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Advanced Reprocessing – The Potential for Continuous Chromatographic Separations

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Abstract

This concept paper, discusses the challenges and opportunities for an extractive chromatographic process for the separation of fission products and minor actinides from uranium and plutonium isotopes in irradiated nuclear fuel. The paper highlights the constraints of the PUREX process, a process that is universally accepted for reprocessing of spent nuclear fuel now and for GEN IV reactor systems. It also identifies the challenges that a new separation process would have to overcome to dislodge its acceptance by both the operators and regulators. Although the concept of using a chromatography technique for this separation is challenging, recent developments of continuous chromatography such as simulated moving bed (SMB) and/or continuous annular chromatography (CAC) provides a degree of encouragement. Equally the development of new stationary phases in particular inorganic exchangers, many of which have not been examined for this application enhances confidence that an alternative to the PUREX process is possible.

Keywords: Chromatographic; Liquor concentrations; Separations; Uranium

Introduction

The PUREX process [1] has for nearly 60 years been largely unchallenged separation technology for the reprocessing of irradiated fuel for nuclear weapons production and/or for commercial nuclear power generation. The merits and efficiency of this process are unquestionable since it achieves the objectives of highly purified plutonium and uranium which both can be eventually recycled. Although well proven and predictable the PUREX process is not without its challenges, the generation of significant quantities of highly active aqueous liquid containing fission products (FPs) and minor actinides (MAs), the degradation of the solvent phase reagents and non-specific nature of the extractant, Tri-Butyl Phosphate (TBP), have to be addressed [2]. To ensure the uranium and plutonium are decontaminated to the required levels the PUREX process requires strict control of process conditions (flow sheet parameters); largely due to the lack of specificity of TBP. In addition the process requires appropriately sized, large, contactors as it is the bulk of the heavy metals (U and Pu isotopes) that are extracted from the aqueous phase in to the organic phase. It is accepted in many quarters that the PUREX process significantly reduces the waste management disposal problems [3].

The development of alternative nuclear fuel reprocessing schemes is being evaluated some as add-on to PUREX, others as updated PUREX process. Many of these developments are targeting better waste management of high active waste for future GEN IV fuel cycles [4]. The incorporation of the PUREX process, whether updated or not, into future reprocessing will still have inherent disadvantages, and these may be further exacerbated with future fuels that will have significant higher burn ups [5].

Any new process must overcome the PUREX challenges as well as offering some distinct advantages as both regulators and operators have become acclimatised to sixty year old technology.

The concept developed at the University of Central Lancashire [6] is a radical departure from PUREX and will offer many advantages as described later in this paper. It is based on the separation of FPs and MAs from uranium and plutonium isotopes using continuous chromatographic (cc) separation (Figure 1).

The paper explores the developments that have been achieved in chromatography in the past few decades and the advent of new stationary phases. It also describes some of the criteria that any new process will have to address and potential opportunities for this new process.

Continuous chromatography

Chromatography is one of the most relied upon technologies available to engineers and scientists in a variety of fields that include pharmaceuticals, forensics, environment, and energy and has found uses over a wide range where the separation of compounds would be incredibly difficult, prohibitively costly or due to the chemistry involved, impossible by other means. Chromatography is based on the principle of multiplication of single-stage separation factors by arranging the separation medium such that the products of one separation stage directly feed additional stages, thus significantly enhancing the degree of separation obtained. The physical arrangement usually employed is to put the separation medium (typically an ion exchange resin) in a vertical column [7]. The feed solution enters from the top or bottom of the column where it attaches to the exchange sites of the resin. The chromatographic process occurs as the ions to be separated are eluted preferentially through the column with a carefully chosen eluent.

The single biggest challenge associated with chromatography has always been the inability of the technique to scale up from the laboratory scale to an industrial process [8].

To counter this, a number of attempts have been made towards developing a continuous chromatographic system. These have included; moving and approximated moving beds, counter flow,

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Figure 1: UCLan's Chromatographic separation concept.

annular beds, radial flow, and disk chromatographic systems [9]. However, wide spread industrial use of these techniques is rare even within biological and organic applications and virtually non-existent in inorganic separations, in particular nuclear reprocessing.

