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FLOTATION TECHNIQUES IN WATER TECHNOLOGY FOR METALS RECOVERY: THE IMPACT OF SPECIATION

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ABSTRACT

Toxic metals exist in the effluents of many industrial operations. The impact of chemical speciation was stressed during various flotation applications for metal separation from the effluent. Examples of recent investigations include the removal of arsenic ions by iron oxides, speciation studies of chromium ions, the selective separation of molybdate anions (and verification of extant phosphate, arsenate, and silicate impurities), the recovery of tungstates, the biosorption of metals (i.e., the selective removal of copper), the use of pyrite and other solid wastes as adsorbents, and the classical case of mixed sulfide mineral flotation (pyrite oxidation, use of surface complexation modeling, etc.). Thermodynamic equilibrium diagrams and software packages were employed to interpret the removal mechanism involved.

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INTRODUCTION

Several industrial activities are responsible for the production of toxic and heavy metals in wastewaters and are known as point-sources. Chemical metallic equipment production and petroleum refining activities are mainly responsible for the toxicity found around Thessaloniki. Plating workshops also create related problems with metal-laden liquid wastes, but because they are small, the contaminants are diffused/dispersed throughout their source wastewater. The main toxic metals present in the wastewaters of these industries are Pb, Cd, Hg, As, and Mn. The chemical-producing industry is responsible for arsenic pollution, but also releases the wastewater that contains Mn, Cu, and Zn. Lead and mercury pollution is mainly created by the petroleum refineries. The metallurgical industry, which produces iron and other metals from scrap and recycling raw materials, create wastewaters containing Fe, Cu, and Zn at concentrations of 0.35, 0.15, and 0.1 mg/L, respectively.

All these industries have installed wastewater treatment units. However, in various developing countries, several small and medium metal-plating plants produce wastewaters with relatively high concentrations of heavy metals, but they do not have their own treatment units for these wastewaters. Therefore, they are mainly responsible for environmental pollution with heavy metal ions. The bioavailability and toxicity of dissolved metals are closely linked to the chemical speciation of metals in solution.

The wastewater treatments used for removal of toxic metals include the conventional physicochemical treatment of addition of inorganic coagulants and polymers, subsequent precipitation, aeration, and final neutralization. However, the final step, which should involve the treatment and safe disposal of toxic sludge, has been largely ignored.

In the treated industrial wastewaters, depending on reuse/recycling options, some of the values often exceed legal limits. Therefore, the necessity of innovative, simple, and economical treatment methods for the final polishing step or tertiary treatment are needed.

Our aim was mainly to examine the metal speciation and its great impact on the flotation process as applied by different techniques to metal ion removal from dilute aqueous solution. The paper was an outcome following a presentation of a similar topic given at the European Research Conference on “Natural Waters and Water Technology: Impact of Metal Speciation on Water Technology” held in Albufeira (Algarve), Portugal, 7–12 October 2000.

A few meetings on metal speciation have been held (1). Patterson addressed the aspect of metal separation and recovery, concluding that this area is fertile for scientific research and development; also, Patterson noted that engineers and scientists should focus efforts toward the development of new and improved recovery technologies that are based upon a scientific foundation governed by clearly identified chemical and physiochemical principles. By comparing the environmental risk and the reserve depletion rate, he gave an example of prioritization for the recovery of several metals with combined factors.

The field of flotation and its advances, specifically of dissolved-air flotation in water treatments, was covered in a 2000 conference (2). Furthermore, the state-of-the-art flotation process was the subject of many reviews (3,4). The flotation process originated from mineral processing, and therefore deserves some attention despite differences that make comparisons of it with water treatment difficult, such as the particle size and concentration, economic significance, type of separation required (selective or total), and the respective applied technique.

According to the method used for bubble generation, 2 broad categories of the flotation process exist:

1. dispersed-air flotation, which generates bubbles by introducing air directly into the flotation cell (tank), usually through the bottom of an agitator shaft. It is conducted in small cells as well as in flotation columns, and a sparger or diffuser is often used.
2. dissolved-air flotation, which is based on varying solubility of air in water as a function of pressure (Henry's law). Initially, air is dissolved in effluent water at 5–6 atm in the saturator, and when this water is introduced in the flotation vessel, the change to normal pressure releases the air bubbles.

FROTH FLOTATION

With a history of more than a century, flotation constitutes one of the most significant beneficiation methods of ores and industrial minerals. Today, almost 100 different types of ores and approximately 2 000 000 tons of them are processed every year by froth flotation, which is a dispersed-air flotation technique. Electroflotation, in which fine gas (mainly hydrogen and oxygen) bubbles are generated by electrolysis of the medium, is also a dispersed-air flotation technique.

Mineral processing and the environment are quite interrelated. For example, acid mine drainage is a principal pollution problem resulting from sulfide minerals, even after the mining activities has ceased, due to poor deposits and disposals left untreated. Relatively high concentrations of metallic ions in water were reported in the United States, both in mine tailings and from the natural leaching of ore (5). Mineral processing meanwhile has created appreciable know-how, which has then been transferred to other fields, like environmental technology; for instance, flotation application has been used as a remediation technique for polluted dredged sediment (6). Of course, in this case the speciation of the heavy metals and the particle size distribution was of outmost importance for successful flotation.

In mixed sulfides beneficiation, the heart of the whole enrichment method is flotation, usually by xanthate collectors. One major cause of inefficient mineral separation during flotation is the poisoning of mineral surfaces, which results in atypical flotation behavior. So, during the flotation of lead-zinc ores, unwanted activation of sphalerite interferes with galena flotation, contaminating the PbS concentrate and causing a lowered ZnS recovery. The problem is caused by lead ions in the flotation pulp being released during oxidation. As this phenomenon is widespread, several investigations have focused on the problem. The nature of lead speciation on the surface of sphalerite was examined with modern analytical techniques that have relevance to mineral flotation (7).

One common characteristic of sulfide minerals (which can be used to explain the unwanted production of acid mine drainage) is their instability under atmospheric conditions: They are often transformed into more stable, oxidized forms. The spontaneous oxidation of pyrites was studied through electrokinetic measurements (8). The zeta-potential of freshly ground pyrite in the presence of added ferric ions in the solution (400 and 800 ppb) had a similar behavior to that of aged pyrite, showing a reversal of surface charge. Cationic flotation processing of pyrites was investigated with a quaternary ammonium compound; cationic surfactants find extensive application as flotation collectors mainly for nonsulfide metallic and silicate ore processing. Pyrite flotation is of particular interest both in sulfide ores and in coal processing. Pyrite is not especially significant from an economic point of view, unless it is associated with gold (or uranium), but it often coexists with arsenopyrite, an unwanted admixture.

