Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Germanium from Lead in Solutions by Flotation

A. I. Zoumboulis[a]; K. A. Matis[a]; N. K. Lazaridis[a]
[a] LABORATORY OF GENERAL & INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY (BOX 114), UNIVERSITY OF THESSALONIKI, THESSALONIKI, GREECE

To cite this Article Zoumboulis, A. I. , Matis, K. A. and Lazaridis, N. K.(1990) 'Separation of Germanium from Lead in Solutions by Flotation', Separation Science and Technology, 25: 4, 463 — 476
To link to this Article: DOI: 10.1080/01496399008050343
URL: http://dx.doi.org/10.1080/01496399008050343

SEPARATION SCIENCE AND TECHNOLOGY, 25(4), pp. 463-476, 1990

Separation of Germanium from Lead in Solutions by Flotation

A. I. ZOUMBOULIS, K. A. MATIS,* and N. K. LAZARIDIS

LABORATORY OF GENERAL & INORGANIC CHEMISTRY
DEPARTMENT OF CHEMISTRY (BOX 114)
UNIVERSITY OF THESSALONIKI
THESSALONIKI 54006 GREECE

Abstract

Flotation of lead as the hydroxide by dodecylamine (in ethanolic solution) proved to be an effective separation method from germanium ions. The experiments were carried out in dilute aqueous solutions of pH 10, on a laboratory scale, and at different concentration ratios. Germanium was further concentrated as a second stage by flotation by using pyrogallol as the activator and dodecylamine as the collector at pH 7. The latter technique was found to float both germanium and lead ions from solution. Germanium separation and its scale-up is discussed.

INTRODUCTION

Germanium is known to rarely form minerals of its own. It occurs as a scattered element in different ores such as mixed sulfides; for instance, at the mineral processing plant in Tsumeb (South Africa) (*1*). Among the main recovery methods for germanium from concentrates is a hydrometallurgical route (possibly in combination with pyrometallurgy) which usually results in the production of great volumes of dilute solutions in which germanium coexists with other metal ions (arsenic, lead, zinc, etc.). The separation of germanium from arsenic was accomplished elsewhere (*2*) by ion flotation, and the method was investigated in depth, but on a

---

*To whom correspondence should be addressed.

small scale, for germanium alone (*3*, *4*). Lead and germanium belong to the same group in the Periodic Table, so they should have similar properties and behaviors.

The mechanism of germanium ion flotation is described by the following simple chemical reactions:

$$H_2GeO_3 \xrightarrow{3H_2P} H_2GeP_3$$

$$GeP_3 \xrightarrow{2S^+} S_2GeP_3$$

where P stands for pyrogallol (activator) and S for dodecylamine (cationic surfactant). Metagermanic acid (H_2GeO_3), the form in which germanium predominately exists in dilute solutions, is rather undissociated, $pk_1 = 8.585$ (*5*). Therefore, a ligand for complex formation is needed. It is seen from the reactions that the relationship of reagents at least requires a stoichiometry for germanium/pyrogallol/dodecylamine equal to 1:3:2.

Lead, on the other hand, has been studied more extensively, notably by the research teams of Rubin (*6*, *7*) and Wilson (*8*). The former examined the foam separation of lead by using the anionic surfactant sodium lauryl sulfate, and observed maximum removal at pH 8.2. The latter paper examined the adsorbing colloid flotation of lead in a pilot plant by hydrocomplexes of ferric chloride and the same collector.

The flotation removal of lead ions by dodecylamine (laurylamine) and the effect of pH in dilute solutions was briefly reported (*9*) and correlated successfully to the theoretically expected amount of lead hydroxide precipitation. It was stated that as lead hydroxide is soluble in aqueous solutions up to 3.65×10^{-4} *M*, precipitate flotation was not expected (*6*, *7*).

EXPERIMENTAL

Batch flotation experiments were conducted in the laboratory with artifical solutions or mixtures, following the dispersed-air flotation technique. The apparatus consisted of an air compressor connected to the cell through a needle valve, a washing trap, and a rotameter. The compressor outlet excess pressure was set at 1 atm. The flotation cell was a cylindrical Perspex column with a liquid volume of about 2 L (80 mm i.d. by 420 mm height), having a Scott No 4 diaphragm (porosity 10–16 μm) at the bottom. A weir was provided at the top for the foam. It was also used as a part of a continuous rig in the separation of copper and zinc as sulfides from solutions by precipitate flotation (*10*). The foam layer was removed continuously throughout the experiments.

Certain small-scale experiments (*11*) also reported on Ge-Pb ion flotation by the pyrogallol/dodecylamine system. They were conducted with a microcell of approximately 100 cm^3 content (34 mm i.d. by 140 mm height), connected to a nitrogen cylinder. This flotation apparatus was earlier used for germanium (*3*, *4*). Nitrogen was later replaced by air. No selective separation was achieved with these experiments, so they were not repeated on a larger scale.

