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ScienceDirect

Procedia Engineering 138 (2016) 258 – 266

Procedia Engineering

www.elsevier.com/locate/procedia

“SYMPHOS 2015”, 3rd International Symposium on Innovation and Technology in the Phosphate Industry

Carbamoylalkylphosphonates type ligand for uranium extraction from phosphates ores

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Abstract

Carbamoylphosphonic acid and carbamoylphosphonate ligands have been synthesized and studied for uranium extraction from phosphates ores. From a structure-selectivity approach, the molecular design of such ligands was optimized leading to a specific one called DEHCNPB which exhibits outstanding results for the selective extraction, and quantitative recovery of uranium in phosphoric acid compared to the URPHOS reference system.

Keywords: Bifunctional extractants; Uranium extraction; Phosphoric acid; DEHCNPB

1. Introduction

Natural phosphates rocks, commonly used for the production of phosphoric acid or fertilizers, contain uranium (from 20 to 200 ppm depending on deposits) as well as other common impurities such as rare earths, chromium, vanadium, titanium (hundreds ppm) and mainly aluminium and iron (ranging from 2000 to 5000 ppm).

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doi:10.1016/j.proeng.2016.02.083

Considering the amount of phosphate rock processed annually for the production of phosphoric acid, it represents one of the most attractive unconventional resources of uranium to supply the global uranium demand [1,2].
For this purpose, several solvent extraction processes such as the URPHOS [3], OPAP [4] and OPPA [5] processes have been implemented for recovering uranium from WPA.

While the OPAP and OPPA processes are very attractive in regards to the uranium extraction efficiency from WPA, the use of iron powder in order to reduce the uranium(VI) in uranium(IV) is a major drawback which results in a poor uranium(IV) selectivity toward iron(III) [4]. The degradation of OPPA by hydrolysis into monoalkylorthophosphoric acids is also an important issue [5].

The URPHOS process, which consists in a synergistic combination of di-2-ethyl-hexyl-phosphoric acid (HDEHP) as a cationic exchanger and trioctyl-phosphine oxide (TOPO) as a neutral donor is recognized as the best system since it extracts hexavalent uranium U(VI), avoiding the reduction step of uranium, and is a more stable and selective solvent (especially against iron) than OPAP and OPPA. However a multiple cycle scheme is needed to offset the low extraction strength and the iron contamination as a consequence of an insufficient selectivity of HDEHP-TOPO system.

For these reasons, the development of new efficient, selective, and robust extractants, for the recovery of uranium in high concentrated phosphoric acid media, used in synergistic mixtures or singly have been proposed [6].

Various works reported the substitution of the HDEHP or the TOPO in HDEHP-TOPO mixtures leading to other synergistic reagents [6-8] or the improvement using new cation exchangers and solvating agents involved in synergistic mixtures such as the URPHOS-bis process [9] which combine two different ligands: bis(di-n-butoxy-1,3-propyl-2-)phosphoric acid (HBiDiBOPP) and di-n-hexylmethoxyoctylphosphine oxide (DinHMOPO). With respect to the efficiency of the different systems studied the selectivity toward iron remains low.

The second approach consisting in the use of a single molecule or “autosynergistic” molecule which combine both cationic exchanger and neutral donor functions in a same molecular architecture is less described in the literature. O-methyldihexylphosphine oxide O′-hexyl- 2-ethyl phosphoric acid such as bifunctional extractants containing both phosphine oxide and phosphate groups have been developed for this purpose [10]. Whatever the extraction conditions, this bifunctional extractant results in higher extraction abilities than URPHOS system but a lower selectivity towards iron(III). However, some limits are inherent to the use of such phosphate ester function such as its hydrolysable ability in acidic conditions and the formation of a third phase during extraction which is not applicable for industrial process.

Considering the potential of this approach, we synthesized bifunctional extractants based on an amide group and a phosphonic acid [11] or a phosphonate group [12]. This system is a combination of a cationic exchanger (the phosphonic acid or phosphonate part) and a solvating exchanger (the amido part) (Fig. 1). The influence of the molecular design including the nature of alkyl chains on the amide part, the spacer length between the two functions, and the degree of steric hindrance on the spacer of such carbamoylphosphonic acid or carbamoylphosphonate ligands are discussed here and highlight the impact of the molecular structure on the efficiency to extract selectively the uranium(VI) from phosphoric acid solutions.

2. Results and discussion

The influence of the molecular design on the properties of the amido-phosphonic acids and amido-phosphonate ligands to selectively extract uranium(VI) over Fe(III) from phosphoric acid solutions have been studied including (Fig. 1).:

- length and ramifications of alkyl chains on amide group (**R1** and **R2**)
- spacer length and degree of steric hindrance on the spacer (**n**, **R4** and **R5**)
- length of alkyl chain of phosphonate (**R3**)

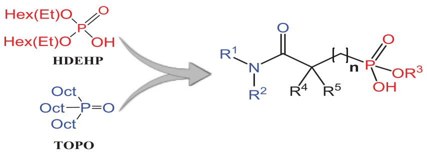

Fig. 1. Structural modifications considered for the amido-phosphonic acid and amido-phosphonate ligands