The interaction between sulfide minerals and thio-collectors takes place by a corrosion-type, mixed potential mechanism that involves simultaneous electrochemical processes (5). The significance of redox potential was demonstrated through computations of the mineral surface speciation in a flotation system of sulfide minerals; electrochemical potential constitutes one of the parameters that influence the behavior of metals in aqueous solutions. Surface complexation modeling was introduced and found to be a useful tool for describing chemical reactions (9). An uncontrolled increase of the dimensionless pe (the negative common logarithm of electronic energy) would be incompatible with the use of sulfide ions as depressants. At moderately oxidizing conditions, S^{2-} species in solution are oxidized and the mineral surface speciation is radically changed to permit xanthate readsorption.

Sulfide flotation by sulfydryl collectors is an immediate function of the dissolved oxygen of the flotation liquid. An industrial concentrate consisting mainly of pyrite and arsenopyrite was further enriched by xanthate flotation of pyrite through the use of various reducing sulfur-containing agents as arsenopyrite depressants, such as, sodium salts of sulfide, sulfite and dithionite. Gold had previously been found to be associated with arsenopyrite in this ore; therefore, the separation was of interest (10). The solution pH determines the equilibrium distribution of the species of sulfite and related compounds.

Dissolved gases present in flotation pulps have a serious influence on the process. Electrochemical potentials, measured in the pulp, may be indicators of the readiness of sulfide minerals to float because every charge transfer reaction, which is responsible for sorption of surfactant, corresponds to a specific electrochemical potential (5).

Figure 1 shows the result from thermodynamic calculations for the system iron-(ethyl)xanthate-water (Fe-EX-H_2O). It explains an observed difference in flotation behavior between the conventional (dispersed-air) and electrolytic flotation (11). Under strong oxidizing constants, ferric hydroxide is formed at acidic pH values ($pH > 3.5$), while in less strong oxidizing conditions, dihydroxy-ferric ethyl xanthate is formed. In electrolytic flotation (or electroflotation), very active hydrogen is produced. This could reduce the oxidizing effect of permanganate (a strong oxidizing reagent and a depressant in pyrite flotation) and create the necessary conditions for dihydroxyxanthate to be formed instead of ferric hydroxide. The activation of pyrite electrolytic flotation at pH values 5.0–8.0 corresponds well with the formation of dixydroxyxanthate under mild oxidizing conditions. Even though $Fe(OH)_2EX$ is slightly hydrophobic, its formation may aid the co-adsorption of xanthate and/or dixanthogen and make the pyrite surface hydrophobic.

The exclusion of cyanides, traditionally used in sulfide mineral processing (it is cheap and effective), is of particular interest as they are considered highly toxic substances. Due to increasing environmental concerns and particularly after the recent accidents in Europe, their use should be gradually restricted. Organic polymeric depressants, such as starches, dextrins, and related products may be interesting alternatives (12). The depressing effect of dextrin on flotation separation of an artificial mixture of sphalerite-pyrite was reported.

The effects of oxygen in the oxidation/adsorption of xanthate on sulfide minerals were the result of various reducing agents applied to an auriferous bulk concentrate that showed selective depression of arsenopyrite. Electrochemical measurements were also conducted in the presence of nitrogen instead of air (4); Fig. 2 gives a relevant example. With the application of nitrogen, a decrease of redox potential corresponded with the depression of the minerals. An increased selectivity over the conventional case was also noted.

SORPTIVE FLOTATION

Sorptive flotation is a combined method that involves the preliminary abstraction or scavenging of metal ions using proper adsorbents, which exist at the

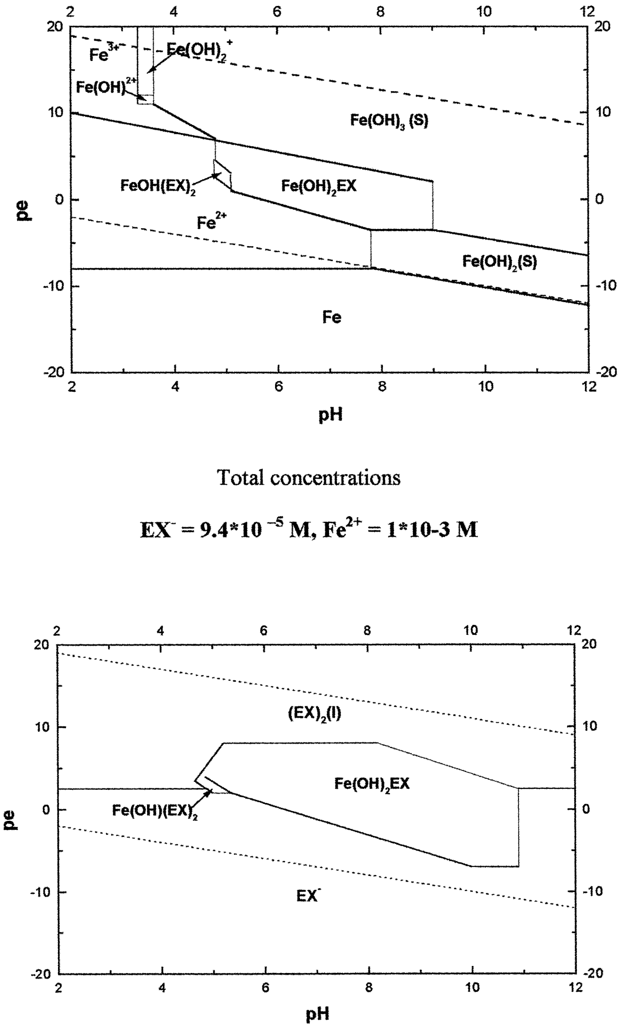


Figure 1. Electrolytic flotation of pyrite: pe-pH predominance diagram for the Fe-EX-H_2O system at a total concentration of 9.4×10^{-5} mol/L ethyl xanthate and 1.0×10^{-3} mol/L iron; (a) iron and (b) xanthate species. Reprinted with permission from (11); copyright SCI.