Chemical analysis of the solution samples left after flotation was carried out by atomic absorption for lead in the usual manner and for germanium by the colorimetric phenylfluorone method at 520 nm (*12*). The latter was found to be very accurate and specific for solutions with concentrations up to 1 ppm germanium. From the technological point of view, germanium is expected in dilute aqueous solutions during its recovery. The experimental results were expressed as flotation recoveries (usually given as average values).

Germanium solutions were prepared from GeO_2 and lead from $(CH_3COO)_2Pb \cdot 3H_2O$ (both Merck). Sodium hydroxide and hydrochloric acid solutions were used for pH modification. As surfactant or collector, dodecylamine, $CH_3(CH_2)_{11}NH_2$ (Fluka, purity 99%), in ethanolic solution was used. In some experiments pyrogallol, $C_6H_6O_3$ (Merck), was also used as a ligand activator. The key reagent in germanium analysis was 2,3,7-trihydroxy-9-phenyl-6-fluorone.

RESULTS AND DISCUSSION

Ion Flotation of Ge

In small-scale laboratory experiments of germanium ion flotation (*3*), the following conditions were used. A tested volume of 100 cm^3 with an initial concentration of $1 \times 10^{-4}\,M$ Ge at pH 7, a reagent ratio for pyrogallol/dodecylamine/Ge equal to 3:2:1 plus 10% excess and 0.5% ethanol (frother), without any stirring, and flotation (through a D_4 glass frit) by 3.33 cm^3/s nitrogen at a pressure difference of 26.6 kN/m^2 for 300 s as the retention time. Germanium removal from the solution was over 90%. The flotation rate was observed to follow a first-order kinetics equation.

The present, larger-scale experiments on 2-L samples of germanium alone (i.e., 20 times greater in solution volume) were carried out in a flotation cell scaled up in an area ratio of 5.5 times and a height ratio of approximately 3 times. Note that the top of the cell was left for the foam layer. The initial germanium content was again 1 × 10^{-4} *M* (i.e., of the order of 7 ppm). Preliminary experiments showed that no conditioning was needed and that pH modification from the value of 7.0 was not necessary. Pulse addition of collector did not improve flotation recovery. Also, when the cell height was doubled, there were similar results. For bubble columns used in the chemical industry, the ratio of height to diameter is important.

Figure 1 shows the results at different retention times with gas flow rate variations. The same reagents ratio was kept (no excess). Generally, germanium recoveries became constant after 1.2 ks with 8.3 cm^3/s, but still they were rather low (60%). The technique was also tested by varying the initial concentration, but gave similar results, as shown in Fig. 2. The germanium concentration left in solution after flotation was slightly increased, from approximately 3 to 14 ppm. With an increase in pyrogallol of more than three times (3 × 10^{-4} *M*), the germanium concentration

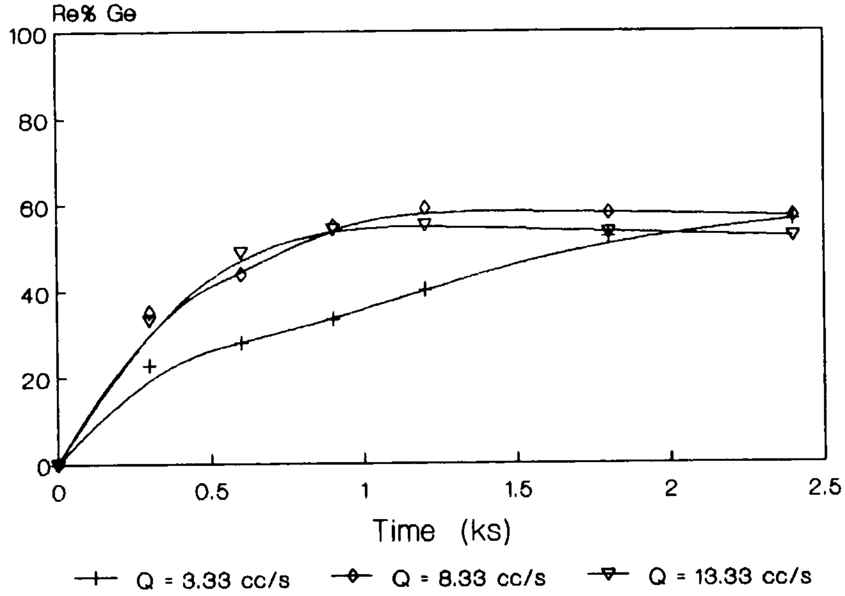

FIG. 1. Flotation of germanium: effect of flotation time at various gas flow rates on recovery (%). Initial Ge concentration 1 × 10^{-4} *M*, pH 7, pyrogallol 3 × 10^{-4} *M*, dodecylamine 2 × 10^{-4} *M* in 0.2% ethanolic solution.

