

Circular Economy Model of Cathode Waste Processing

BLAŽ TROPENAUER, DUŠAN KLINAR, NIKO SAMEC & JANVIT GOLOB

Abstract The production of aluminium achieved significant step regarding energy efficiency while one of important waste stream remains untreated. Namely, waste, known as Spent Pot Lining (SPL) derives from each individual electrolytic cell, or more precisely from the material of the cathode electrode bath. The SPL stream contributes to about million tons per year of hazardous waste in the world's smelters production. The carbonaceous content represents 60 % of the whole SPL mass and consists of a great part of graphite. This part of waste represents a great opportunity to harvest its usable material flows. Laboratory tests confirmed the inefficiency of onestep treatment separation of different impurities as needed. With the help of laboratory investigations, the possibilities of material utilization of SPL have been studied. Comprehensive aspects of preliminary inquiry allow placing a new model for the preparation of products that satisfy customer's needs. This approach improves process economics and effectively close the loop of mass flow.

Keywords: • spent pot lining • carbon • waste treatment • cryolite • circular economy •

CORRESPONDENCE ADDRESS: Blaž Tropenauer, TALUM d.d. Kidričevo, Strategic research department, Tovarniška cesta 10, 2325 Kidričevo, Slovenia, e-mail: blaz.tropenauer@talum.si. Dušan Klinar, Scientific Research Centre BISTRA, Slovenski trg 6, 2250 Ptuj, Slovenia, e-mail: dusan.klinar@bistra.si. Niko Samec, PhD, Full Professor, University of Maribor Faculty of mechanical engineering, Smetanova ulica 17, 2000 Maribor, Slovenia, e-mail: niko.samec@um.si. Janvit Golob, PhD, Full Professor, University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, 1000 Ljubljana, Slovenia, e-mail: janvit.golob@fkkt.uni-lj.si.

1 Introduction

The origins of SPL formation lie in the electrolysis cells entire life of the operation. During start-up, melts of cryolite and alumina salts penetrate and fully impregnate the carbon cathodes. On the overall, the rate of sodium and bath penetration into the cathode is a function of its graphitization rate, current density, cryolite ratio (CR) and time of electrolysis (Soerlie, 1994).

Disposal or landfilling will soon not be an option in the future. The important starting point of research activities is based on possible applications of products in the regional economy. Namely, different applications direct the criteria for the product and consequently determinates the more precise concept of processing SPL.

The target of the research is to elaborate the concept and define the conditions for setting up efficient technologies for SPL treatment for already separated carbon and brick parts. A special emphasis is put on the local solution to these environmental problems.

Following modern trends, the effort directs to prepare SPL material for the full reuse, what means, establishing a circular economy, connected to several industries like metallurgy, cement production, construction and mineral wool production. Regarding self-usage of the processed waste (back to the electrolysis process or/and anode production) the preliminary investigations show that such a treatment can cause some quality problems regarding increasing sodium content despite positive economic effect.

2 Materials and Methods

A circular model to solve the environmental problem is difficult to conceive. This is partly the result of the wrong starting points, which put the existing methods and techniques in the forefront, and partly because of the many factors that influence the definition of the appropriate concept. The fact is that the development cycle started, which the stakeholders generally do not realize, but they are forced to initiate certain actions with which they have not met before. Therefore, a systematic approach is needed, which leads through the model of problem-solving.

2.1 The approach

In the beginning, it is necessary to be acquainted with the problems and existing solutions while further decisions are made upon these basics. Research strategies and actions follow, depend on developed technology concept. Therefore, a research and development phase necessary thoroughly examine the information about the origin of an environmental challenge, the problems caused by and recognize consequences. As enough knowledge is gathered about the environmental problem, the solution investigations begin. They can vary in different economic models and can offer outsourcing turnkey solutions or solutions that require own knowledge and efforts. In any case, an in-depth analysis of economic as well as technological solutions is required. Especially if the waste collection service express difficulties in running this activities or prices rise constantly, another model for an environmental solution should be pursued. This model extends the research phase to the technical level. Environmental problem owners must gather not only local but also professional and scientific knowledge to evaluate the existing state of the art technical solutions to choose the right technology provider. As Raymond (Raymond, 2010) exposes, this interdisciplinary knowledge integration is very demanding and linked with a significant degree of confusion. Problem owner can carry out laboratory tests or try to find on a market convincing information upon given technical solutions. The analytic results present strong support for the decision upon selected technology that would most likely solve the specific environmental problem of the company.

2.2 Standard and innovative models

Because the aluminium production industry, besides electrolysis aluminium, produces castings and foundry alloys, the technical knowledge is merely based on pyrometallurgical processes. Therefore, processes linked with this kind of technology is the first to be pursued by the techno-developing teams.

