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

Supporting Information

Table S1. Selected examples of fluoride uptake on to various sorbents reported in the literature

Metal-loaded resins					
Resin (functional group)	Loaded metal	Optimum pH	Initial F⁻ concentration (mg L⁻¹)	Maximum F⁻ uptake capacity (mg g⁻¹)	Reference
Purolite S940 (aminophosphonic)	Al	2.5	50	12.17	Bhatt <i>et al.</i> , 2004 [1]
Purolite S950 (aminophosphonic)	Al	2.5	50	6.02	Bhatt <i>et al.</i> , 2004 [1]
Duolite C467 (aminophosphonic)	Al	5-7	50	1.976	Ku <i>et al.</i> , 2011 [2]
Amberlite 200CT (sulfonic acid)	La	1-8	15	25.46	Luo & Inoue (2004) [3]
Unnamed (aminophosphonic)	La	3.5	50	31.13	Kanesato <i>et al.</i> , 1988 [4]
Indion FR10 (sulfonic acid)	La	7	11	0.470	Viswanathan & Meenakshi, 2008 [5]
Indion FR10 (sulfonic acid)	Ce	7	11	0.456	Viswanathan & Meenakshi, 2008 [5]
Duolite C466 (iminodiacetic acid)	Al	7	10	1.875	Prabhu & Meenakshi, 2014 [6]
Duolite C466 (iminodiacetic acid)	La	7	10	4.760	Prabhu & Meenakshi, 2014 [6]
Duolite C466 (iminodiacetic acid)	Ce	7	10	4.519	Prabhu & Meenakshi, 2014 [6]
Unnamed (hydroxamic acid)	Ce	4	95	9.5	Haron & Wan Yuuns, 2001 [7]
Other sorbents					
Support matrix	Functionality	Optimum pH	Initial F⁻ concentration (mg/L)	Maximum F⁻ uptake capacity (mg/g)	Reference
Activated alumina	La ³⁺	4-8	20	6.7	Cheng <i>et al.</i> , 2014 [8]
Activated carbon	La oxyhydroxides	7	80	9.96	Vences-Alvarez <i>et al.</i> , 2015 [9]
Chitosan	Mixed lanthanides	unspecified	20	4.73	Liang <i>et al.</i> , 2013 [10]

PLS aqueous speciation data using Aqion version 6.4.7

Experimental

Known concentrations of cations and anions in the PLS at 1/100 dilution, to simulate experimental conditions in section 3.2. of the main research article were inputted into the Aqion software [11]. Appropriate adjustments to pH, [Cl⁻] and [Na⁺] were made. Necessary adjustments to charge balance were made by adjustment of dissolved inorganic carbon. Output speciation took precipitation of minerals into account.

Results

The concentrations of key aqueous species (these being mainly anions, cations and neutral complexes present in significant quantities and containing Al³⁺ and F⁻) are shown in Table S2.

Table S2. Aqion calculations for Al³⁺ and F⁻ speciation in the PLS at different pHs.

Species	Concentrations (mmol L ⁻¹)		
	pH 2	pH 4	pH 8
AlF ²⁺	0.0228	0.00140	< 0.0001
AlF ₂ ⁺	0.163	0.0820	< 0.0001
AlF ₃	0.0363	0.132	< 0.0001
[Al(OH) ₄] ⁻	< 0.0001	< 0.0001	0.190
F ⁻	0.0223	0.140	0.785
HF	0.297	0.0428	< 0.0001
H ⁺	11.0	0.223	< 0.0001
OH ⁻	< 0.0001	< 0.0001	0.00139

Table S3. Manufacturer specifications for Purolite[®] S950+ [12]

Parameter	Value
Appearance	Spherical beads, off-white
Commercial equivalents	Duolite [®] C467 Lewatit [®] MonoPlus TP 260 Amberlite [®] IRC 747
Moisture retention	60-68%
Particles < 300 μm	≤ 1%
Reversible swelling H - Na	≤ 50%
Capacity (Ca ²⁺)	74 mg g ⁻¹ (1.84 mmol g ⁻¹)

