Development of a combined leaching and ion-exchange system for valorisation of spent potlining waste

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Abstract

This work aims to contribute to addressing the global challenge of recycling and valorising spent potlining; a hazardous solid waste product of the aluminium smelting industry. This has been achieved using a simple two-step chemical leaching treatment of the waste, using dilute lixiviants, namely NaOH, H_2O_2 and H_2SO_4 , and at ambient temperature. The potlining and resulting leachate were characterised by spectroscopy and microscopy to determine the success of the treatment, as well as the morphology and mineralogy of the solid waste. The acidic and caustic leachates were combined and the fluoride component was selectively extracted, using a modified ion-exchange resin, in fixed-bed column experiments. Solid-state analysis confirmed that the potlining samples were a mixture of contaminated graphite and refractory materials. A large quantity of fluoride was solublised by the leaching process, as well as numerous metals, some of them toxic. In column-loading studies, the resin performed above expectations, based on previous studies, which used a simulant feed, extracting fluoride efficiently from leachates of significantly different compositions. Overall, the study accomplished several steps in the development of a fully-realised spent potlining treatment system.

Keywords: Spent potlining, leaching, ion-exchange, fluoride, aluminium, resource recovery

1. Introduction

Spent potlining (SPL) is a hazardous waste product of aluminium smelting operations, which is generated at the end of the lifespan of a smelter electrolysis cell. There are two distinct fractions, these being "first-cut", composed mainly of graphitic material from exhausted cathode blocks, and "second-cut", formed mainly of cement and brick from the refractory lining underneath. Both cuts are heavily contaminated with fluoride-bearing compounds, with reported fluoride concentrations $\leq 20 \%$ [1]. Various other chemical species are also present, including $\leq 1 \%$ cyanides [2]. Estimates for the average mass of SPL generated per tonne of aluminium produced vary between 7 and 50 kg [3], but an average of ~25 kg is frequently given [4, 5]. The estimated global production of aluminium in 2018 was 64.3 MT, meaning ~1.61 MT of SPL was also created [6]. Of this, it is estimated that 50 - 75 % of the waste was deposited either in landfill facilities or over-ground buildings [1, 7].

SPL has been explicitly classified as hazardous waste in a number of countries, due to its leachable fluoride and cyanide components and potential to evolve flammable mixtures of CH₄, NH₃ and H₂ gases [4, 8]. A number of utilisation strategies have been developed for the waste: SPL may be added to cement clinker kilns, to improve firing conditions [9]. It can be partially substituted for fluorite (CaF₂) in Arc furnaces for steelmaking [10], or used as an additive in pig iron and rock wool production [11, 12]. The issue with all such uses is only relatively small amounts of SPL may be used, otherwise process complications ensue [9, 13]. Accordingly, various treatment systems for SPL are also in use, with the goal of converting the waste to an environmentally-benign form. The majority are pyrometallurgical, using the calorific value of the SPL to power a furnace and combust the carbon component [14, 15]. These however, are undesirable from a CO_2 emissions perspective. The only

operational hydrometallurgical process is the low caustic leaching and lime (LCLL) method developed by Rio Tinto Alcan. This has a throughput capacity of 80,000 T yr⁻¹ and produces an inert carbon/cement mixture, which is landfilled, and CaF₂, which can be reused by smelters [16].

The LCLL process recovers the fraction of fluorides which are water-leached from SPL. Lisbona *et al.* however, showed that the great majority of fluoride compounds remain within the SPL matrix after water-washing [17]. Fluoride is rapidly becoming a scarce resource, as the only major geological reserves are in the form of fluorite, of which there are < 35 years-worth remaining globally. Fluorite has been classified as a "critical" mineral by the European Union for future conservation since 2014 [18] and its market price is on a long-term upwards trend [19]. Therefore, there is a clear impetus for a more efficient hydrometallurgical treatment, which will solublise and moreover, *recover* a greater fraction of the fluoride content of SPL.

