Highly efficient fluoride extraction from simulant leachate of spent potlining via La-loaded chelating resin. An equilibrium study

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GRAPHICAL ABSTRACT
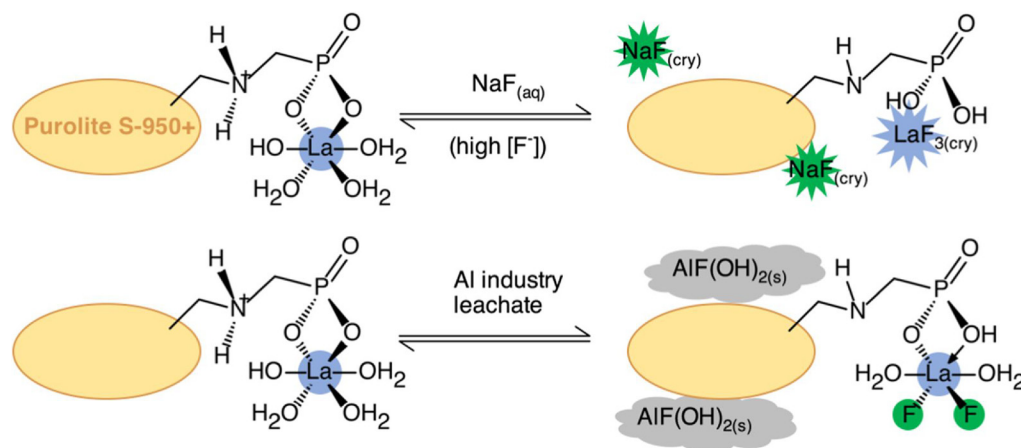
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ABSTRACT

Spent potlining (SPL) hazardous waste is a potentially valuable source of fluoride, which may be recovered through chemical leaching and adsorption with a selective sorbent. For this purpose, the commercially available chelating resin Purolite® S950+ was loaded with lanthanum ions, to create a novel ligand-exchange sorbent. The equilibrium fluoride uptake behaviour of the resin was thoroughly investigated, using NaF solution and a simulant leachate of SPL waste. The resin exhibited a large maximum defluoridation capacity of 187 ± 15 mg g^{-1} from NaF solution and 126 ± 10 mg g^{-1} from the leachate, with solution pH being strongly influential to uptake performance. Isotherm and spectral data indicated that both chemisorption and unexpected physisorption processes were involved in the fluoride extraction and suggested that the major uptake mechanism differed in each matrix. The resin demonstrates significant potential in the recovery of fluoride from aqueous wastestreams.

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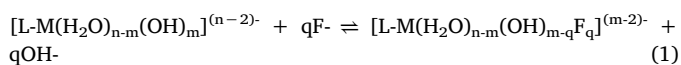E-mail address: tjrobshaw1@sheffield.ac.uk (T. Robshaw).

1. Introduction

Spent pot-lining (SPL) is a hazardous, carbonaceous waste product of the primary aluminium industry, formed from the exhausted cathodes of electrolytic cells. Over the lifespan of a cell, contaminants such as cryolite and AlF_3 diffuse through the graphite cathodic lining and ultimately into the refractory material below, causing a degradation in performance [1]. The cell is then decommissioned and the contaminated material excavated. The cathode material is known as "first-cut" SPL and the refractory shell as "second-cut". The amount of SPL currently being generated worldwide is likely in excess of $1 MT yr^{-1}$ [2,3].

The composition of first-cut SPL includes $\leq 18\%$ fluorides and $\leq 0.5\%$ cyanides [4], thus presenting a risk of fluorosis and poisoning to both humans and animals [5,6].

SPL is however, a potentially valuable resource, partially because of its high fluoride concentration. Fluorspar (CaF_2) is the root of practically all major fluro-chemicals and was recognised by the European Union in 2014 as one of the 20 most crucial minerals to recycle effectively in the immediate future [7]. Numerous industrial processes have been devised for the treatment of SPL and recycling of minerals, but at present, only the Rio Tinto Alcan low-caustic leaching and lime (LCLL) process regenerates CaF_2. This involves leaching of ground and screened SPL with water, then evaporation to precipitate NaF, before a final treatment with $Ca(OH)_2$ [8]. A large percentage of fluoride-bearing compounds are not solublised by the initial wash [9] and must be leached by a combination of NaOH and H_2SO_4 to allow safe disposal of the solid residue, yet no fluoride recovery is attempted from these waste-streams. We propose an alternative strategy, in which the separate aqueous leachates are combined, then contacted with a sorbent material that selectively extracts the fluoride.

