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

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To cite this Article Zouboulis, A. I. , Matis, K. A. , Lanara, B. G. and Loos-Neskovic, C.(1997) 'Removal of Cadmium from Dilute Solutions by Hydroxyapatite. II. Flotation Studies', Separation Science and Technology, 32: 10, 1755 — 1767
To link to this Article: DOI: 10.1080/01496399708000733
URL: http://dx.doi.org/10.1080/01496399708000733

SEPARATION SCIENCE AND TECHNOLOGY, 32(10), pp. 1755–1767, 1997

Removal of Cadmium from Dilute Solutions by Hydroxyapatite. II. Flotation Studies

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ABSTRACT

Dissolved-air flotation has been investigated in the present paper as a suitable solid/liquid separation technique, applied downstream for hydroxyapatite ultrafine particles which were used in a preliminary stage for the removal by sorption of toxic cadmium cations. The main parameters affecting this process were evaluated, including the necessary quantity of sorbent material in the dispersion, the proper pH values of Cd solutions, the type and concentration of supplementary inorganic flocculant agents (ferric chloride and aluminum sulfate), and the presence of additional surfactant added. The results obtained were considered to be promising. Under optimum conditions, over 95% of Cd-loaded hydroxyapatite particles were separated in a very short retention time.

INTRODUCTION

The existing literature on flotation of apatites has mainly come from the mineral processing field; flotation is a widely used method for beneficiating endogenic and sedimentary phosphate ores (1–4). In general, this separation process is applied mainly to remove siliceous or carbonate gangue from phosphate ores. Salts of fatty acids, such as sodium oleate,

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are overwhelmingly the main surfactants (collector agents) applied (5). In Ref. 5 mention was also given to the adsorption of organic modifiers.

The mechanism of oleate adsorption on salt-type minerals, in general, has been extensively examined based on adsorption, zeta-potential, and infrared studies, as well as on theoretical thermodynamic calculations (5). The role of surface area and porosity of apatites (of different types and origins) has also been commented upon (1). It appears that the internal surface, constituted of pores, has a lesser influence than the external surface on the adsorption and dissolution characteristics.

Many sorbent materials are often manufactured (mostly for economic reasons) as fine or even ultrafine particulates. In this case their application has to be carried out in mixed-flow type equipment and not in columns due to the high pressure loss. Consequently, an effective solid/liquid (S/L) separation process is required for the subsequent separation of sorbent-loaded particles from the treated solution. The separation of fines (and ultrafines) by applying flotation techniques has been reviewed (6). A series of fine sorbents has been applied for the removal and recovery of toxic or precious metals by the application of a combined process constituted of both a sorption and a flotation process. This may be termed *sorptive flotation*; for example, powdered activated carbon was used for the recovery of gold–thlourea complexes (7) and pyrite fines for the enhanced removal of copper hydroxo-precipitates (8), as well as of arsenic oxyanions (9).

Sorption of Cadmium by Hydroxyapatite

In the first part of this work (10) the removal of cadmium, a priority pollutant, from dilute aqueous solutions was examined by sorption onto synthetic hydroxyapatite fine particles. In the same study the calculation of typical adsorption isotherms (of the Langmuir type) was also presented. For the present paper the dissolved-air bubbles generation method was selected, being the rather dominant flotation technique in water and wastewater treatment (11). The only published work similar to the present one was the removal of cadmium ions by bentonite particles, employing adsorbing particle flotation (as it was termed) (12). The removal of cadmium from dilute solutions by (dissolved-air) flotation, but without the use of a sorbent, has also been published (13), therefore permitting a comparison of the two methods. The mechanism of precipitate flotation as the respective hydroxide was followed in that case, and the best separation was obtained in the pH range between 10 to 11.

In our previous paper (10), electrokinetic measurements for the same system were also conducted, and these indicated a point of zero charge for hydroxyapatite particles at pH values less than 5. Nevertheless, the zeta potential of sorbent particles in the presence of cadmium was observed to change toward less negative values due to the attachment of metal cations onto their surface, a fact consequently expected to favor the applied flotation process.