A number of different leaching treatments for SPL have been researched. Only a very small number of single-step treatments have been proposed, one using chromic acid as the lixiviant [20]. This reduced the fluoride content in the solid output to < 150 mg kg⁻¹, but an estimated 10 - 11 % alumina (Al₂O₃) remained in the waste, Al³⁺ salts, in acidic conditions, have also been favoured as lixiviants [17]. The advantage of this approach is that an aluminium hydroxyfluoride (AHF) hydrate product can be precipitated from the leachate, which may then be converted to AIF₃ and recycled directly back into aluminium smelters [21]. However, it achieves only 76 - 86 % fluoride extraction [22, 23]. Dilute caustic leaching has also been investigated and found to extract 70 - 90 % of the total fluoride content of SPL [24]. More recently, caustic leaching has been enhanced by ultrasonication techniques, as shown by Xiao et al. [25]. This technique has afforded a solid residue of \leq 94.7 % carbon. It should however be noted that the SPL used in this study was first-cut material only and the majority fraction of SPL excavated from decommissioned smelter cells is a mixture of first- and second-cut [17]. It is generally recognised that multi-step leaching is required to reduce the concentrations of fluoride and other contaminants in the solid residue to a level safe to landfill [16, 26]. Shi et al. used leaching conditions of 2.5 M NaOH, then 9.7 M HCl, both at 100°C, attaining carbon of 96.4 % purity [26]. Li et al. achieved a carbon purity of 95.5 % after a leaching treatment using first, deionised water and second, acidic aluminium anodizing wastewater [3]. However, the SPL used in the instance was again first-cut in origin. The residual fluoride concentration in the carbon residue was also not reported. Neither previous study addressed the issue of labile cyanide destruction in the leachate. It is arguably necessary, from an environmental and economic perspective, that an optimum treatment system should recover close to 100 % of the trapped fluorides within SPL waste. It should furthermore deal effectively with all grades of the waste, rather than a selected fraction.

Our research group has conceptualised a treatment system, capable of dealing with all SPL cuts (Figure 1). It aims to mobilise > 95 % of fluoride-bearing contaminants via a two-step leaching treatment. The two leachate streams are then combined, whilst ensuring minimal precipitation, producing a liquor of high ionic strength. This however is likely too complex to afford recovery of commodity chemicals of high purity by precipitation. Therefore, an ion-exchange step must be introduced, to immobilise the fluorides within a solid-phase extractant, before they are eluted as an analytically pure and concentrated solution. A lanthanum-loaded, chelating, weak acid cationexchange (WAC) resin was chosen for this purpose. The chemical functionality, modification and uptake behaviour has been reported in our previous work and is beyond the scope of this study. However, key information is seen in Figures S1 – S2. The adsorbent has extracted fluoride from a simulated SPL leachate with an efficiency of 126 mg q⁻¹ via a unique complexation reaction between La centres and aqueous aluminium hydroxyfluorides (AHFs) [27]. It was also observed to load efficiently in simulated industrial conditions using a mini resin column [28]. We were able to elute a solution of aluminium and fluoride ions, relatively free of cocontaminants, from which it was calculated that synthetic cryolite (Na₃AIF₆) was a viable and valuable recovery product. However, the elution behaviour of this column was not optimised and it is vital to prove that the ion-exchange system performs equivalently in treating actual SPL leachate, as opposed to a simplified simulant solution.



Fig. 1 Simplified flow diagram showing the leaching side of the proposed SPL treatment system

This article presents a simple, rapid leaching treatment of mixed-cut SPL, based on the principles of the LCLL process, consisting of first, NaOH/H₂O₂, then H₂SO₄, at mild concentrations and temperatures. The leachates are characterised in detail, with attention paid to their anionic make-up, which is a feature inadequately documented in the literature so far. Finally, we demonstrate the feasibility of the proposed ion-exchange circuit implementation via column loading studies, showing that resin uptake performance actually exceeds results achieved previously with a simulant feed.

2. Experimental

2.1. Materials and Reagents

Mixed-cut SPL, of various grades and ages, was kindly provided by Trimet Aluminium (Essen, Germany). All purchased reagents were of analytical grade or better. Deionised water was used throughout. H_2SO_4 and H_2O_2 (30 % aqueous solution) were purchased from Sigma Aldrich. NaOH pellets were purchased from Fisher Scientific. PurometTM MTS9501 was kindly donated by Purolite and converted into La-loaded form (which will be referred to as La-MTS9501) by the procedure previously reported [27].

2.2. Preparation of SPL prior to leaching treatment

The as-received SPL ranged from a fragment size of fine powder to pieces ≤ 5 cm in diameter. The larger pieces were fed into a jaw crusher to be reduced in size. The fractions of each sample were then separated, by sieving, into 3 grades, these being > 3/8 inch, 3/8 inch – 1.18 mm and < 1.18 mm. Three different samples, designated A, B and C, were identified by visual inspection as having significantly different ratios of cementious to carbonaceous material (Figure S3), thus representing reasonable limits of material that could be provided for processing. Previous research has shown that a particle size of ~1.18 mm represents the threshold, below which, leaching treatments are generally not more effective [17]. Therefore, the smaller two grades for samples A, B and C were carried forward to the chemical leaching trials.

2.3. Solid-state characterisation of materials

For powder X-ray diffraction (PXRD) spectroscopy and scanning electron microscopy (SEM) analysis, SPL samples, at various process stages, were ground with a mortar and pestle, inside a glove bag. PXRD was performed using a Bruker D2 phaser, with diffractograms matched using the ICDD database [29]. SEM samples were mounted onto aluminium stubs, using carbon tape and were analysed, without any coating treatment, using a Jeol JSM6010 microscope. Quantification of C, H, N and S for leached samples was performed using a Perkin Elmer 2400 CHNS/ 0 Series II Elemental Analyzer.

