

## AL19 - A Novel, Zero-Waste Technology for Spent Pot Lining Recycling

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### Abstract

Each tonne of aluminium produced in aluminium smelters generates approximately 20 kg of hazardous waste, known as spent pot lining (SPL) which is a mix of the carbon lining and the refractory lining. The waste contains high levels of leachable cyanides and fluorides, as well as components that form combustible gases (mainly CH<sub>4</sub>). The current practice of the waste management of hazardous SPL is still often landfilling or incineration, which costs aluminium producers on average 200 €/tonne of SPL waste (240 million € annually on a global level).

A novel zero waste process has been developed and optimized in the frame of the SPL-CYCLE project (<http://splcycle.zag.si/>) for wastes originated from two aluminum smelters. The new process consists of five main separation and purification stages which are dilution, filtration, crystallization and flotation, resulting in the production of four products: a) fluoride salts for aluminium production, b) graphitized carbon for aluminium production, c) aluminosilicates for refractory industry, and d) manufactured aggregate for construction (supplementary cementitious materials, lightweight aggregates, geotechnical fill, bricks, concrete).

The current research paper presents major aspects of SPL and SPL-CYCLE process, including characterization results from raw materials (1<sup>st</sup> and 2<sup>nd</sup> cut) and the products, description of the process' flowsheet and the pilot plant, and presentation of thermodynamic data.

**Keywords:** Aluminum spent pot-lining (SPL), carbon cathode lining, aluminum reduction cell, industrial waste valorization, waste detoxification.

## 1. Introduction

Spent potline constitutes the bottom part of Hall-Héroult electrolytic cells that are used in aluminum production. It constitutes the spent carbon cathode (1<sup>st</sup> cut) and high temperature resistant bricks (2<sup>nd</sup> cut). During cell operation, the lining is subject to reducing conditions and fails after 5–9 years depending on the operating conditions, materials quality and construction technique. All the parts are toxic due to the impregnation with molten electrolyte during the operating period, containing leachable fluoride salts and cyanides. The best available technologies for non-ferrous metals describe many options to treat SPL: use SPL in cement production, as a carbonaceous substance in ironworks, as a secondary raw material (glass wool, salt slag) and as a substitute fuel [1].

A novel zero waste process has been developed and optimized in the frame of the SPL-CYCLE project (<http://splcycle.zag.si/>) for SPL 1<sup>st</sup> and 2<sup>nd</sup> cut recycling. The new process consists of five main separation and purification stages which are extraction and detoxification for fluoride salts and cyanide removal, filtration for solid-liquid separation, crystallization of fluoride salts, and flotation, resulting in the production of four products: a) fluoride salts for aluminium production, b) graphitized carbon for aluminium production, c) aluminosilicates for refractory industry, and d) manufactured aggregate for construction (geotechnical filler, bricks, concrete) [2].

The SPL-CYCLE project is exploring the potential customers for technology and recycled products markets (graphite, fluoride salts, aluminosilicates) and is preparing the techno-economic study and tailored-made business strategies for addressing various industrial needs in order to bring the sustainable supply of critical resources close to the local industry. Through the SPL-CYCLE project, the foreground for the smooth market penetration is in preparation to avoid common bottlenecks in the successful commercialization. The SPL-CYCLE technology is utilizing zero waste principle by closing material loops as all products could be recycled or reused in other industries.

## 2. SPL-Cycle Process Flowsheet

The SPL-CYCLE technology is a hydrometallurgical detoxification process at ambient temperature and pressure that transforms the SPL into a non-hazardous material suitable for recycling. The technology is self-sustained, and thereby ideally adapted to the needs of small-scale Al smelters looking for a local, on-site solution. Further to detoxification, the method succeeds in the production of 2 high purity products that can be considered as carbon and aluminosilicate-source material on various industrial branches.

In the frame of the SPL-CYCLE project, a pilot plant was built in 2019 with a capacity to treat at least 5 kg SPL/h (40 kg/day). For a full-scale Al smelter, it is assumed that 200–250 kg/h SPL treatment is needed, depending on the Al-smelter capacity. The tests on the pilot plant are set to get sufficient information for the preparation of the scale-up configuration in the intended industrial applications. The process is applied separately for the 1<sup>st</sup> and 2<sup>nd</sup> cut and takes place in the following steps presented in Figure 1.