Many techniques exist for the defluoridation of water. Established precipitation methods however, result in large volumes of low-value slurry, from which fluoride recovery is difficult [10]. Adsorption and ion-exchange techniques are a promising alternative, as the fluoride may be selectively removed under mild conditions, with no waste generated. This has led to numerous fluoride uptake studies, using sorbents such as alumina [11], activated carbon [12], chitosan [13], synthesised microporous polymers [14] and layered double hydroxide clays [15]. Some sorbents may be repeatedly regenerated and reused, with hydroxide treatment being the most common strategy [14,16]. Commercial anion-exchange resins cannot produce selective uptake, since fluoride is the least selective of all common anions towards such materials [17]. This may be overcome via a cation-exchange or chelating resin, pre-loaded with metal ions, which have a high affinity for fluoride, thereby allowing uptake via the ligand-exchange processes shown in Eq. (1) [18,19].

$$[L\text{-}M(H_2O)_{n\text{-}m}(OH)_m]^{(n\text{-}2)\text{-}} + qF\text{-} \rightleftharpoons [L\text{-}M(H_2O)_{n\text{-}m}(OH)_{m\text{-}q}F_q]^{(m\text{-}2)\text{-}} + qOH\text{-} \quad (1)$$

where L = resin functional group ligand, M = coordinated metal centre and q = 1 or 2. Al itself has been a popular metal for this purpose, given its light molecular weight, abundance and high stability constants associated with AlF_n complexes [20]. The highest reported uptake capacity for Al-loaded resins is $\sim 12 mg$ fluoride per g resin [21].

Rare earths have been similarly investigated, as they are hard metals, therefore strongly binding fluoride ligands [22]. A barrier to their industrial use for this purpose is their perceived scarcity and high cost. However, this is applicable mainly to Pr and Nd, which are desirable for production of lightweight magnets, used in hybrid car engines [23]. La and Ce in particular, have more limited industrial uses and this is reflected in the market value for their oxides, which remained in the region of £1400-1600 T^{-1} throughout 2017. In contrast, Nd and Pr oxide prices were $> £30,000 T^{-1}$ [24].

The most common resin functional groups for La-loading have been either sulfonic or aminophosphonic acids [19,25,26], with highest reported uptake capacities being higher than for the Al-loaded equivalents; in the region of $25–30 mg g^{-1}$ [27]. Most literature studies on aqueous fluoride extraction focus on uptake from analytical grade NaF solutions [28,29], sometimes with controlled amounts of competing anions added, or mildly contaminated water from aquifers [26,29]. However, data for concentrated waste-streams, containing multivalent cations, which may complex fluoride and displace resin-bound metals is lacking. Indeed, this factor compelled us to choose a more expensive chelating resin for the intended purpose, as in solutions of high ionic-strength, the loaded species of a conventional strong acid cation exchanger would be displaced by other cations in the aqueous waste, according to concentration gradients and order of selectivity, hence ruining the fluoride affinity of the resin. The only studies on actual SPL industrial leachate used calcite as a sorbent and focussed on modelling the kinetics of the uptake process [30,31]. To the best of our knowledge, no work exists on the selective removal of fluoride from leachate of SPL via metal-loaded chelating resin. Additionally, uptake behaviour has only been studied over initial fluoride concentrations $< 100 mg L^{-1}$ (Supporting Information, Table S1), whereas the leaching of SPL produces aqueous waste of fluoride concentration > 2 orders of magnitude higher [9,32]. Therefore, from a water-conservation perspective, it is desirable to investigate such uptake conditions, even though the mechanisms of uptake may be complicated. The same applies for simpler NaF-based waste-streams.

Purolite® S950+ is a macroporous, weak acid, chelating resin, consisting of a styrene/divinylbenzene backbone, with aminophosphonic acid functional groups. The Al-loaded form has previously been investigated for fluoride-removal capabilities [21]. A similar Al-loaded resin has been commercialised for industrial use [33], although only as a final water-polishing step, rather than as part of a fluoride-recovery loop. Rare earth-loading has not yet been trialled. We envisage a treatment system (Fig. 1) for SPL leachate, using La-modified S950+ columns, with NaOH treatment to elute the fluoride as NaF, then precipitation of CaF_2 with $Ca(OH)_2$ [34]. However, the thermodynamics and kinetics of uptake in such an unusual sample matrix as spent potlining leachate must first be understood. Thus we report here an investigation into the isotherm behaviour of fluoride uptake on to La-loaded Purolite® S950+, with detailed comparison between PLS and NaF solution matrices.

2. Experimental

2.1. Reagents and stock solutions

A simulant pregnant leach solution (PLS) of first-cut SPL was prepared, with concentrations calculated from characterisation work of Holywell & Bréault [4], Mahadevan & Ramachandran [35] and Pong et al. [36]. The major components of this liquor are given in Table 1.

NaF, $NaHCO_3$, NaCl, NaCNO, $K_4[Fe(CN)_6]$, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$ and $Ca(OH)_2$ (analytical reagent grade) were purchased from commercial suppliers and used without further purification. Sodium and sulfate salts were used where possible, to reflect the leaching agents used in the LCLL process [8]. Reagents were dissolved in deionised water in a polypropylene beaker. The ionic strength of the undiluted leachate was $24.8 mmol L^{-1}$, compared to $6.23 mmol L^{-1}$ for a NaF solution of equivalent fluoride concentration. The pH was 5.5. Aqueous speciation was carried out using the Aqion software package v6.4.7 [37]. Full methodology is shown in the Supporting Information, p2.

2.2. Pre-conditioning and metal-loading of the resin

Purolite® S950+ resin was kindly donated by the manufacturer in Na form. Specifications are given in Supporting Information, Table S3. Conversion to H form [38], was achieved by contacting 25 g resin (wet mass) with 1 L of 1 M HCl in a Nalgene® bottle, which was sealed and