The first mention of continuous chromatography in the literature is attributed to Martin [10] who envisaged methods to move chromatography into the large scale, i.e., an industrial separation technique. He described two methods in which this may be achieved which generally persist today; the first is a moving bed configuration in which the stationary phase is forced against the flow of mobile phase within a thin tube. If the balance between mobile and stationary phase flow rates is balanced correctly, components with higher affinity for the mobile phase would be carried further with this than the stationary phase. Movement of the mobile phase is inherently plagued with hydrodynamic challenges; to overcome them a certain number of fixed beds are connected in series to form a closed loop, and the counter-current movement of the solid and liquid phase is simulated by periodically shifting the fluid inlets and outlets in the direction of the fluid flow i.e., simulated moving bed (SMB) [11]. An example of a laboratory SMB reactor is shown in Figure 2.

The other idea was continuous annular chromatograph (CAC), it employs continuous feed and separation of several species simultaneously. The innovation is embodied in equipment that permits continuous feed and separation of chemical species on an apparatus consisting of an annular bed of adsorbent particles. The apparatus is rotated slowly about its axis while eluent and feed solution are fed into one end of the bed. Eluent is fed to the entire bed circumference while the feed mixture is introduced into a narrow sector of the circumference at a single point. Helical component bands develop with the passage of time extending from the feed point, with slopes dependent on eluent velocity, rotational speed, and the distribution coefficient of

the component between the fluid and sorbent phases. The separated components are continuously recovered once steady state is attained as they emerge from the annular column, each at its unique position on the circumference of the annular bed opposite the feed end (Figure 3). Separations can be carried out with simple or gradient elution, wherein the eluent concentration is changed continuously [12].

Current developments have largely concerned biological separations based on simulated moving bed (SMB), although there have been attempts to further promote CAC for both organic molecules (biotechnology and protein separations) and on a limited scale inorganic ions (metals) [13]. The practical applications which have been reported generally give very encouraging results with good separation and efficiencies equivalent to that of conventional batch chromatography [14]. In addition to equipment selection chromatography comprises of two components: The mobile phase, and the stationary phase.

In developing an alternative to the PUREX process both components will require significant effort, but past research has provided a good foundation on which to build.

The mobile phase

The composition of the mobile phase will be dependent on the upstream operations, i.e., dissolution and downstream, post-separation circuit requirements such as waste management. At this stage of the development of this alternative PUREX process a nitrate base system is under consideration, but this does not exclude other aqueous systems. As discussed later the process feed liquor U and Pu concentration will not dominate the cc process conditions unlike the PUREX process.

The head-end operations of the PUREX process involve the de-cladding of the irradiated nuclear fuel which is then dissolved in hot nitric acid to produce a uranium solution of ~ 300 g/l concentration