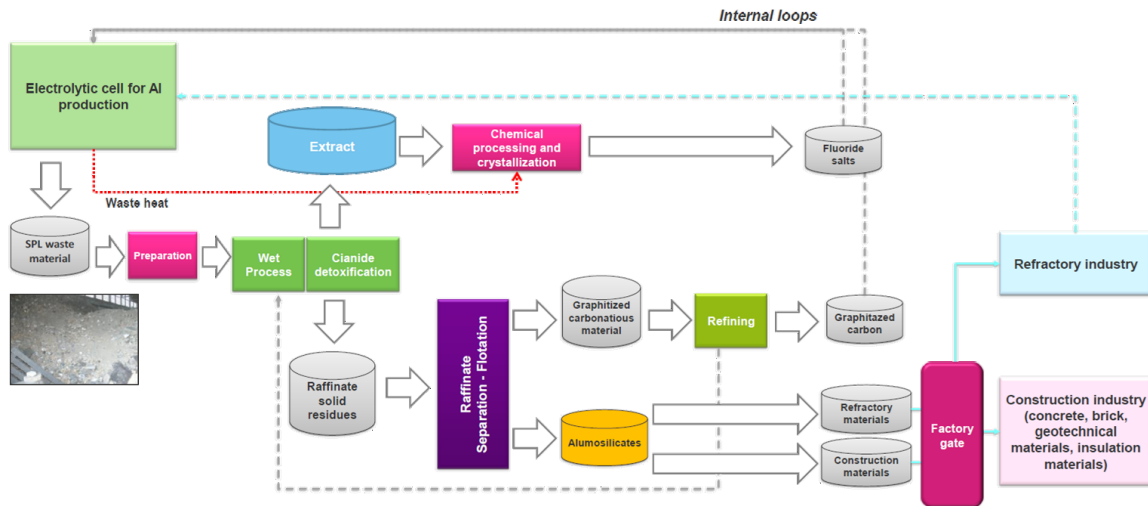


Figure 1. The SPL-cycle process flowsheet.

Major processing stages are the followings:

- 1) Grinding of the SPL to appropriate size (mainly < 4 mm, other sizes are also possible)
- 2) NaOH leaching to remove the salts (mainly cryolite) with parallel detoxification (cyanide removal by activated H<sub>2</sub>O<sub>2</sub>). Reactive gases formed by the interaction with water are flared off. This step is applied both to the first and second cut.
- 3) Flotation to remove C → this step is only applied if necessary, for recycling of the second cut (alumosilicates).
- 4) Precipitation of CaF salts; Extracted NaF leachate (after 2<sup>nd</sup> step) is mixed with Ca(OH)<sub>2</sub> to obtain a slurry. This is separated by a filter press into two components, CaF<sub>2</sub> crystalites and NaOH liquid fraction.

The process results in the following end-products:

- A C-rich fraction (85-90 % graphite) with a small proportion of alumina and silicates, as well as CaF<sub>2</sub> which is beneficial for metallurgy. Ideally, this fraction can be reused on site to produce anodes, if the purity is high enough (i.e. Na content very low). Alternatively, the C-fraction has potential for use as slag former or fuel (cokes replacement) in the steel industry. It is estimated that the C-rich fraction has a potential value of around 350 EUR/tonne (based on discussions with industry).
- Detoxified sandy material with or without C (depending on flotation step). This can potentially be used in cement production, as geotechnical filler, concrete mixes, refractories, etc.
- Fluoride salts that can be used in back in the Al production, in metallurgy as a flux agent and in cement production.

### 3. SPL Characterization

The current section contains characterization analyses results for both SPL grades towards identification of their properties of interest. 10 kg of 1<sup>st</sup> and 2<sup>nd</sup> cut SPL were obtained from Talum aluminum industry from Slovenia. To obtain representative samples, the company collected material from various locations of a single cell. After sampling, and to ensure safe handling of the material in the laboratory both 1<sup>st</sup> and 2<sup>nd</sup> cut samples were subjected to leaching with NaOH and UV-activated H<sub>2</sub>O<sub>2</sub> towards removal of fluoride salts and cyanides. Samples for characterization were obtained using a riffle splitter.

### 3.1. Characterization Methodology

Chemical analysis of both samples was performed on an energy-dispersive X-ray fluorescence (ED-XRF) instrument Xepos (SPECTRO A. I. GmbH Company). To ensure the non-toxic nature of the samples, their content in CN was measured using continuous flow analysis (CFA) according to the ISO 14403-2 standard [3]. An ASTM method (proximate analysis) that is designed to be used for coal samples was also applied in order to determine the content of moisture, ash, volatiles and  $C_{\text{fix}}$  in the 1<sup>st</sup> cut. [4]. Individual standard procedures are applied to determine the sample content in each of the basic components, and are presented in Table 1, together with sample treatment.

