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SOLVENT EXTRACTION AND EMULSION SEPARATION IN MAGNETIC FIELDS

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ABSTRACT

In two-phase emulsion separations, it is customary to employ large settling volumes (for mixer-settling apparatus) or large centrifugal forces (for centrifugal contactors). Improvement can sometimes be achieved by using an extractant with magnetic properties in the presence of a variable field. In the work reported in this paper, two different extractants (D-2EHPA and TBP) were employed in magnetic field experiments. These compounds are both stable and resistant to acid (15% H_2SO_4) and basic (NaOH, pH = 10) media. The test results for extraction of Cu^{2+} (with D-2EHPA) and UO_2^{2+} (with TBP) from aqueous media were positive. The emulsion separation for these two systems in the presence of a magnetic field was 160 times faster than in the gravitational field alone.

INTRODUCTION

The idea of the application of external fields in solvent extraction has attracted scientists for many years. The influence of electric or ultrasonic fields on mass transfer has been investigated (1,2,3). Application of electric fields allows the decrease of the settling volume of the mixer-settler extractor (4).

In the present work, the possible interaction of the magnetic field with the extraction process was investigated. A new extractant possessing certain magnetic properties was proposed. Its preparation was based on the "magnetic liquid" principle.

Magnetic liquids have been known for years and have found numerous applications, such as sealings (5), lubricants (6), etc. The only reported investigations concerning mass transfer between the gaseous phase and the magnetic liquid droplets were carried out by Kozubov (7). Not much information is available on the preparation of magnetic liquids. It is known, however, that they are formed by the dispersion of small ferromagnetic particles (e.g., Fe_3O_4) in a liquid. Surfaces of such particles are covered by purposely added stabilizer that prevents their sedimentation.

PREPARATION OF EXTRACTANT FEATURING MAGNETIC PROPERTIES

A magnetic extractant should contain a selective metal complexing agent; in our case, the agent was tributylphosphate (TBP) or oxym. The extractant obtained should be resistant to electrolyte solutions. Figure 1 shows a schematic diagram of the preparation procedure (8).

Following the above procedure, some magnetic liquids were obtained. The high consistency of the results should be noted. Kerosene solutions of some popular extractants were used in the process. The following extractants were applied: TBP, di-2-ethylhexyl phosphoric acid (D-2EHPA), tri-n-octylamine (TnO), AC-1, and 5ME-529 oxyms (similar behavior to LIX-type extractants). The concentration of these extractants was in the range of several and below 20%, while the concentration of magnetite (Fe_3O_4) varied between 10 and 15%.

A considerable negative influence of the sediment aging upon the Fe_3O_4 dispersion efficiency was observed during the preparation process. The magnetite sediment could not be stored, even for several hours, after precipitation without a stabilizing agent (oleic acid).

PROPERTIES OF THE MAGNETIC EXTRACTANTS

Photographs of the extractant obtained on the base of the TBP/kerosene solution were made using an electron microscope.

The particle-size distribution in the magnetic extractant was determined by means of the photographic method (Figures 2 and 3).