2.4. Leaching treatment of SPL

All leaching treatments were performed at ambient temperature (~ 20°C). In a typical caustic leaching experiment, 2.0 g SPL was weighed into a large polypropylene beaker, fitted with a large magnetic stirrer. A 100 mL solution of NaOH at pH 11.0, including 10 mL H₂O₂ was added and the suspension was stirred at 200 rpm for 3 hrs. In initial studies, the complete oxidation of cyanide was checked using ion chromatography (IC), which is described in section 2.5. After this time, the NaOH concentration was increased to 1 M and the total volume to 250 mL. Leaching proceeded for a further 3 hrs, after which the suspension was gravity filtered. The leachate was conserved for analysis and subsequent ion-exchange studies. The solid residue was briefly rinsed with 250 mL water, then dried in an air-flow oven at 50°C for a minimum of 24 hrs, before being conserved for future experimentation. In a typical acidic leach, 2.0 g SPL was again weighed into a large polypropylene beaker, with stirrer. To this was added 250 mL 0.5 M H₂SO₄ and the suspension was stirred at 200 rpm for 3 hrs. Similar separation procedures to the caustic leach were then used. The solid:liquid ratio was chosen based on the efficiency reported by previous researchers [17, 23] and the aim to match the resulting [F-] and [Al3+] with the simulant leachate used in previous work. The rinsing water used between leaches was analysed for fluoride and cocontaminant concentration. However, levels were found to be insignificant compared to caustic and acidic leachate and this water was not conserved.

2.5. Characterisation and mixing of leachates

The majority of elemental quantification was achieved by inductively-coupled plasma mass spectroscopy (ICP-MS), using an Agilent 7500CE spectrometer by diluting samples appropriately in a 1 % HNO₃ matrix (Trace Select grade). Anions were quantified using a Metrohm 883 Basic IC plus IC system, fitted with a Metrosep A Supp 5- 4 x 150 mm column and using Na₂CO₃/NaHCO₃ eluent. Samples were diluted appropriately with deionised water. Fluoride was also quantified by potentiometry, using a Sciquip ion-selective electrode (ISE), using total ionic strength adjustment buffer (TISAB) solution. A number of samples were cross-measured by both methods during data collection and results were consistently in agreement within 2 %.

Acidic and basic leachates were combined by pipetting appropriate volumes into polypropylene vials, followed by any necessary pH adjustment, using H₂SO₄ or NaOH. Any precipitates were collected by vacuum filtration of the suspension through a sintered glass funnel, followed by drying of the solids via air-flow oven as previously described. Precipitates were characterised by PXRD, as previously mentioned. Theoretical aqueous speciation data was determined using the Aqion computer programme [30]. Concentrations of each species were inputted to the programme, according to ICP-MS and IC data. Charge balance was achieved by adjusting either [Na+] or [SO4²-].

2.6. Fluoride uptake by La-MTS9501 in fixed-bed column studies

La-MTS9501 resin (5.50 mL wet settled volume, 1.79 g dry mass) was packed into a miniature polypropylene column, fitted with porous frits above and below the resin bed. This was connected, as a reverse-flow system, to a Watson Marlow 120U peristaltic pump, using Watson Marlow Marprene[®] tubing (0.8 mm internal diameter). The experimental setup is shown in the Supporting Information, Figure S4. The system was calibrated over a period of 24 hrs to give a flow rate of 1 bed volume (BV) per hr (BV = an equivalent volume of inlet solution to that of the mass of the resin bed). The combined leachates were thus passed through the resin column. Eluent was collected in 0.5 BV fractions and analysed for fluoride concentration, using the ISE. A number of dynamic breakthrough models were used to attempt to describe the data (Supporting Information, p3).

3. Results and Discussion

3.1. Solid-state characterisation

The attained PXRD diffractograms, as expected, showed a large variety of crystalline species in the untreated SPL samples and substantial variation in the amount of mineral contamination between the

three samples, relative to their graphitic content (Figure 2). In the mixed-cut samples, there was also an amorphous component, which is believed to be closely related to NaAlSi₃O₈ (albite) [31]. After the caustic leaching treatment, some crystalline species were absent or obviously reduced in concentration in the diffractograms, but only the full leaching process returned diffractograms that showed principally graphite and only trace levels of contaminants. The effect of the leaching treatment is shown in Figure 2. The full array of diffractograms may be seen in Figures S9-S22.