**Table 1. Standard procedure code and process for SPL proximate analysis.**

ASTM no	Species determination	Sample treatment
D3173-03	Moisture	Heating at 104-110 °C for 1 h
D3174-02	Ash	Sample heating in the following ramp profile: 25 to 450 °C in 1 <sup>st</sup> hour, and from 450 to 750 °C in the 2 <sup>nd</sup> hour
D3175-02	Volatile	Sample retention at 950 °C for 7 min
D3172-89	Fixed carbon	Mass balance to determine fixed carbon content. $C_{\text{fix}}$ (%) = 100-moisture (%) - ash (%) - volatiles (%)

Phase identification was performed through X-ray powder diffraction analytical technique (XRD) on a Bruker D8 Advance device, under the following analysis conditions; scanning rate of 5°·min<sup>-1</sup>, 2 $\theta$  range from 5 to 75 °, graphite-monochromatized CuK $\alpha$  radiation ( $k = 0.15406 \text{ \AA}$ ). The composition of the treated 1<sup>st</sup> and 2<sup>nd</sup> cut was analysed through ICP-MS on leachates that were produced according to a standard procedure [5].

SEM images were obtained using a JEOL JSM-IT500 LV equipped with EDS (Oxford Instruments). Operating conditions were as follows: low vacuum, accelerating voltage 15 kV, probe current 50 A. Thin cuts were prepared by samples embedding in epoxy resin and polishing.

### 3.2. Characterization Results

Two SPL samples (1<sup>st</sup> cut and 2<sup>nd</sup> cut) possess very different appearance as a consequence of their different composition. The 1<sup>st</sup> cut is grey to dark due to the high carbon content, while the aluminosilicate-rich sample (2<sup>nd</sup> cut) is yellow to brown (Figure 2).



**Figure 2. View of the SPL 1<sup>st</sup> cut (left) and 2<sup>nd</sup> cut (right).**

The CN concentration of the 1<sup>st</sup> and 2<sup>nd</sup> cut was found to be 682 mg/kg and 22mg/kg, respectively, while after treatment with H<sub>2</sub>O<sub>2</sub> was measured as 26 mg/kg and 1.7 mg/kg. The sample treatment with H<sub>2</sub>O<sub>2</sub> constitute an efficient way for cyanide removal and elimination of SPL toxicity.

The chemical composition of 1<sup>st</sup> and 2<sup>nd</sup> cut, and proximate analysis for the 1<sup>st</sup> cut are presented in Table 2 and Table 3, respectively. The 1<sup>st</sup> cut has high carbon content and this causes considerable Loss On Ignition (LOI) value; during sample heating the carbon is burned and sample weight is considerably reduced. Moreover, in carbon rich samples LOI analysis is often applied for determination of the sample carbon content since carbon is burned out during sample heating at 1050 °C. The identification of silicon and aluminum in the 1<sup>st</sup> cut is due to inevitable mixing with the 2<sup>nd</sup> cut during cell dismantling. The 2<sup>nd</sup> cut mainly consists of aluminum and silicon which are the main components of chamotte and insulation bricks.

**Table 2. Chemical composition of 1<sup>st</sup> and 2<sup>nd</sup> cut sample.**

Oxide	Content (wt. %)	
	1 <sup>st</sup> cut	2 <sup>nd</sup> cut
Na <sub>2</sub> O	6.38	3.34
MgO	0.21	1.29
Al <sub>2</sub> O <sub>3</sub>	4.11	16.31
SiO <sub>2</sub>	4.86	63.50
P <sub>2</sub> O <sub>5</sub>	0.05	0.09
K <sub>2</sub> O	0.48	2.84
CaO	2.81	4.99
TiO <sub>2</sub>	0.10	0.77
Fe <sub>2</sub> O <sub>3</sub>	0.63	2.84
Other	0.36	0.30
LOI	79.78	3.51

The proximate analysis results revealed that the 1<sup>st</sup> cut sample mainly consists of fixed carbon and ash by approx. 41% and 45%, respectively.