It is noted that at acidic pH values (less than approximately 5), sorption was not effective because almost complete dissolution of the synthetic sorbent was taking place, as previously presented (10). The respective minerals are often called semisoluble (5) or sparingly soluble (3). Solubility properties of particles (mineral, etc.) are of importance from the point of view of flotation because of their role in determining the chemical composition of the aqueous phase and the charge characteristics of the interface. The case of apatites has been specifically discussed, and a series of hydrolysis and complex formation reactions has been given (14). Elsewhere, it has been commented on whether the interactions and conversions predicted by thermodynamics practically occur during the relatively short time (in the range of few minutes) available for flotation (3). An answer was provided later by experiments performed with synthetic materials; it was found that the thermodynamic detailed predictions were indeed not confirmed (15, 16).

EXPERIMENTAL

Apparatus

Dissolved-air flotation was the selected flotation technique for the generation of air bubbles. Dissolved-air flotation generates fine bubbles in a size range from 10 to 120 μm, with a mean size of approximately 40 μm (11). Therefore, this technique offers a hydrodynamically quiescent region, suitable for the flotation of fine particulate matter such as the HAP particles. A laboratory test unit (purchased from Aztec, UK) was used for the flotation batch experiments in 1 L feed solutions, as described elsewhere (17); in the same paper this flotation technique was applied to cadmium ion removal by using nonliving biosorbents. The recycle ratio was kept constant at 30% for all the experiments following saturation at 4–5 atm, from which the amount of air actually used for flotation can be calculated.

Materials

The presence of hydroxyapatite (denoted hereafter as HAP) particles, with diameters even below 1 μm, was found by scanning electron microscope (10). The size distribution analysis of the sorbent also revealed that 50% of the particles were under 3.5 μm; hence, the need for a specific

S/L separation downstream was justified because simple settling is not sufficient under these conditions. The experimental part (as far as cadmium removal is concerned) and the analytical procedures were previously described (10).

As flotation surfactants, typical cationic and anionic ones were tested, i.e., cetyltrimethyl-ammonium bromide (denoted as CTMA-Br) and sodium oleate (SO), respectively, usually at concentrations of 1×10^{-4} M. Preliminary experiments were also performed testing other anionic surfactants, such as sodium dodecyl sulfate, but as the results obtained were not improved, in the following experiments only SO was used. For comparison reasons, 0.5% v/v ethanol was also used during experiments performed without any surfactant present (collectorless runs). Two typical inorganic flocculating agents, ferric chloride ($FeCl_3 \cdot 6H_2O$) and aluminum sulfate [alum, $Al_2(SO_4)_3 \cdot 18H_2O$], as well as an organic anionic polyelectrolyte flocculant (marked A305 and kindly supplied by Kemira Kemi Finland), were also examined in order to further enhance the required S/L separation. Ethanol was used as a convenient frother at a concentration of 0.5% v/v.

Procedures

After an initial contact time of 600 seconds between the sorbent and the metal solution, which was found during preliminary experiments to be sufficient for almost quantitative sorption/removal of metal, a further 300 seconds conditioning time was applied, followed by an additional 300 seconds in certain cases when flocculant and surfactant were added. HAP addition in the feed (metal-laden solution in deionized water) was usually 1.0 g/L, unless otherwise stated. The natural pH value of the dispersion was around 6.7 and the initial concentration of cadmium in the solution was 10 mg/L. The pH value of the dispersion, when required, was adjusted by the addition of sodium hydroxide or nitric acid solutions and controlled throughout the sorption/conditioning time. The dispersion was subsequently treated by dissolved-air flotation; the flotation time was in the range of 2 minutes.

The floated HAP was removed by suction from the surface of the flotation cell, filtered through a glass crucible (Gooch, No. 4), dried, and weighed. Simultaneously, a proper sample from the treated dispersion was taken, filtered, and analyzed for the residual cadmium concentration by employing standard atomic absorption spectrophotometry procedures. Both percentage removal (denoted as Re%) of cadmium (by sorption onto HAP) and percentage recovery (also denoted as Re%) of HAP by flotation are shown in the figures. Zeta-potential values were calculated by measuring the respective electrophoretic mobilities using the Mark II apparatus (Rank Brothers, UK).

