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Extraction studies of gadolinium relevant to its use as neutron poison in the PUREX process

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ABSTRACT

The extraction behavior of gadolinium into tri-*n*-butyl phosphate (TBP) (0.37–1.1*M*) in *n*-dodecane (*n*-DD) as diluent from different concentrations of nitric acid (1–13.5*M*) has been systematically investigated to establish the feasibility of using gadolinium as soluble neutron poison for ensuring nuclear criticality safety during the processing of FBR spent fuel containing higher concentrations of fissile material. The effect of acidity, temperature, metal loading and gadolinium concentration on the distribution co-efficient of Gd(III) are established. The obtained results clearly indicate the feasibility to decontaminate Gd(III) under typical FBR fuel reprocessing conditions thereby enabling to qualify the final product to be pure from the point of view of nuclear poison impurity.

1. Introduction

The plutonium content in a typical Fast Breeder Reactor (FBR) spent oxide fuel ranges from 10 to 30% by weight depending on various factors. While processing this fuel through aqueous reprocessing methods employing PUREX process, nuclear criticality is an important safety issue to be addressed. To overcome this in the design of process equipment, many possibilities exists viz, designing of poison tube tanks, strategically including neutron poison sheets in the layout to reduce the effective neutron multiplication factor (k_{eff}) and so on. But all these possibilities take a large toll on the capacity of the plant if they are to be adopted effectively. Alternately, addition of soluble neutron poison was found to be more effective (Morrison et al., 1966; Eggert, 1974). Among all the elements, gadolinium is the best possible choice because of its high thermal neutron absorption cross section and its chemical compatibility with the PUREX process streams. As a result it is required only in very small quantity to ensure nuclear criticality safety even when handling higher quantity of fissile material. In addition, the solubility of gadolinium in typical PUREX process streams is high enough to be employed very effectively (Lloyd et al., 1972; Dutta et al., 2006; Vijayalakshmi et al., 2014; Desigan et al., 2012; Baumann, 1980; Gilbert et al., 1985; Rodenas et al., 1990; Rohde and Lewis, 1972; Nichols, 1962). Gadolinium nitrate has been used earlier as a soluble neutron poison to study the criticality safety of uranium (Durazzo and Riella, 2009) and plutonium solutions (Rohde and Lewis, 1972). The solvent extraction of several rare earth ions from nitric acid medium has been extensively reported. Prominent extractants that have been employed are high molecular weight amines (Feng et al., 2014), carboxylic acids (Preston and Du Preez, 1990), tri-n-butyl phosphate (TBP) (Mathur and Choppin, 1998; Ishimori and Watanabe, 1960; Peppard et al., 1957) and di-(2-ethylhexyl) phosphoric acid (D2EHPA) (Torkaman et al., 2016). As the recycled fuel specification sets a very stringent upper limit for neutron poison impurities, it is imperative to study the distribution behavior of gadolinium in PUREX solvent. Thus, the primary purpose of the present work is to generate the distribution data for gadolinium at conditions prevalent in FBR fuel reprocessing. Though extensive work has been carried out, the effect of nitric acid concentration at equilibrium both in presence/absence of uranium is yet to be studied in detail. When short cooled FBR spent fuel is reprocessed, due to the higher decay heat of the fuel, the process solutions may get heated up to temperatures as high as 50 °C depending on the process conditions and irradiation history of the spent fuel. Hence, the effect of temperature on the distribution behavior of gadolinium in TBP-nDD/HNO_3 system also has to be evaluated which is address in the present article.

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2. Experimental

2.1. Reagents and instrumentation

Nitric acid used for the experiments was 70% analytical grade of Fischer make TBP of purity 99.9% from Fluka and *n*-dodecane with purity of 99.9% from Aldrich were used. Gadolinium was used in the form of $Gd(NO_3)_3 \cdot 6H_2O$ which is 99.9% (REO) chemically pure from Alfa Aesar. The gadolinium in the stock solution was analyzed by ICP-AES (Hennebruder et al., 2004) which was then used for calibrating the spectrophotometric method using 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol (Br-PADAP) as chromogenic reagent for gadolinium estimation (Ganesh et al., 2014; Martinez et al., 1993). Stock solution of uranyl nitrate was prepared and standardized by Davies and Gray method (Davies and Gray, 1964). Free acidity was estimated by potentiometry (Ganesh et al., 2011). All other reagents used for the experiments were of analytical grade (99.9% pure) from Sigma Aldrich and Merck. Fiber optic aided spectrophotometric technique with 1 cm path length dip type probe was used to measure the absorbance.

