Progress in Nuclear Energy xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Progress in Nuclear Energy

journal homepage: www.elsevier.com/locate/pnucene

Removal of radionuclides from a HCl steel decontamination stream using chelating ion exchange resins – Initial studies

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ARTICLE INFO

Keywords:
Chelating resin
Chloride media
Radionuclide extraction
Intermediate-level waste
Breakthrough
Decommissioning

ABSTRACT

Extraction behaviours of Co(II), Cu(II), Fe(III), Ni(II), U(VI), Th(IV) and Zn(II) mixed metal solutions were examined in chloride media using chelating ion exchange resins Purolite S930+, Purolite S950, Purolite S957 and Dowex M4195 to understand mechanisms of extraction and to identify a potential steel decontamination process to reduce intermediate-level waste volume from nuclear reactor decommissioning. Effects of acidity and ionic strength were considered in batch extraction tests. Breakthrough behaviours were modelled with the Dose-Response model to give an indication to maximum loading capacities. A two-stage process for radioactive steel decontamination is proposed.

1. Introduction

Over the next decade, there are plans to decommission half of the current 15 operational nuclear power facilities in the UK (Smeed, 2016). One of the challenges presented by this decision is the potential to generate a large volume of radioactive waste that must be treated and disposed of, or stored. A report by the Nuclear Decommissioning Authority evaluated the material components of ILW waste from all sources (Nuclear Decommissioning Authority, 2013) and from a total of 310,000 tonnes of ILW, reported up to April 2013, of this 28% was steel, 26% graphite 19% was concrete, cement and sands.

Using this previous assumption of 28% steel, the predicted volume of radioactive waste that needs to be managed by the UK (CoRWM, 2006) of 353,000 m^3 of ILW, and projected median costs for generic ILW disposal and transport as £9630 per m^3 (Environment Agency, 2013), a calculated cost for steel disposal will run to an approximate value of £952 million. Thus, waste volume reduction must be a key strategy in dealing with this waste. Typical processes from the decontamination of steel involve the use of hydrochloric acid (Winard, 1991). We are currently coupling a chelating ion exchange process to remove problematic contaminants and activation products from the decontamination stream.

The Dowex M4195 bispicolylamine functionality has been shown to suppress iron extraction to below 20% while exhibiting extremely high extraction for copper in acidic media (Diniz et al., 2002). Cobalt and nickel displayed similar trends above a pH of 1 and M4195 was shown to far surpass extractive performance of iminodiacetic chelating cation exchangers for these metals in sulphate media (Mendes and Martins, 2004). The S950 aminophosphonic acid functionality has been shown to be more effective than iminodiacetic functionalities for cobalt and nickel in acidic nitrate media, and that nickel adsorption varied with acidity while that of cobalt is more dependent on resin nature (Deepatana and Valix, 2006). Bi-functional polymers aim to combat the dependence of extraction on contact time (Alexandratos and Bates, 1988; Alexandratos et al., 1991; Alexandratos and Natesan, 1999). The S957 sulfonated monophosphonic acid functionality was shown to be extremely effective for uranium; sulfonate ligands aided rapid complexation (Chiarizia et al., 1994) while the phosphonic acid ligands aided selective complexation once ions entered the matrix (Alexandratos and Natesan, 1999).

In the present study, the extractive performance of chelating ion exchange resins Purolite S930+, Purolite S950, Purolite S957 and Dowex M4195 have been examined in a series of static batch extractions for Co(II), Cu(II), Fe(III), Ni(II), U(VI), Th(IV) and Zn(II) in chloride media over a range of pH and chloride concentrations from which extraction mechanisms can be determined. Breakthrough kinetics and loading capacities of these resins have also been explored.

2. Experimental procedure

2.1. Materials

All chemicals and ion exchange resin Dowex M4195 used were of analytical grade or better and supplied by Sigma-Aldrich. Purolite

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http://dx.doi.org/10.1016/j.pnucene.2017.10.007
Received 2 February 2017; Received in revised form 27 September 2017; Accepted 16 October 2017
0149-1970/ © 2017 Published by Elsevier Ltd.

Table 1
Supplier-specified physical and chemical properties of the tested resins (Purolite®, 2017a, 2017b, 2017c; Dow®, 1998), experimentally determined wet resin density and rough small volume cost.

Name	S930+ (Purolite®, 2017a)	S950 (Purolite®, 2017b)	S957 (Purolite®, 2017c)	M4195 (Dow®, 1998)
Commercial Equivalent	Chelex 100, Diaion CR11, Lewatit TP-208, Amberlite IRC748i	Amberlite IRC747, Lewatit TP-260,	–	Lewatit TP-220, Purolite S960
Appearance	Spherical beads	Spherical beads	Spherical beads	Opaque beads
Polymer Structure	Polystyrene-DVB	Polystyrene-DVB	Polystyrene-DVB	Styrene-DVB
Type	Macroporous chelating	Macroporous chelating	Macroporous chelating	Macroporous chelating
Functional Group	Iminodiacetic	Amino- phosphonic	Phosphonic & sulfonic acid	Bis-picoyl-amine
Ionic Form	Na^+	Na^+	H^+	Weak base/partial H_2SO_4 salt
Moisture Retention	52-60% in Na^+ form	60-68% in Na^+ form	55-70% in H^+ form	40-60%
Particle Size	425-1000 μm	> 300 μm	> 425 μm	297-841 μm
Specific Gravity	1.18	1.13	1.12	–
Wet Resin Density (g/mL)	0.278	0.378	0.427	0.319
Small volume cost (£/L)	~10	~10	> 30	~120