RESULTS AND DISCUSSION

HAP Flotation by Surfactants

Preliminary collectorless flotation experiments, performed at natural pH values (6.7), showed that although cadmium removal was over 95%, the flotation recovery of HAP particles was lower than 40%. These experiments were also not found to be substantially influenced by the presence of cadmium ions, by changing the initial HAP concentrations, and by changing the initial pH values in the range between 5 to 11. Therefore, the presence of a surfactant seemed to be necessary in order to achieve efficient separation recoveries of HAP particles.

Figure 1 presents selected dissolved-air flotation results, examining the influence of added surfactant SO concentration, which was found to perform better than CTMA-Br, increasing the flotation of metal-loaded HAP particles up to 80%, while the second one only slightly improved the flotation experiments (up to 50%). Cadmium removals were found to be over 80% for both cases. It was also shown that cadmium removal was decreased to 30% when the sorption of the toxic metal and the conditioning of oleate did not occur in separate conditioning steps.

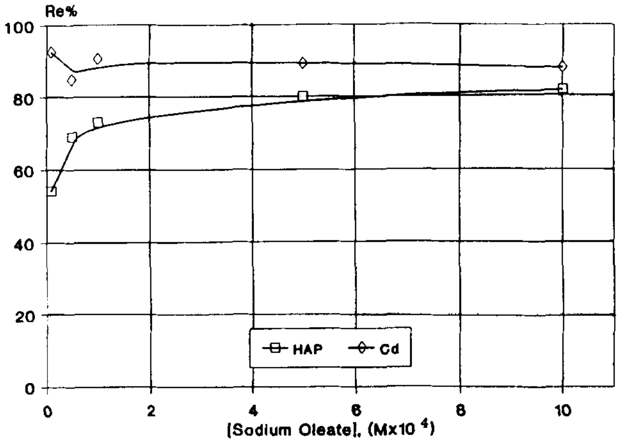

FIG. 1 Influence of surfactant SO concentration on dissolved-air flotation of Cd-loaded HAP particles (pH value: 7.2).

Chemisorption of oleate onto calcium sites of mineral apatite is the more widely accepted surfactant adsorption mechanism (1). It was elsewhere reported that a two-dimensional condensation of oleate on a heterogeneous surface gave rise to a bi-layered structure of oleate on apatite, prior to precipitation of calcium oleate (5).

Addition of Inorganic Flocculants

When the particles to be removed have very small diameters, thus not permitting a separation method to take place effectively, their size can be substantially increased by causing them to form larger aggregates. Flocculation is an important preliminary stage in many S/L unit operations and is widely used in water and wastewater treatment (18). In the past, inorganic flocculants have been used in order to separate toxic metals by the application of adsorbing colloid flotation; for instance, the removal of molybdate and arsenate from aqueous solutions was recently reported (19). At an earlier time the use of flotation was proposed to measure indirectly the degree of aggregation of minerals, the latter obtained by shear flocculation (20). This method was based on the observation that flocs float sooner than dispersed particles.

Conventional S/L separation processes, such as filtration, sedimentation, and flotation, usually become more effective as the size of suspended particles is increased from the initial ultrafine or fine range up to a certain maximum diameter. Applying this approach, two common inorganic flocculants were tested, followed by collectorless flotation; the respective results are presented in Fig. 2. The recoveries of HAP particles by flotation were found to be higher when alum was used compared with the case of ferric chloride addition, while the respective removals of cadmium were over 90% in most of the experiments.

The subsequent addition of surfactant SO, following the addition of flocculant, was also tried (Fig. 3). In the case of alum, the presence of SO was found to improve further both HAP flotation recovery and Cd removal, while for the case of ferric chloride, a lower increase was noticed. By comparison with the results previously presented (in Fig. 1), a certain increase in HAP flotation results can be observed after flocculation, caused by alum addition.