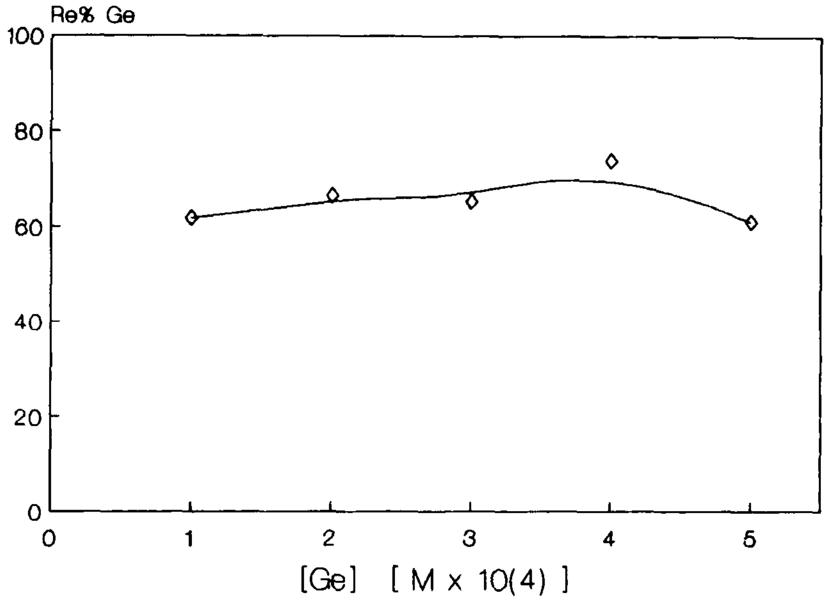

FIG. 2. Effect of initial germanium content on germanium recovery. Flotation time 1.2 ks, gas flow rate 8.33 cm^3/s (other operating conditions as before).

showed a small increase in recovery. An increase of dodecylamine more than two times (2×10^{-4} *M*) the germanium concentration and a change of ethanol did not affect the process.

The added reagents were therefore increased simultaneously while keeping the stoichiometric ratio constant. The results are presented in Fig. 3. A 100% excess of reagents was found necessary in this case for total recovery. Therefore, the experimental conditions found optimum for small-scale operation needed revamping, mainly in the flotation retention time and reagent additon, depending on the specific cell.

Preliminary dissolved-air flotation experiments for germanium (and later lead) alone were then carried out, but the results were unsatisfactory. It seemed that this technique for bubbles generation could not work in such dilute solutions without any previous coagulation. Dissoved-air flotation is, more or less, the conventional flotation technique in effluent treatment. It has been applied, for instance, in the selective separation of copper, zinc, and arsenic ions from solution (*14*).

Lead alone was earlier reported (*13*) for the same flotation mechanism, and it showed effective removal. From simple stoichiometry, a ratio of Pb/

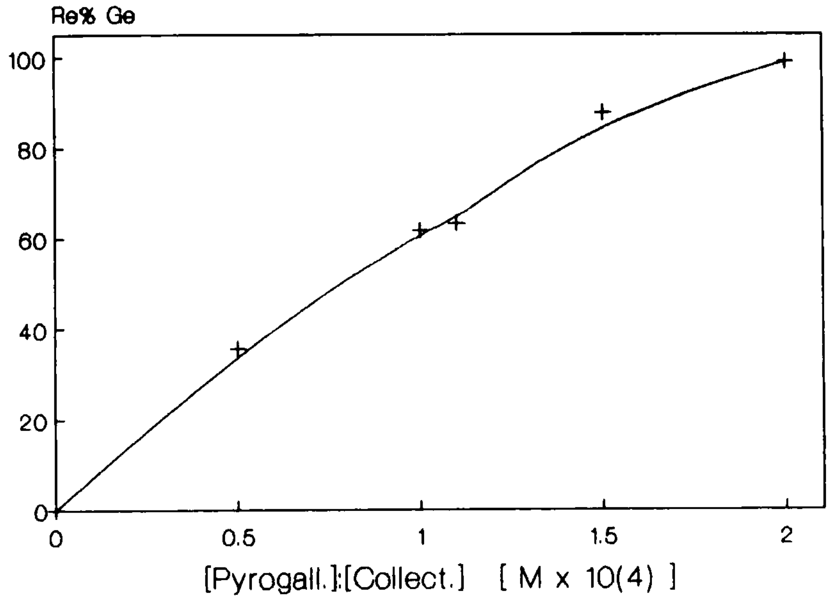

FIG. 3. Effect of increased reagents addition on germanium recovery at a constant 3:2 ratio of pyrogallol/dodecylamine (in *M*).

pyrogallol/dodecylamine equal to 1:2:2 is expected. This, however, was not certified experimentally, possibly due to the fact that lead in aqueous solution forms polynuclear species [$Pb_6(OH)_8^{4+}$ and $Pb_4(OH)_4^{4+}$ in the pH range studied], and its removal does not follow a simple model. Increased foaming was also noticed (*11*) in these experiments, and it was usually a problem in flotation.

For germanium-lead artificial mixtures at their physical pH (as found for germanium alone), Fig. 4 presents the initial results for a small-scale while following the same ion flotation mechanism. In these mixtures the germanium concentration was kept constant and that of lead was increased. The added reagents (pyrogallol and dodecylamine) were calculated only for germanium because at this stage only selective separation was aimed for. It was found that the two metal ions cofloated. Germanium recoveries decreased, but lead gave high recoveries, over 80%. Germanium recovery decreased because of the pH, which is a known crucial parameter in flotation techniques (*3*).