Fig.2 Selected PXRD spectra of SPL samples. (a) sample B 1.18 mm – 3/8 inch as received, (b) sample B 1.18 mm – 3/8 inch after full leaching treatment, (c) sample C 1.18 mm – 3/8 inch as received, (d) sample C 1.18 mm – 3/8 inch after full leaching treatment

Compared to previous SPL characterisation attempts, sample C appeared to be relatively free of contamination, with NaF being the only significant species present, apart from graphite. Li *et al.* reported a similar XRD spectrum for, first-cut SPL, to Figure 2c [3]. Other researchers have reported high levels of alumina (Al₂O₃), CaF₂, cryolite and diaoyudaoite in first-cut material [17, 26]. There have been few attempts to characterise second- or mixed-cut SPL by PXRD, with the exception of Tschope *et al.* [32], who did not find evidence of Na₂CO₃ hydrate or SiC. However, the species observed in this instance are predictable, given the known components of a smelting cell. Portland cement and fire brick would be expected to contain a large SiO₂ component [33], whilst the sidewall bricks of a smelting cell can made entirely of SiC, depending on design [34].

Selected SEM data is seen in Figure 3. Again, the full set of micrographs may be viewed in the Supporting Information, S23-S25. The elemental composition of the material, determined by point EDX analysis in the regions denoted with Greek symbols, is shown in Table 1.



Fig. 2 SEM images of SPL samples: (a) sample A < 1.18 mm as received, (b) sample A < 1.18 mm as received EDX fluorine mapping, (c) sample C < 1.18 mm as received, (d) < 1.18 mm after full leaching treatment. α , β and γ symbols denote areas in which point EDX analysis was performed

Region	Element	Mass %	Atomic %	Sigma	Line
αa	0	42.07	51.85	8772	К
	Na	45.85	39.32	12730	K
	Al	12.08	8.82	2615	K
β	С	75.15	83.70	31340	К
	0	11.98	10.02	3959	K
	Na	8.70	5.06	8348	К
	Al	1.26	0.63	1160	К
	Zn	2.91	0.59	1614	L
γ	С	34.48	45.59	2438	K
•	0	22.61	22.45	2809	К
	F	16.03	13.40	1865	К
	Na	26.88	18 56	5925	к

Table 1	Point	EDX	analysis	of	selected	regions	of SPL	samples

^aThis point also produced a peak in the spectrum corresponding to Si K line (expected at 1.739), but this was not recognised by the detection software.

Figure 3a confirms that a large fraction of second-cut material was present in sample A. The accompanying EDX mapping (Figure 3b) suggested that the distribution of fluorides within the material, at the microscale, was strongly heterogenous. The visible crystalline precipitation in Figure 3c appeared to be NaF, according to elemental composition (Table 1) and was unsurprisingly absent following the leaching treatment (Figure 2d). Needle-like formations of NaF crystals have previously been reported from investigations of exhausted smelter cells [31].

3.2. Leachate characterisation

Table 2 shows the quantities of major chemical species that were mobilised by the two leaching treatments. Data for the more minor contaminants are shown in Table S1.

Table 2 Quantities of major chemical species leached from each SPL sample, determined by ICP-MS (cations) and IC (anions)

Leaching treatment	Sample	Leached species													
		F ⁻ (%)	NO₃ ⁻ (mg g⁻¹)	SO₄²- (mg g⁻¹)	PO₄ ³⁻ (mg g⁻¹)	AI (%)	Na (%)	Ca (%)	Si (%)	Cu (mg g⁻¹)	Fe (mg g⁻¹)	K (mg g ⁻¹)	Ti (mg g⁻¹)	Mg (mg g⁻¹)	Zr (mg g ⁻¹)
caustic	A < 1.18 mm	5.64	<10	755	152	1.15		0.0372	1.71	0.960	155	1240	78.7	3.84	<5
caustic	A 1.18 mm - 3/8 inch	22.1	<10	480	69.2	0.196		0.0435	1.18	3.28	52.6	612	48.0	11.5	<5
caustic	B < 1.18 mm	7.58	<10	785	97.6	1.12		0.0325	1.56	0.936	138	833	53.4	1.87	<5
caustic	B 1.18 mm - 3/8 inch	9.72	<10	620	133	2.49		0.0264	1.39	<0.5	65.4	757	83.1	1.65	<5
caustic	C < 1.18 mm	9.70	<10	1150	146	2.00		0.0470	0.409	2.45	102	564	5.39	4.41	<5
caustic	C 1.18 mm - 3/8 inch	9.04	<10	3270	89.3	1.06		0.0383	0.460	<0.5	88.6	394	26.5	3.48	<5
	average	10.6	<10	1180	114	1.34		0.0374	1.12	1.44	100	734	49.2	4.46	<5
	Standard deviation	5.83		1050	33.7	0.804		0.0074	0.559	1.16	39.9	293	29.9	3.62	
acidic	A < 1.18 mm	0.403	3060		179	4.42	6.43	1.32	4.63	35.8	15500	2900	742	845	141
acidic	A 1.18 mm - 3/8 inch	0.129	669		164	4.43	8.93	1.99	5.18	5.72	5550	6670	794	103	251
acidic	B < 1.18 mm	0.364	279		86.0	3.31	4.63	1.20	3.50	14.2	3540	618	760	814	122
acidic	B 1.18 mm - 3/8 inch	0.103	667		<15	2.94	4.03	0.792	3.69	11.2	2650	102	819	802	88.9
acidic	C < 1.18 mm	0.651	2940		123	1.20	1.27	0.754	0.519	47.6	16100	178	227	424	16.7
acidic	C 1.18 mm - 3/8 inch	0.761	2930		162	1.25	1.54	0.675	0.401	295	8090	96.0	150	444	25.3
	average	0.402	2180		143	2.92	4.47	1.12	2.99	68.3	8570	1760	582	727	108
_	Standard deviation	0.267	1170		37.9	1.44	2.93	0.500	2.05	112	5910	2640	307	242	86.5