Fluoride ion-selective electrode analysis and synthesis of total ionic strength adjustment buffer (TISAB)

The fluoride concentration of solutions before and after resin-contact were analysed using a Cole-Palmer fluoride ion-selective electrode. The electrode was calibrated using standards of known fluoride concentration from 0.1-10 or from 10-100 mg L⁻¹. These were made by dissolving $\geq 99.999\%$ NaF, which had been dried in an air-flow oven for a minimum of 24 h, in deionised water. Electrode readings for each sample were averaged from at least three replicates. Error values were calculated from 2 x standard deviation, then propagated as necessary. Each sample contained 50 % total ionic strength adjustment buffer and were sufficiently diluted to ensure ionic strength did not vary significantly between samples.

For synthesis of TISAB, all reagents were of analytical grade and used without further purification. In a 1 L beaker, 45.0 g NaCl was dissolved in ~500 mL deionised water, followed by 4.00 g 1,2-Diaminocyclohexanetetraacetic acid hydrate. 57 mL acetic acid were added and the water volume increased to ~800 mL. 5M NaOH was added dropwise, to increase pH to 5.5. The solution was then transferred to a 1 L volumetric flask and water volume increased to exactly 1 L.

Analysis of resin at various process stages by X-ray photoelectron spectroscopy (XPS)

Experimental

Samples were washed, ground and dried as described in the main research article. The samples were mounted for XPS analysis by pressing into In foil.

Analysis was carried out using a Kratos Supra spectrometer, with monochromated Al source and 2 analysis points per sample. The area of analysis was 300 x 700 μm . Charge neutralisation was used throughout. Survey scans were collected between 1200-0 eV binding energy, at 160 eV pass energy, with 1 eV intervals and 300 s per sweep with 2 sweeps being collected. High-resolution Al 2p, C 1s, Cl 2p, F 1s, La 3d and 4d, N 1s, O 1s and P 2p scans were collected over appropriate energy ranges (see spectra), at 20 eV pass energy, with 0.1 eV intervals. For C 1s, F 1s, La 4d and O 1s, 1 x 5 min sweep was collected. For Al 2p, Cl 2p, N 1s and P 2p, 2 x 5 min sweeps were collected and for La 3d, 4 x 5 min sweeps were collected. The increased collection time was due either to reduced sensitivity, extended energy range or both.

Attained data was calibrated for intensity, using a transmission function characteristic of the instrument, then quantified using Schofield theoretical relative sensitivity factors. All data was calibrated relative to a C 1s position of 285.0 eV for aliphatic C environments.

Results and commentary

Table S4. Average surface composition (atomic %), of the resin at various process stages

Sample	Al	Ca	C	Cl	F	La	N	O	P	Na
H-950+	<0.1	<0.1	76.2	<0.1	<0.1	<0.1	3.8	15.2	4.9	<0.1
La-S950+	<0.1	0.8	74.5	<0.1	<0.1	0.6	3.0	14.6	6.3	<0.1
La-S950+ post-NaF-contact	<0.1	<0.1	69.7	<0.1	6.7	1.6	2.2	10.8	5.0	4.2
La-S950+ post-PLS-contact	3.9	0.3	67.8	<0.1	2.9	0.7	4.2	14.6	5.8	<0.1