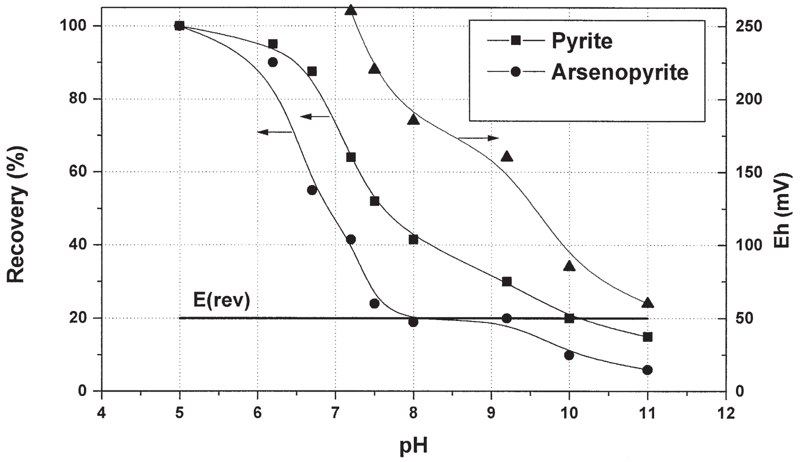


Figure 2. Flotation of an industrial bulk pyrite concentrate with nitrogen bubbling instead of air (in conditioning and flotation stages): recoveries and Eh (electrochemical potential) versus the pH of solution. The straight line represents the reversible potential of the xanthate-dixanthogen for the specific concentration. Reprinted with permission from (4); copyright Marcel Dekker.

fine or ultrafine particle size range, followed by a subsequent flotation stage for the separation of metal-loaded particles from the treated (cleaned) solution (13). The adsorbents for the initial sorption process could be either conventional (powdered activated carbon, zeolites) or industrial solid by-products, i.e. originated in the mineral industry or of a biological nature (biosorbents), such as those produced during fermentations. So, pyrite was tried in the laboratory as an adsorbent in a number of applications, including one for arsenic oxyanion removal (14). Arsenic removal by lime precipitation as calcium arsenate has long been practiced. Arsenic has been found in well water due to geological reasons; the most notable contamination of drinking water was the crisis experienced in Bangladesh where thousands of people showed symptoms of chronic arsenic poisoning (15).

As presented in Fig. 3, the action of pyrite (iron sulfide mineral) was not similar to the two species of arsenic studied. As(III) could be removed in the weak alkaline range, in contrast to the As(V) anions, which were preferentially removed in acidic medium. The results were evaluated by electrokinetic studies and stability data. In a pH range higher than their respective i.e.p. values, the interactions between arsenate and the hydroxylated pyrite surface seemed to be of a specific nature because the pK_2 of arsenate acid has an approximate pH value of 7. Similar specific interactions are possible in the case of arsenite adsorption in a pH range higher than its pK (pH = 9). Arsenite adsorption in a pH range lower than 9 may be facilitated by the superficial formation of arsenic sulfides. The knowl-

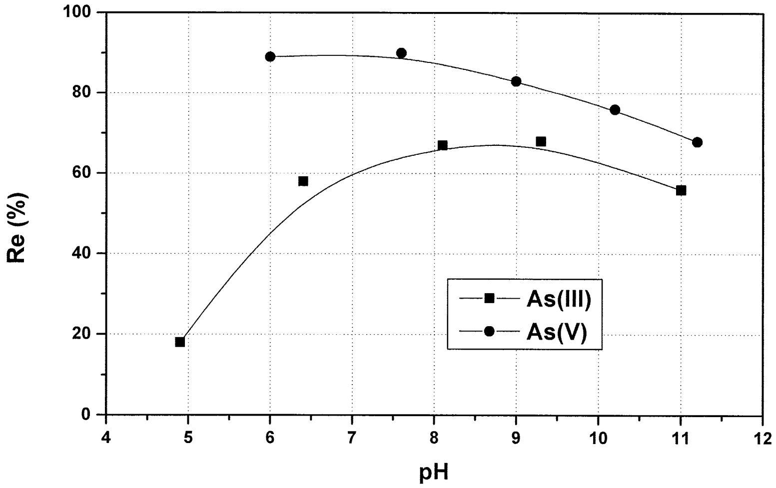
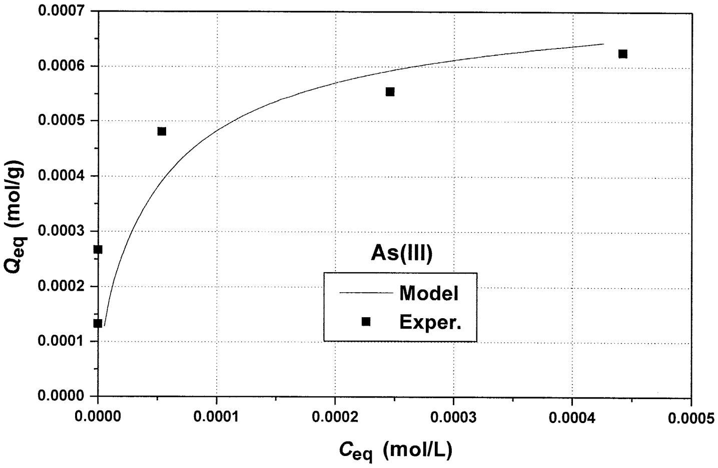


Figure 3. Removal of trivalent and pentavalent arsenic from aqueous solutions by pyrite fines: influence of pH (variation by lime addition) on arsenic species removal in the presence of 5 g/L pyrite. Reprinted with permission from (14); copyright Marcel Dekker.

edge of the oxidation state of pollutant ions is often a prerequisite for the application of efficient treatment methods. In practice, trivalent arsenic (which is the most toxic species) is first oxidized to As(V) and then treated; for this reason, ozone and oxygen was used in groundwater samples (16). With sorptive flotation, this first stage of oxidation was proven to be unnecessary.

The modeling of sorption processes has been recently applied to predictions of sorption rates under various environmental conditions, such as the pH, temperature, concentration of sorbent and metal ions, and ionic strength. Many approaches were developed, such as the constant capacitance, stern, diffuse double layer, and triple layer models. The fundamental concepts upon which all these models are based remain, more or less, the same (17). Often, diffusion effects (external, or liquid film, and intraparticle transport resistance) should be also taken into consideration.

Figure 4 shows the results of diffuse double-layer modeling for the soprtion removal of arsenic anions onto goethite; a comparison is presented with the experimental values for 2 main valencies of arsenic, and a good agreement is observed (18). One of the limitations of the computer program PHREEQC is the uncertainty in the appropriate surface-complexation reaction constants. As an example, the program described the case of hydrous ferric oxide and zinc ions at different concentrations. Strong and weak surface sites were assumed (19). Protons and zinc compete for the 2 types of binding sites. Zinc is more strongly sorbed



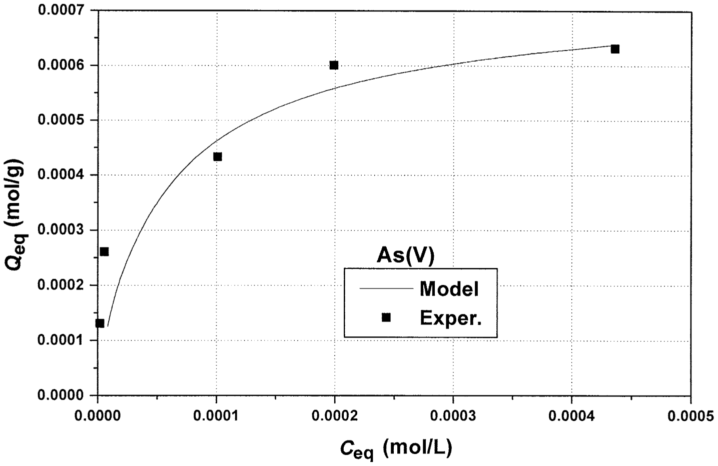


Figure 4. Sorption of trivalent and pentavalent arsenic oxyanions from solution onto goethite mineral: experimental vs. theoretical (diffuse double-layer modeling) values, using the PHREEQC program for surface complexation. Reprinted with permission from (18); copyright Kluwer Academic Publishers.

at high pH values than at low pH values. The results of simulation were consistent with the literature (17).

