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Investigation of uranium(VI) extraction mechanisms from phosphoric and sulfuric media by ^{31}P -NMR

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Abstract

Uranium extraction using DEHCNPB (butyl-1-[N,N-bis(2-ethylhexyl)carbamoyl]nonyl phosphonic acid, a bifunctional cationic extractant) has been studied to better understand mechanism differences depending on the original acidic solution (phosphoric or sulfuric). Solvent extraction batch experiments were carried out and the organic phases were probed using ^{31}P -NMR. This technique enabled to demonstrate that phosphoric acid is poorly extracted by DEHCNPB ($[\text{H}_3\text{PO}_4]_{\text{org}} < 2 \text{ mM}$), using direct quantification in the organic phase by ^{31}P -NMR spectra integration. Moreover, in the presence of uranium in the initial phosphoric acid solution, uranyl extraction by DEHCNPB competes with H_3PO_4 extraction.

Average stoichiometries of U(VI)-DEHCNPB complexes in organic phases were also determined using slope analysis on uranium distribution data. Uranium seems to be extracted from a phosphoric medium by two extractant molecules, whereas more than three DEHCNPB on average would be necessary to extract uranium from a sulfuric medium. Thus, uranium is extracted according to different mechanisms depending on the nature of the initial solution.

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1. Introduction

Phosphate rocks are widely exploited for the production of phosphoric acid, which is used to make fertilizers and others industrial products¹. These ores also contain uranium (~100 ppm on average), and are considered as a secondary source for uranium production². Therefore, there is a double interest to recover uranium from phosphate rocks: it would decontaminate industrial phosphoric acid while valorizing uranium as a by-product for the nuclear industry. This context drove the CEA, in collaboration with AREVA, to develop new liquid-liquid extraction processes designed to extract, purify and concentrate uranium from phosphate ores. A process using DEHCNPB^{3,4} (butyl-1-[N,N-bis(2-ethylhexyl)carbamoyl]nonyl phosphonic acid, cf. Fig. 1) was developed and successfully tested during pilot scale trials in mixer-settlers. This bifunctional extractant allowed to recover uranium with high yields and purity, filling U/Fe selectivity requirements⁵. DEHCNPB was also used for the extraction of uranium from conventional ores (after sulfuric lixiviation)⁶. This process was adapted to a sulfuric feed solution and pilot tests were performed as well. However, uranium leaks were observed in aqueous phase in the scrubbing steps when the solvent was loaded from a sulfuric medium. In order to better understand differences of performances observed during those tests, a comprehensive study was initiated in order to explore the possible existence of different uranium extraction mechanisms, depending on the nature of the acidic solution (phosphoric or sulfuric). This paper presents an experimental study performed to achieve a better understanding of uranium extraction mechanisms. Phosphoric acid extraction by DEHCNPB was studied using ³¹P-NMR to probe the organic phases, allowing quantification of phosphoric acid. Uranium distribution ratios were measured as a function of DEHCNPB concentration and combined to NMR integrations to determine average stoichiometries of U(VI)-DEHCNPB complexes formed in organic phases. These results will then be helpful to develop a thermodynamical model for the simulation of uranium extraction from sulfuric and phosphoric media.

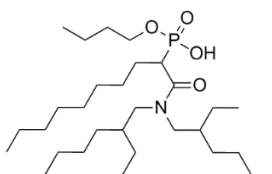


Fig. 1. Molecular structure of DEHCNPB extractant.

Nomenclature

DEHCNPB Butyl-1-[N,N-bis(2-ethylhexyl)carbamoyl]nonyl phosphonic acid

D_i Distribution ratio of species i

ESI-MS ElectroSpray Ionization coupled with Mass Spectrometry

GC-FID Gas Chromatography coupled with Flame Ionization Detector

HL Acidic extractant (DEHCNPB)

ICP-AES Inductively Coupled Plasma-Atomic Emission Spectroscopy

ICP-MS Inductively Coupled Plasma- Mass Spectrometry

IR Infra-red spectroscopy

NMR Nuclear Magnetic Resonance

O/A Ratio of organic volume to aqueous volume

SANS Small-Angle Neutron Scattering

SAXS Small-Angle X-ray Scattering

TPH Hydrogenated TetraPropylene

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