This series was repeated with the pH modified to the optimum (around 7), and the results are shown in Fig. 5, where germanium recoveries also

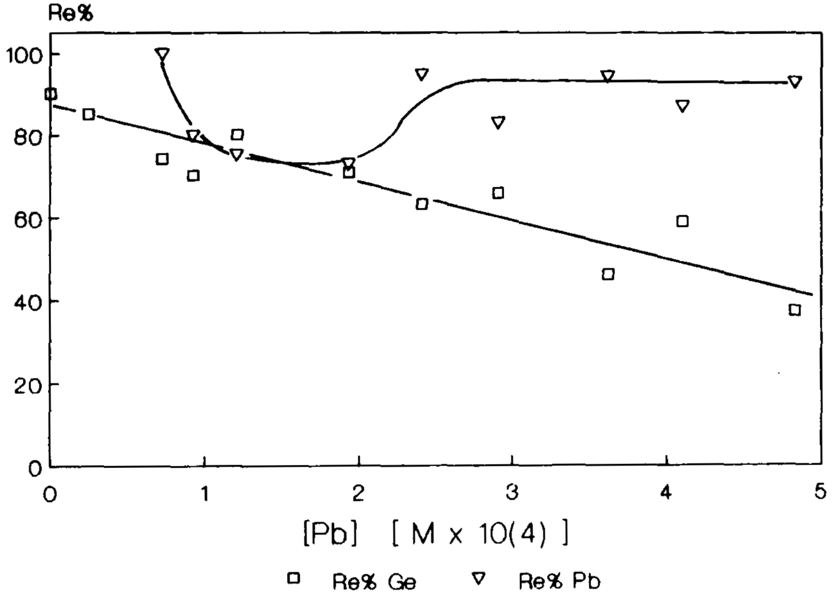

FIG. 4. Small-scale flotation of germanium-lead. Effect of initial lead content in the mixture on recoveries of both ions (initial Ge 1 × 10^{-4} *M*, 10% excess of reagents, time 300 s, gas flow rate 3.33 cm^3/s, varying pH from 5.4 to 7.1).

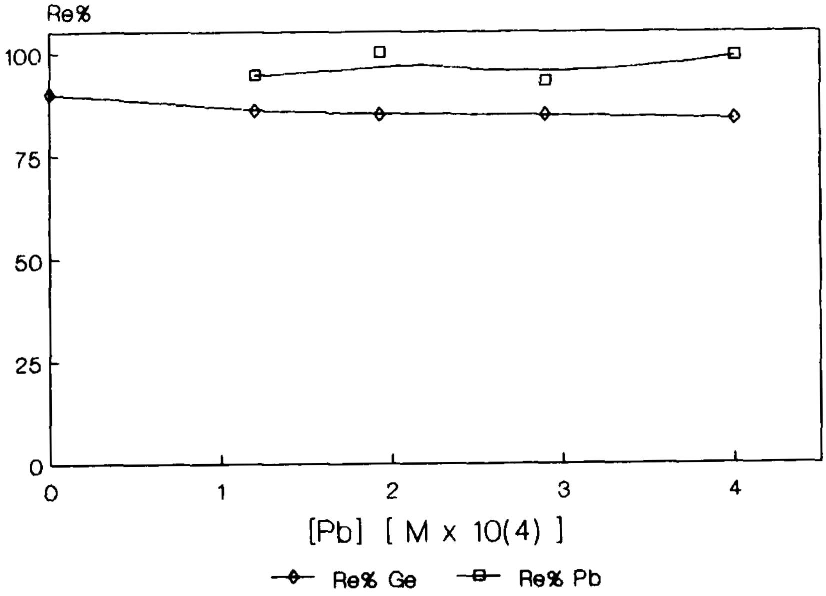

FIG. 5. Small-scale experiments on Ge-Pb. As in Fig. 4, but pH 7.0 to 7.1.

increased compared to Fig. 4. Taking into account that the pyrogallol quantity was only proportional to that of germanium and that lead floats, it is suggested lead could float without any pyrogallol.

This flotation technique was found satisfactory only as a concentration method for both germanium and lead from dilute aqueous solutions. However, in the absence of lead, it is promising in germanium recovery, for instance, in separation from arsenic. Adsorbing colloid flotation, also examined, proved ineffective (*2*). Therefore, it is proposed as a second stage process following lead separation.

Separation of Pb from Ge

Knowing the aqueous chemistry and metals speciation is a prerequisite in flotation when applied to solutions. This is particularly the case with hydrolyzable metals such as lead. For pH values less than about 8, the main existing species in solution are Pb^{2+} and $PbOH^+$, which makes it possible to use an anionic flotation collector. For pH values greater than 8, $Pb(OH)_2$ is mainly formed and the species $HPbO_2^-$ also exists, so removal by an aninoic collector is expected to decrease, as reported elsewhere (*6*, *7*). The heterogeneous equilibrium of lead hydroxide in dilute solutions is

$$Pb(OH)_2(s) \rightleftharpoons Pb(OH)_2(aq) \qquad pK = 3.44$$

However, a cationic collector may be used (*9*) in the pH range 9–11. In the more basic region, competition occurs with hydroxyl ions, generally making these separation techniques unsatisfactory. For example, at pH 12 no lead flotation was found.

