

Rapid Computer Aided Ligand Design and Screening of Precious Metal Extractants from TRUEX Raffinate with Experimental Validation.

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ABSTRACT

Although half of the world's spent nuclear fuel (SNF) is treated in a "once-through cycle", reprocessing allows for recycling of U, Pu, and other fission products. The traditional PUREX process can extract U and Pu but does not completely inhibit the extraction of minor actinides. Further isolation of transplutonium elements can be achieved using TRUEX with minimal additional waste generation, yet valuable and desirable elements reside in SNF and in the raffinates of high level liquid wastes (HLLW). HLLW contains ca. 1 kg/m³ of Ru, Rh, and Pd, after PUREX reprocessing of 1 ton of initial heavy metal (IHM) with burnup of 33,000 MWd/t IHM and after cooling for 3 years. While the retrieval of these precious metals from SNF would minimize waste generation and improve resource utilization, it has been difficult to achieve thus far. We propose a novel solution to this problem through the design of software that uses computational combinatorial chemistry with empirical corrections for realistic separations conditions to rapidly design and screen new ligands for the extraction of precious metals from nuclear fuel cycle (NFC) raffinates. Though computer aided ligand design is generally accepted and sometimes utilized, its full capability has not been realized because: 1) the most accurate computational methods for heavy metals are not routinely used in ligand screening algorithms, and 2) the effects of realistic extraction conditions are not taken into account.

An algorithm will be developed that is interfaced with common codes for the computer-aided design of sequestering agents for precious metals from NFC raffinates. It incorporates a "tree expression" algorithm to screen large ligand libraries utilizing a database of statistics regarding the physico-chemical properties of known precious metal extractants. A combination of molecular mechanics, semi-empirical and density functional based information will be obtained for reported ligands so as to establish criterion for ligand screening based upon ligand binding energies, atomic electrostatic properties, as well as metal ion selectivity. Using previously established computational protocols, a thermodynamic cycle representative of the bulk reaction for extraction will be calculated to ascertain the favorability of the metal-ligand complex toward extraction. Experimental data collected within the proposed work will be used to add empirical corrections that account for experimental conditions. These will include the stability constants of the metalligand complex under varying ionic strengths, from which the free energy may be determined, as well as the distribution/partition coefficients for the metal-ligand complexes, which are representative of the favorability of extraction from the aqueous to organic phases. This goaldriven, science-based approach will demonstrate that advanced modeling and simulation tools (when used in conjunction with smaller-scale, phenomenon-specific experiments) can reduce the need for large, expensive integrated experiments. This mission-supporting activity will produce a tool that can be broadly used within the separations community providing advanced resource utilization and creative solutions for the management of SNF.