

# Studies on Separation of Heavy Metals from Acidic Solutions by Foam Fractionation with Respect to an Application on Acidic Soil Extracts

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An experimental investigation is presented on the batch foam fractionation of the heavy metal cations  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Sb^{3+}$  and  $As^{5+}$  from diluted aqueous solutions with hexamethylenedithiocarbamate (HMDC) as complexing agent and sodiumdodecylsulfate (SDS) as surfactant. Among the considered pH-values of 2, 4 and 7 the pH 2 experiments allow a direct application of foam fractionation on acidic extracts from heavy metal contaminated soil. The experiments at pH 2 and pH 4 show better results than those at

neutral pH. Although a simple device was used, a maximum enrichment factor of 13.8 and a minimum removal factor of 0.01 have been measured. The flotation with weak organic acids like citric acid (CA) and acetic acid (AA) show about 50–70% smaller enrichment factors than those acidified with hydrochloric acid. The dissolution and mixing of the reacting components as well as the concentration of the detergent and the gaseous volume flow can be regarded as basic parameters of foam fractionation.

## 1 Introduction

Heavy metals distributed in atmosphere, water and soil represent a severe environmental load because these substances are both persistent and in many cases very toxic. Elimination of heavy metals from contaminated soils is a special problem. It is known that heavy metals adsorbed on solids are desorbed when the pH-value decreases because protons compete for adsorption sites. Based on this, processes have been developed that use acids to clean heavy metal contaminated solids like soils. The heavy metals can be removed from these acidic soil extracts by several processes reviewed by Kümmel et al. [1], but a particular problem still remaining to be solved is the removal of heavy metals from dilute solutions at concentration levels below 20 mg/L.

Foam fractionation is a promising method here. This technique uses the property of interfaces to concentrate ions or other charged particles such as colloids. In its simplest form, a surface active agent (surfactant) ion having a charge opposite to the ion to be concentrated is added to the solution and gas bubbles are introduced at the bottom of the vessel. They collect the surface active material, that carries the oppositely charged ions and forms a froth on the surface. It collapses there and produces a head product which contains the collected ions as a concentrate. In cases, where collector and frother are two different components the ions are complexed by the collector, the complex enters into the frother or detergent and is pulled out of the liquid phase. The complexing reaction between free electron pairs of the complexing agent and the metal ion forms a covalent bond.

In foam fractionation, soluble ion pairs are formed at the gas/solution bubble interfaces (Moussavi et al. [2], Grieves [3]). On the contrary, ion flotation (Kawalec-Pietrenko et al. [4], Grieves [3], Sebba [5]) and precipitate flotation (Kawalec-Pietrenko et al. [4]) result in insoluble products which form a sublimate (ion flotation) or a precipitate (precipitate flotation).

Foam fractionation has not yet been applied to the purification of sewage in industrial scale. To date, in industrial purification plants heavy metal ions are mostly removed from aqueous solutions by precipitation and flocculation combined with sedimentation or filtration of the precipitate. This procedure, however, has severe disadvantages, in particular concerning the resulting ecological loads. First of all, the consumption of great amounts of chemicals used for precipitation and neutralization causes high and undesirable concentrations of neutral salts in the solution to be purified. In order to guarantee a nearly complete precipitation, the pH-value must be adjusted carefully. In presence of foreign ions, in particular with high ionic strength or complexing agents, evident increases in solubility occur so that the separation may be unsuccessful (Kümmel et al. [1]). Furthermore, often difficulties in sedimentation of the precipitates occur so that flocculation agents are needed. Thus, large amounts of chemicals are consumed which cannot be recycled in a metal recovery plant and must be disposed. These problems can be avoided by foam fractionation. Moreover, this method needs only little equipment, is highly selective, good enrichment factors can be obtained and it can be combined with a biological sewage purification plant. Obviously, until now only a few authors applied foam fractionation on solutions at low pH-values (Hualing et al. [6], Stalidis et al. [7], Walkowiak [8]). At almost neutral pH-values of 6–8 precipitation flotation and ion flotation, respectively, seem to be predominant i.e., insoluble metal-hydroxides are formed. However, to allow any selective separation of the single metal species e.g., by electrolysis, it is necessary to get the metals concentrated but still dissolved. It has been tried to apply weak organic acids like citric acid (CA) or acetic acid (AA) on the extraction of heavy metal contaminated soil (Heining [9]) because these acids show the following advantages: They are biologically well decomposable and, partly remaining in the soil, they form no toxic metabolites. Denaturation of soil, which may occur with application of mineral acids, can be avoided. Moreover, by the use of mineral acids problems arise in the following electrolysis because the formation of toxic electrolysis products like nitrosous gases ( $HNO_3$ ) or chlorous gases (HCl) may take place.