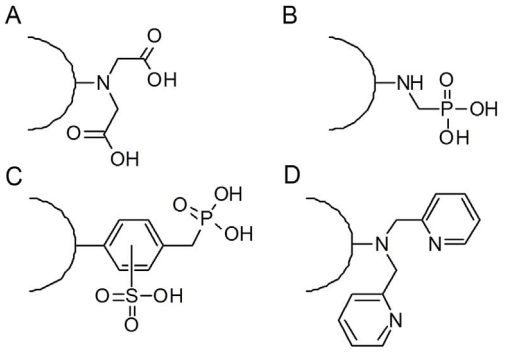

Fig. 1. (**A**) Iminodiacetic functionality of Purolite S930+ resin; (**B**) amino-phosphonic acid functionality of Purolite S950 resin; (**C**) mixed sulfonic/phosphonic acid functionality of Purolite S957 resin; (**D**) bis(picolyl)amine functionality of the Dowex M4195 resin.

S930+, S950 and S957 were kindly donated by Purolite. Some resin properties and rough costs can be seen in Table 1, and resin functionalities can be seen in Fig. 1. Note that at the time of submission, the naming of resins S950 and S957 on the Purolite production line have been replaced with “Puromet MTS9500” and “Puromet MTS9570” respectively. Small volume costs for resins were obtained from communication with Purolite.

The resins were converted from their sodium or free base forms to their hydrogen forms by contact with deionised water (DI water) followed by 20 BV of 1 M hydrochloric acid for 24 h. After this time, the resins were washed three times with 10 BV of DI water and then stored under DI water prior to use.

Stock mixed metal solutions were prepared by dissolving the respective chloride salts of Co(II), Cu(II), Fe(III), Ni(II) and Zn(II) in DI water, to which uranyl nitrate hexahydrate and thorium nitrate solutions were added. Metal analysis was carried out using either a Perkin Elmer Atomic Absorption Spectrometer AAnalyst 400 or a Thermo Scientific iCAP 6000 series ICP-OES. Calibration for both instruments was performed using standard solutions (Inorganic Ventures) diluted with 1% nitric acid.

2.2. Metal loading experiments as a function of pH and chloride concentration

A known volume of wet settled resin was contacted with a known volume of solution containing metals at a set pH (± 0.05) and shaken on a mechanical shaker for 24 h. The pH was controlled using dilute solutions of hydrochloric acid. No attempt was made to control the ionic strength of the experimental systems. The solid was allowed to settle under gravity and the solution pH measured and an aliquot taken for elemental analysis.

Uptake was determined by difference between the initial solution and the solution post contact. The extraction percentage (E%) and distribution ratio, K_d, were calculated as follows:

$$E\% = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$K_d = \frac{C_i - C_e}{C_e} \times \frac{V_{sol}}{m_{resin}} \quad (2)$$

where C_i is the initial concentration of metal (g mL^{-1}), C_e is the concentration of metal in solution at equilibrium (g mL^{-1}), V_{sol} the volume of solution in contact with the resin (mL) and m_{resin} the mass of wet resin (g). The mass of resin was calculated by converting the volume of wet settled resin using the experimentally determined wet resin densities for each preconditioned material; 0.278 g mL^{-1}, 0.378 g mL^{-1}, 0.427 g mL^{-1} and 0.319 g mL^{-1} for S930+, S950, S957 and M4195 respectively.

2.3. Slope analysis

Slope analysis is a graphical approach to determine stoichiometric coefficients in postulated equilibria from straight-line portions of appropriate plots of extraction data. In the straight line portions using equilibrium analysis, it can be theorised that a metal being extracted by an immiscible phase containing a cation exchanger, in our case a strong acid cation exchange resin, which has been preconditioned with acid, would follow the equilibrium;

$$M^{J+} + J\overline{HR} \rightleftharpoons \overline{MR_J} + JH^+$$

where the bar denotes the immiscible phase species. The value J can be determined by the slope analysis of a logarithmic plot of distribution versus pH (-log [H^+]). This plot can give an insight into the extraction mechanism and also the possible aqueous speciation of the metal ion. The caveat of slope analysis lies in the simplicity of the technique (Moyer et al., 1991). The application of slope analysis can provide simple, and often robust, answers but often as not these are more qualitative in nature and sometimes mask the complexity of the system. Non-integer values of *J* often indicate a more complex system and can be related to the activity of the immiscible phase (Danesi et al., 1970), in this case the functionality on the surface of the resin. To overcome this problem experimental work is carried out at low concentrations, low loadings, and/or constant ionic strength, where extraction behaviour is usually simpler.

2.4. Dynamic kinetic tests

The breakthrough kinetics were determined by pumping the mixed metal solution through a cylindrical column of 15.5 mm internal diameter packed with a 6 mL BV of wet settled resin at a rate of one bed volume per hour maintained by an iPump i150 peristaltic pump. Post-

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