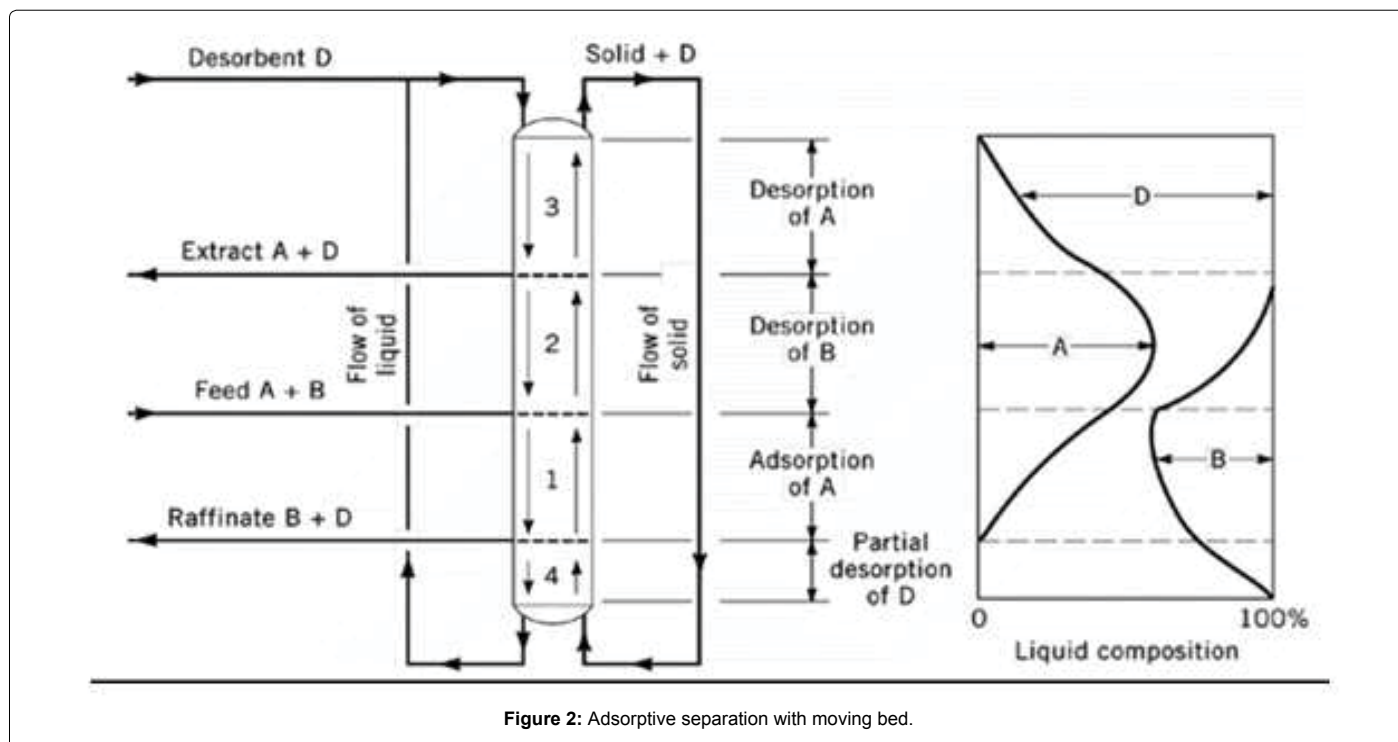


Figure 2: Adsorptive separation with moving bed.

with a free acidity of about 3M. At this uranium concentration some of the more important fission products (FPs) and minor actinide (MA) concentrations are reported in Table 1, these concentrations are based on a typical irradiated PWR 3.5% U-235 fuel with a burn up of 33 GWd/tHM, cooled for 3 years [15].

As the UCLan's conceptual process will remove FPs and MAs from the aqueous it will not be dominated by the concentration of U and Pu.

The stationary phase

A vast number of stationary phases have been developed for chromatographic separations, but few, if any for nuclear reprocessing applications [16]. Both organic and inorganic ion exchangers have been used, however, in chromatographic separations largely for nuclear waste management applications [17]. The exchangers have included conventional polystyrene-divinyl benzene copolymers with sulphonic acid groups, but the greater number has involved inorganic materials such as zeolites, hydrous oxides, titanates, phosphates, and silicates. Some have demonstrated very good separation factors for Cs and Sr from other radionuclides in highly active liquors; however such liquors are depleted of uranium and plutonium isotopes [18] i.e., the major heavy metals. In addition to good separation factors some inorganic exchangers have demonstrated good resistance to gamma radiation [19].