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## 2 Experimental Setup

The aim of this investigation was to apply the method to soil extracts with pH-values of 2–3. Hexamethylenedithiocarbamate (HMDC) was used as complexing agent and sodiumdodecylsulfate (SDS) as surfactant. The metals tested were Pb and Sb because they occur at high concentrations in the extracts of the examined soil, which should be regenerated later. On account of their toxicity and importance concerning environmental pollution Cd, Cu and As were to be tested, too.

In the first experimental series the pH-values were adjusted with hydrochloric acid. The pH-values investigated were 2, 4 and 7, the complexing agent concentrations varied between 1 and 25 mg/250 mL and the ratio complexing agent: metal (molar ratio, MR) was 2 and 4. The metal tested first was Pb. Because HMDC is not very soluble in water, it was first dissolved in ethanol in a mass ratio of 1:100 (HMDC: EtOH). After addition of 250 mL of a diluted Pb solution 25 mg SDS was added and the pH-value was adjusted. Finally, the sample was shaken by hand and filled into the flotation vessel.

In the second series of experiments all four metals and one metalloid (As) were floated simultaneously. A pH-value of 2 was adjusted with acetic acid (AA) and citric acid (CA), respectively, so that the metal standard solutions were diluted with 0.05 M CA and 1 M AA, both of pH 2. By doing this, dissolution problems concerning the HMDC occurred again: Unwanted sublation was caused by using ethanol to dissolve HMDC in the manner described above. Finally, the attempt to use 0.2 g SDS/L organic acid as solvation agent was successful. In all tests the initial volume was about 230 mL and that of the head product about 10 resp. 15 mL (in the second test series).

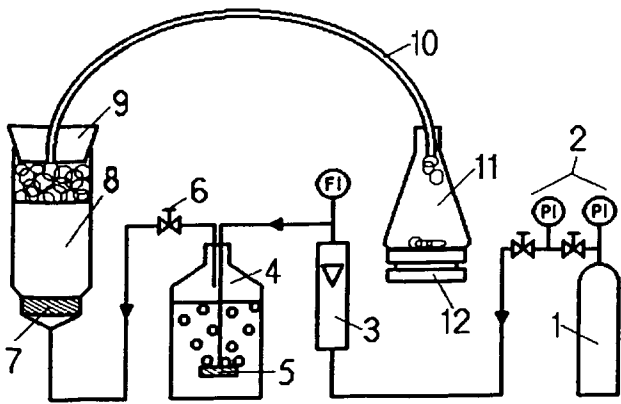


Figure 1: Experimental device: (1) pressure vessel with nitrogen, (2) manometer and valve unit, (3) flowmeter, (4) washing bottle, (5) frit, (6) plug valve, (7) bubble generating frit, (8) flotation vessel, (9) plug, (10) hose, (11) collecting vessel, (12) scales, FI and PI signify „flow indicator“ and „pressure indicator“ respectively

Fig. 1 shows a schematic of the experimental device. To avoid errors in estimation caused by evaporation the nitrogen was saturated with water vapour in a washing bottle (4). The plug valve (6) served as a stop-cock between washing bottle and flotation vessel (8). The bubbles were generated by the frit (7) which had a diameter of 50 mm, a maximum pore width of 10–16  $\mu\text{m}$  and a porosity of 4. The flotation vessel was 110 mm high and had a diameter of 60 mm. The froth was conveyed to the collecting vessel (11) by the hose

(10), which had a length of 580 mm and an inner diameter of 10 mm.

### Reagents

The reagents HMDC, the 1000 mg/L standard solutions of  $\text{CdCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{SbCl}_3$  and  $\text{As}_2\text{O}_5$  and the acetic acid (96%) were of analytical grade and obtained from Merck (Darmstadt, Germany). Analytical grade SDS was obtained from Fluka (Neu-Ulm, Germany). Citric acid of synthetic grade was obtained from Merck (Darmstadt, Germany). All aqueous solutions were prepared by using desalted water with a conductivity of 0.4  $\mu\text{S}/\text{cm}$ . The gas used was technical grade nitrogen.