Nevertheless, attention is also needed to the form of the collector with the pH of the solution whether flotation is active or not. Above approximately pH 10 the solution concentration of amine cations is reduced due to the formation of neutral molecules, as explained from the ionization and the p*K* = 10.68 of dodecylamine (*15*):

$$RNH_2 \overset{H^+}{\rightleftharpoons} \overset{+}{RNH_3} \overset{OH^-}{\rightleftharpoons} RNH_2 + H_2O$$

Large-scale flotation experiments at pH 10 on lead alone are shown in Figs. 6 and 7 for 1 × 10^{-4} *M* Pb, initially (of the order of 20 ppm) without any pyrogallol. The corresponding optimum conditions on a smaller scale

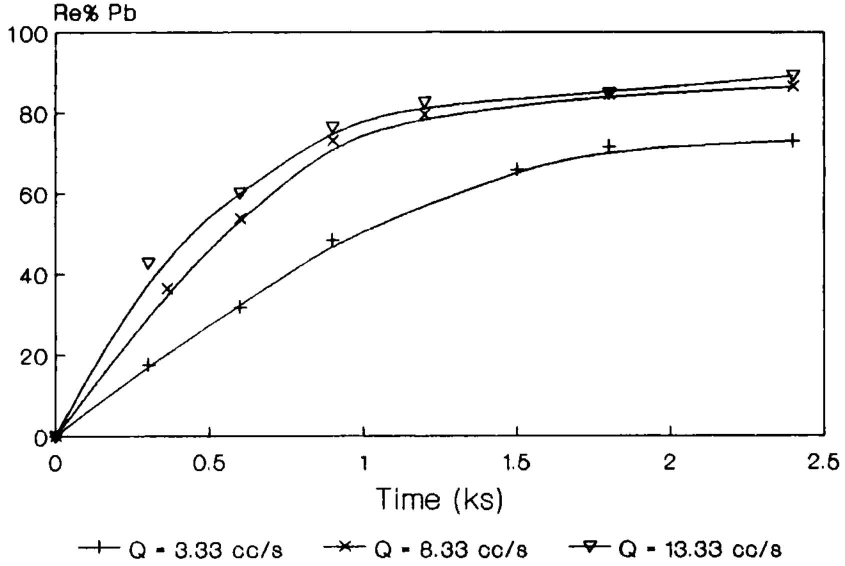

FIG. 6. Flotation of lead as hydroxide: effect of flotation time at various gas flow rates. Initial Pb 1 × 10^{-4} *M*, dodecylamine 5 × 10^{-5} *M* in 0.2% ethanolic solution, pH 10.

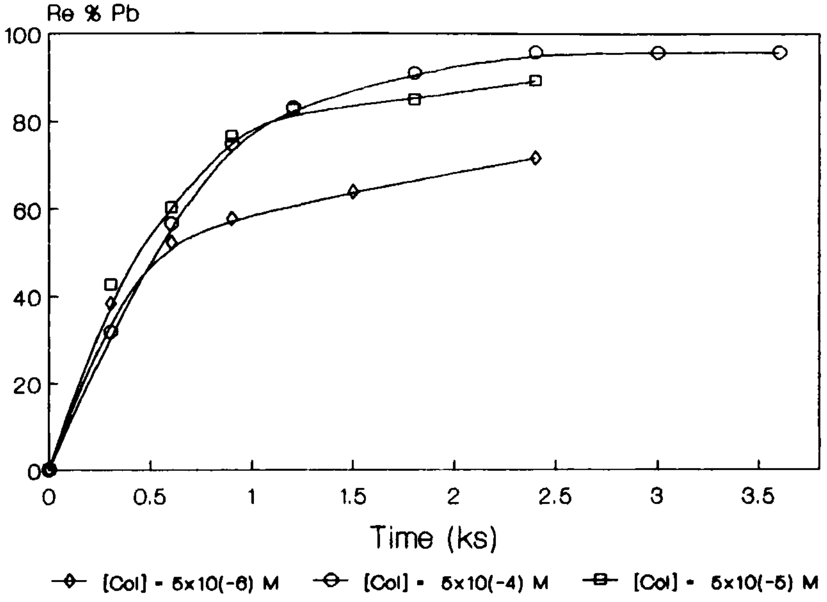

FIG. 7. Effect of collector (dodecylamine) concentration and flotation time on lead removal. Gas flow rate 13.33 cm^3/s (other operating conditions as in Fig. 6).

were 300 s flotation time, 3.3 cm^3/s gas flow rate, with 2×10^{-4} *M* dodecylamine in 0.5% ethanolic solution (*9*). In the present case, as shown by the figures, a 13.33 cm^3/s gas rate for 1.8 ks and a 5×10^{-4} *M* collector in 0.2% ethanol were selected. A 2.5×10^{-4} *M* dodecylamine concentration was also found suitable.