As expected, a large fraction of the SPL fluoride content was mobilised by the caustic leach [24]. This would have included most of the NaF originally present, which previous studies, and indeed the LCLL process, have shown to be mainly removed by water washing [3, 16]. Our work however, shows that both caustic and acidic leaching conditions decrease the quantity of NaF within the solid material (this is seen for example, in Figures S11-S13). NaF is highly water soluble (~ 4 g L⁻¹ at ambient temperature), hence it is likely that the different lixiviants solublise different fractions of the SPL matrix, allowing the leaching solution to access further trapped NaF crystals. NaF was only observed in large quantities in sample C, with most fluoride in the other two received samples being more complex species. The other main SPL contaminants soluble in base are Na₃AlF₆ and Al₂O₃. The latter was surprisingly not detected in this study, although it is not always present in SPL samples [31]. Major contaminants diaoyudaoite and CaF₂, in contrast, are only soluble in acidic conditions. This is seen most clearly in Figure S12.

Although the quantity of fluoride mobilised by the acid leach was, on average, ~ 20 times less than by the basic leach, it is likely a necessary step to reduce the fluoride concentration in the residual solid to a level that would allow classification as non-hazardous waste. There are a range of national and international classifications for solid waste-forms, which govern the level of control required with respect to landfill disposal. This paper will refer throughout to criteria used by the European Union (Council Decision annex 2003/33/EC) [35]. It can be seen from Table 2 that the caustic leaching treatment also does not fully solublise a number of hazardous metals. Considering an average across all samples studied, the SPL, post-caustic leaching, would contain leachable quantities of fluoride (\leq 4,000,000 mg kg⁻¹), Cu (\leq 68,000 mg kg⁻¹), Cr (\leq 33,000 mg kg⁻¹) and Ni (\leq 20,000 mg kg⁻¹). All of these are greatly in excess of the EU maximum allowable levels for 'landfilled hazardous waste', these being 50, 100, 70 and 40 mg kg⁻¹ respectively [35]. This demonstrates the necessity of the

acidic leach. This research group is currently conducting trials on the residual barren SPL samples to determine leachability of remaining contaminants.

The total amount of fluoride in the SPL is lower than has been reported for previous samples. Lisbona *et al.* analysed samples from a now disused smelted in the United Kingdom and found the fluoride concentration to be > 19 % [17]. Xiao *et al.* reported a concentration of ~13 % in a sample sourced from China [25]. These examples however, were both first-cut only material, in which the fluoride and Na content is markedly higher [1].

Any labile cyanide in the samples was oxidised to cyanate via the initial peroxide treatment, then caustic leachate samples were checked, during IC analysis, for the presence of a cyanate peak. This peak was not detectable above the baseline for any of the samples analysed, at a dilution factor of 10. It can therefore be assumed that the great majority of cyanide present in this particular source of SPL was converted to ferrocyanides or ferricyanides, most likely Na₄Fe(CN)₆ and Na₃Fe(CN)₆, which is known to occur when the waste is exposed to the environment over time [36]. These species may ultimately end up in the ion-exchange circuit and specifically, the wastewater from the fluoride and Al elution process. This water would also contain other toxic species and its potential treatment has been discussed in previous work [28].

The approximate composition of the SPL material, derived from the leaching data can be compared to values given by Holywell and Bréault [1] (Table S3), which is often quoted in the literature as being an accurate range [27, 37]. Given the relatively low fluoride and cyanide contamination identified in this report, it is likely that the original cells were of prebake, rather than Söderberg design [1]. The apparent concentrations of AI Fe, Ti and Mg were considerably lower than expected, although it should be noted that our values are based on the total leachable content under the conditions stated and should not be considered total quantification values. Our data suggested there was no increase in leaching efficiency between the two size fractions.