### Analysis

The metal ion concentrations of most of the samples were determined by atomic absorption spectrometry (AAS). Only the content of Sb and As of the second series of tests were determined by ICP – atomic emission spectrometry (AES). These analytical methods are described in detail by Welz [10].

## 3 Results

The following Figs. 2–5 show results from the first series of experiments.

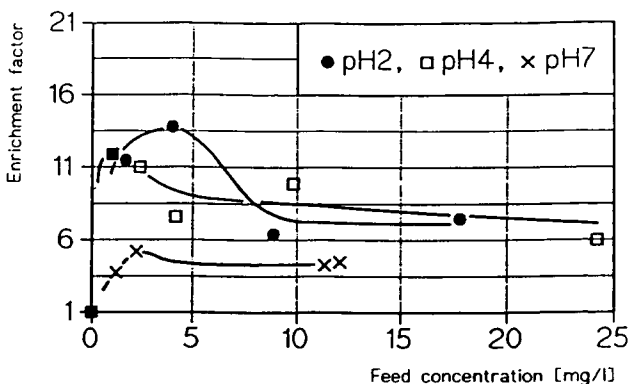


Figure 2: Enrichment factor versus feed concentration of Pb in HCl. The lines serve as guides for the eye

Fig. 2 shows the enrichment factor (= final concentration of Pb in foam divided by initial concentration in pool) as a function of the initial Pb concentration and the pH-value. The enrichment factors are maximum if the feed concentration is between 1 and 5 mg/L and reach a maximum value

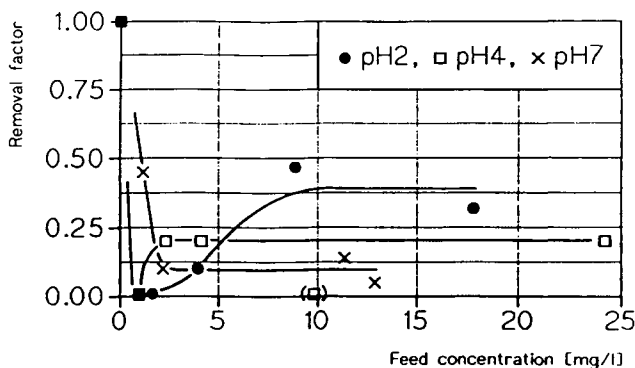


Figure 3: Removal factor versus feed concentration of Pb in HCl. The lines serve as guides for the eye

of about 13.8. The pH 2 and pH 4 tests show greater enrichment factors than the pH 7 tests.

Fig. 3 illustrates the removal factors (= final Pb concentration in pool divided by initial Pb concentration in pool) versus the feed concentration.

The removal factors of the best foam fractionation results are almost zero i.e., the corresponding bottom concentrations are near the detection limit of the flame AAS. For Pb this is about 0.01 mg/L. The Figs. 2 and 3 are corresponding, i.e. Fig. 3 shows minima of removal factors where Fig. 2 shows maxima of enrichment factors.

In Fig. 4 an attempt is made to show the enrichment factor as a function of flotation time. Linear regression results in a straight line with the equation  $y = 0.14x + 6.04$  and a correlation coefficient of 0.74.

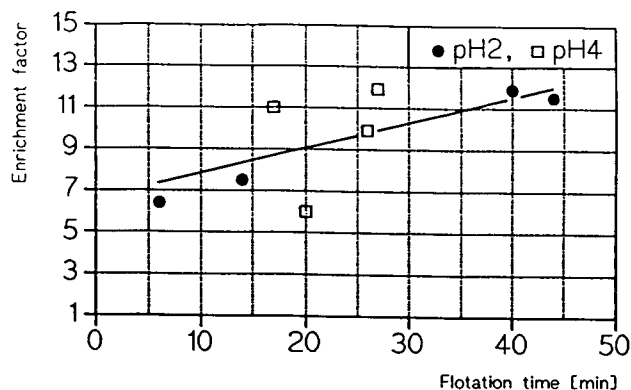


Figure 4: Enrichment factor of Pb in HCl as a function of flotation time

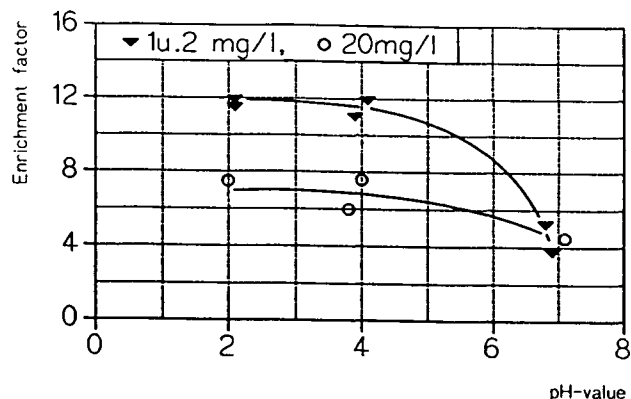


Figure 5: Enrichment factor of Pb in HCl versus pH of the feed. The lines serve as guides for the eye

In Fig. 5 it can be seen that the enrichment factors of the pH 2 and pH 4 tests are similar, whereas those of the pH 7 experiments are only a half to a third of these values.