An explanation of these results can be seen from the zeta-potential measurements presented in Fig. 4. Without the prior addition of inorganic flocculants, the surface charge of HAP particles remains negative in the examined pH range when the anionic surfactant SO was used, while a maximum 70% of HAP separation by flotation was observed. Through the use of adsorption studies this behavior has been attributed to the

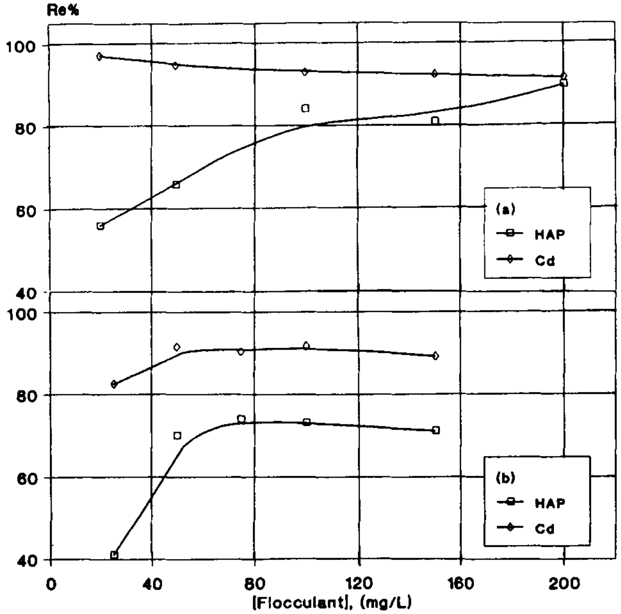

FIG. 2 Influence of flocculant concentration without any surfactant present: (a) alum, (b) ferric chloride (pH value: natural).

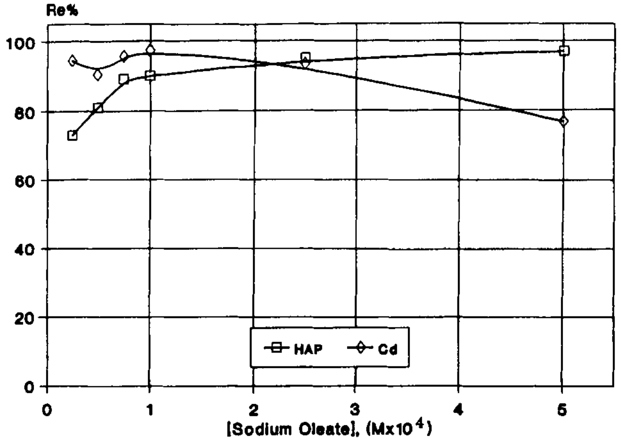

FIG. 3 Influence of surfactant SO concentration, added supplementary to alum; [Al(III)]: 100 mg/L at a pH value of 7.2.

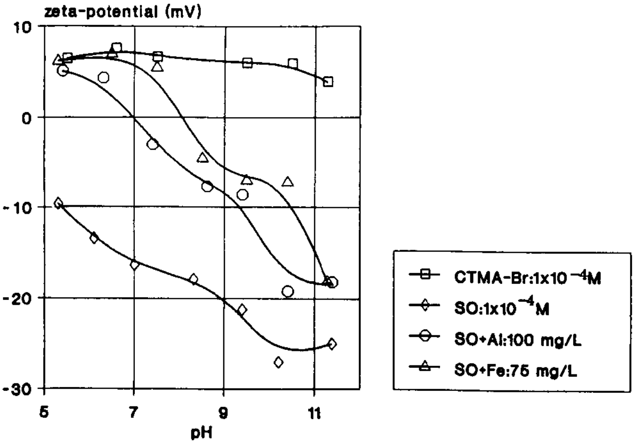

FIG. 4 Zeta-potential measurements against the solution pH values.

formation of a monolayer coverage of HAP particles by SO, followed by the precipitation step of calcium oleate (21).

Later the surface charge is reversed, becoming positive (in the examined pH range) when the cationic surfactant CTMA-Br was added. The addition of alum was found to neutralize the negative surface charge of HAP particles at the pH value of around 7. This pH range (6.7–7.2) was also found to be optimum for the flotation experiments when the aforementioned (in Fig. 2) optimum conditions were applied, i.e., [Al(III)] = 100 mg/L and [sodium oleate] = 1×10^{-4} M. The addition of ferric chloride was also found to neutralize the surface charge of HAP particles at a higher pH value (around 8).

Addition of Organic Flocculants

An anionic polyelectrolyte was also examined, in addition to the inorganic ones, and the results are presented in Fig. 5. Flotation was again found to be efficient only after the simultaneous addition of a suitable surfactant. This organic flocculant increased the flotation of HAP particles, although it did not have a substantial influence on cadmium removals which were always over 98%. Lower removal/recovery results were obtained when a cationic polyelectrolyte was examined (data not presented). Application of the anionic polyelectrolyte, even at the low concentration of 0.1 mg/L, was generally capable of flocculating the fine HAP particles.