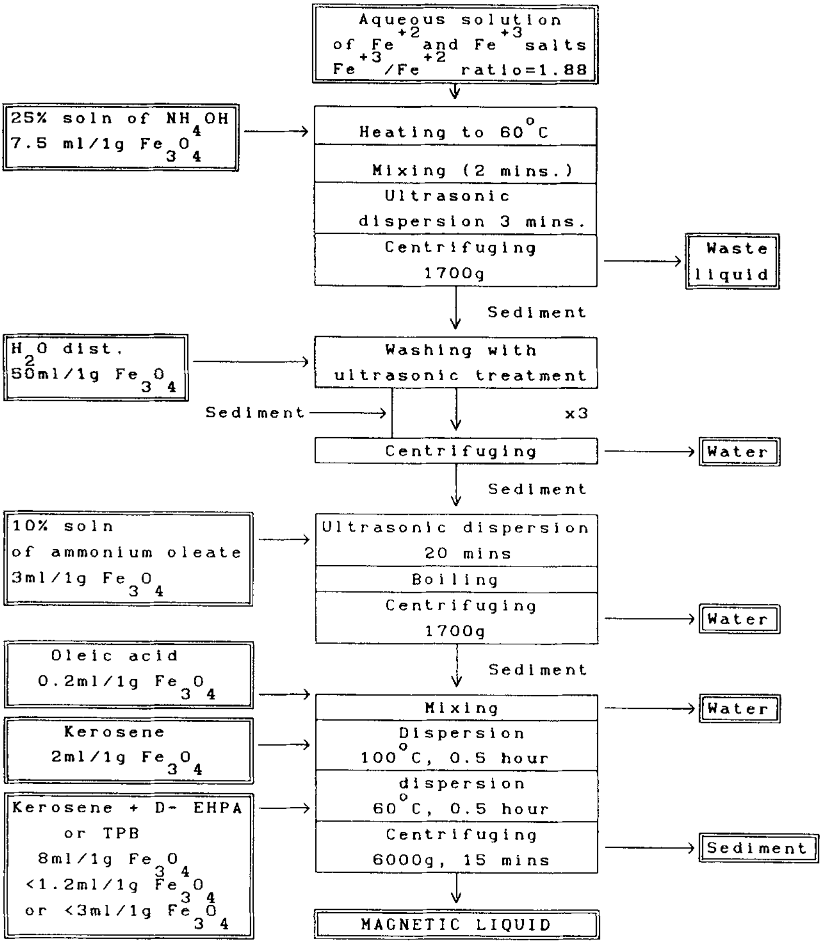

FIGURE 1. Schematic diagram of the production process of an extractant featuring magnetic properties.

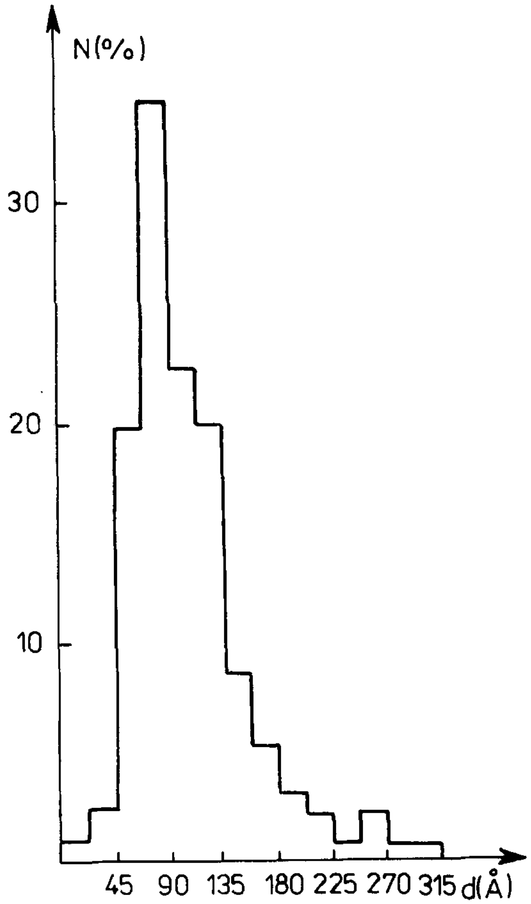

FIGURE 2. Distribution of the dispersed-phase particle size.

The magnetic extractant features the following properties:

1. low viscosity, 3.47 cP;
2. density 0.82 to 0.86 g/cm^3;
3. stability in the field of gravity of 60 m s^{-2};
4. stability in the magnetic field of a permanent magnet (field intensity - 130 g A^{-1} s^{-2});

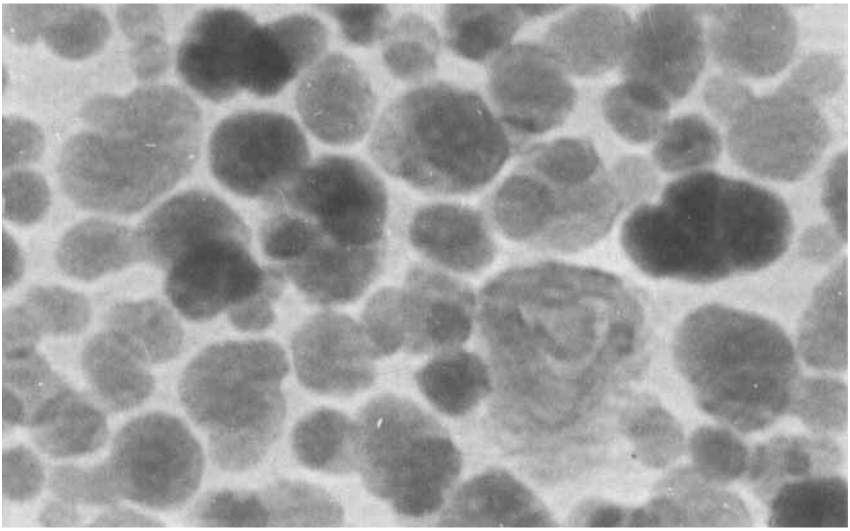

FIGURE 3. Electron microscope photograph showing ferromagnetic particles in a magnetic liquid. Image magnification: 877500x.