Nowadays, the problem of industrial solid waste and by-product handling and disposal is increasing continuously, as more strict environmental regulations must be taken into account. Such by-products exist often in finely divided form (the energy costs for size reduction are generally high) and were investigated as cheap adsorbents or substrates (20). Appropriate methods for the subsequent solid-liquid separation were examined, among them flotation. Figure 5 presents the case of dolomite-lead ions; dolomite is a common alkaline-bearing semi-soluble salt mineral. In the same figure, the fraction distribution of lead species as a function of the solution pH is also included. Lead removal in presence of dolomite is pronounced at considerably lower pH values than those required for the precipitation of lead in the bulk solution as hydroxide. We also observed the deleterious effect that the very alkaline values had on adsorption.

Pyrite fines were also tried in the laboratory for the possible removal of hexavalent chromium (a highly toxic metal) oxyanions, which are commonly treated by reduction first of Cr(VI) to its trivalent form at acidic pH (approximate value of 2) and the subsequent hydroxide precipitation of Cr(III) by increasing the pH to alkaline values (around 9–10) through the use of added lime (21). Figure 6 is a selected example and shows electrokinetic measurements of the system with and without preliminary treatment with Cr(VI). In the presence of chromium, an excessive positive surface charge of pyrite was observed, indicating a reduction process because hexavalent chromium exists in aqueous solution only as anionic species. For comparison, the electrokinetic behavior of chromium hydroxide precipitate (5×10^{-2} mol/L dispersion) is also presented in the figure as is the computer-assisted calculated speciation of the trivalent chromium; the latter shows the distribution of hydroxocomplexes, which are responsible for the altered electrokinetic behavior of Cr(VI)-treated pyrite. The charge reversal to negative values becomes possible at pH value of approximately 8.8, above which the formation of only neutral or anionic Cr(III)-species is reported.

However, these chemical speciation models based on thermodynamic principles are sensitive to the quality of their thermodynamic databases: Errors inherent in the databases supplied with the widely available computerized programs are discussed in (22). In another paper (23), the results of Cr(VI) removal by polyacrylamide-grafted sawdust (a solid waste) were published. The effect of pH on the adsorption was interpreted with the help of a Pourbaix diagram considering the structure of the sorbent and chromium speciation.

In Fig. 7 the chemical speciation is presented for an aqueous solution containing simultaneously hexavalent chromate and ethylenediaminetetraacetic acid (EDTA) species (0.1 mmol initial concentration of each). The Mineql+ computer program (Environmental Research Software) was used for the construction of thermodynamic equilibrium diagrams for the examined systems. This is a power-

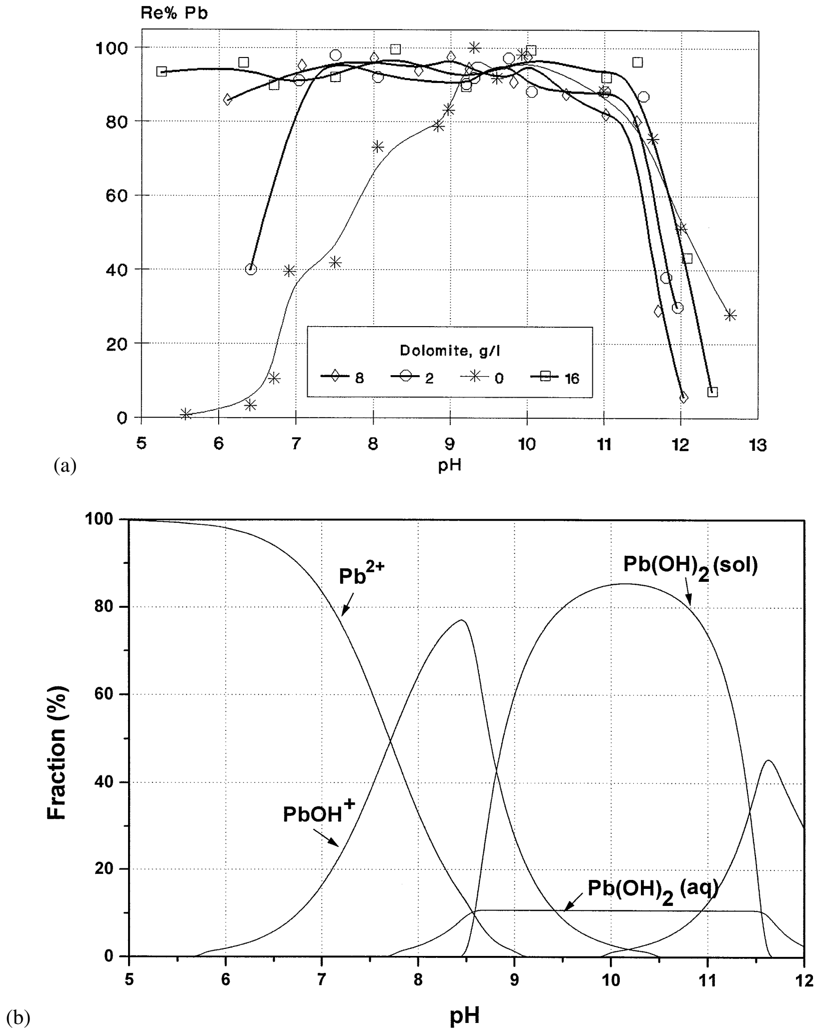


Figure 5. Removal of toxic metal ions through the use of industrial solid by-products as sorbents: application of dolomite for lead; (a) Pb removal as a function of pH at varying mineral additions and (b) aqueous distribution of lead species. Reprinted with permission from ref. (20); copyright IAWQ.