Company Talum has many foundries and produces cast alloys, billets, castings, and slugs out of its own produced primary or electrolysis aluminium. Company's experts decided to follow trends in the thermal waste decomposition of SPL waste as their expertise and education originated mostly in this engineering field.

The standard model

A classic path to decide appropriate technology was chosen. Only thermal review of SPL waste treatment was performed. Classical thermal treatment technologies reported troubles processing SPL as difficult grinding, clogging of feeding equipment, material adhesion, 30 % of inorganic residues and incomplete destruction of fluorides. Therefore, a new, innovative thermal technology was chosen for investigations, namely plasma technology. Pro and contras were investigated. This technology is believed to have many advantages like only 5 to 10 % glazed and inert residues, complete destruction of toxic waste components, high throughput, modularity, small-scale economics, production of calorific and combustible gas and no environmental impact.

To proof of these benefits, it is important to contact few technology providers and test their equipment for SPL processing. Detailed specifications of the waste must be carried out to submit as much as possible information to the provider. The goal is to convince the provider for laboratory and pilot test examination and receive feedback information. The provider can submit a bid, namely for simulation of the solution, laboratory tests or to continue with more tests.

Thermal tests on existing pilot devices offered by the equipment provider usually become very expensive. This turns out as a crucial hindrance to proceed with investigations as technology provider requests substantial cost refund to perform tests on a larger amount of waste sample. The customer is subjected to two choices. First, it can rely on the provider's simulation results and then it can secure the purchase of new technology with specific guarantees in the contract. However, there is no guarantee that with a new technology and special waste the economic outcomes will be the same as described in the business plan. In addition, the risk of the provider's business failure is always present. Therefore, very little customers are willing to take the risks by installing new environmental technologies that are not proven in practice.

The innovative model

Environmental solutions are usually technologically demanding and innovative. Because the standard approach does not give a solution to this environmental problem, some new, innovative approaches are many times considered. Such an approach can secure customers' investments in new technology to a far better extent than a standard approach does. It extends the design phase and allows the customer to convince himself upon the suitability of technological solutions.

The first difference is integrity. Namely, all the existing technological solutions should be considered and not just the staff's expertise. Therefore, a complete review of existing technologies is essential. An interdisciplinary approach to management is the next step. Combining interdisciplinary knowledge reduces the degree of complexity. Interdisciplinary knowledge is necessary to include understanding the state-of-the-art solutions. With a team of experts with diverse knowledge, the problem is covered comprehensively to gain an overview of the current state of managerial solutions and current technologies. External experts are usually part of such teams, as companies do not possess enough expertise in knowledge. Prior to checking the selected technological solution at the experimental level, it is necessary to familiarize with the complexity of the technological solution and the processing of the resulting products. Insofar, as the technological solution is based on laboratory tests, it is appropriate to check the results with different types of knowledge that can be either within the company itself or outside. The results stimulate new thinking and form the basis for the development of tacit knowledge and the delivery of this knowledge. New conceptual solutions and a combination of interdisciplinary knowledge renew the concept of the solution itself. From the many times discussed ideas and new concepts, requirements are defined that determine the quantitative scope, location, and user of the technology. It seems the solution lies in the local economy where derived products can circulate. New innovative technology needs to provide SPL detoxification and deactivation and consequently decomplex waste to the final inert material.

To be able to provide the appropriate technological solution and the products obtained, it is necessary to switch from the laboratory level to the pilot technology tests. Users of waste-derived products require an appropriate quantity to check the quality of products themselves. Positive results from the pilot plant confirm technological relevance and minimize risks associated with up-scaling technology and investment on a real scale.

If the technological solution and derived products can be confirmed, the environmental approval is close to being obtained. The priority of the solution lies not in the economies of scale of the investment, while local relevance and integration into the ecological circle of the local economy are quite more important. Also, the possibility to obtain relevant approvals for the issuance of an environmental permit given by the state. In this process, the team of experts also acquire local, tacit knowledge to finalize the solution. Tacit knowledge is personal and gained from direct interaction with suppliers, customers and people within the company (Nonaka, 1998).

If there is a suitable technology provider on the market, it is possible to negotiate for the delivery of most of the equipment. Because the basic engineering skills for this type of technology has been mastered, the provider's suitability can easily be checked. However, the equipment can also be bought, as a component on a market and finally assembled with own engineering knowledge to whole technology.

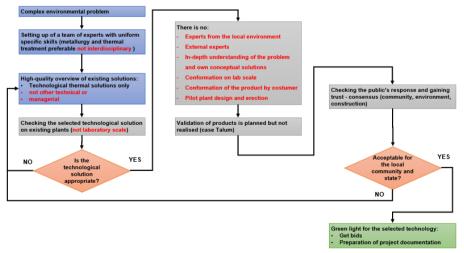


Figure 1: The shortcomings of the standard model (exposed with red text).