Due to adsorption of lead hydroxide on the bubbles, it was possible for a large local concentration to occur so the lead hydroxide becomes an insoluble precipitate. This is negatively charged at the pH studied, and the positively charged collector can be attracted electrostatically; the product is certainly hydrophobic. Hence, a kind of precipitate flotation was followed.

The next stage was Pb–Ge mixtures. The initial ideas for a possible selective separation come from a PhD thesis (*11*). It was known that germanium does not float in dodecylamine. Even in the presence of pyrogallol at pH 10 it has a flotation recovery of less than 40%. In the range here examined, germanium exists in dilute solutions mainly in the form of the $GeO(OH)_3^-$ species.

In the first attempt for separation, the initial concentration of lead in the mixture was kept constant at 1×10^{-4} *M* and the concentration of germanium increased up to $5 \times 10^{-}$ *M* at a modified pH. This round of experiments was of theoretical interest because, in practice, germanium is not expected to exist in higher concentrations in leach solutions than lead. Lead recoveries decreased dramatically with increased germanium content as shown in Figs. 8 and 9, possibly due to the increased ionic strength.

With an increased ionic strength of solution, the surfactant can more easily form micelles due to a decrease of the critical micelle concentration, with the final result being a decrease in active concentration of collector. The zeta potential of the precipitated particles is also reduced because of the increased ionic strength, and the attachment of the collector to them becomes less secure.

In Fig. 8 an increase in germanium recoveries is also observed (in more dilute solutions), which was further improved by using less collector (0.1×10^{-4} *M* dodecylamine rather than 2.5×10^{-4} *M*, in 0.2% ethanol) and more flotation time (1.8 ks) (see Fig. 9). However, the technique seemed to give a promising selective separation of germanium–lead for solution concentration ratios of 1:1 or perhaps less, leaving germanium in solution and transferring lead to the surface, from which it can be easily removed. This is the so-called reverse flotation.

When the initial concentration of lead in mixtures was increased while maintaining a constant germanium content (1×10^{-4} *M*), the amount of

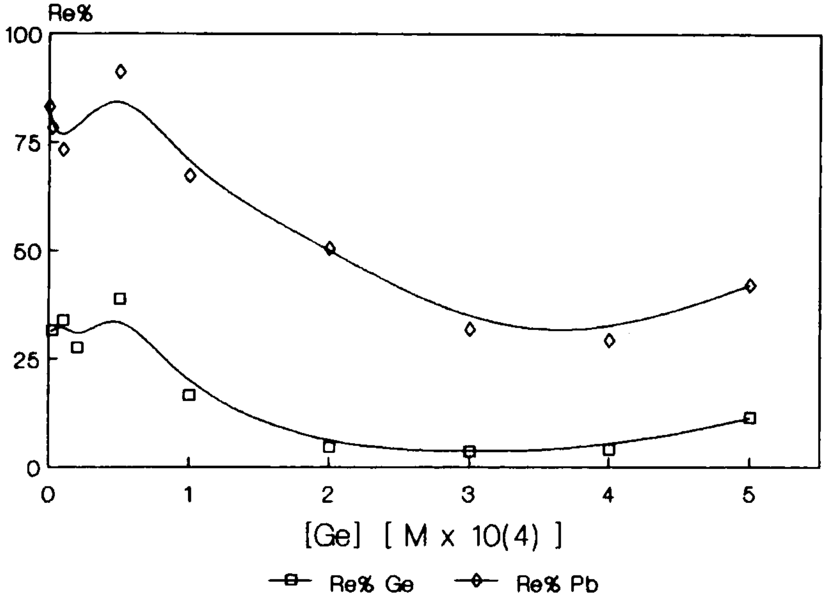

FIG. 8. Effect of initial germanium content in mixtures on flotation recoveries in the separation of Pb-Ge. Flotation time 1.2 ks, dodecylamine 2.5×10^{-4} *M* (initial Pb 1×10^{-4} *M*, 0.2% ethanol, pH 10, gas flow rate 13.33 cm^3/s).