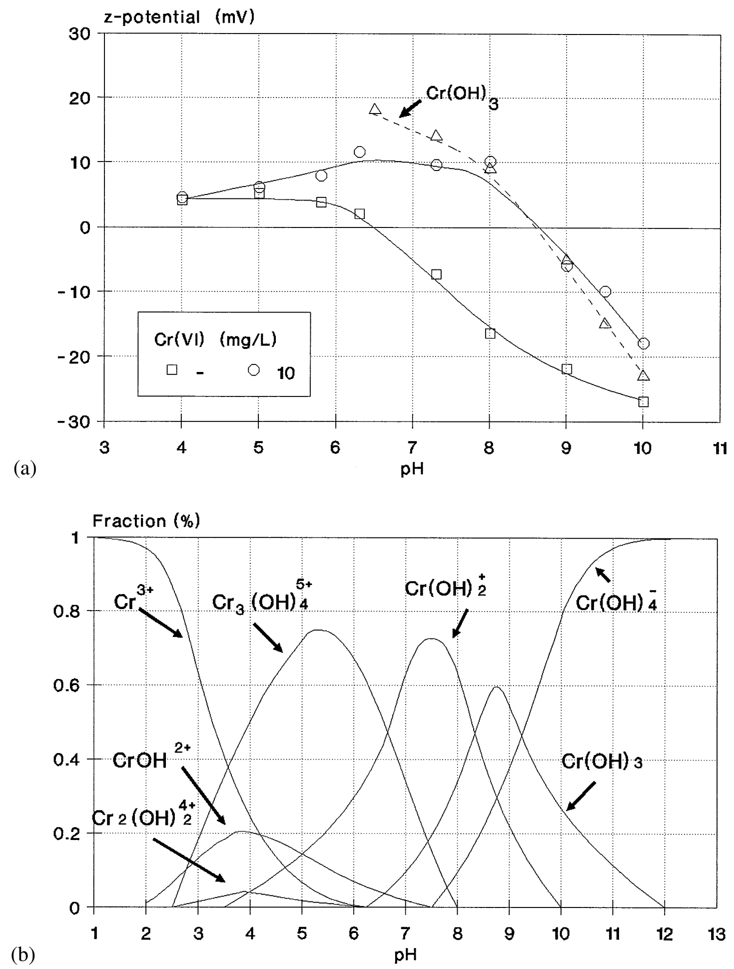


Figure 6. Removal of hexavalent chromium anions from solutions by pyrite fines: (a) zeta-potential measurements of the system and also of trivalent chromium hydroxide; (b) a speciation diagram of Cr(III) for total chromium activity of 10 mg/L. Reprinted with permission from (21); copyright Elsevier.

ful and convenient chemical equilibrium modeling system that can be used to perform calculations on aqueous systems with moderate ionic strengths at ambient temperatures. A comparative study of inorganic sorbent materials for the removal of metal ions by granulated geothite was published; the sorption results were found to fit the classical Langmuir isotherm (24).

Although Cr(VI) and EDTA species are both anionic such that an interaction between them may not be feasible, because of their distribution CrO_4^{2-} and $EDTAH_2^{2-}$ may each strongly compete for the same sorption sites. This competition results in lower efficiency of chromate adsorption in the Cr(VI)/EDTA mixed

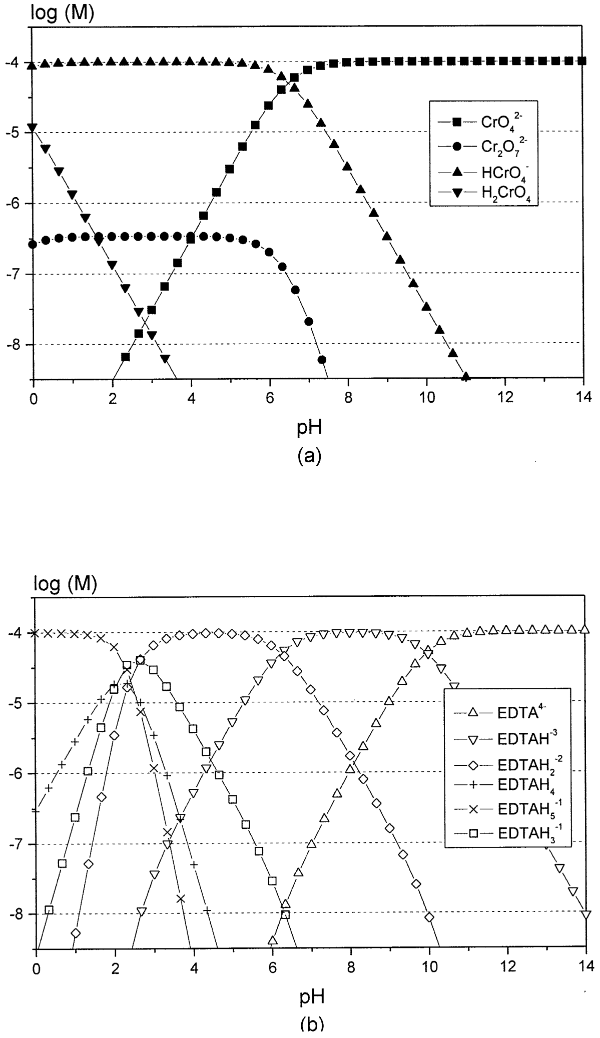


Figure 7. Speciation in an aqueous solution containing Cr(VI) and EDTA as a function of pH for [Cr(VI)] = [EDTA] = 0.1 mmol/L as determined through use of the Mineql+ program: (a) chromium species, (b) EDTA species.

solution than in the Cr(VI) solution. EDTA is a common representative of aminopolycarboxylic chelating agents, the most widely used complexing agents for chemical process industries. The inhibition of conventional metal precipitation, due to the presence of chelating/complexing compounds, such as acetate, citrate and tartrate ions, and ammonia, as well as nitriloacetic and EDTA, that may be