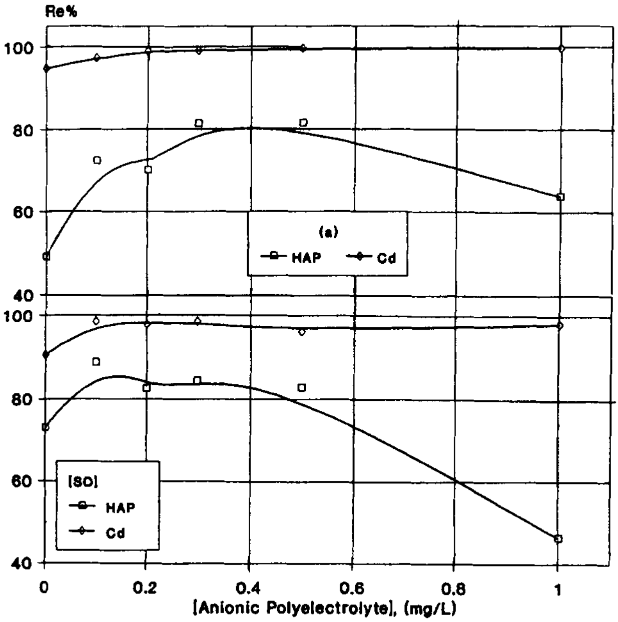

FIG. 5 Influence of polyelectrolyte concentration (surfactant at a concentration of 1×10^{-4} M was also added, pH value: 7.2): (a) in the presence of CTMA-Br, (b) of SO.

When the added concentration was increased above a certain value (0.5 mg/L), detrimental effects on flotation recovery were noticed.

When the polyelectrolyte concentration was kept constant and the respective additions of surfactant were increased, both removals were slightly increased (Fig. 6a). The influence of pH value after the addition of 0.1 mg/L anionic polyelectrolyte is presented in Fig. 6(b); relatively minor differences were observed.

The addition of organic flocculants resulted in lower floatabilities of HAP particles in comparison with the addition of inorganic ones. Therefore, in the following experiments the important parameters of pH value of the dispersion and of HAP addition were examined only in the presence of inorganic flocculants.

Influence of Dispersion pH Values and of HAP Concentration

The influence of pH value on the combined process (sorption and flotation) was also investigated using alum and two different initial HAP con-

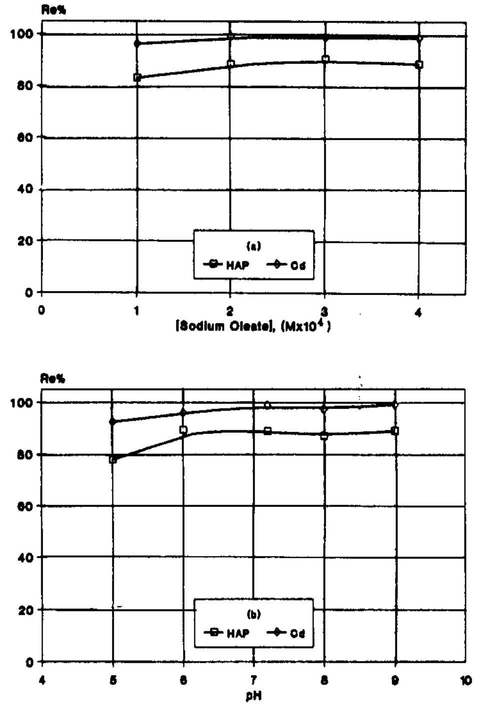

FIG. 6 (a) Effect of SO concentration following 0.5 mg/L anionic polyelectrolyte addition, and (b) influence of pH value after 0.1 mg/L polyelectrolyte addition and 1 × 10^{-4} M SO.

centrations. Sodium oleate was used as the surfactant (Fig. 7). The presence of CTMA-Br in this case again proved to be ineffective because the recovery of HAP particles by flotation was lower than 20% (data not shown). At the higher HAP concentration examined (1 g/L), a decrease in flotation of HAP particles was observed in the alkaline pH range (Fig. 7a); this may be due to the existence of soluble $Al(OH)_4^-$ as a result of alum hydrolysis (18). In the pH range from 6 to 7, flotation was successful and recoveries over 95% were obtained for both HAP particles and Cd ions and for both HAP concentrations applied.