The variation of the molar ratio (MR) of 2 and 4 did not give any relevant information. So, further experiments with bivalent ions were run with a MR of 2.

The following Figs. 6–9 reveal results from the second series of tests. The Figs. 6 and 7 show the enrichment factors of Cd, Pb and Cu as functions of the initial metal concentration, now in citric acid and acetic acid, respectively.

It is obvious that there is no significant difference between the results of both organic acids. The highest enrichment factors of 5–6 have been obtained at the lowest initial concentration of 1 mg/L, but they are about 50–70% lower than those of the first test series.

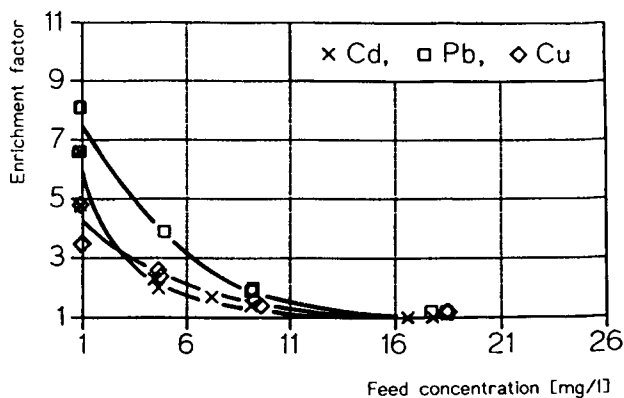


Figure 6: Enrichment factor versus feed concentration of Cd, Pb and Cu in citric acid. The lines serve as guides for the eye

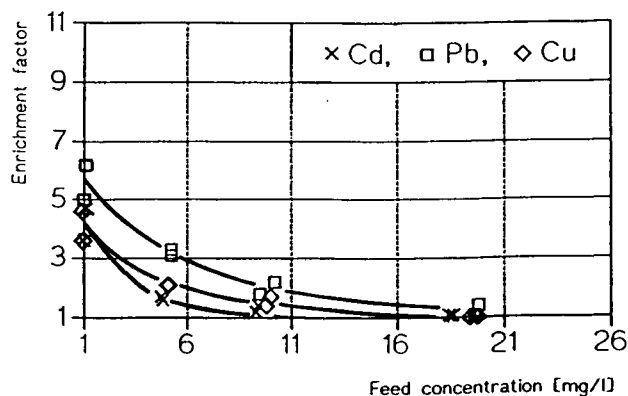


Figure 7: Enrichment factor versus feed concentration of Cd, Pb and Cu in acetic acid. The lines serve as guides for the eye

The Figs. 8 and 9 reveal that there is no enrichment of head products concerning Sb and As.

The error of measurement could be estimated by a second determination which has been made for the second experimental series. This error is the sum of foam fractionation error and analysis error. The deviations of the enrichment factors lay between 0.0 and 15.8%, on the average 8.8%, related to the mean of both measurements. The analysis error can be taken to be about 10%, so that the error of foam fractionation can be estimated by maximum of 3–4%.

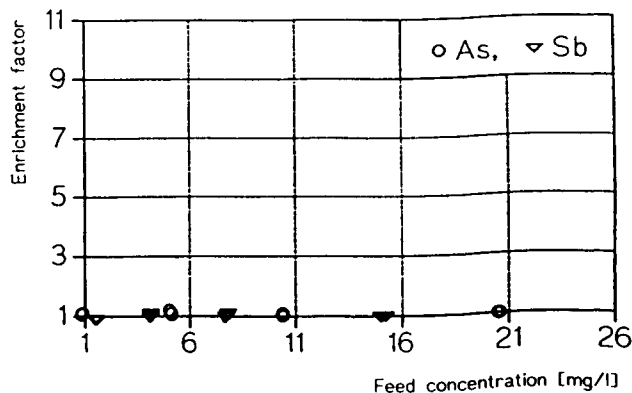


Figure 8: Enrichment factor versus feed concentration of As and Sb in citric acid