5. excellent keeping properties – >2 years without a trace of sedimentation;
6. resistance to mineral acids of several percent concentration; and
7. resistance to alkaline solutions at pH ≤10.

APPLICATION OF MAGNETIC EXTRACTANTS

Emulsion-Phase Separation in Magnetic Fields During the Liquid-Liquid Extraction Process

A number of comparative tests on the phase-separation rate from emulsion were conducted, the investigated processes being copper extraction using D-2EHPA and uranium extraction with TBP. The aqueous phase was a water solution of $CuSO_4$ with a concentration of 10.3 mg Cu/cm^3, acidified to the pH value of 4.05. The organic phase was an 11% solution of D-2EHPA in kerosene and another solution containing an identical quantity of D-2EHPA plus 15% of dispersed magnetite (Fe_3O_4). The organic-to-aqueous-phase ratio varied in the range 1:1 to 1:2.5.

The second investigated system was a uranyl nitrate $UO_2(NO_3)_2$ solution with a concentration of 1.025 mg U/cm^3 in water. Sodium nitrate was added to the aqueous phase as a salting-out agent in a quantity sufficient to obtain a concentration of 5 M/L. The organic phase was, in that case, 8% TBP solution in kerosene and, in this case, another similar solution of TBP in a magnetic liquid.

The total-phase separation rate in a 1300-*g* magnetic field of a permanent magnet ranged from 20 to 160 times higher than the gravitational separation. The highest separation rate was observed in the experiments in which the magnetic extractant constituted a water-dispersed phase. With the reversed-emulsion type, the rate of the separation process only increased 20 times.

No signs of magnetic extractant destruction were observed after its direct contact with the water phase, which made the liquid-liquid extraction experiments possible.

Liquid-Liquid Extraction in Magnetic Fields

It is a widely known fact that the presence of solid particles or a detergent at the phase boundary of two nonmixing liquids inhibits the diffusion processes, which results in decreasing the rate of the extraction process. It was expected that the magnetic extractants would provide sufficient quantities of solid particles to decrease the extraction efficiency. In order to determine the significance of the above effect, a series of laboratory experiments on copper extraction and reextraction were carried out in a tap-funnel. The initial concentration of Cu^{2+} was 10.3 mg/cm^3; the water/organic phase ratio was 1:1 and 2:1 for extraction and reextraction, respectively. The copper reextraction process was conducted using a 1% H_2SO_4 solution. The results obtained are listed in Table 1.

No significant influence of the solid particles on the extraction and reextraction process run was observed in the investigated system.

Magnetic and conventional extractants can be compared only if the mass transfer interface area is constant and exactly known.

The investigations of both types of extractants were carried out in a Lewis extractor (no magnetic field applied). Extraction of uranium by means of TBP was selected as the model process. The aqueous phase, in that case, was a 5 M solution

TABLE 1. RESULTS OF THE EXTRACTION AND REEXTRACTION OF THE COPPER

No.	D-2EHPA conc. (%)	Fe_3O_4 conc. (%)	Cu^{2+} conc. after extr. (mg/mL)	Cu^{2+} conc. after reextr. (mg/mL)
0	7	0	7.6	0.74
1	5	40	9.7	0.09
2	5	22	9.8	0.05
3	5	4.3	9.8	0.01
4	5	1.2	9.5	0.04