**Table 3. Proximate analysis of SPL 1<sup>st</sup> cut sample.**

Sample	Ash (%)	Moisture (%)	Volatile (%)	Fixed carbon (%)
SPL 1 <sup>st</sup> cut	44.76	0.75	13.57	40.92

The mineralogical analysis of the 1<sup>st</sup> cut grade revealed that carbon is in the graphite phase (Figure 3). The presence of a quartz phase on the 1<sup>st</sup> cut grade is due to inevitable contamination from the 2<sup>nd</sup> cut. Other phases present in the 1<sup>st</sup> cut are villaumite, sodium silicate and nepheline. Amorphous carbon is expected to be present in the sample, however its identification with XRD is impossible due to the lack of peaks, which is attributed to its non-crystalline structure. Concerning the 2<sup>nd</sup> cut, further to quartz which is the main component of the sample, also mullite is present (Figure 4). The presence of both substances is normal since they are used in the production of high temperature resistant bricks.

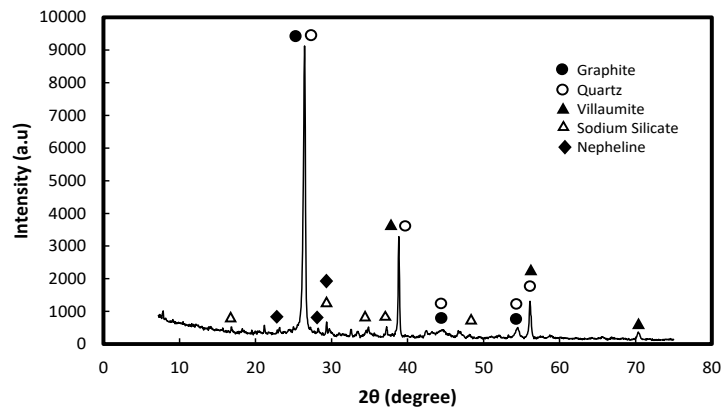


Figure 3. XRD diagram of SPL 1<sup>st</sup> cut sample from Talum.

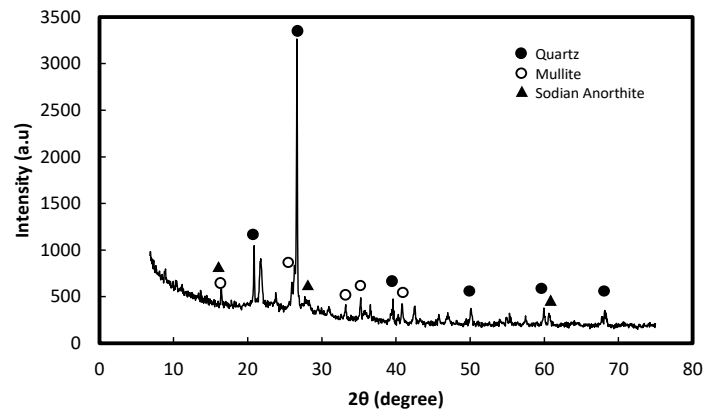


Figure 4. XRD diagram of SPL 2<sup>nd</sup> cut sample from Talum.

The 1<sup>st</sup> cut sample was also subjected to thermogravimetric analysis under atmospheric conditions and the thermogram is presented in Figure 5. The sample weight loss initiates at about 435 °C, and continues to approx. 1110 °C. The overall sample weight loss was 67.7 % and is mainly attributed to carbon burning.

