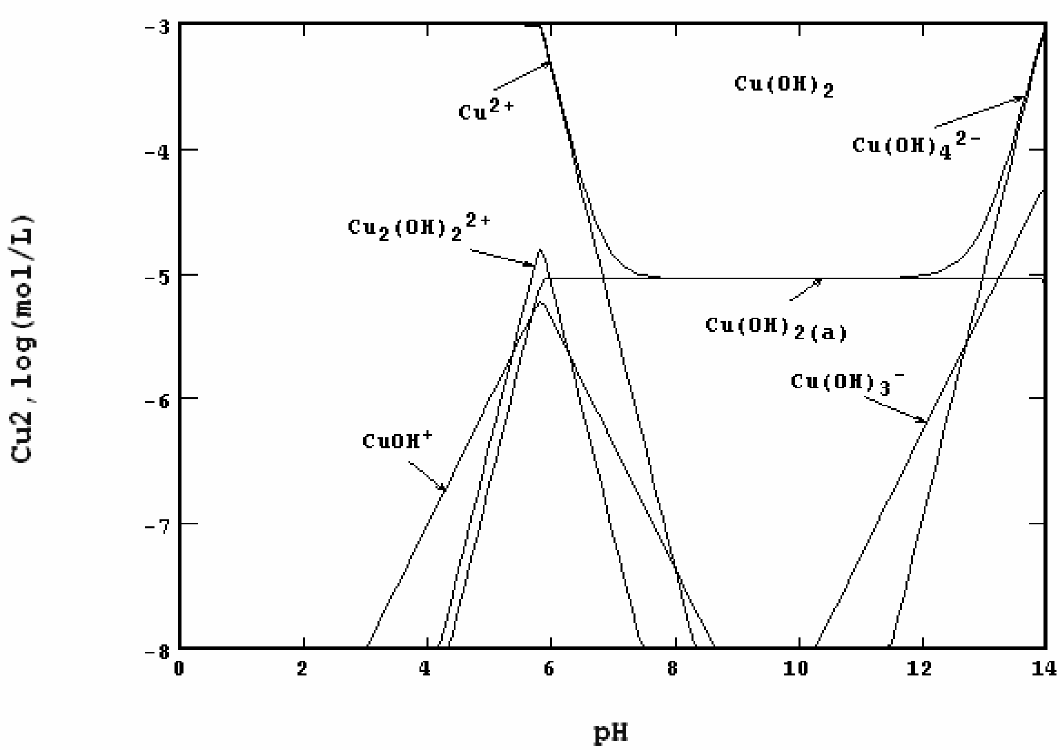

Figure 1. Speciation for Cu (II) species as a function of pH. Calculated using Stabcal and the MinteqA2 database.