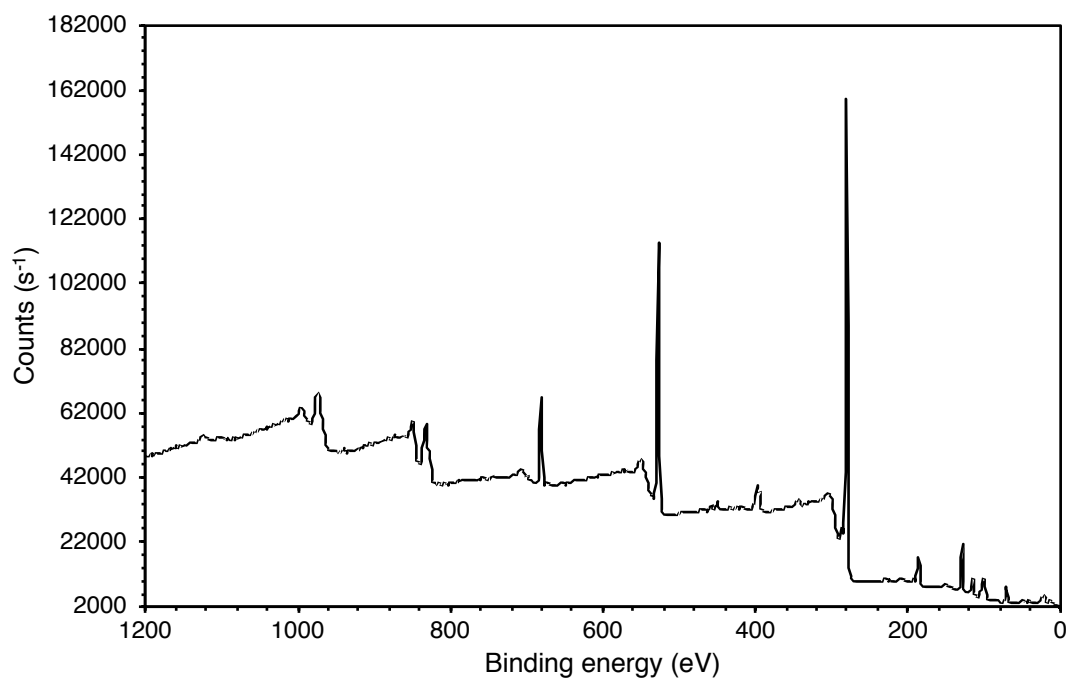


Fig. S1. Survey scan of La-S950+ treated with PLS, $[F^-] = 1500 \text{ mg L}^{-1}$. \blacklozenge = La 3d_{5/2}, \square = F 1s, \star = O 1s, \bullet = N 1s, \blacklozenge = C 1s, \blacktriangleright = P 2p.