The anionic composition of the leachates is of particular interest compared to our previous studies, with respect to competition and suppression effects on the uptake of fluoride during the ion-exchange treatment. We predicted a greater NO_3^- concentration, but under-predicted the SO_4^{2-} concentration [28]. This was partially due to considering only the contribution from the acid lixiviant, rather than this and the contribution from the material itself [38]. SO_4^{2-} has only weak affinity for AI^{3+} , but at such high concentrations, $AISO_4^+$ and $AI(SO_4)_2^-$ are predicted to form [30] and this could partially suppress the formation of aqueous aluminium fluorides, hence interfering with the resin uptake mechanism.

In terms of the timescale required for effective leaching, the treatment described herein is Comparable to most literature procedures. The alkaline H_2O_2 pre-leaching cyanide-oxidation step could possibly be shortened to improve efficiency, but because of the complete absence of labile cyanide in these samples, this could not be assessed. One advantage of this treatment is that it operates at ambient temperature, whereas most studies have performed leaching at elevated temperature, finding the efficiency to be improved [20, 26]. A comparison of laboratory-scale leaching treatments is shown in Table S2. This demonstrates that our proposed treatment uses much higher dilutions of lixiviants than has been previously attempted [26]. Temperature was not considered as a variable in this work, as the uptake capacity of La-MTS9501 decreases at elevated temperature [28]. Hence it would be more practical industrially for both the leaching and ion-exchange sides of the process to operate at ambient temperature.

The variability of key chemical species concentrations within the range of samples appears to be very high (Table 2), which is rarely discussed in previous studies. This reinforces the need for the proposed ion-exchange system to handle an inlet stream of variable composition.

3.3. Combination of leachates and resulting precipitates

Parameters from the theoretical mixing of caustic and acidic leachates for selected samples and fraction sizes were inputted into Aqion. Sample A, < 1.18 mm and sample A, 1.18 mm – 3/8 inch were chosen, as they represented the limits for the sample range studied, with respect to the F⁻:Al³⁺ molar ratio in the final mixed leachate. For sample A, < 1.18 mm, this was 1.54 and for sample A 1.18 mm –

3/8 inch, it was 7.66. The choices were made because our previous work suggested that the performance of the La-MTS9501 resin was sensitive to this parameter [28]. We also acquired data for sample C, 1.18 mm – 3/8 inch, to compare first-cut with mixed-cut leachates. We finally acquired data for a theoretical average that would be produced by mixing the leachates from all samples and size fractions together. Previous ion-exchange experiments, using synthetic leachate, were run at pH 5.5. However, Aqion predicted substantial precipitation of SiO₂ and CaF₂ under these conditions, which experimental observations, at small scale, appeared to confirm. Therefore, pH was adjusted to 3.0 to minimise any precipitation. Our equilibrium work suggested this would result in a minimal decrease in resin performance [27].

The aqueous speciation results are presented in Table 3. For brevity, only major F, Al and S species are shown. It should also be noted that Aqion does not account for the following elements, which would all have been present in the mixed leachates, though all at concentrations of < 1 g L⁻¹: Ba, Be, Li, Ti, V, Y and Zr.

Chemical species	Sample A < 1.18 mm	Sample A 1.18 mm – 3/8 inch	Sample C 1.18 mm – 3/8 inch	Average of all samples
		Concentrat	tion (mmol L ⁻¹)	
AIF ²⁺	5.49	0.0218	6.71 x 10 ⁻³	0.0351
AIF ₂ +	11.9	2.20	0.904	2.82
AIF ₃	1.21	10.5	5.72	10.6
AISO ₄ +	1.38	1.09 x 10 ⁻⁴	2.67 x 10⁻⁵	2.35 x 10 ⁻⁴
Al(SO ₄) ₂ -	1.38	1.06 x 10 ⁻⁴	2.68 x 10⁻⁵	2.36 x 10-4
CaSO ₄	2.07	0.329	0.197	0.560
F-	0.0214	1.03	1.36	0.801
HF	0.0145	1.56	1.29	1.00
HSO4-	3.82	8.57	5.49	7.13
Na+	353	422	476	396
NaSO4-	57.7	67.4	67.4	64.8
SO42-	161	162	165	162
Total ionic strength	554	605	581	568

 Table 3 Selected Agion theoretical speciation data for combined leachates, with pH adjusted to 3.0

Table 3 shows that, at both the lower and upper limit of the F-:Al³⁺ ratio, the dominant fluoride-bearing species is an Al complex, due to the well-known mutual affinity of the two species. This was also the case for the simulant leachate used in previous ion-exchange experiment, which produced excellent resin uptake performance [28]. The real leachates possess greater relative concentrations of AlF₂⁺ and AlF₃, rather than AlF²⁺. This may be advantageous to resin efficiency, assuming the main complexation reaction involves stoichiometric binding of one AHF with one La centre on the resin surface, as this would lead to the loaded resin being more fluoride-rich (Figure S2). It can also be seen that some leachates contain significant concentrations of free aqueous fluoride and HF. We had not previously examined a system with these species *and* aluminium fluoride complexes co-existing and the effect on uptake behaviour was unknown at this point.