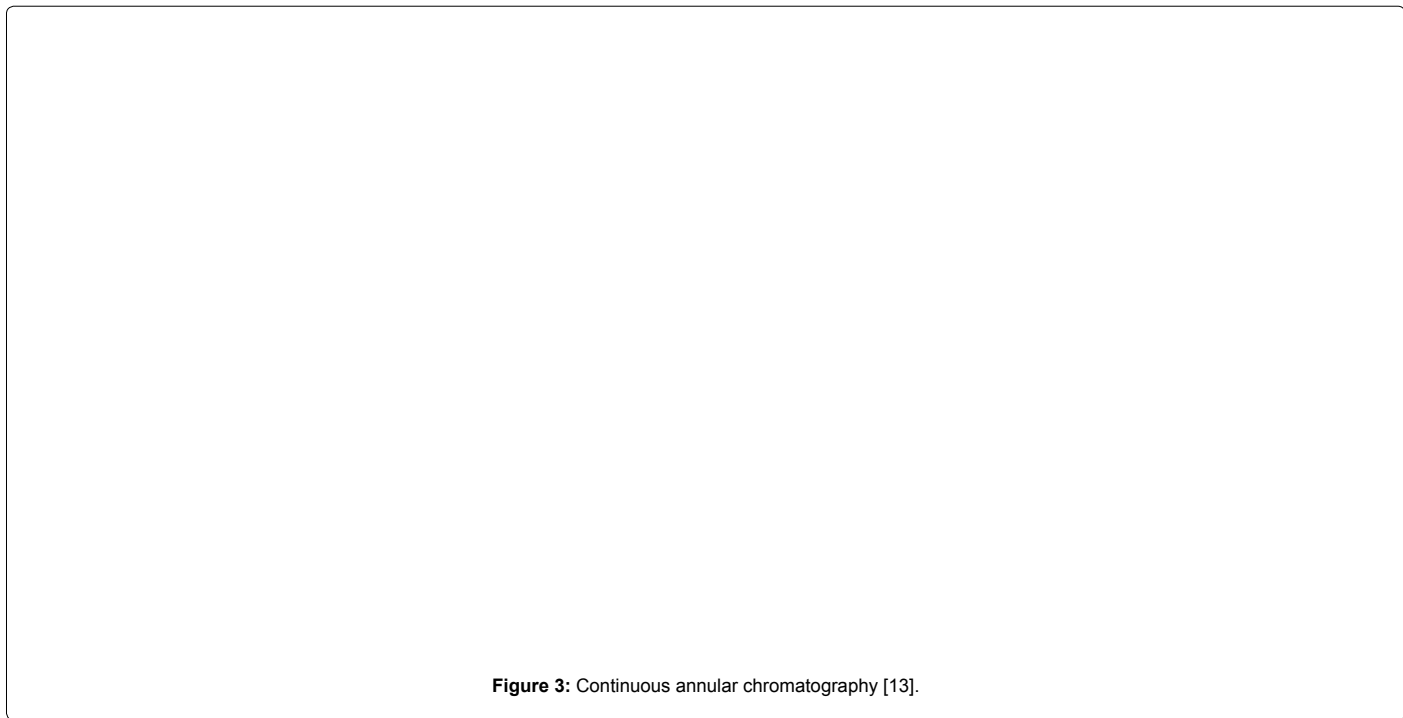
In developing stationary phases for the Uclan process it is important to take account of:

1. Ease of preparation to minimize cost and availability
2. Appropriate kinetic and thermodynamic characteristics
3. Robustness, as harsh process environments could be involved
4. Recyclability to minimize environmental impact
5. Predictable exchange mechanism to assist modelling and regulator confidence.

The challenges for continuous chromatography

The concept of replacing the PUREX process for reprocessing of irradiated uranium fuel is a significant challenge as several key conditions/considerations will require critical assessment and comparison with a technology that has been accepted and unchallenged for nearly sixty years. The more important challenges are addressed in this section. Separation processes, such as the PUREX process, have to satisfy not only a variety of interested parties such as regulators and operators, but also meet some stringent specification conditions such as reliability, throughput, product quality, environmental impact etc. The PUREX process 'ticks many of these boxes' but has some inherent disadvantages, which have been previously described. Unquestionably the separation of uranium and plutonium from FPs and MAs is one of PUREX's major attributes; for most elements decontamination factors (D_f) of 10^7 are achieved except for Np (1.5×10^4) and Tc (5×10^3) relative to the U product and U (5×10^4), Np (100) and Tc (100) relative to the plutonium product [20], however to achieve these D_f s the aqueous and solvent phases have to be brought in to contact numerous times. It is highly unlikely that these D_f s can be achieved by single contact and therefore alternative separation processes will still require multi-stages, but the number of stages can be reduced if the stationary phase has a superior separation factor for the target radionuclide. Improved separation efficiencies, hence reduced number of stages, will have a direct impact on the overall size of contactors and therefore on the capital cost of reprocessing facilities.

Contactor dimensions are also influenced by kinetics and for a liquid-liquid extraction system the phase disengagement for mixer-settler contactors will predominate. In general the settler area/volume will be at least 5 times the mixer area/volume, but this will depend on the dispersed phase drop size, mixing regime and density difference between the aqueous and solvent phases. The extraction of uranium and plutonium from nitric acid solutions is rapid [21], in some cases a few seconds for centrifugal contactors, but longer for less intensive mixing regimes. These and other considerations are required when



Radionuclide	Approximate concentration
U	300 g/l
Pu	3.2 g/l
Np	150 mg/l
Am	200 mg/l
Cm	7 mg/l
Alkali metals (Cs, Rb)	1 g/l
Alkaline earth metals (Sr and Ba)	0.9 g/l
Y and lanthanides	3.5 g/l
Zr	1.2 g/l
Se and Te	150 mg/l
Mo	1.1 g/l
Tc	260 mg/l
Ru, Rh, Pd	1.3 g/l
Ag, Cd, Sn, Sb	30 mg/l

Table 1: Dissolver liquor concentrations.

selecting the PUREX system. Chromatographic separations will need to consider kinetics, and also particle size, porosity, density etc. of the stationary phase, but in comparison with liquid-liquid extraction system such as PUREX, fewer others.