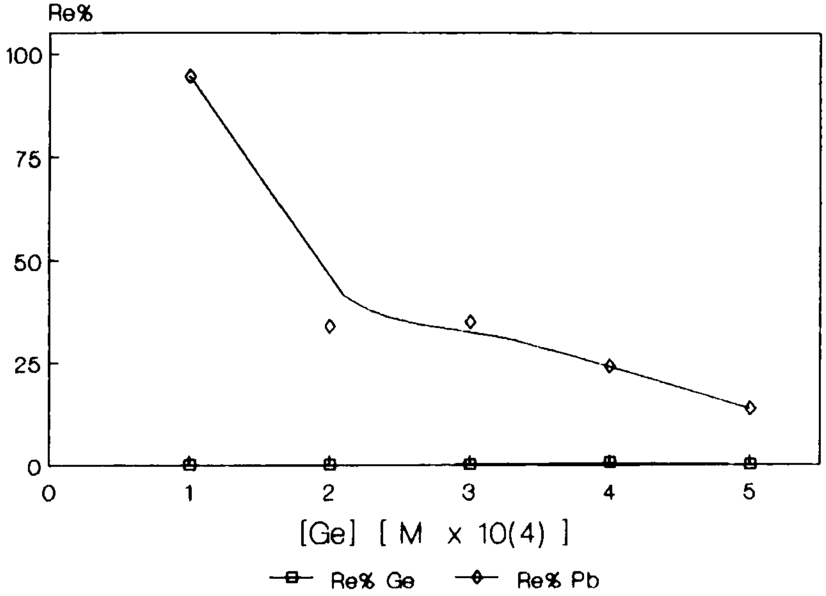

FIG. 9. Experiments on the separation of Pb-Ge. As in Fig. 8, but flotation time 1.8 ks, dodecylamine 0.1×10^{-4} *M*.

dodecylamine added (in 0.2% ethanol) should be increased at the same time in order to accomplish flotation. The variation of the ratio of collector to colligend (here, lead), usually expressed as ϕ, was adopted with the increased initial lead concentration. The results are presented in Figs. 10–12, with ϕ values equal to 2, 0.5, and 0.1, respectively. The lead concentration was varied from 1×10^{-4} *M* to 5×10^{-4}*M*, and the solution pH was kept at 10–10.3. The flotation time was 1.8 ks, and the gas flow rate 13.3 cm^3/s.

The increased germanium recovery at a concentration ratio of [Pb]:[Ge] equal to 2:1, in *M* and $\phi = 2$ (Fig. 10), was due to increased foaming, hence entrainment in the foam layer. In this way the quantity of collector used was reduced. In high [Pb]:[Ge] ratios the separation results were not as good (see Fig. 11), possibly due to the presence of excess collector. In this case, less foam was noticed and the solution was turbid.

The phenomenon of the negative effects of an excess of collector in flotation from solutions is known and has been discussed elsewhere (*16*). Finally, the experimental results and separation by $\phi = 0.1$ were further improved as shown in Fig. 12.

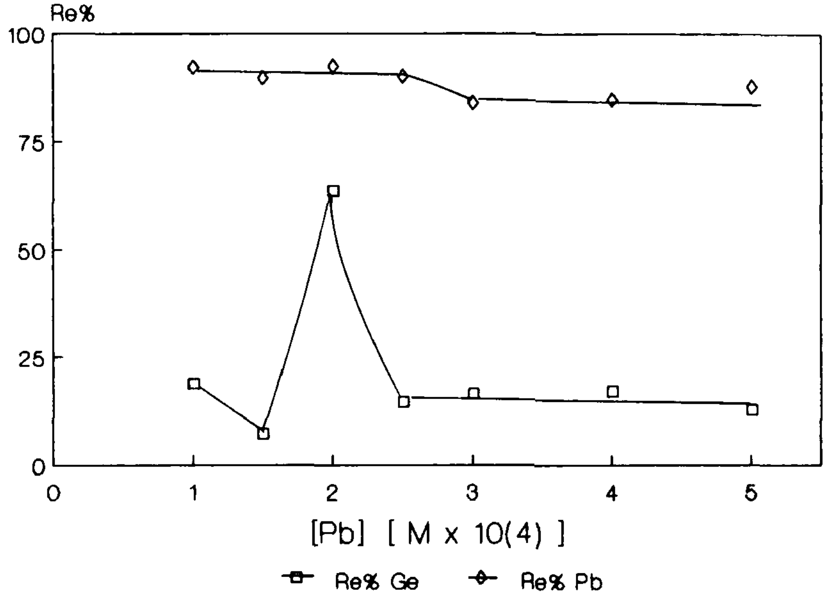

FIG. 10. Separation of Pb-Ge. Effect of initial lead content. Ge 1×10^{-4} *M*, pH 10.0–10.3, collector ratio $\phi = 2$.