Important differences are notable between standard and innovative model. There are highlighted in the standard model shortcomings (Fig. 2). The standard model does not propose the interdisciplinarity of environmental issues and not

incorporate needed experts. Therefore, the problem cannot be discussed comprehensively. The main disadvantage of the standard model is, however, the lack of laboratory scale experiments. This phase gives low budget solutions of the studied technology with costumer conformation of the gained products. In a next step, a pilot plant can be built to test technological solutions, type of the equipment and gain product samples for tests.

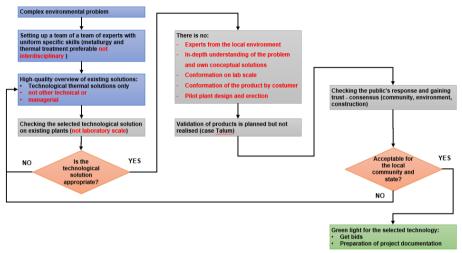


Figure 2: The shortcomings of the standard model (exposed with red text)

3 Results and Discussion

With the pursuing of the given innovative development model (Fig. 1), a new approach for the special environmental problem of the cathode SPL waste is addressed more adequately.

3.1 Environmental issues

SPL waste generating companies have constant environmental challenge linked with material handling, processing, and delivery. Dismantling process of an electrolysis cell starts with the mechanical demolition of various material layers. First, the cryolite layer is removed as it can be easily used again for the start of the electrolytic process. In next phase, the carbon part or the cathode is crushed and the firebrick layer separated. The carbon part is called the First cut, as it is cut off firstly, analogous to the Second cut represent the firebrick part.

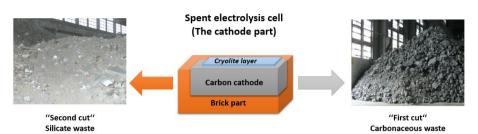


Figure 3: The spent cathode waste parts generation: first and second cuts.

3.1.1 Waste problematics

Above discussed "first and second cuts" contain cyanides and fluorides and are therefore toxic. An additional dangerous feature is fire hazard and explosiveness. The first cut contains a large amount of carbon with a relatively high calorific value. In the event of contact with moisture and water, some amounts of inflammable, toxic and explosive gases are generated as well (methane, ammonia, hydrogen). Also, by the dismantling process lot of toxic dust particles become airborne. Consequently, the process needs to be maintained in a closed storage hall.

The upon described properties make SPL a very dangerous and hard to process waste. Usually, an electrolysis plant has a dismantling team which is an everyday challenge to handle, process and deliver this waste to a waste disposal company. Such companies deliver waste to cement plants and incinerators which need fine material of rather small particles (approx. 200 micro m). The bulky waste is still toxic, flammable, and explosive. Grinding is very difficult due to graphite and sodium content, which cause the material to be sticky and slippery at the same time (Li, 2007). Besides, if grinding is proposed it must be processed by the support of water spray action to prevent over dusting. In short, the waste disposal companies also have a huge challenge and therefore the prices for SPL destruction rises.

3.1.2 Waste properties

The SPL waste is impregnated with soluble salts like NaF and insoluble cryolite and further with approx. 2 % of different types of cyanides. The silicate brick part can be used in construction, brick, cement works and glass wool production. The carbonaceous part of SPL is of special interest as it has energetic and material potential. The carbon can be utilized as an energy source to produce heat in various melting, combustion and incinerator applications. The carbon is partly graphitized and can, therefore, be a rich source of graphite products.

The silicate or brick part of the waste contains besides impurities like NaF merely possesses Quartz (SiO₂) and Mullite (Al₄Si₆O₁₀). Carbon content in the first cut reaches on average approx. 60 % of the whole sample, the NaF part covers about 20 to 30 % and the cryolite about 15 %.

3.2 Overview of existing technical solutions

Peer review of possible approaches and technologies for the processing of SPL provides comprehensive information disseminated in recent decades. This information spreads from individual research efforts to existing technological solutions.

Generally, two basic processes are in progress. Those are chemical and pyrometallurgical (or thermal) approaches with important weaknesses and advantages. The standard waste processing starts with waste mechanical preparation and later treatment process used, gives some intermediate products in form of energy and material. The products are for economic reasons subjected to further conversion to reach commercial products. Usually, there is always some waste present at the end of the process.

Mentioned processes have the same basic approach technique but differ in the flow of intermediate and final products. It is common to produce useful products out by the treatment process. Aluminium fluoride is a chemical product used in the production of electrolysis of the alumina and represents a high value and desirable product.