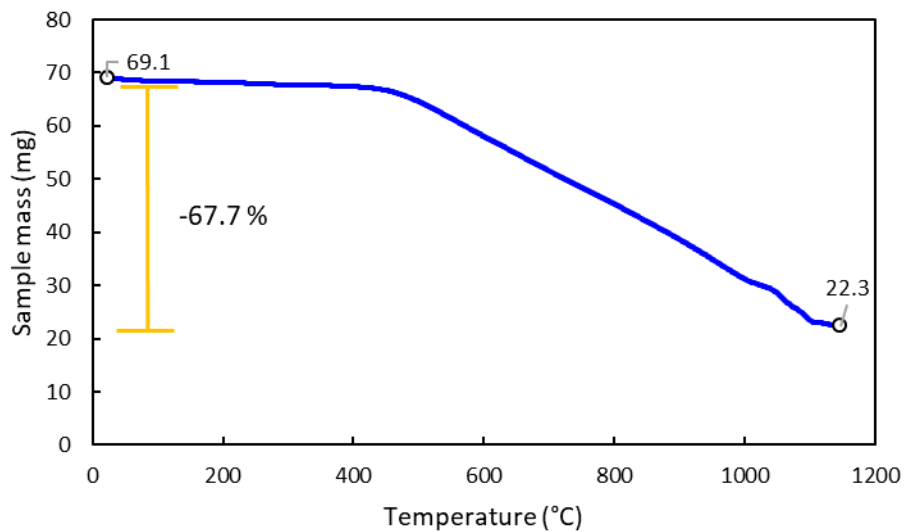
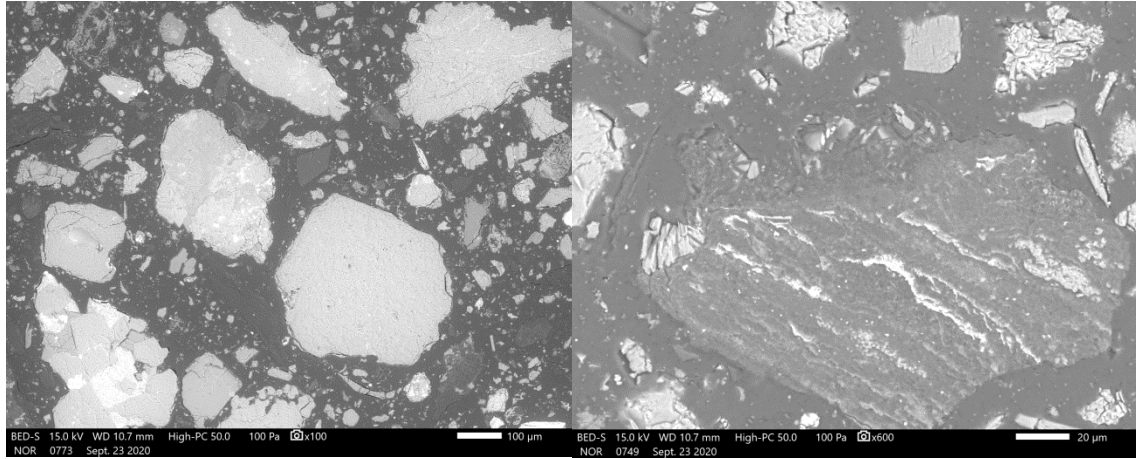
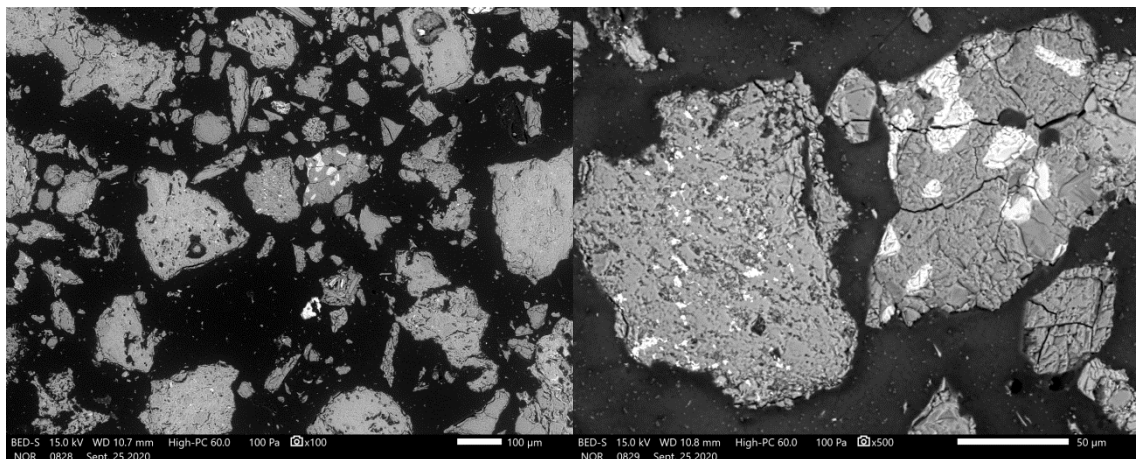


Figure 5. Thermogravimetric curve of Talum 1<sup>st</sup> cut sample at temperature range between 25 and 1150 °C, 3°C per min heating rate and air atmosphere.

The morphologies of 1<sup>st</sup> and 2<sup>nd</sup> cut from SPL sample are shown in Figure 6 and 7 in 2 different magnifications. The 1<sup>st</sup> cut consists of graphite grains and cryolite and fluoride salts in the form of large grains. A considerable penetration of fluoride salts is identified in the graphite particles. Regarding the 2<sup>nd</sup> cut, it mainly consists of aluminosilicate grades, while fluoride salts are also identified.



