INNOVATIVE WASTE TREATMENT CYCLE FOR ALUMINIUM INDUSTRY

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Abstract - Nowadays challenges in industries abroad are environmental oriented. As landfilling is getting more restricted, new, innovative options are addressed. Also, the aluminium industry is not immune to this problem as it generates tons of hazardous wastes. One of them is especially critical as no proposed treatment technology is economically justified. Spent Pot lining (SPL) is a hazardous waste material which originates from the primary aluminium production – the electrolysis cathode pot. Suggestions from the professional and scientific sources on how to approach the problem with state-of-the-art solutions were taken into account. A robust model to economically treat SPL is presented.

Keywords - Alkaline – Acidic treatment, flotation, spent pot line, waste treatment.

I. INTRODUCTION

Target is aluminium primary producers (smelters), produced aluminium in the electrolysis process mainly by a Hall-Héroult process with prebaked anodes.

In such productions, electrolysis cells consist of a cathode pot which lasts from 6 to 10 years. After finishing its lifetime replacement take place and old materials are mechanically dismantled, demolition or de-lining process take place by hydraulic equipment like on Fig. 1 to get spent pot lining (SPL) materials. By the manual separation process metal parts, cathode graphite (carbon) parts and two types of chamotte bricks (refractory and insulating) see Fig. 2 can be separated as "First cut" – mainly carbon (Cfix ≈ 55 %) and "Second cut" – mainly brick part (Cfix ≈ 10 %). There exists also a mixture of both with Cfix around 40 %.

Both materials are impregnated with NaF and Na_3AlF_6 - cryolite salts from the electrolyte in a significant amount. There is about 25 % of both salts, about 12 % water-soluble NaF and 13 % water insoluble cryolite. Beside presented salts, some parts of cyanide salts (around 0.5 – 1.5 %) can be found. In the First cut, more water-soluble NaF is presented up to even 25 %. Some small amounts of carbides react with water and form methane – CH4 explosive gas. Amounts of gas are relatively small approx. 0.2 L/kg of SPL but if calculated per 1 t of SPL about 200 L of methane appear. Such an amount represents fire treats and needs to be systematically separated and destroyed to assure safety.

As the material is sensitive to water contact due to explosive gas generation and to leaching NaF salt with some cyanides, producers keep them stored inside objects. The frequency of cell change is usually around 1-2 per month and this gives the impression of relatively unimportant quantities of SPL material. But with some period of operation, several 1000 t of SPL can be found in store places around. Dry SPL material form some unpleasant dark dust of carbon (can be explosive also).

Due to mentioned composition SPL is declared as hazardous toxic waste (HTW).
SPL is usually not in a focus of attention inside production company due to its relatively small amounts and possibilities to simply and cheaply throw in the deposit – landfilling. Many thermal treatment techniques are presented in literature, but the problem of remaining fluorides leachable content remains even at elevated temperatures above 1.200 °C [1]. Hollywel [2] concentrates on active processes and some of them have also promising solutions on chemical basis.

II. METHODS FOR TREATMENT

Comparing to anodes which amount is relatively large the spent anodes cannot be simply landfilled. Companies with own anode production line have also a line (or even production plant) for anodes recycling. Such a plant is usually a part of primary Aluminium production factory where 100 % of anode waste is recycled inside the process. Comparatively, a small plant of SPL recycling can be added to a smelting plant. Components of SPL do not allow to be applied inside the smelting plant, the application needs to be found outside the company (danger of sodium contamination).
The idea starts to process SPL in a way it can be incorporated in a circular economy. First hazardous

toxic waste - HTW needs to be detoxified and cleaned from water leachable material [3]. This way, clean and safe material can be available to different industrial applications around the regional/national economy.

To reach first goal material is leached with pure water and parallel detoxified in oxidation (activated H2O2) process. As some components (carbides) react with water and form an explosive gas, the material is, in the same process also deactivated for gas production. Gas is separated and burned on the flare.

The second goal is the elimination of cryolite what mean mostly sodium – Na and fluorine – F. This is done with reactive extraction and cryolite are converted to water solvable NaF. Remaining is purified graphitized carbon contains from 85 to 90 % of carbon and CaF_2 as the main residue. In case of processing the second cut (mainly chamotte) pure material came as result almost free from sodium and fluorine (also detoxified and no water leachable content). The material contains a certain amount of carbon (approx. 10-15 %) which can be in case of interest separated by flotation [4], otherwise can be used as a mineral raw material for mineral wool production or become a component in fresh concrete mixtures.

An extracted solution of NaF is separately processed toward useful products e.g. solid CaF_2 and NaOH solution. There is also another possibility of processing depending on the final user.