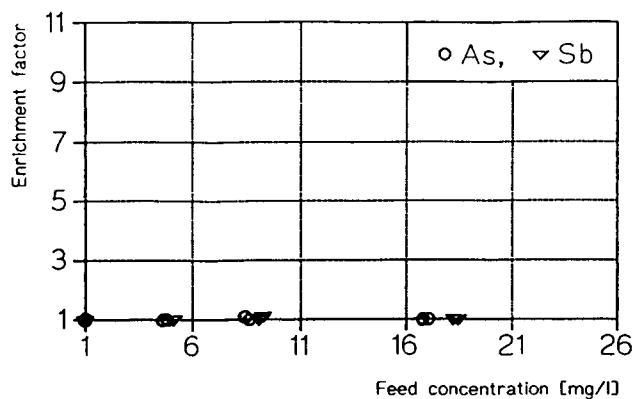


Figure 9: Enrichment factor versus feed concentration of As and Sb in acetic acid

Probably it is mostly caused by fluctuations of the gas volume flow.

A third series of tests has been carried out similar to the second one but with a detergent concentration of 0.12 mg/L instead of 0.2 mg/L. No separation was achieved in this series.

#### 4 Discussion and Conclusions

It has been shown that foam fractionation with the complexing agent HMDC and the detergent SDS can be carried out in principle. Good dissolution and mixing of the reactants, the concentration of detergent and gas volume flow seem to be essential for the separation result. The enrichment factor increases with increasing flotation time (cf. Fig. 4) which may be a result of better froth drainage from water molecules. That is possible when the froth is ascending slower. On the other hand, if the flotation takes too much time i.e., if the gas volume flow is too low, the gas bubbles would collapse before they reach the collecting vessel. This means there must be the choice of an optimum flotation time and a corresponding optimum gas flow rate.

The first test series showed maxima between 1 and 5 mg/L feed concentration of Pb which may result from an optimum ratio between the number of Pb complexes and free surface adsorption sites. If the initial Pb concentration is too low, there are less Pb complexes than free surface adsorption sites. If the initial Pb concentration is too high, not all of the complexes can find an adsorption site on the surface, so that they remain in the bulk solution. There is only one maximum visible in the diagrams of Cu, Cd and Pb in acetic acid and citric acid, respectively (Figs. 6 and 7), but it might be that there are other hidden maxima that could not be detected because of the lack of samples with initial metal ion concentrations between 1 and 5 mg/L. The tests gave best results when the initial concentration was low, which may be another hint that foam fractionation can be regarded as a surface-controlled process which could be optimized by an enlargement of surface.

The highest enrichment factors (13.8) have been measured for Pb in HCl at pH 2, whereas those of the multiple ion samples of Cd, Pb, Cu, Sb and As in CA resp. AA were only about 5–6 for Cd, Pb and Cu. The difference between mineral acids and weak organic acids can be explained by the fact that citric acid and acetic acid are able to form complexes with metal ions, too. Probably these complexes are not hydrophobic enough to be carried out of the bulk solution. The fact that the foam fractionation tests show better

results at low pH-values will be examined in further studies. As and Sb could not be enriched in the head product, possibly because of the formation of neutral or anionic complexes with water molecules (hydrolysis). In further experiments the use of cationic complexing agents will be tested to concentrate and separate these two substances. A comparison of the removal factors reveals bottom concentrations of minimum 0.01 mg/L for the first experimental series whereas the second series of tests shows minimum 0.3 mg/L. Foam fractionation results of CA- and AA-experiments are similar.

Compared with enrichment factors from reference literature quite good results could be obtained: Moussavi and Carleson [2] got relative enrichment factors (final head products concentration divided by final bottom products concentration) of maximum 140 when they floated zinc. The relative enrichment factors of our experiments are about 1900 in the first testing series.

Although the results are encouraging, further investigations on influences of foam fractionation under the described conditions are still necessary. The aim of all investigations should be a depletion of bottom products until drinking water quality is achieved and the enrichment of head products permits separate recovering of the metals.

#### Abbreviations

AA	acetic acid
AAS	atomic absorption spectrometry
AES	atomic emission spectrometry
CA	citric acid
HMDC	hexamethylenedithiocarbamate
ICP	inductive coupled plasma
MR	molar ratio
SDS	sodiumdodecylsulfate
surfactant	surface active agent

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