**Figure 6. SEM pictures of 1<sup>st</sup> cut SPL materials; (a) brighter grains are representing cryolite and fluoride salts, darker are graphite grains, (b) enlarged grain of graphite with the interlayered fluoride salts.**

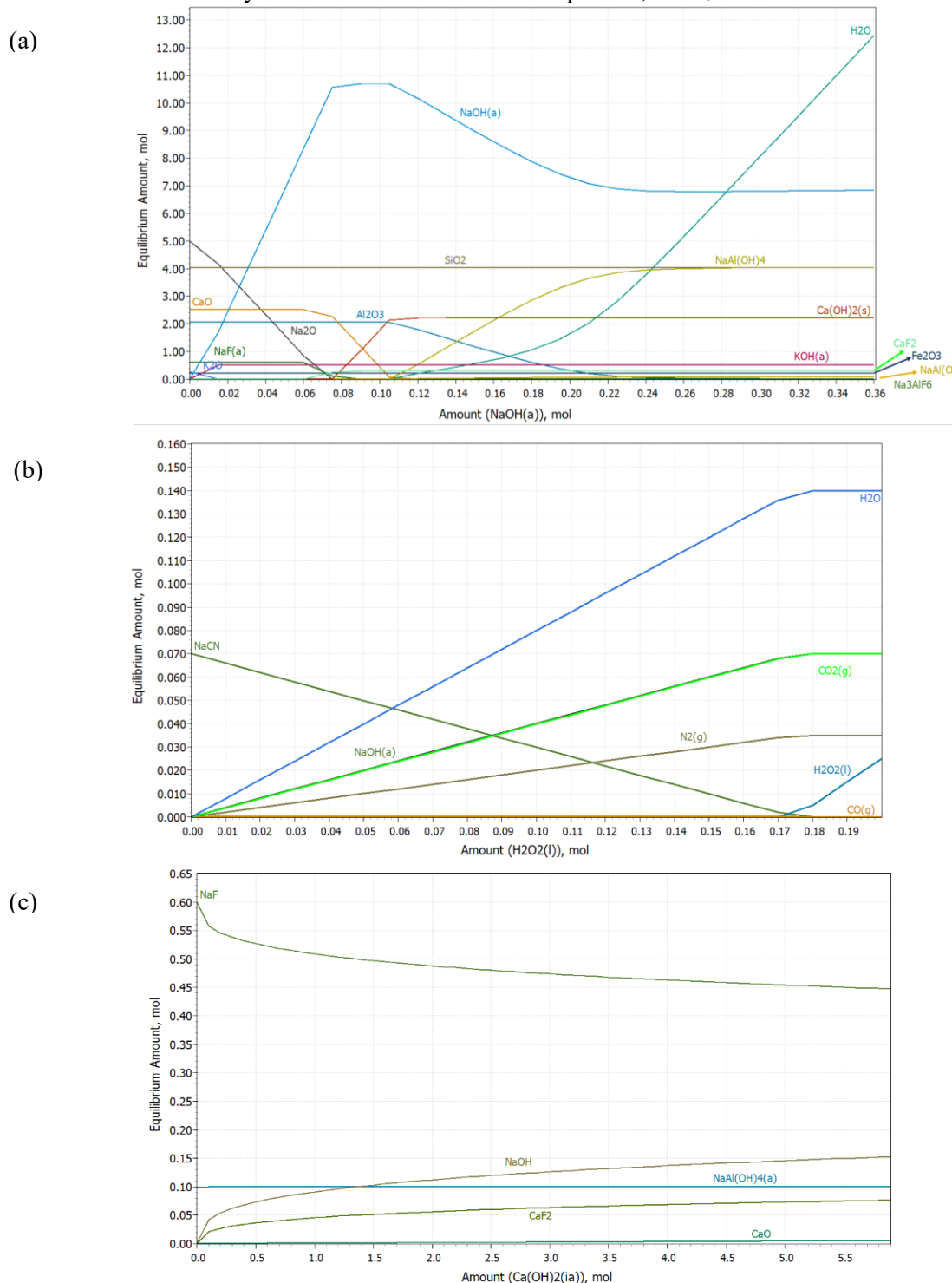


**Figure 7. SEM pictures of 2<sup>nd</sup> cut samples with porous grains of aluminosilicates (a) and loose grains of fluoride salts (b) composed of NaF (grey) and CaF<sub>2</sub> (brighter inclusions).**