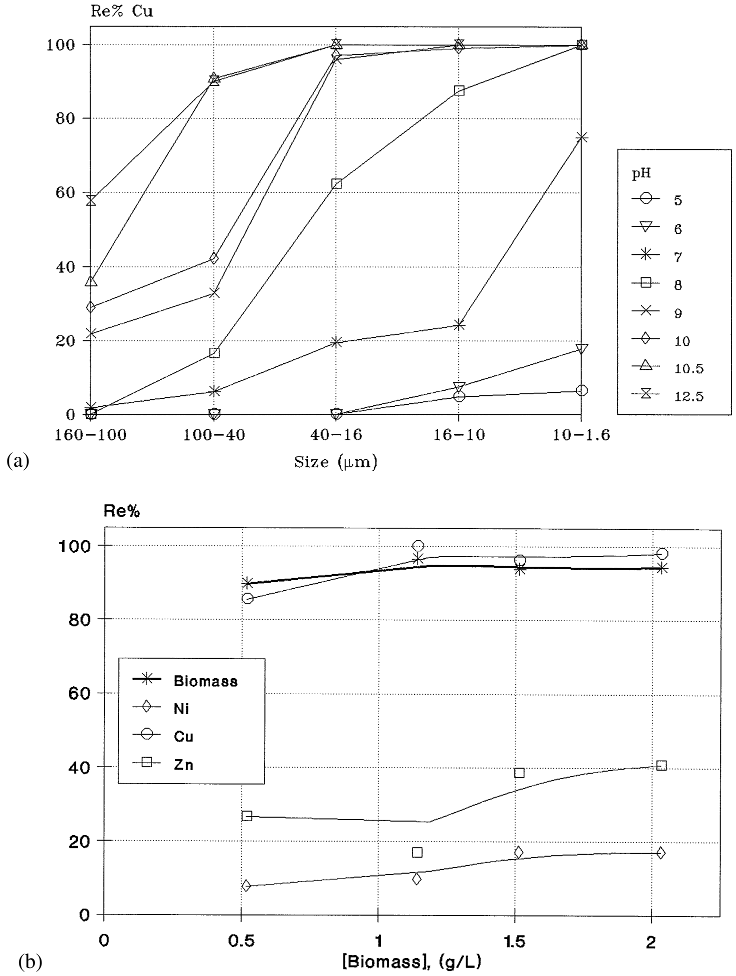


Figure 8. Metals (copper, zinc, and nickel) removal from wastes: (a) experimental work on size distribution of copper hydroxide precipitates at various pH values; adapted from (27). (b) Both biosorption of metals and flotation recovery of loaded by *Streptomyces rimosus* biomass, at pH 7, are also shown in (b).

present in most real wastewater streams was reported (25). The bed depth–service time model was applied to the experimental results to model the column operation.

Biosorbents, i.e. industrial wastes from large-scale fermentation processes, such as *Streptomycetes* from pharmaceutical production, are also efficient materials for metal ion removal (26). Figure 8 presents some results for zinc, copper, and nickel removal from an aqueous mixture in the presence of calcium and sodium ions. On biomass surfaces several chemical groups may be present, such as acetamido groups of chitin, amino and phosphate groups of nucleic acids, amino, amido, imino, sulfydryl groups of proteins, which could attract and subsequently sequester metals from the surrounding aqueous environment. Attention should be paid to the possible influence of pH on these chemical groups.

In the figure, the results show a selectivity of biosorption for copper. This selective separation was obtained in only one stage of operation. A good explanation for this limited selectivity can be found in the literature (27). In this earlier work, with copper alone and using appropriate Gooch filtration, researchers examined the size distribution during copper precipitation as a function of pH. The existence of ultrafine particulates, of less than 50 μm, was observed at pH values up to approximately 9, where according to thermodynamic principles, copper precipitates as an hydroxide.

A surface-induced hydrolysis reaction mechanism was proposed for the adsorption of divalent cations on mineral surfaces like pyrite (28). The respective electrokinetic investigation of pyrite as a function of pH in the presence of increasing amounts of copper ions favored the hydrolysis reaction mechanism. Due to mineral surface coverage by the hydrolyzed copper cationic species, a reversal of zeta-potential was observed around the neutral and slightly alkaline pH range. This interfacial precipitation of the metal hydroxide occurred at a lower pH than that required for the hydrolysis of the respective cation in the bulk solution.

As promising alternatives to the conventional pump-and-treat practice for contaminated soils and groundwater, in situ chemical treatment was demonstrated (29). Treatment walls based on sorption have been tested to intercept and treat migrating inorganic and organic contaminants. Nevertheless, these methods have limited use due to regulatory barriers.

ADSORBING COLLOID AND ION FLOTATION

Ion flotation is perhaps the simplest flotation technique that involves the removal of surface inactive ions from aqueous solution by the addition of surfactants (30). Figure 9 presents an example on the separation of germanium cation, which is not the typical case of ion flotation. In this application, an activator such as pyrogallol should be initially introduced before attempting to remove germanium by a surfactant (collector) such as dodecylamine. At low concentrations,

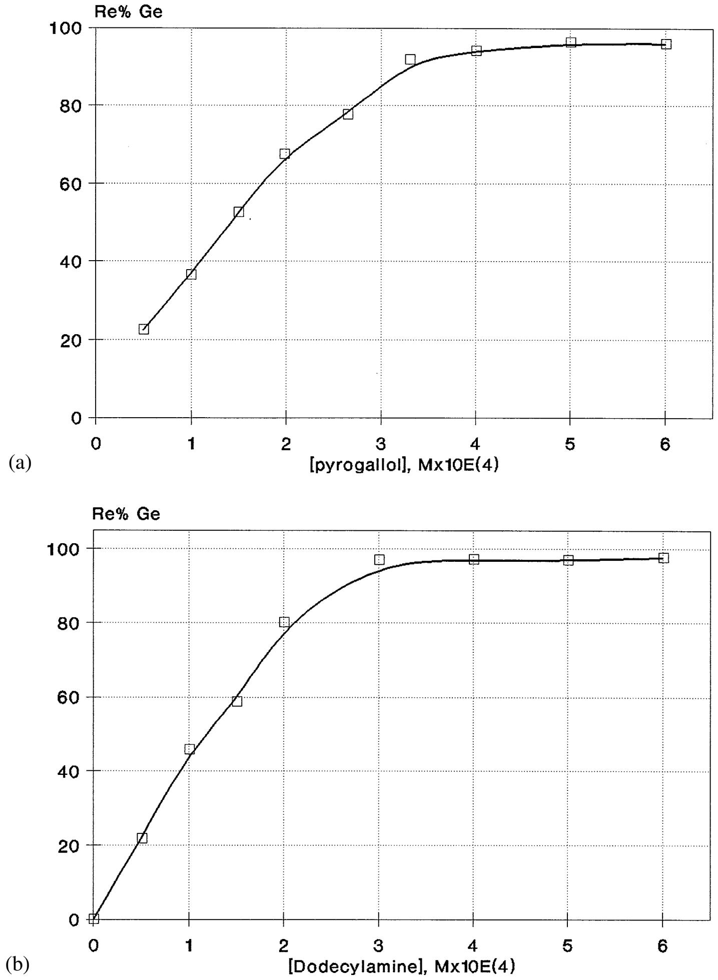


Figure 9. Ion flotation of germanium from dilute solutions: (a) effect of pyrogallol (activator) concentration on germanium ion recovery; laurylamine (collector) concentration kept at 2.2×10^{-4} mol/L. (b) Varying the concentration of laurylamine with 3.3×10^{-4} mol/L pyrogallol added; effect on recovery and certification of flotation mechanism of germanium. Reprinted with permission from (30); copyright Elsevier.

Ge(IV) is present in solution of pH 2–7 in the form of a very slightly dissociated metagermanic acid (H_2GeO_3), so it cannot be floated. Pyrogallol can form a strong complex acid with composition $(H_2Ge)L_3$, and in this form it can be floated by a cationic surfactant with 10% excess of chemical reagents. The foam that was collected contained a precipitate (sublate) with proven composition $S_2(GeL_3)$, where

S is the cation of amine-type surfactant and L represents the ligand. The stoichiometric mechanism of this separation process was clarified as it is illustrated in the figure.