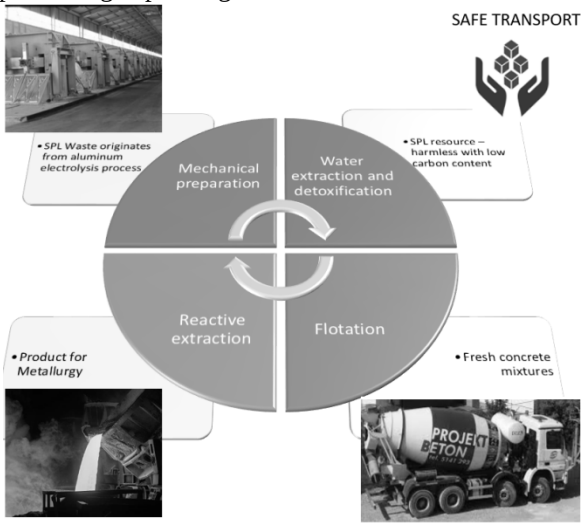


Fig.1: The SPL treatment cycle solution

The proposed solution has many advantages:

- Closed recycling loop. The originating waste from the metallurgical industry returns as products
- Waste is detoxified and made safe
- Marketable products in form of carbon, fluorspar and silicates
- No residue. Also, filtrates transform into usable products
- Sustainable economics

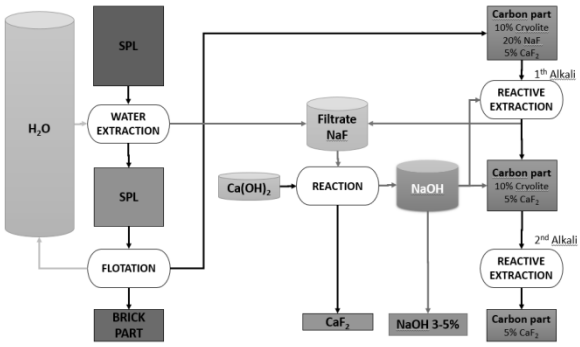


Fig.2: A rough presentation of the proposed process to treat SPL.

The process starts with a water extraction step in order to extract soluble salts. Thereafter a flotation is needed to separate the silicates from the carbon part of the waste. Next, an alkali reactive extraction is dissolving the sparingly soluble salts. In the last reaction step, the dissolution of other compounds continues. The last reaction step can be acidic but instead, an additional alkali step is preferable. The result showed 4 % lower carbon content in comparison with acid extraction. However, this process step is beneficial as it does not introduce new species or ion in the system. In addition, this method is significantly cheaper compared to acid extraction as high operating costs and an investment in additional equipment is avoided. It prevents the occurrence of complex filtrates as other complex ions are not introduced. The filtrate from water extraction and reactive extraction steps has a high level of NaF content which is very near saturation. One possibility is CaF_2 and NaOH formation with the help of mixing NaF with Slaked lime.

A. Application of obtained products and potential partners for use

The product was introduced to potential customers and received a positive feedback in the form of cooperation interest. However, it is desirable to have a granulation with a size greater than 0.5 mm and the price of our product increases with the size of the delivered granulation (up to 6 mm). Namely, there is a problem with introducing too small particles of carbon material in the incinerator chamber as it burns before it touches the slag.

We can point out that tests were performed under the same conditions but with granules of 1 mm sizes and the results of extractions were the same. Therefore, the conceptual platform is very good, and we chose the right direction to transform the SPL waste in product form. The second product is the filtrate of extraction steps. Without proper treatment, the filtrate can present an obstacle in project economics as this

byproduct presents an open mass flow model with no recycling loop closed. Therefore, a proper solution must also be present for filtrate transformation. Some authors prefer to mix the filtrates from alkali and acid steps to produce cryolite [5]. But the cryolite is not a desirable product in modern electrolysis any more. Therefore, some new chemical techniques are researched to gain valuable products as electrolysis additive like AlF_3 [6]. The filtrate from water extraction has a high level of NaF content which is very near saturation. Therefore, direct NaOH extraction of waste is not advisable or meaningful. As NaF is formed from the first and second extraction step, the filtrate has very high pH and is unsuitable for outflow. One possibility is CaF_2 formation if we mix NaF with Slaked lime:

$2NaF + Ca(OH)_2 \rightarrow CaF_2 + 2NaOH$

The refined CaF_2 is useful in ironworks. The gained NaOH, which is also an expensive agent, can be introduced to the next, alkali extraction process, to close the material loop and save resources. As Slaked lime also contains anions for effective Cryolite extraction it would be possible to use this agent directly, without introducing the expensive sodium hydroxide. The problem would result than in too high CaF_2 content that would contaminate the surface of the carbon product and the CaF_2 extraction is not possible.

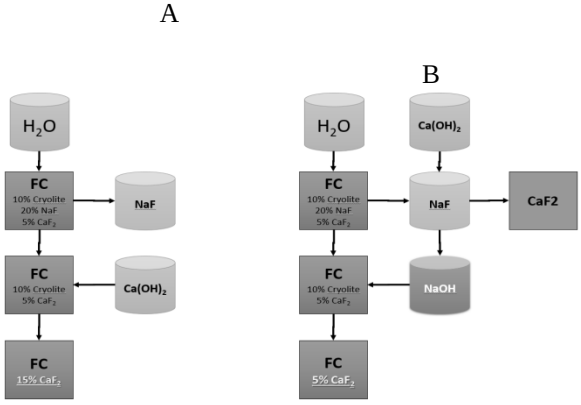


Fig.3: Comparison between the direct – slaked lime introduction (A) and NaOH recycling (B) procedure expressed as a percentage by mass

Although the acid-reactive extraction is effective to dissolve CaF_2 content, new species are present in the acid filtrate. Besides HCl, undissolved CaF_2, $CaCl_2$, and $AlCl_3$ are present and the problems to treat a complex filtrate continue. It is sensible to omit the acid extraction step.