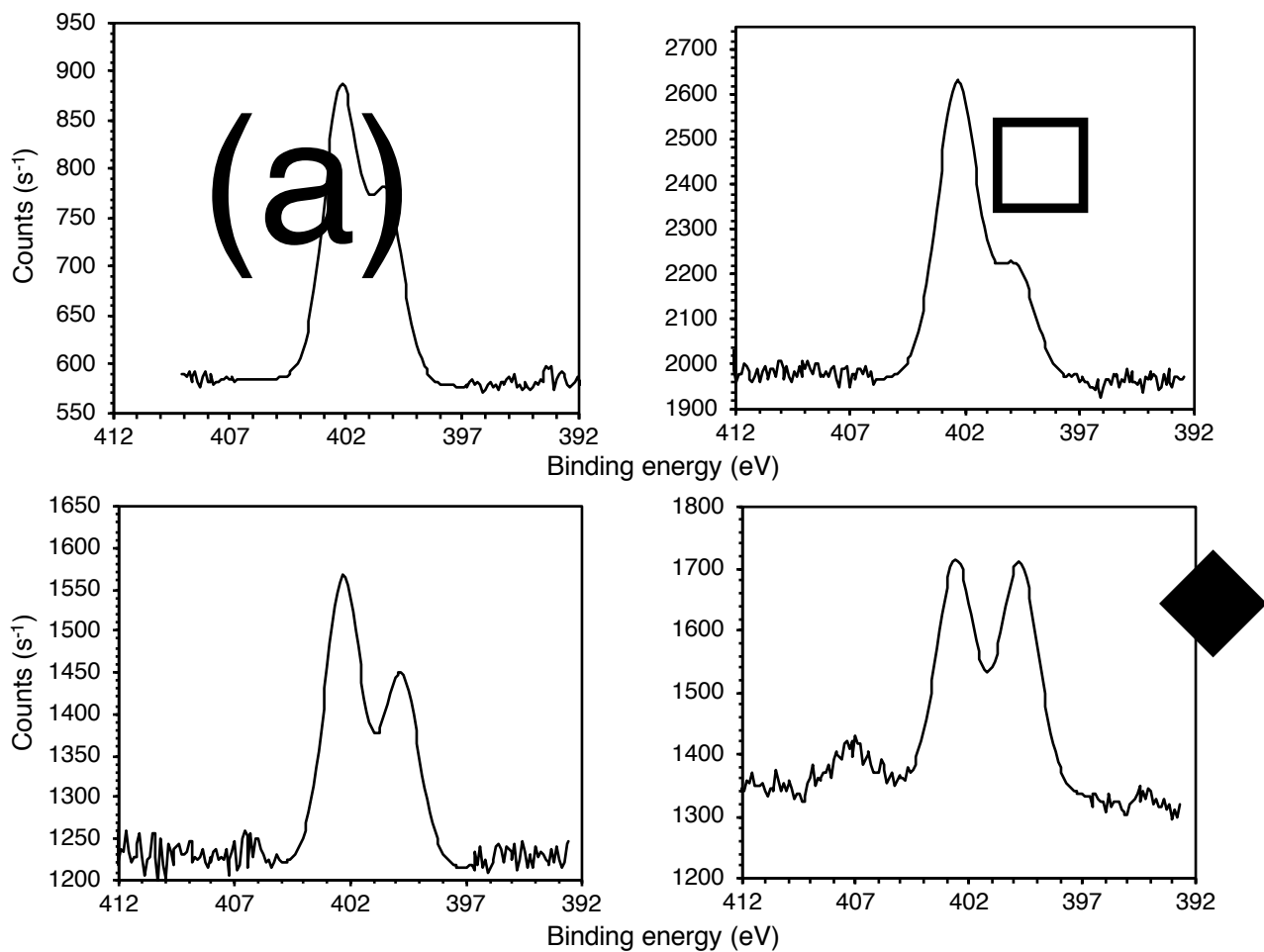


Fig. S2. High resolution N 1s spectra for the resin at various process stages: (a) H-S950+, (b) untreated La-S950+, (c) La-S950+ treated with NaF, [F⁻] = 1500 mg L⁻¹ and (d) La-S950+ treated with PLS, [F⁻] = 1500 mg L⁻¹. ◆ = trivalent N. □ = protonated N.

Table S5. Results of curve-fitting and analysis of N, O and La chemical environments present in samples of H-S950+ and La-S950+ at various process stages

Sample	Binding energy (eV)	Atomic concentration (%)	Assignment
N 1s			
H-S950+	400.0	39.1	Trivalent amine
	402.1	60.9	Protonated amine
La-S950+ untreated	399.9	27.4	Trivalent amine
	402.3	72.6	Protonated amine
La-S950+ NaF-treated	399.9	40.2	Trivalent amine
	402.3	59.8	Protonated amine
La-S950+ PLS-treated	399.8	50.2	Trivalent amine
	402.6	49.8	Protonated amine
O 1s			
H-S950+	531.5	49.2	P=O
	533.0	50.8	P-O-H
La-S950+ untreated	531.5	62.3	P=O
	533.3	37.7	P-O-La
La-S950+ NaF-treated	531.4	51.6	P=O
	532.9	48.4	P-O-H*
La-S950+ PLS-treated	532.6	100	AlF(OH) ₂
La 3d 5/2			
La-S950+ untreated	835.8 / 839.1	100	Coordinated La with OH / H ₂ O ligands
La-S950+ NaF-treated	829.9 / nd	14.8	Unknown*
	833.5 / nd	12.6	Unknown*
	837.4 / 841.5	72.6	LaF ₃
La-S950+ PLS-treated	831.9 / nd	29.2	Coordinated La with 2 F ⁻ ligands
	836.2 / 839.4	70.8	Coordinated La with 1 F ⁻ ligand

nd = not detectable.