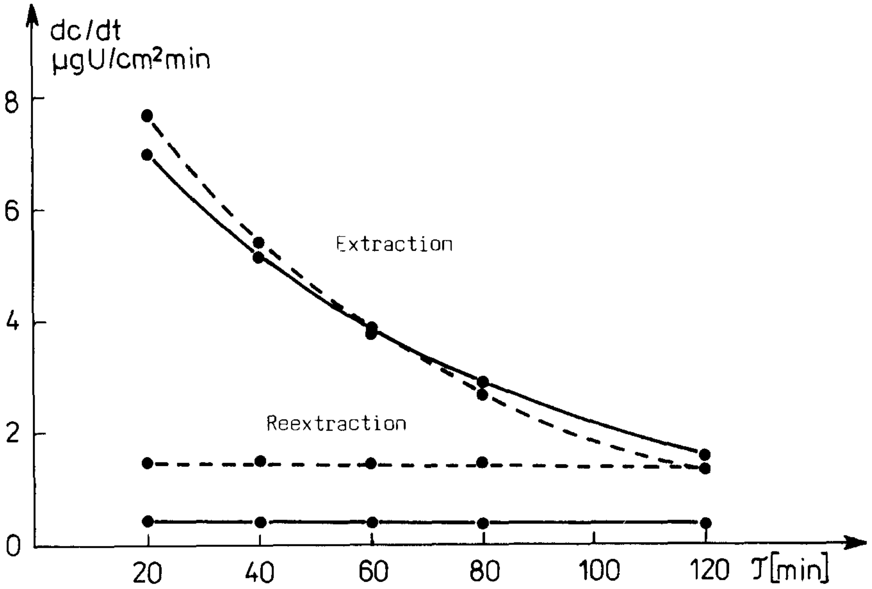

FIGURE 4. Comparison of the mass transfer rate in uranium extraction and reextraction processes in a Lewis extractor per unit of the interfacial area for magnetic and standard extractants.

- - - - - - - standard extractant

——— magnetic extractant

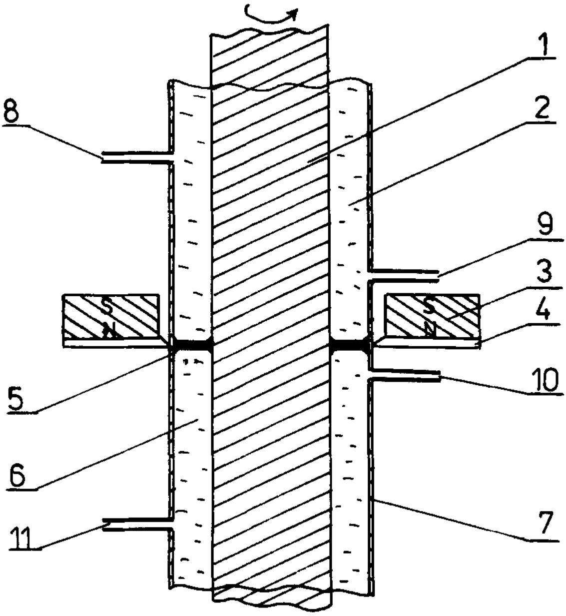

FIGURE 5. Construction of the extractor.
1-polyethylene-coated steel cylinder
2-primary aqueous phase subject to extraction (AP1)
3-permanent magnet
4-steel ring
5-organic-phase membrane (e.g., extractant containing TBP)
6-aqueous phase used as reextractant (e.g., distilled water, AP2)
7-Plexiglass® tube
8-AP1 outlet
9-AP1 inlet
10-AP2 inlet
11-AP2 outlet

of $NaNO_3$ containing $UO_2(NO_3)_2$ at a concentration of 2.091 mg U/cm^3. The organic phases used were a 15% TBP solution in kerosene as a standard and 15% TBP plus 10% dispersed Fe_3O_4 in kerosene as the extractant of magnetic properties.

The UO_2^{2+} concentration was determined during the extraction and reextraction processes. The results of analyses, combined with the knowledge of the mass transfer interfacial area, permitted a calculation of the uranium mass transfer rate. A comparison of conventional and magnetic extractants is shown in Figure 4.

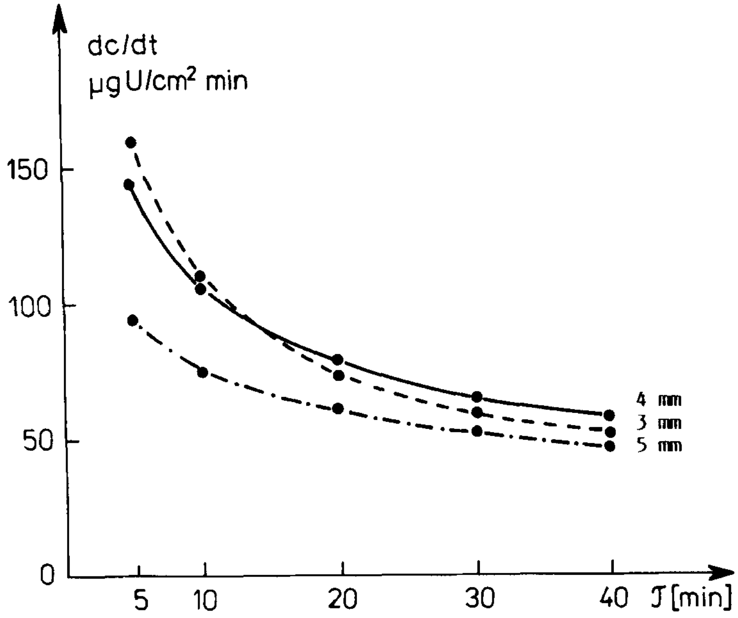

FIGURE 6. Mass transfer rate through a unit of the interfacial area vs extraction time for different thicknesses of the organic-phase membrane.