#### 4. Process Thermochemistry

The process thermodynamics was investigated by HSC Chemistry 9 software using the chemical composition of the 1<sup>st</sup> cut SPL material based on a 5 kg sample. Equilibrium compositions were calculated using Gibbs free energy of all possible reactions depending on determined reactants and products. In the calculations, the *add amount* approach was applied which means that material was added step by step. Figure 8 shows the equilibrium diagrams of the caustic leaching (Figure 8a), cyanide destruction (Figure 8b) and CaF<sub>2</sub> precipitation using Ca(OH)<sub>2</sub> precipitation agents (Figure 8c). All cyanides in the material were accepted as NaCN. In the first stage, the sample was leached by a 3 wt% NaOH solution and the graph represents the increasing addition amount of leaching solution. According to the thermodynamic results, Na<sub>3</sub>AlF<sub>6</sub> decomposes directly in the reaction system and forms NaF<sub>2</sub> and NaOH at the initial stage. However, increasing the addition of the solution starts a second reaction leading to the formation of NaAl(OH)<sub>4</sub>. Besides,

CaF<sub>2</sub> and Ca(OH)<sub>2</sub> are formed and cause a slight dissolution of NaAl(OH)<sub>4</sub>. K<sub>2</sub>O is not stable in the high pH leaching environment and forms KOH(a). Although the calculations were considered the all different iron hydroxide forms and silicon compounds, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> become stable.



**Figure 8. Equilibrium diagrams of (a) leaching, (b) cyanide destruction and (c) precipitation by Ca(OH)<sub>2</sub> for 1<sup>st</sup> cut-sample.**

For the cyanide destruction unit, the cyanide weight percentage of the sample was converted to moles for the 5 kg sample. According to the thermodynamic calculations, sodium cyanide decomposes to NaOH, H<sub>2</sub>O, CO<sub>2(g)</sub> and N<sub>2(g)</sub> by hydrogen peroxide treatment as given in Fig 8b.

The required amount of H<sub>2</sub>O<sub>2</sub> is 0.18 mol for 5 kg sample considering no-side reactions take place. It was assumed that the process solution will contain NaF after the two process stages and possible precipitation unit designed using Ca(OH)<sub>2</sub> addition. Although CaF<sub>2</sub> precipitates in the identified system, the reaction requires much more dosing than the stoichiometrical amount, which is half of the NaF in molar units. Thus, other precipitation agents should be considered to obtain CaF<sub>2</sub> with higher efficiencies.

## 5. SPL-Cycle Process Implementation

A pilot plant has been built to implement and test the SPL-CYCLE technology at larger scale. The pilot plant consists of the extraction unit (Figure 9) and the precipitation part (Figure 10). The process is operated through an automated control system utilizing several sensors for monitoring the process parameters such as electrical conductivity, liquid levels and pH during the treatment. It is operating under normal atmospheric conditions and untreated tap water is used during the processing.



Figure 9. Extraction unit of the SPL-CYCLE pilot plant (left) and filled extractor during SPL processing (right).

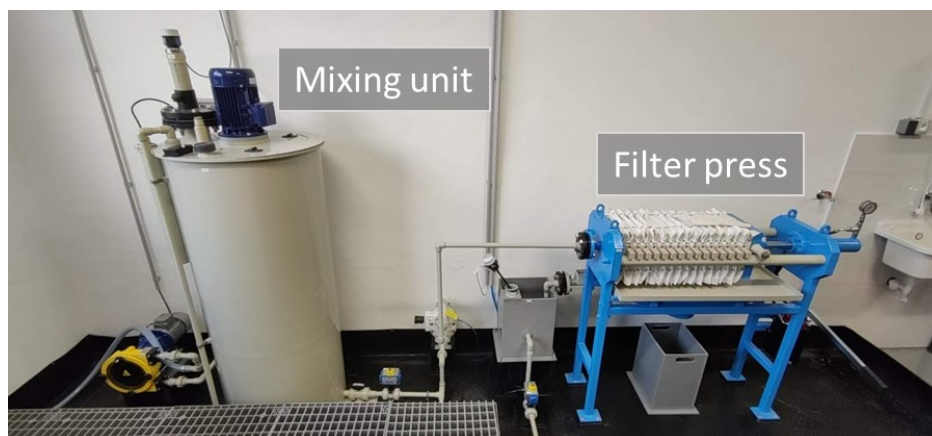


Figure 10. Precipitation unit on the SPL-CYCLE pilot plant.