The back extraction of U and Pu from the solvent phase is readily achieved by changing the nitric acid concentration of the aqueous phase and change in oxidation state of the target metal respectively; in other words the reaction is reversible and hence the solvent can be re-cycled; a prerequisite for the PUREX process. Extracting the minor radionuclides (FPs and MAs) from the aqueous phase in preference to U and Pu does not necessarily require reversibility, and for disposal of the loaded solid phase (stationary phase) this irreversibility would be regarded as beneficial.

Tri butyl phosphate which is the ‘work horse’ of the PUREX process, has a preference for uranyl nitrate and plutonium nitrate [Pu(IV) and Pu(VI)] relative to other radionuclides; this should not infer that some of these radionuclides could not be extracted into the solvent

phase. By controlling the heavy metal concentration, aqueous phase nitric acid concentration and the solvent to aqueous feed ratio of the feed materials, good separation factors are achieved. This tight control renders the PUREX process somewhat inflexible. A separation process capable of removing the minor radionuclides would be far more flexible as the concentration of U and Pu would be largely immaterial.

Most solvent extraction processes, and PUREX is no exception, suffer from the loss of extractant and diluent to the aqueous phase; the solubility of TBP in aqueous systems is of the order a few hundred ppm. The loss of TBP, due to its solubility in the aqueous phase, is further exacerbated by its degradation due to either acid hydrolysis or radiolysis. Previous work Krishnamurthy et al. [22,23] has demonstrated that radiation chemical yields of di-butyl phosphate and mono-butyl phosphate were considerably enhanced in the presence of nitric acid in the TBP phase. The nitric acid hydrolysis of TBP is also influenced by the acid concentration [24] with 10% TBP hydrolysing in 0.35, 0.55 and 1.9 hours at 8.6, 5.4 and 1.04 molar nitric acid respectively at the boiling points of the acid systems.

The loss of TBP, either via degradation and/or solubility, adds further challenges for the PUREX process, which results in additional process circuits required culminating increased costs and complexity of the PUREX process.

The aqueous solubility of solids such as ion exchangers is insignificant and may only occur if the exchange materials are degraded/decomposed and part of the polymer is cleaved from the polymeric skeleton. Other losses may occur due to particle attrition but well designed contactors will minimize this.

The acid and radiation stability of TBP presents several problems for the PUREX reprocessing operator. The formation of mono- and di-butyl phosphates and eventually phosphoric acid influences the separation of other radionuclides from U and Pu. Unless removed these TBP degradation products remain in the solvent phase and are capable of extracting other radionuclides such as FPs, in particular Zr [25] and

retard the extraction efficiency of Pu isotopes [26] thus potentially impairing the effectiveness of the PUREX process. In extreme conditions will accelerate the formation of a third phase [27,28]. These impingements are overcome by the inclusion of a solvent wash circuit. This circuit produces secondary wastes that require treatment in specifically designed equipment, e.g., evaporator. The solvent clean-up circuit with inclusion of waste treatment facilities is additional burden on capital cost.

UCLan's perceived sequential chromatographic separation (Figure 1) of fission products and minor actinides from U and Pu is unique and novel, but a major challenge. If successful it would provide a major improvement to nuclear waste management, considerably reducing the volume of high level waste, as the major offending radionuclides e.g., Cs and Sr will have been separated in the first stage from the rest of the activity. The removal of these two radionuclides would a significantly small volume in comparison to today's vitrified waste.

This versatile process could be used in conjunction with the PUREX process and/or its replacement. Positioning Stage 1 of UCLan's process up front of PUREX would significantly diminish the radiolytic degradation of TBP/diluent thus eliminating the need for solvent washing on a regular basis.

Current research at UCLan is focussing on Stage 1 i.e., to ascertain if any commercial materials are capable of selectively removing Cs and Sr from nitric and their stability under such conditions and the preparation of highly selective and stable inorganic composites for these two radionuclides.

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