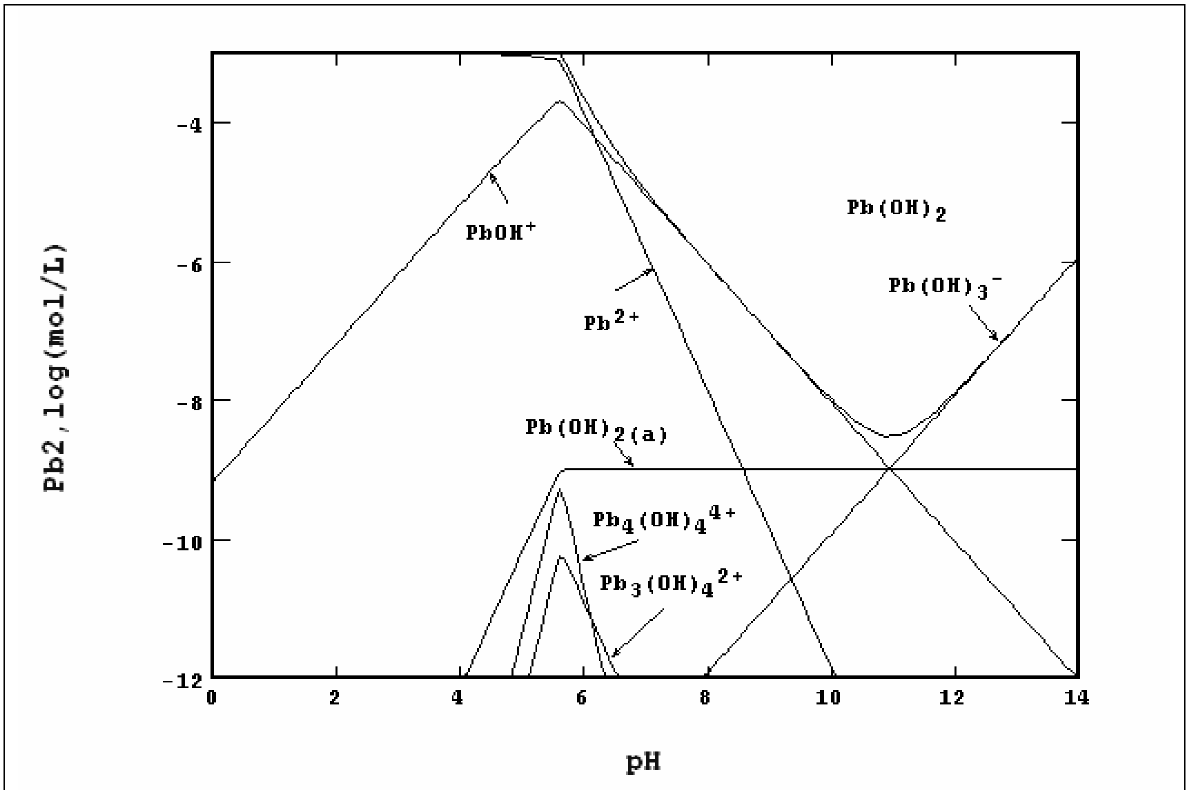

Figure 2. Speciation for Pb (II) species as a function of pH. Calculated using Stabcal and the MinteqA2 database.

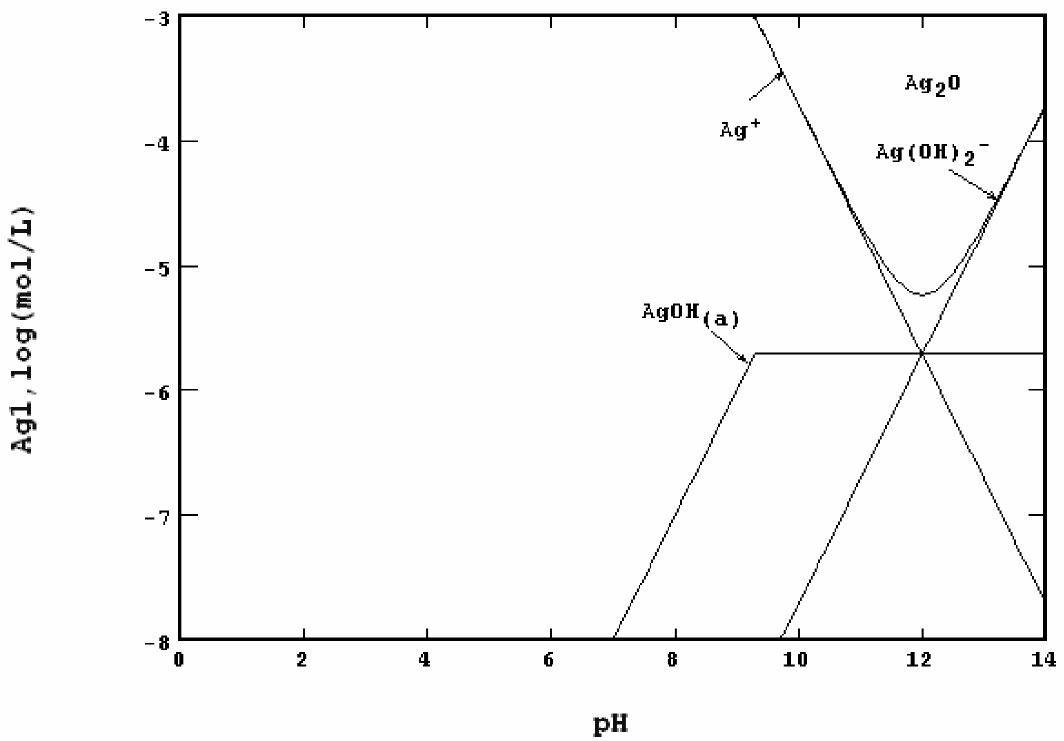

Figure 3. Speciation for Ag (I) species as a function of pH. Calculated using Stabcal and the MinteqA2 database.