2.2. Procedures

Solvent extraction was carried out with equal volume of organic and aqueous phases in a centrifugal vial with sufficient free volume space for effective mixing using a vortex shaker of Heidolph Reax make at a speed of 1700 *rpm* for 30 min. The two phases were then allowed to disengage completely, after which the acidity and gadolinium concentration were measured, with appropriate dilution wherever needed. The free acidity of both phases was estimated using titration with standard sodium carbonate. Gadolinium estimation in both phases was made by spectrophotometry using 5-Br-PADAP as the chromogenic reagent. All the measurements were carried out in duplicate and their average was used for the calculation of distribution coefficients. The distribution coefficient of gadolinium (D_{Gd}) was determined by the ratio of concentration of gadolinium in organic to aqueous phase at equilibrium. For studying the temperature effect on gadolinium distribution, the experiments were carried out in a double walled glass container with provisions for mixing and external jacket for temperature control as shown in Fig. 1. In all the experiments, mixing was carried out for 30 min which was sufficient for the equilibrium to be established, and then allowed to settle for about 5 min for phase separation. Experimental values were within the error band of ±5%.

3. Results and discussion

The extraction behavior of Gd(III) in TBP-HNO_3 system is very similar to the trivalent lanthanides (Bednarczky and Siekierski, 1989) and have three TBP molecules coordinated to Gd(III) in the extracted species. The overall chemical reaction is represented by the following equation (Desigan et al., 2012):

$$Gd^{3+}{}_{aq} + 3NO_3^- aq + 3TBP_{org} \rightleftharpoons Gd(NO_3)_3 \cdot 3TBP_{org} \quad (1)$$

The apparent equilibrium constant, which is defined as the product of the equilibrium constant and the activity coefficients raised to appropriate power of stoichiometric coefficients as per Eq. (1) is represented as follows:

$$K = \frac{[Gd(NO_3)_3 \bullet 3TBP]}{[Gd^{3+}][NO_3^-]^3[TBP_f]^3} \quad (2)$$

The distribution coefficient of gadolinium (D_{Gd})is defined as,

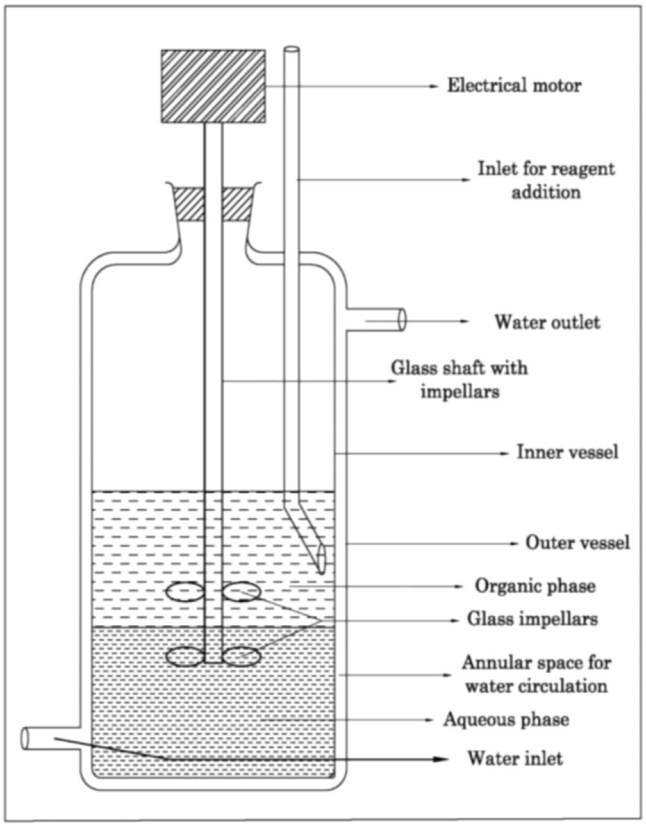

Fig. 1. Jacketed vessel with mechanical agitator.

$$D_{Gd} = \frac{[Gd(NO_3)_3 \bullet 3TBP]}{[Gd^{3+}]} \quad (3)$$

$$K = \frac{D_{Gd}}{[NO_3^-]^3[TBP_f]^3} \quad (4)$$

$$\ln K + 3\ln[TBP_f] = \ln \frac{D_{Gd}}{[NO_3^-]^3} \quad (5)$$

$$\ln K + 3\ln[NO_3^-] = \ln \frac{D_{Gd}}{[TBP_f]^3} \quad (6)$$

Classical slope analysis techniques of the data obtained from this work were performed. A plot of $\ln(D_{Gd}/[NO_3^-]^3)$ vs $\ln[TBP_f]$ results in a straight line with the slope as the stoichiometric co-efficient of TBP and intercept as ln K which is represented in Fig. 2 (Stas et al., 2005). The results indicate that, the slope of the line was 2.74 which confirmed that almost three TBP molecules is coordinated to Gd(III) in the extracted species. The influences of concentrations of Gd(III), TBP, HNO_3, $UO_2^{2+}$and temperature on the distribution coefficient of gadolinium are discussed below.

3.1. Effect of metal ion concentration

Extraction behavior of gadolinium of various concentrations (1–5 *g/L*) from nitric acid solution of fixed concentration of 3.5*M* into TBP of three different concentrations (10, 20 and 30% by

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