Walkowiak determined that ion-water and cation-surface active anion interactions govern ion flotation selectivity when a sublate was not formed in the bulk solution (31). If precipitation takes place in the bulk solution, the surface charge of sublate was the key factor influencing the floatability of an ion. Basic properties such as solubility, ionic potential, and viscosity were discussed.

In a review on the possible application of metal ion flotation in hydrometallurgy, precipitate flotation was also examined; zinc, among others, was found to coexist with germanium (4). Zinc can be removed by flotation as the respective hydroxide when the solution pH is 9.0–9.5 (see Fig. 10a). The recovery curves were compared with theoretical data of zinc solubility and showed good correlation.

Flotation has been also used, mainly as a preconcentration technique, in chemical analysis (32). Zouboulis, Matis, and Stalidis (31) found that it may be suitable for speciation studies and presented the case of Cr(III/Cr(VI) for selective separation (Fig. 10b). The need for simple, precise, relatively cheap, and selective speciation methods for environmental pollution research and control or for wastewater engineering is noted. Electrodialysis, ion chromatography, and anodic stripping voltammetry were other speciation methods commonly used.

Adsorbing colloid flotation involves the removal of a solute by adsorption on or co-precipitation with (depending on the conditions) a carrier floc, such as ferric hydroxide, which is then floated. The advantage of the technique is the in situ preparation of the “sorbent” has a high surface area. Such separation of arsenic ions, in which approximately 30 mg/L ferric ions were found necessary for the removal of 10 mg/L As(V), was reported (33). For comparison, approximately 0.5 g/L of synthetic goethite (α-iron-hydroxy-oxide) was used under the same conditions as those for arsenic ion separation. The synthesis of this sorbent material required 19 hours of ageing after its preparation and thorough washing (34). Also, adsorbing colloid flotation is a good separation technique for colloids and is often used in effluent treatment.

Matis et al. (34) also found that the flotation separation of arsenate was accomplished without the use of a surfactant; the key to the process was an effective flocculation prepared in advance (33). Flocculation of contaminant microparticles was recently examined in depth in the flotation process and was found to be affected by smaller bubbles such as those generated by electrolysis of water (35).

Spectrometric analyses have been recently used to study the sorption of molybdate oxyanions on chitosan (a constituent of biosorbent cell walls) and cross-linked beads; the sites of interaction with the metal species were discussed (36). The metals, including molybdenum, are nonrenewable resources being consumed at an exponential rate as a result of population and capital growth. In another publication (37), adsorbing colloid flotation was investigated for the removal of molybdates as

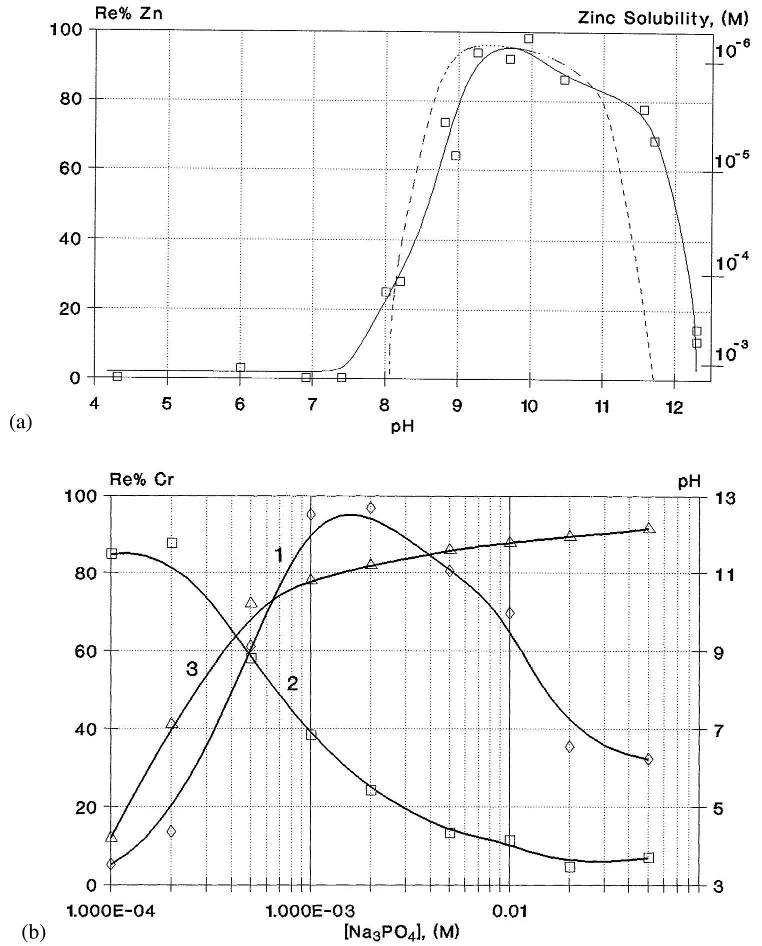


Figure 10. (a) Precipitate flotation removal of zinc. Effect of solution pH at the following concentrations: zinc 1×10^{-4} mol/L and dodecylamine 2×10^{-4} mol/L. The dotted line is a theoretical curve and shows the precipitation of zinc as $Zn(OH)_2$, i.e. the free ion concentration remains in the aqueous solution after precipitation. Reprinted with permission from (4); copyright Marcel Dekker. (b) Speciation laboratory studies by ion flotation and the separation of Cr(VI)/Cr(III) with sodium dodecylsulfate as surfactant; the effect of ionic strength of solution by adding trisodium phosphate: (1) removal of Cr(III), (2) removal of Cr(VI), (3) solution pH. Reprinted with permission from (31); copyright Kluwer Academic Publishers.

well as ion flotation with dodecylamine. Adsorbing colloid flotation was shown to be successful for the selective separation of arsenate from molybdate anions for wastewaters of hydrometallurgical origin at pH 9 when the same collector (dodecylamine) and the typical ferric hydroxide as co-precipitant were used. The flotation mechanism by dodecylamine was compared with that of sodium dodecyl-sylfate (pH 3.5–4.5), an anionic surfactant; except at high concentrations (10–40 g/L), conventional removal methods are usually based on precipitation. Nevertheless, these methods are not suitable for relatively low concentrations of molybdate oxyanions (lower than 1 g/L) due to simultaneous losses of the valuable metal. All the species of molybdenum and its hydrometallurgical impurities, as well as their heteropoly-molybdic complexes (at pH higher than 2 and for the usual range of concentrations) exist mainly as anions, making their separation a difficult task.

For solutions containing low concentrations of molybdate anions, Mo was proposed to be concentrated and recovered by ion flotation at pH 2–4 by dodecylamine; however, if other impurities, such as silicates are present, they would be co-floated with molybdates. In high silicate concentrations in aqueous solutions, most of the silicates could be precipitated out by partial acidification at pH 8–9 before flotation would be applied (37). The chemical speciation of this system is quite complicated.