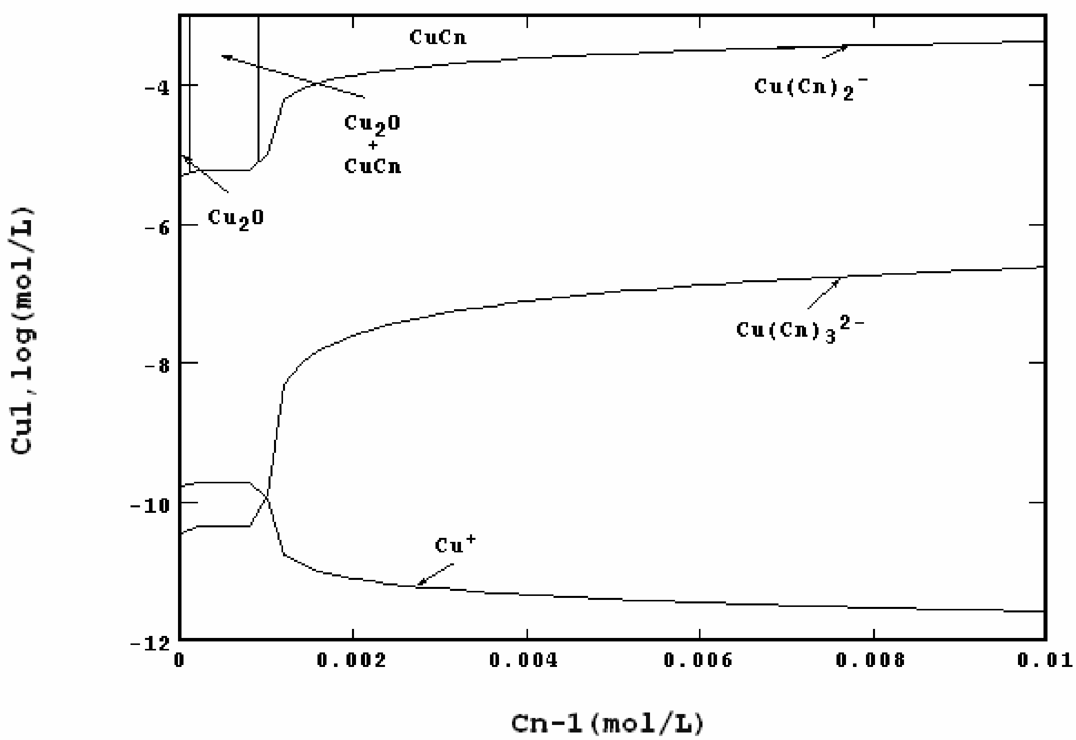

Figure 4. Speciation for Cu (I) species at pH 9 as a function of cyanide concentration. Calculated using Stabcal and the MinteqA2 database.

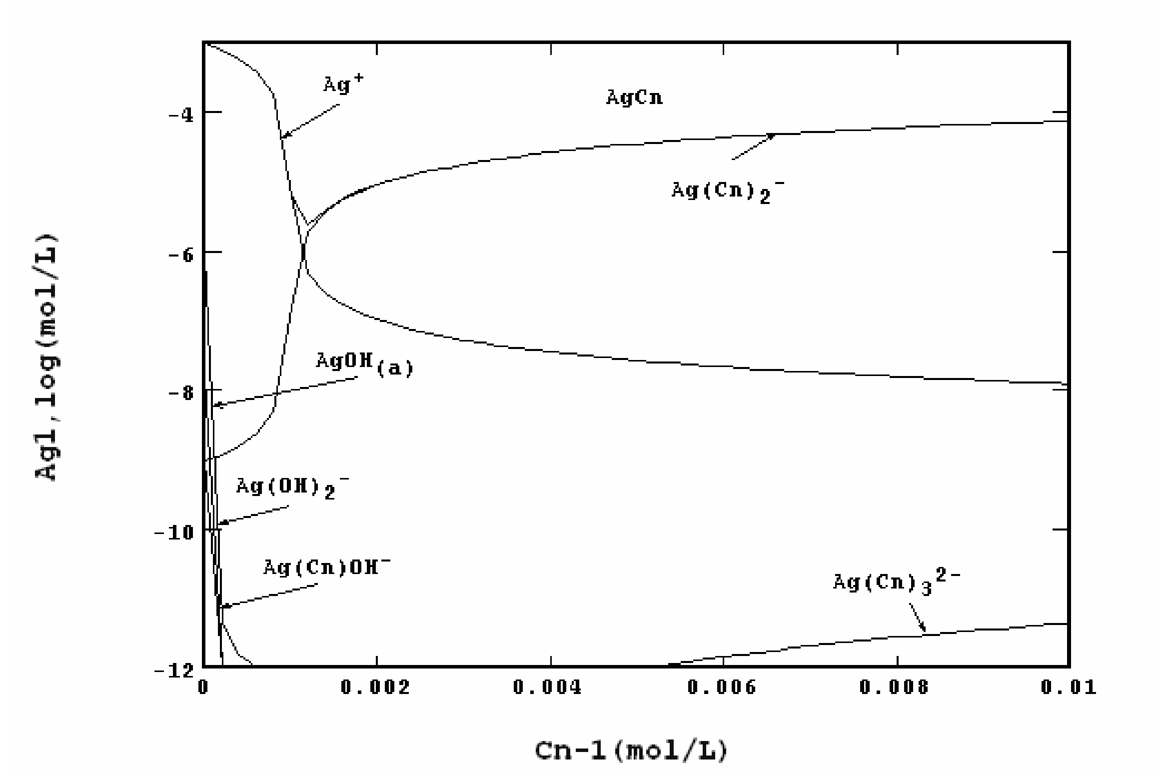

Figure 5. Speciation for Ag (I) species at pH 9 as a function of cyanide concentration. Calculated using Stabcal and the MinteqA2 database.

