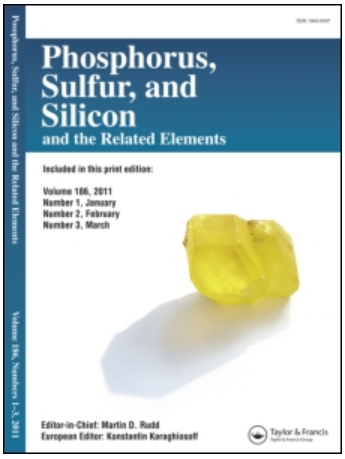

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The Uses of Organo Phosphorus Compounds in Liquid-Liquid Extraction of Metal Ions

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THE USES OF ORGANO PHOSPHORUS COMPOUNDS IN LIQUID-LIQUID EXTRACTION OF METAL IONS

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Abstract A survey of the uses of organo phosphorus compounds in liquid-liquid extraction processes is presented. Some modern aspects of solvent extraction including the development of new extractants, the development of the liquid membrane technique, the design of more selective organophosphorus extractants and the use of organo phosphorus compounds as extraction catalysts, are discussed.

INTRODUCTION [1]

Liquid-Liquid extraction (or Solvent Extraction) is by now a well established process for the separation, purification and concentration of metal ions. Its implementation in hydrometallurgical processes has been increasing over the last two decades[2].
If an immiscible liquid organic phase (called "Solvent") is mixed with an aqueous phase containing a solute, this solute distributes between the two phases. In the most general situation, the solvent contains a) the extractant which interacts chemically with the metallic solute b) the diluent which lowers the viscosity of the solvent and facilitates the contact between the two phases c) the modifier which prevents the formation of a third phase and modifies the equilibrium position d) the accelerator which enhances the extraction rate.

General properties are required for the organic phase in liquid-liquid extraction. These are: 1) Selectivity, 2) Loading capacity, 3) Low solubility in the aqueous phase, 4) Low toxicity,

5) Chemical stability, 6) Rapid phase separation, 7) Rapid extraction of the desired solute, 8) Easy stripping and solvent recovery, 9) Reasonable cost.

THE ORGANO PHOSPHORUS EXTRACTANTS

Among the common extractants generally used, the organo phosphorus extractants appear in many processes.

Neutral Extractants

The most familiar extractant of this group is Tributylphosphate (TBP). It is used for the Uranium refining[2], for the Uranium-Plutonium separation[3], for the Iron removal[2], for the individual separation of the light Rare Earths[4 5 6] and for the Zirconium-Hafnium separation[2].

Another extractant of this group is Trioctylphosphine oxide (TOPO), which has been found to be a very efficient synergic agent in the extraction of Uranium VI from phosphoric media[7 8 9]. Alkoxyalkylphosphine oxides ($R_2P(O)CH_2OR'$) have recently been proposed. They have in some cases higher performances than TOPO because of their higher solubility in the organic phase[10].

Neutral phosphonates like Dibutylbutylphosphonate (DBBP) can in some cases advantageously replace TBP.

Bidendate neutral organophosphorus molecules have recently been investigated in solvent extraction. Among them, carbamoyl phosphonates have been found to be suitable for the removal and recovery of Americium III and highly radioactive actinides[11 12].

Cation Exchangers

Phosphoric acids are common extractants, especially Di(ethyl$_2$ hexyl) phosphoric acid (DEHPA). It exhibits a moderate selectivity which enables a complete separation of Rare Earths[4 5 6]. Other hydrometallurgical applications of DEHPA include the Nickel-Cobalt separation[2], the extraction of Zinc[2] and the recovery of Uranium from phosphoric media (with TOPO: The DEHPA-TOPO process).

Two other processes using organo phosphoric acids as extractants have been developed for the recovery of Uranium from phosphoric media[7 8 9]: 1) The MOPPA DOPPA process: The extractant is an equimolecular mixture of mono(octylphenyl)phosphoric acid (MOPPA) and di(octylphenyl)phosphoric acid (DOPPA); 2) The OPPA process: The extractant is octylpyrophosphoric acid (OPPA). Alkoxyalkyl phosphoric acids $(ROCH_2)_2CHO_2P(O)OH$ have also been proposed recently for the extraction of Uranium[13].

Phosphonic and phosphinic acids are more selective than phosphoric acids in the Nickel-Cobalt separation[14] and can also be used for Rare Earth separations[15]. They are now industrial extractants.

RESEARCH AND DEVELOPMENTS

Improvements of Existing Processes

The design of a solvent takes into account many parameters (chemical, hydrodynamical and economical parameters); however, the chemical parameters greatly determine the investment costs (number of stages, volume of solvent,etc). As illustrated above, continuous efforts are therefore devoted to the research of better extractants.

Liquid Membranes

The application of the liquid membrane technique in hydrometallurgy has aroused a great deal of interest for a few years. It has been shown that organo phosphorus extractants can be used as mobile carriers (see for instance ref.[16 17 18]).

Extraction Kinetics and Extraction Mechanism

Phosphoric acids can be used as accelerators in metal extractions which are controlled by the reaction kinetics (e.g. extraction of Copper by acidic chelating agents). A mechanism has been proposed in which the phosphoric acid appears as a phase transfer catalyst[19].

More Selective Extractants

Recent studies have shown the enhancement of the selectivity in

the extractions of alkali and alkaline earths by adding crown ethers to DEHPA solutions[20]. This result could stimulate research to find more sophisticated organophosphorus extractants exhibiting selectivity on the base of macrocyclic effects. The extension of the solvent extraction method to the recovery of metals from diluted complex solutions (leaching solutions of low grade ores, wastes) mainly depends on the discovery of more selective reagents.

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