It is clear that the process efficiency was lower in the cases where the magnetic extractant was used. The figures illustrating the decreasing process efficiency, in comparison to the standard extractant, are 4% and 70% for extraction and reextraction, respectively. As can be concluded from the data shown in Table 1, the presence of Fe_3O_4 particles did not cause the problems observed. Thus, the only explanation of the phenomenon can be a negative influence created by the oleic acid that was added to the organic phase as a stabilizer.

Increasing the rate of the extraction processes is possible in the case when both extraction and reextraction take place simultaneously. With this in mind, another extractor was constructed, in which both processes could be run simultaneously and it would also be possible to apply a magnetic field. The magnetic extractant remains under the influence of the external field and is shaped so as to

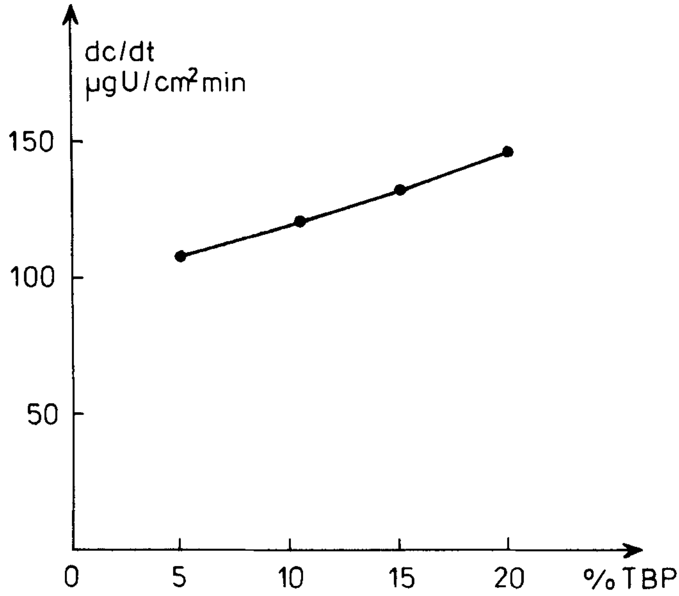

FIGURE 7. Uranium mass transfer rate through a unit of the interfacial area vs TBP concentration in the organic phase.

form a membrane between the primary aqueous phase and another water phase constituting the reextractant. The extractor construction is shown in Figure 5.

The membrane was formed by a kerosene-based magnetic extractant containing 15% TBP and 10% Fe_3O_4. The water phase above the membrane was a 5 M solution of $NaNO_3$ containing $UO_2(NO_3)_2$ at a concentration of 2.091 mg U/cm^3. In the process of uranium reextraction from the membrane, the aqueous phase below the membrane was distilled water.

Since the extractor used in the experiments was just a prototype, a series of kinetic studies were performed to establish conditions of simultaneous extraction and reextraction. The results shown in Figures 6 and 7 indicate that the rate of mass transfer through a unit of the membrane surface area decreases with the growth of its thickness and increases with the concentration of the complexing agent, being, in that case, TBP.

CONCLUSIONS

The developed method of producing a kerosene-based extractant that features magnetic properties and contains popular metal-complexing agents (TBP, D-2EHPA) guarantees >90% consistency of the permanent degree of dispersion of magnetite.

The obtained extractants possess excellent keeping properties and are resistant to most electrolytes. It is entirely possible to obtain such extractants that would be resistant to strong mineral acids and, at the same time, alkaline solutions. Fluoroorganic and fluosilicon-organic compounds are used as stabilizers in such extractants.

The magnetic extractants obtained in the way of the described procedure are suitable for extraction processes. Their extracting properties are slightly inferior to those of extractants without ferromagnetic particles; the situation can most probably be improved by setting the droplets into oscillation-like motion in an alternating magnetic field. Such oscillations are supposed to restore active interfacial area, thus accelerating the diffusion processes, which, in turn, leads to improvement of the whole process efficiency.

The magnetic properties of an extractant enable considerable acceleration of emulsion-phase separation in a magnetic field. It is possible to construct an extractor of the mixer-settler type of much smaller dimensions in comparison with a standard extractor.

In a magnetic field, a magnetic extractant can form a membrane-like shape, a fact that allowed us to design and build a new type of extractor for simultaneous extraction and reextraction of metals. Consequently, we can conclude that similar extractors, particularly multistage ones, can become a useful tool in studies on the kinetic effect in the extraction process.

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