Figure 11 presents an example in aqueous mixtures. Over 95% of the impurities (usually 15 mg/L each) could be selectively removed from solutions that

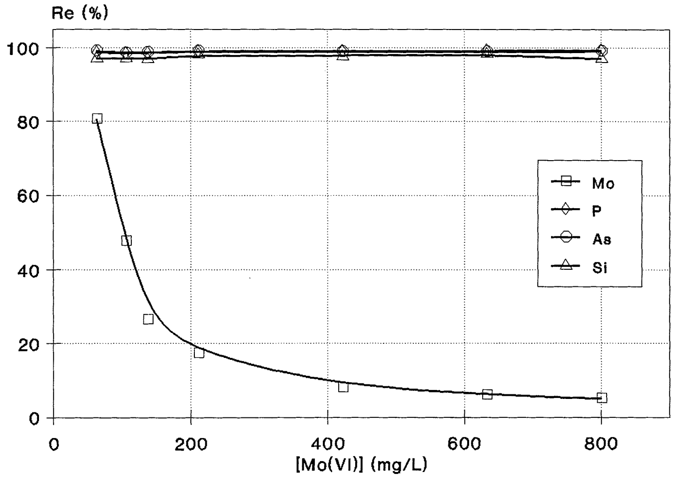


Figure 11. Adsorbing colloid flotation of molybdate oxyanions from mixtures by dodecylamine at pH 9: effect of initial molybdate concentrations on the selective separation of impurities (phosphates, arsenates, and silicates). Reprinted with permission from (37); copyright Elsevier.

contain molybdates (at concentrations exceeding 200 mg/L); the simultaneous co-removal of molybdates was approximately 20%. The possible reason for the behavior observed between the impurities (floatable) and molybdates (unfloatable) is the different solubilities between the ferric compounds of molybdates, which are soluble at alkaline pH, and arsenates, phosphates, and silicates; these are insoluble precipitates at the experimental pH values and hence, they can be sepa-

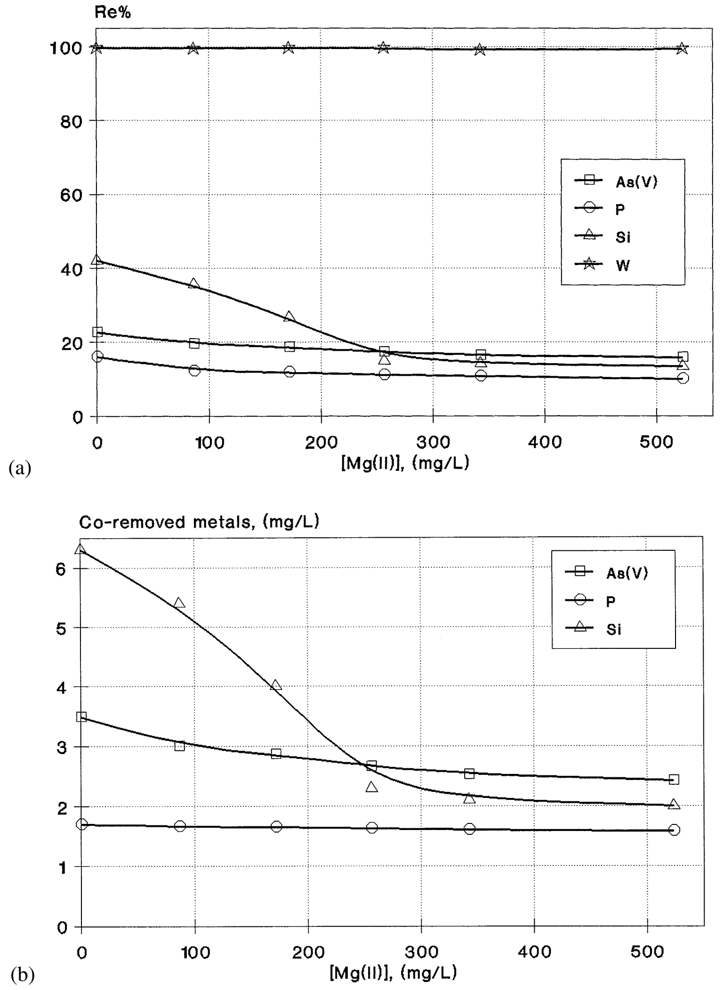


Figure 12. Ion flotation, with magnesium ions as depressant, for the recovery of tungstate anions from quaternary aqueous mixtures at pH range 2–5: effect of Mg^{2+} concentration on the separation of W from arsenates, phosphates, and silicates. Reprinted with permission from (38); copyright SCI.

rated by flotation. The observation implies that precipitation and co-precipitation rather than surface adsorption was the dominant mechanism for the removal of these impurities by the scavenger flocs of Fe(III). Therefore, Si, P, and As anions should be selectively separated prior to recovery of molybdates.

The separation of tungstate anions from mixtures with impurities (arsenates, phosphates, and silicates) (38). Figure 12 gives an example of the study. Ion flotation was successful through the use of dodecylamine as surfactant and magnesium ions as depressant agents. Tungstates when they exist in mixtures present a complex aqueous chemistry, quite similar to that of molybdates, by forming a number of isopoly- and heteropoly-acids and their respective dissociated anions. Magnesium chloride constitutes a common precipitant used for the purification of concentrated W-containing solutions (wastewater or leaching hydrometallurgical solutions) from the co-existing impurities. It forms insoluble precipitates with arsenate, phosphate, and silicate ions in neutral or weakly alkaline solutions, but this does not happen with tungstates.

CONCLUDING SUMMARY

The removal of soluble ionic species, such as metal cations or (oxy)anions, from dilute solutions, as in the case of most wastewater, is the subject of many investigations. For this, as a polishing step, flotation is a promising separation process with moderate costs. The term is used in its broad sense, as various and quite different flotation techniques are available, such as ion flotation, adsorbing colloid flotation, and sorptive flotation. Flotation has been successfully applied to mineral processing, water and wastewater treatment, and even chemical analysis. In general, the recovery of metal ions by flotation is both rapid and almost complete when the main parameters (such as the solution pH, type and concentration of added reagents, redox potential, and ionic strength) are optimized.

The impact of chemical speciation is shown in this paper, in which we reviewed the treatment of a wide range of heavy-metal bearing waste streams. Toxic metals exist in the effluents of many industries, such as the electroplating industry, battery and accumulator manufacture, printed circuit manufacture, metal salt manufacture, the photographic industry, the ferrous and non-ferrous metal industry, the power industry, chemical waste treatment, mine water discharges, landfill leachates, contaminated land reclamation, and even in certain groundwaters. The variety of industries that requires need for wastewater treatment highlights the importance of the present review.

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