* Due to precipitation of crystalline LaF₃ at high [NaF], the aminophosphonic group is no longer chelated to a metal centre and is presumably reprotonated, consistent with the binding energies observed.

*These environments do not match those observed in the untreated or PLS-treated sample. It is possible they may represent coordinated La centres with 1 and 2 fluoride ligands and those environments observed in the PLS-treated sample may be more complicated species where the La interacts with the 1st layer of AlF(OH)₂ precipitation via fluoride or hydroxide bridging ligands.

The binding energy of the quarternary amine environment does not change significantly upon La coordination to the resin, suggesting that it remains protonated, rather than forming a coordination bond to the La centre. Previous XPS studies, for example Lavallee *et al.* [13], have shown that the N 1s binding energy alters by ≤ 0.8 eV upon abstraction of a proton and formation of a coordination bond to a metal centre.

The extent of amine protonation actually increases slightly upon coordination of La centres to the resin, since the process releases protons from the -OH groups, causing the solution to become more acidic. However, the ratio of protonated amines drops markedly upon contact with NaF solution and PLS, indicating the release of protons from the ammonium groups, as described in the main article.

Uptake of mixed anions by H-S950+ and La-S950+

Experimental

Equi-mass solutions of F^- , Cl^- , Br^- , NO_3^- , PO_4^{3-} and SO_4^{2-} (150 mg L^{-1}) were made up by dissolving their Na salts in deionised water $\sim 200 \text{ mg}$ of H-S950+ or La-S950+ (dry weights) were contacted with 25 mL mixed anions solution. Pre- and post-contact solution samples were diluted appropriately and analysed by ion-chromatography using a Thermo-Fisher ICS-900, fitted with a Dionex IonPac® AS23 $4 \times 250 \text{ mm}$ column and using $Na_2CO_3/NaHCO_3$ eluent. The instrument was calibrated with solutions of $1\text{-}10 \text{ mg L}^{-1}$, which were diluted from 1000 mg L^{-1} analytical standards, purchased from Fisher Scientific. The equilibrium uptake capacity for the various anions (q_e) was calculated using the procedure described in the main research article.