It was found that the most efficient way to combine the two leachate streams was to cautiously add caustic leachate to acidic, whilst maintaining pH below 3.5, to minimise precipitation. The masses of precipitates attained were recorded and are shown in Table S4. The amount of precipitation generally increased with the fraction of second-cut material in the sample. PXRD spectra of selected precipitates from all three samples were examined, namely sample A, 1.18 mm – 3/8 inch, sample B, < 1.18 mm and sample C < 1.18 mm (Figures S29 – S32). The only identifiable crystalline component in the spectra was cryolite. There was also an amorphous component, most likely albite, which varied in size between samples, being much lesser for sample C (mainly first-cut). The purity of the cryolite is unlikely to be acceptable for resale as a chemical commodity, again enforcing the necessity of the ion-exchange step in the SPL valorisation process.

A small amount of precipitation appears to be inevitable, upon mixing the caustic and acidic leachates. It would not be feasible to treat acidic and caustic streams individually with La-MTS9501 resin, as it is completely ineffective at extreme pHs [27]. However, it is desirable to avoid loss of fluoride from the leachate by precipitation of impure cryolite, before it enters the ion-exchange system.

There are two potential strategies to negate this. First, the F⁻:Al³⁺ ratio could be kept relatively low via addition of aqueous Al³⁺ salts Anodizing wastewater would be a potential cost-effective candidate for this application [3, 23]. This however, would require monitoring and quantification techniques performed on both leachate streams before mixing [28, 39]. The second strategy would simply be to redissolve the precipitate in the acid leaching vessel, in-lieu of a small quantity of SPL, as suggested in the flow diagram in Figure 1.

3.4. Analysis of leached SPL

The elemental analysis results for the full range of samples and size fractions is presented in Table 4.

 Table 4 Mass % of C, H, N and S of residual SPL samples after leaching treatments, determined by elemental analysis

Leaching	Sample	Elemental composition (mass %)						
treatment	-	С	H	N	S			
Caustic	A <1.18 mm	7.25	0.67	< 0.01	0.26			
Caustic	A 1.18 mm – 3/8 inch	1.67	0.39	0.01	0.18			
Caustic	B <1.18 mm	28.01	0.85	0.12	0.17			
Caustic	B 1.18 mm – 3/8 inch	19.47	0.69	1.38	0.16			
Caustic	C <1.18 mm	78.31	0.41	0.24	0.20			
Caustic	C 1.18 mm – 3/8 inch	76.42	0.31	0.40	0.20			
Caustic + acidic	A < 1.18 mm	7.26	0.57	0.01	0.14			
Caustic + acidic	A 1.18 mm – 3/8 inch	2.98	0.48	0.02	0.26			
Caustic + acidic	B < 1.18 mm	66.06	0.35	0.18	0.50			
Caustic + acidic	B 1.18 mm – 3/8 inch	27.57	0.33	0.01	0.36			
Caustic + acidic	C < 1.18 mm	88.27	0.27	0.19	0.32			
Caustic + acidic	C 1.18 mm – 3/8 inch	87.21	0.25	0.56	0.36			

From the elemental composition of the leached samples, it is seen that the C % of the SPL increases, following the acidic leach, as more contaminants are solublised. The increase is significant for all samples, with the exception of sample A < 1.18 mm. The H % also decreases significantly for most samples between the leaching treatments, which may suggest the original material contained an organic hydrocarbon component, which dissolves during the treatment (also suggested in PXRD spectra by the amorphous region). The N % is very inconsistent across all samples and the S % actually increases slightly, following the acidic leach, which is likely due to residual sulfate not entirely removed by the final water wash. Notably, the C % was always greater in the smaller size fraction, across all samples, but the difference was only very large in the case of sample B. It would not be possible, for example, to separate the carbonaceous and cementious fractions effectively on this basis. The attained carbon purity for our first-cut samples does not approach that reported in previous work [3, 26]. However, since the proposed treatment is designed for mixed-cut SPL, this parameter is of little significance.