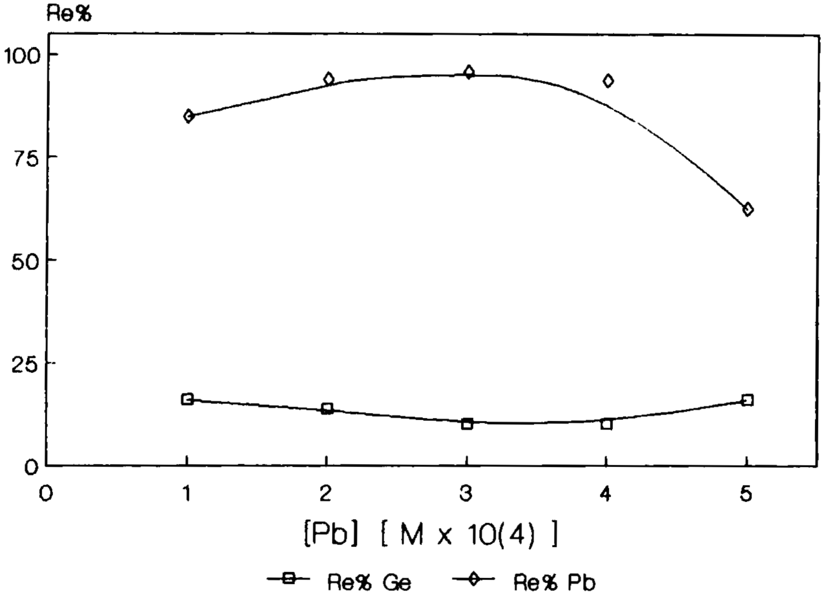

FIG. 11. Separation of Pb-Ge. As in Fig. 10, but ϕ = 0.5

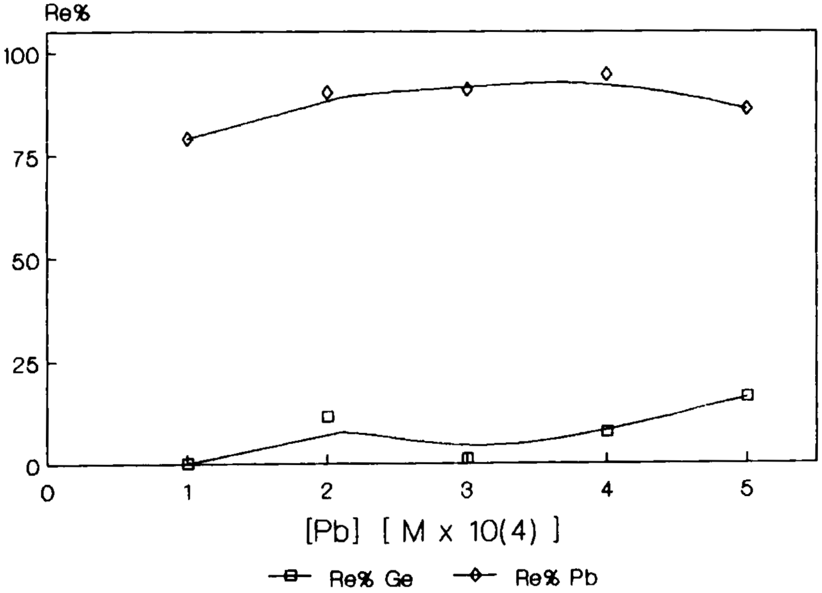

FIG. 12. Separation of Pb-Ge. As in Fig. 10, but ϕ = 0.1.

In conclusion, the selective separation of lead from germanium ions was found satisfactory by flotation at approximately pH 10 and with dodecylamine as collector.

REFERENCES

1. V. A. Glembotskii, V. I. Klassen, and I. N. Plaksin, *Flotation*, Primary Sources, New York, 1972, p. 520.
2. K. A. Matis, I. N. Papadoyannis, and A. I. Zoumboulis, *Int. J. Miner. Process., 21*, 83 (1987).
3. K. A. Matis, G. A. Stalidis, and A. I. Zoumboulis, *Sep. Sci. Technol., 23*(4/5), 347 (1988).
4. G. A. Stalidis, K. A. Matis and A. I. Zoumboulis, *Chim. Chron. (N.S.), 15*(3), 133 (1986).
5. V. A. Nazarenko and A. M. Adrianov, *Usp. Khim., 34*(8), 547 (1965).
6. A. J. Rubin, *Removal of Surface Inactive Substances by Foam Separation Processes*, PB-214510, NTIS, USA, November 1972.
7. A. J. Rubin, in *Adsorptive Bubble Separation Techniques* (R. Lemlich, ed.), Academic, New York, 1972, p. 199.
8. M. A. Slapic, E. L. Thackston, and D. J. Wilson, *J. Water Pollut. Control Fed., 54*(3), 238 (1982).
9. A. I. Zoumboulis and K. A. Matis, in *Pretreatment in Chemical Water and Wastewater Treatment* (H. H. Hahn and R. Klute, eds.), Springer Verlag, Berlin, 1988, p. 159.
10. G. A. Stalidis, N. K. Lazaridis, K. Matis, and I. N. Papadoyannis, *Sep. Sci. Technol., 24*(12/12), 1033 (1989).
11. A. I. Zoumboulis, PhD Thesis, Department of Chemistry, University of Thessaloniki, 1986.
12. V. A. Nazarenko, N. V. Lebedova, and R. V. Ravitskaya, *Zavod. Lab., 24*(1), 6 (1958) (Translation).
13. A. I. Zoumboulis and K. A. Matis, *11th National Conference on Chemistry, Athens*, 1986, p. 76.
14. G. A. Stalidis, K. A. Matis, and N. K. Lazaridis, *Sep. Sci. Technol., 24*(1), 97 (1988).
15. R. W. Smith and S. Akhtar, in *Flotation—A. M. Gaudin Memorial Volume* (M. C. Fuerstenau ed.), SME/AIME, New York, 1976, p. 87.
16. A. I. Zoumboulis and K. A. Matis, *Chemosphere, 16*(2-3), 623 (1987).

Received by editor February 23, 1989