Results

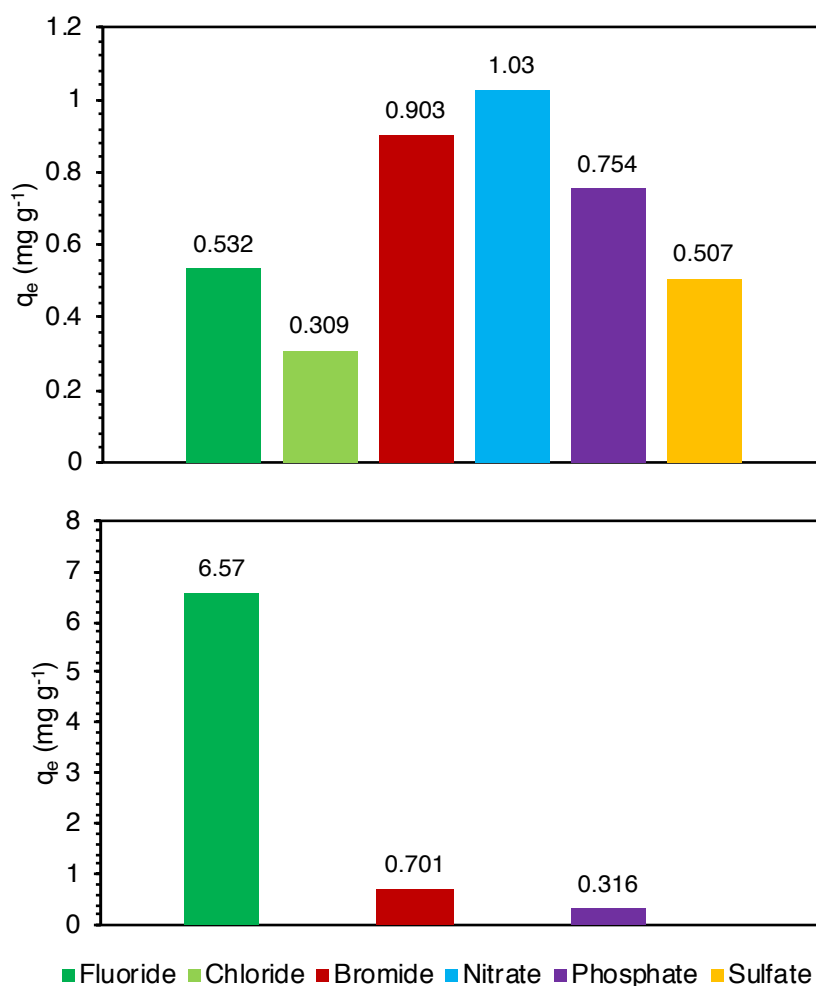


Fig. S3. Uptake of common anions from 150 mg L^{-1} equi-mass solution by (a) H-S950+ resin, (b) La-S950+ resin (Cl^- , NO_3^- and SO_4^{2-} uptake were $< 0.01 \text{ mg g}^{-1}$).

Effect of sorbent dose on resin performance

The standard experimental procedure, detailed in section 2.4. of the main research article, was followed, with variation of the mass of La-S950+ from 100-1000 mg (dry weight), keeping all other variables constant. Results in terms of % fluoride extraction and q_e are presented in Fig. S4.

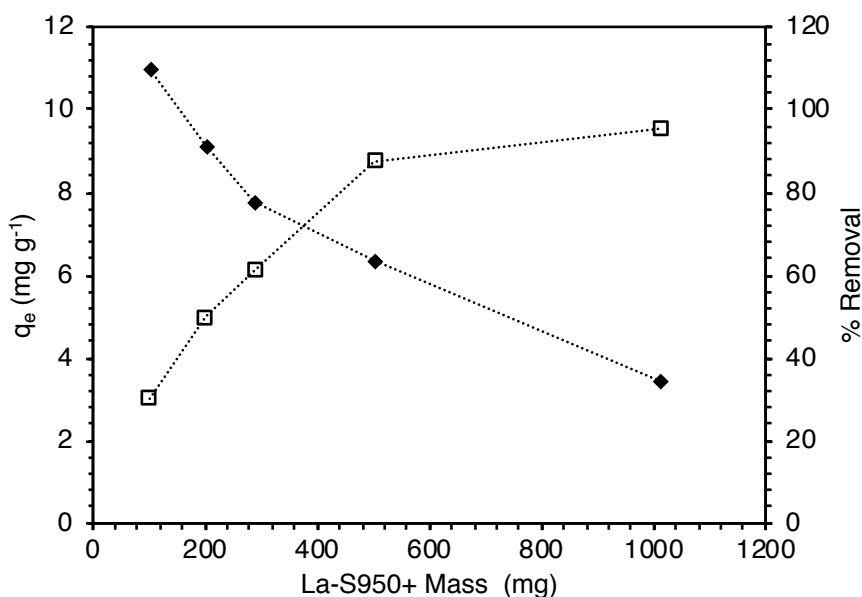


Fig. S4. Fluoride uptake of La-S950+ and % fluoride removal from PLS with varying mass of resin. Liquor dilution = 1/10 (V/V). Volume of liquor = 25 mL. Initial fluoride concentration = 150 mg g⁻¹. Error is too small to be graphically represented. \blacklozenge = uptake capacity. \square = % removal.

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