The treatment process in the pilot plant starts by filling up the extractors with either 1<sup>st</sup> or 2<sup>nd</sup> cut SPL material (Figure 9). The solid to liquid ratio is defined as 1:2 for 1<sup>st</sup> cut and 1:1 for 2<sup>nd</sup> cut due to the lower concentration of fluoride salts. The initial step includes washing with water and the addition of UV activated H<sub>2</sub>O<sub>2</sub> into the loop for the detoxification (cyanide decomposition). The obtained liquid extract of fluoride salts is pumped into the collecting reservoir. Afterwards, a fresh batch of water is mixed with NaOH and the targeted concentration is monitored by electrical conductivity sensors in the liquid circulation loop. The extraction process is completed when the electrical conductivity parameter is stabilized and the obtained liquid is pumped into the

collecting reservoir. For the 1<sup>st</sup> cut, a fresh batch of water with the optimal concentration of NaOH is added three times and for the 2<sup>nd</sup> cut, only one time is sufficient for the cryolite extraction. Afterwards, the SPL material is washed several times with water in liquid to solid ratio 2:1 to reach the leachate electrical conductivity of around 0.5 mS/cm, which is similar to the initial values of the tap water.

Final products of the first part (extraction, detoxification) are a liquid phase, composed of NaF and NaOH, and a solid residue. On a next precipitation stage, the liquid solution is mixed with Ca(OH)<sub>2</sub> to obtain a slurry of CaF<sub>2</sub> and NaOH. Those are separated at the filter press, getting a valuable CaF<sub>2</sub> product and NaOH, which is re-used back in the process.

To assess the efficiency of the SPL-CYCLE technology and possibilities for further utilization, leachates from both samples were collected and analysed. Results are presented in Table 4, where most of hazardous elements are below limitations for classification as inert waste material. The only exception is the concentration of fluorides, which are just a bit above the maximum values. Therefore, the SPL-CYCLE treatment is successful and with the further optimization of the process, all parameters including the amount of fluorides and sodium, will be additionally lowered and tailored to the needs of industry.

**Table 4. ICP-MS analyses of species obtained from first treatment standard leaching tests of treated 1st and 2nd cut SPL materials and maximum values for inert waste materials.**

Parameter	Treated 1st cut material (leaching test after EN 12457-4)		Treated 2nd cut material (leaching test after EN 12457-4)		Maximum values for inert waste * [mg/kg s. s.]
	(mg/L)	L/S = 10 L/kg [mg/kg s. s.]	(mg/L)	L/S = 10 L/kg [mg/kg s. s.]	
Arsenic	0.0064	0.064	0.0023	0.023	0.5
Barium	0.015	0.15	0.0067	0.067	20
Cadmium	0.001	0.01	<0.0002	<0.002	0.04
Chrome tot.	0.0051	0.051	0.0023	0.023	0.5
Copper	0.0042	0.042	0.0026	0.026	2
Mercury	<0.0001	<0.001	<0.0001	<0.001	0.01
Molybdenum	0.0014	0.014	0.0031	0.031	0.5
Nickel	0.0059	0.059	0.0004	0.004	0.4
Lead	0.01	0.1	0.0006	0.006	0.5
Antimony	0.0014	0.014	0.0002	0.002	0.06
Selenium	0.017	0.17	<0.0003	<0.003	0.1
Zinc	0.023	0.23	0.0011	0.011	4
Chlorides	2	20	<1	<10	800
Fluorides	1.35	13.5	1.70	17.0	10
Sulfates	<20	<200	<20	<200	1000
Sodium	110.3	1103	63.2	632	N/a
Aluminium	3.7	37	2.6	26	N/a

\* Acceptability of Alternative Materials in Road Construction. Environmental Assessment. Appendice 3 – Limit Values associated with Level 1 Environmental Characterisation. Table 1.. column 1.. Sétra. France. February 2012.

## 6. Conclusion

The current research paper presents a new method for SPL Recycling that has been developed and optimized in the frame of the “SPL-cycle” research project (<http://splcycle.zag.si/>). The SPL-cycle technology is utilizing zero waste principle by closing material loops as all products could be recycled or reused in other industries. The major processing steps constitute extraction and detoxification (for cyanides and salts removal), filtration for solid-liquid separation, crystallization of fluoride salts, and flotation, resulting in the production of four marketable products: a) fluoride salts for aluminium production, b) graphitized carbon for aluminium production, c) aluminosilicates for refractory industry, and d) manufactured aggregate and aluminosilicates for construction (geotechnical fill, bricks, concrete). Within the project, a pilot plant capable to treat 5 kg SPL/h has been constructed and operated, thus allowing studying of crucial processing stages and optimizing its overall performance under realistic conditions.

## 7. Acknowledgement

The research has been conducted in the frame of the project “SPL-Cycle Closing the loop of the Spent Pot-line (SPL) in the Al smelting process” (PN 17141) that was funded by EIT Raw Materials.

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