The influence of the concentration of HAP particles in the feed suspension was also studied in the presence of alum (Fig. 8). In the range investigated (up to 2 g/L HAP), flotation was effective and recoveries of the order of 90% were found for HAP particles, while cadmium removals were over 95%. A slight decrease in HAP recoveries was noticed when

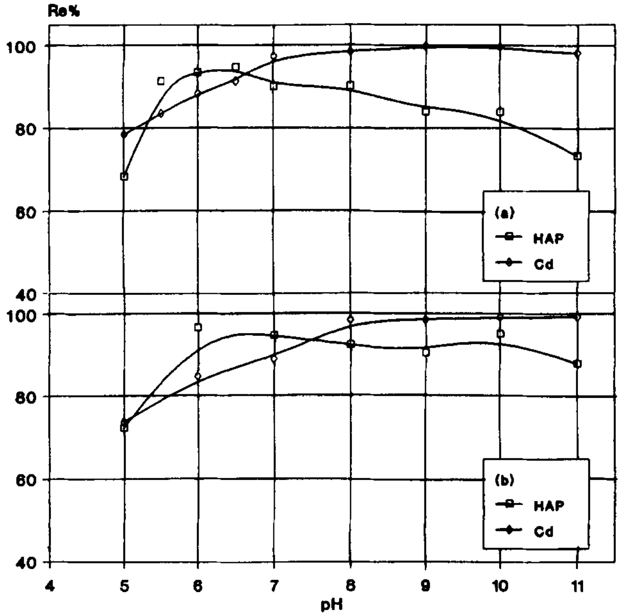

FIG. 7 Effect of pH values on dispersion in the presence of 100 mg/L Al(III) and of 1×10^{-4} M SO: (a) 1 g/L HAP, (b) 0.5 g/L HAP.

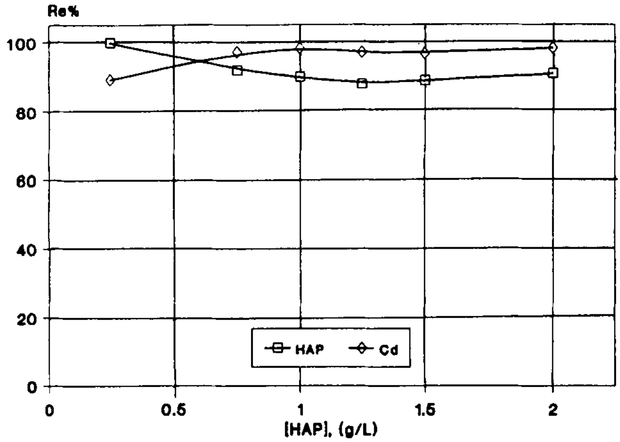

FIG. 8 Effect of initial HAP concentration using 100 mg/L Al(III) in the presence of 1×10^{-4} M SO at a pH value of 7.2.

the HAP concentration in the dispersion was increased, which can be explained as due to relatively insufficient alum addition. Although the addition of ferric chloride did not influenced the removal of cadmium, it produced somewhat lower HAP recoveries.

In conclusion, the solid/liquid separation of dispersed HAP ultrafine particles was found to be effective in the application of dissolved-air flotation; the sorbent was previously applied for the removal of cadmium ions by sorption from dilute aqueous solutions. From the results presented, as well as from others presented in a recent review (22), the main advantages of this method (sorptive flotation), when applied to aqueous solutions containing relatively small concentrations of toxic metals, appear to be the following: high efficiency and possible selectivity for metal removal (therefore, low residual metal concentrations), low space requirements (important where the space available is tight), rapid operation, flexibility of operation to many metals, use at different concentrations, production of small sludge volumes, high enrichment with the contaminant, and moderate cost.

ACKNOWLEDGMENT

This work has been partially supported by a European Union HCM program (Contract CHRX-CT03-0272).

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Received by editor May 17, 1996
Revision received November 1996