3.5. La-MTS9501 column-loading behaviour

Full breakthrough profiles were attained for column-loading treatment of combined leachates from sample A < 1.18 mm and sample A 1.18 mm – 3/8 inch (these again being chosen for representing the extremes of the F-:Al³⁺ molar ratio). The breakthrough behaviour was generally best-modelled as a pair of individual breakthrough curves, seemingly describing two discreet breakthrough stages, though occurring in quick succession. Column data are shown for sample A < 1.18 mm in Figure 3 (data for sample A 1.18 mm – 3/8 inch shown in Supporting Information, p15). Parameters for model-fitting are shown in Table S5.



Fig. 3 Fluoride breakthrough behaviour via loading of La-MTS9501 resin column from combined leachate of SPL sample A, < 1.18 mm size fraction: (a) raw data, (b) modelling of first breakthrough region, (c) modelling of second breakthrough region. Error bars indicate 95 % confidence limits. Column volume = 5.500 mL. Resin mass = 1.792 g. Flow rate = 0.50 BV hr⁻¹. T = 20°C.

The Dose-Response model provided the most accurate modelling of the two breakthrough regions (Table S5). This model has previously been observed to minimise the errors produced by other breakthrough models [28, 40]. The resulting maximum dynamic uptake capacity values (q_0 , in units of mg g⁻¹) were therefore considered the most valid to compare the different experiments. These values for sample A < 1.18 mm were 5.01 ± 0.11 and 26.7 ± 0.4 mg g⁻¹ respectively for each breakthrough region. For sample A 1.18 mm – 3/8 inch, they were 4.23 ± 0.07 and 33.4 ± 0.7 mg g⁻¹. The leachate of sample A < 1.18 mm had a significantly greater inlet fluoride concentration (434 mg L⁻¹, compared to 275 mg L⁻¹). Previous work with simulant leachate showed that the q_0 parameter is strongly influenced by this variable [28], so the difference in resin uptake performance is not as great as would be expected. This is especially surprising, given the differences in F⁻:Al³⁺ ratio and speciation (Table 3). Our previous kinetic work however, suggested that, as the uptake process approaches equilibrium, ligand-exchange reactions occur with the surface-bound AHFs (Figure S2). This causes some release of fluoride back into solution and leads to the dominant adsorbed species tending towards Al(OH)₂F [28]. This may explain the similar resin performance over the two experiments.

Our previous work also provided strong evidence that the uptake of AHFs by La-MTS9501 is heterogenous, with an initial chemisorption complexation between La centres and aqueous AHFs, followed by a secondary uptake where further AHFs bind to the resin through much weaker interactions, again involving F or O bridging ligands (Figure S2) [27, 28]. This would explain the two discrete breakthrough regions, the first representing the full saturation of the La centres, while the secondary adsorption is still proceeding; the second representing full breakthrough for both adsorption mechanisms. In previous work, using simulant leachate, there was not significant evidence of a two-stage breakthrough process [28]. However, the ionic strength of the inlet was much greater in this work (554 and 605 mmol L⁻¹ in these experiments verses 24.8 mmol L⁻¹ for the simulant leachate), which is likely to have retarded the adsorption kinetics [41].

Overall, the efficiency of the resin, using SPL leachate, compares well to data produced using a simulant feed and otherwise similar conditions. This produced a q_0 value of 66.7 \pm 9.1 mg g⁻¹, with the inlet fluoride concentration being substantially higher (1500 mg L⁻¹) [28]. It can be concluded that the more complex chemistry and higher ionic strength of the real leachate is not detrimental to resin performance. Work is currently underway to optimise the elution process for the leachate-loaded columns, to enable maximum recovery of Al and fluoride.

4. Conclusions

A simple leaching treatment for spent potlining (SPL) has been developed, with a view to valorisation of the waste, via fluoride and aluminium uptake in an ion-exchange column system, using chemicallymodified La-MTS9501 resin. The leaching employs economical lixiviants (NaOH/H₂O₂, then H₂SO₄) at high dilutions, works at ambient temperature and is effective for a variety of SPL grades. First-cut and mixed-cut SPL samples, of two different size fractions, were subjected to both stages of the leaching treatment. The SPL was characterised by PXRD and SEM, which confirmed both the strongly heterogeneous nature of the material and the effectiveness of the leaching in terms of mobilising the contaminants. The residual leachable contamination in the barren SPL material is to be assessed. The leaching produced a variety of liguors, which were characterised by ICP-MS and IC, again revealing large differences in elemental composition. The aqueous fluoride and aluminium speciation were predicted, using the Agion software package. Caustic and acidic leachates were combined and pumped through an ion-exchange column to assess the performance of La-MTS9501 with a real industrial leachate feed. The resin performed similarly well in the uptake of fluoride from two inlet solutions of substantially different composition. Dynamic maximum uptake values were in excess of 30 mg q⁻¹ in both cases. The next stage in establishing proof of concept will be optimisation of elution of fluoride and aluminium from the loaded resin column.

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