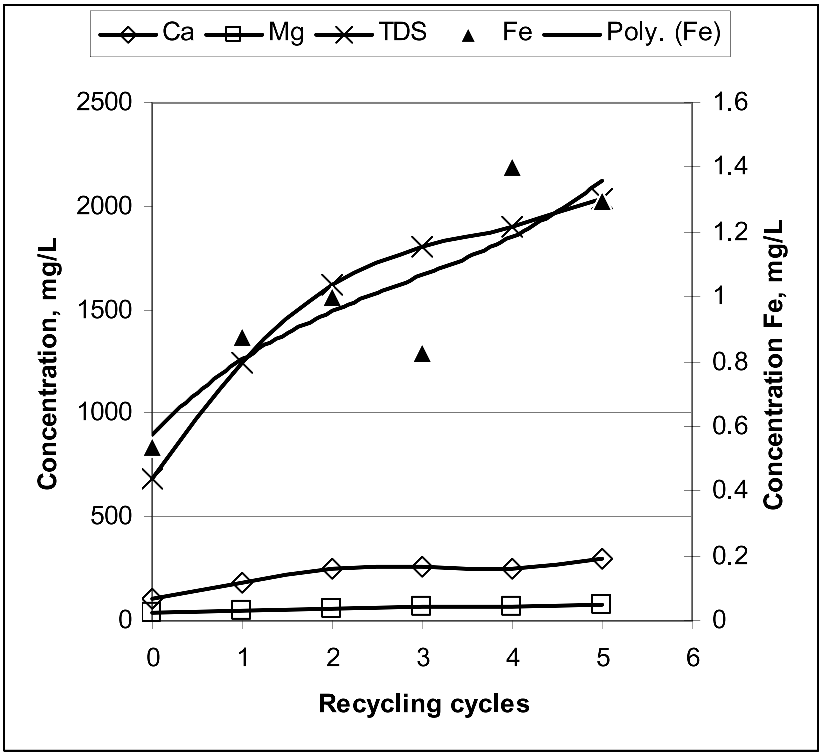

Figure 6. Effect of recycling on water used in the flotation of fresh Rosh Pinah ore samples.

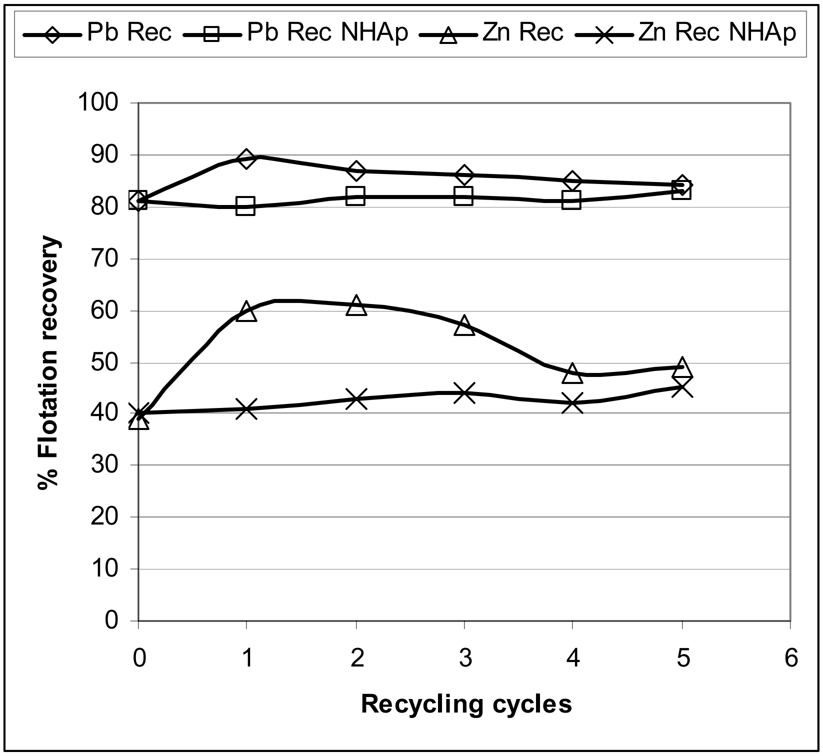

Figure 7. Effect of recycling water and treatment with natural hydroxyapatite (NHAp) on the flotation recovery of galena (%Pb) and sphalerite (%Zn) from Rosh Pinah ore.