Additional testing was performed as to increase the efficiency of alkali reactive extraction of Cryolite. The experiments showed that a second alkali leaching is reasonable as the carbon content of the waste product rises to about 4 % (Cfix raised from 79,6 % to 83,2 %).

As can be seen from the Fig. 2, the indirect usage of Slaked lime gives us the opportunity to treat the filtrate from the first step of extraction and produce the NaOH at the same time which is then introduced to the second step (alkali) reactive extraction. The result is three times smaller CaF_2 content and the advantages described earlier. As the NaOH is dissolving Cryolite, the filtrate is again NaF rich.

$Na_3AlF_6 + 4NaOH \rightarrow 6NaF + NaAl(OH)_4$

The loop with Slaked lime repeats in order to obtain NaOH for the first alkaline leaching of the next batch.

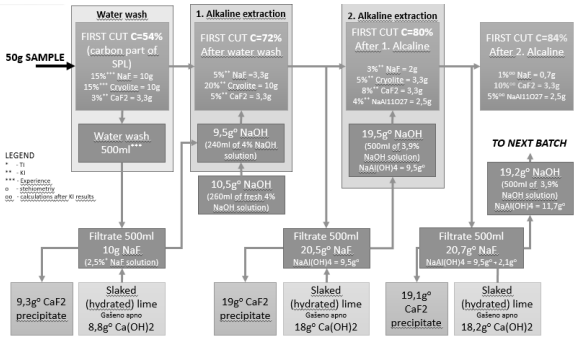


Fig. 1: Mass balance and carbon purity at different extraction stages of the proposed final model for SPL treatment

III. RESULTS AND DISCUSSION

Results showed a carbon content of 82 % after 2 step alkali reactive extraction and 90 % after acid reactive step. The acid step can, therefore, be omitted as the difference is not essential. The benefits of using just alkali instead of the additional acidic step are much greater. This prevents the occurrence of complex filtrates, while at the same time, with the absence of an acidic reagent, we avoid high operating costs and an investment in additional equipment. In addition, the CaF_2 reduction is not a significant factor for purification effectivity, as the metallurgical industry to some extent needs this additive.

The carbon product with a carbon content between 85 and 90 % can be used in ironworks while the silicate part is useful in brickwork.

The by-products of the process are also useful. They appear in form of fluorspar which is used as a flux to lower the melting point of raw materials in steel production to aid the removal of impurities. The other by-product is NaOH which is mostly used in the process itself.

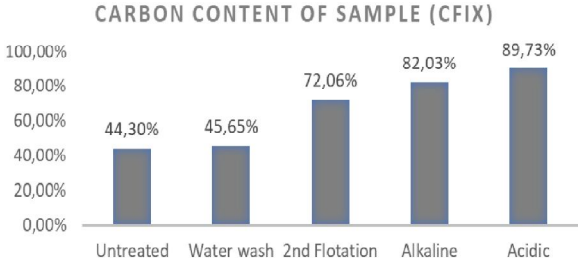


Fig. 2: The carbon content results after each treatment step

A **B**

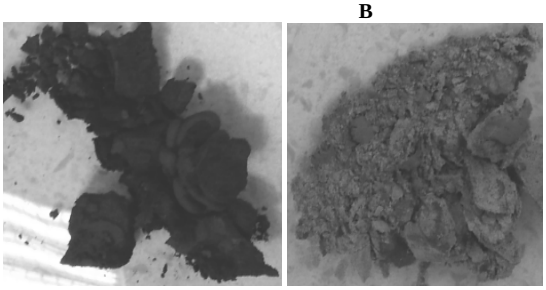


Fig. 3: Obtained products in form of carbon part (A) and mineral part (B)

CONCLUSION

A four-step treatment of SPL waste has been demonstrated as a suitable approach to obtain commercial products in form of high carbon content, silicates, fluorspar and sodium hydroxide. After each step, the product is richer in carbon content (Cfix).

With experiments we managed to achieve the goal, this is enough carbon content of the treated Carbon waste product. This kind of product is useful in ironworks as carbon is introduced to the process in induction and arc furnaces. The CaF_2 fraction is not decisive, as it is even desirable in the iron production industry and plays a similar role as fluorspar (lowering of the viscosity and melting temperature of the slag). The share of Fluorite and Sodium is lowered substantially. The most problematic element for ironworks is Sulphur but, in our product, the share of this element is well below allowed limits. Therefore, a simple, robust and economic model is proposed to treat SPL, especially the carbon part of it. A final model with mass balance is presented, taking into account all the benefits of alkali leaching: recycling, CaF_2 capture, no acid treatment, low operational and capital costs.

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