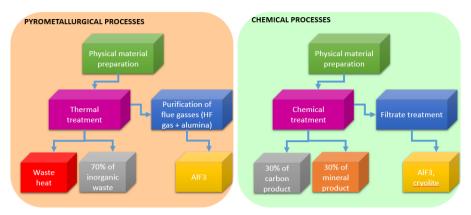


Figure 4: Two different processes with the same approach.

Chemical processes take place in several stages, and quite, different equipment is required. In thermal processes, one, the main phase, is predominant, and this is the thermal decomposition of the material. This phase, however, is very energy intensive and demands extensive maintenance. Although chemical processes seem to be more complex, they can offer a complete sustainable solution at normal environmental conditions (temperature, pressure). Finally resulted in commercial products with low CAPEX and OPEX with significant possibilities of material utilization.

3.2.1 The review of existing technical solutions

Thermal processes reduce the amount of SPL waste to the level of only mineral remains and brick parts. The carbon part burns, cyanides decompose at high temperatures, and fluorides are partially discharged in the form of gaseous HF. Afterwards, they are adsorbed using an alumina, where the product of aluminium trifluoride (AlF₃) is formed. This is the desired input compound in the chemical composition of electrolyte in the electrolysis cell. There are also cases of SPL use in cement plants and ironworks, but due to increasingly stringent legislation, these plants demand sorted and pre-processed input flow. The challenges are high levels of Sodium, Fluorine and toxic Cyanides and a high proportion of water-soluble part (like NaF) respectively (Holywell, 2013).

Best available technologies for non-ferrous metals describe many options to treat SPL: re-use of SPL in cement production, as a carbonaceous substance in the ironworks, as a secondary raw material (glass wool, salt slag) and as a substitute

of fuel (BREF, 2014). Oye describes both thermal and chemical methods of SPL processing, emphasizing the challenges of salt separation, which account for as much as 30 % of the total SPL content. Another technology considers solutions to produce graphite and the inclusion in the mass fraction of the cathode as well as the anodes (Hop, 2004).

In cement plants, the carbon part is used as a substitute for fuel, while the brick part becomes a part of clinker (Pawlek, 2012). Consequently, there is a noticeable decrease in the process temperature in the clinker production mass, which in turn reduces the consumption of heat per kilogram of clinker produced (Renó, 2013).

Aluminum Pechiney and Ciment D'Origny from France use a brick part as a substitute for the raw material for cement production in South Africa (CSIR, 2002). Care must be taken when grinding, storing and transporting crushed material and dosing, as there is a risk of gas formation (Rahman, 2015). The problem in cement plants is also caused by the diverse chemical composition of the waste that affects the industrial process. It is therefore important to prepare an appropriate and rather a constant mixture composition of the material used as the input raw material (Black, 2015).

In the ironworks, carbon part is used as a fuel and a reducing agent. Fluorides increase the flow rate of the slag and lower the melting point, but at the same time, they are also harmful to the pot wall (Meirelles, 2014). The metallurgical fluorspar contains between 60 and 85 % CaF2. It is widely used in the manufacture of iron, steel, and other metals. It acts as a flux to remove impurities (S, P) from the melt while improving the slag flow rate. The carbon part of the SPL can successfully replace fluorspar or fluorite (CaF2). Successfully increases the flow rate of the slag and reduces the levels of sulphur and phosphorus. The tests were successfully carried out in Russia (Personnet, 2016).

For special steel alloys with silicon and magnesium manufactured using an arc furnace, only the carbon section (first cut) should be used. It has the most suitable chemical, physical and metallurgical composition and properties as an addition to iron Si-Mg alloys. The brick part has an excessively powdery structure [Krüger, 2011].

Some also suggest other thermal techniques. One of them deals with the heating of the spent bricks above 750 °C to remove volatile impurities (Oliveira, 2000). Some recommend grinding spent cathodes and incineration in the fluid bed (Courbariaux, 2001), while others propose the glazing of this kind of waste by adding ingredients needed for the formation of glass (Balasubramanian, 2000). The problem with the fluid bed is the agglomeration of SPL particles with sand. Several authors (Saxena, 1994, Oye, 1994)] report about this, and it was also observed in our own tests (Mele, 2015).

We have noticed that a high temperature is needed for the decomposition of the spent carbon part (above 950 °C) and that these temperatures begin to liquefy the soluble salts. This leads to the prevention of oxygen access to the carbon structure and consequently greatly complicates thermal decomposition. The spent cathode sample without soluble salts ignites at substantially lower temperatures; also, thermal decomposition of the sample is effective.

According to own tests, it is obvious that soluble salt fraction must be removed before any treatment is proceeding as its negative influence prevail.

Chemical methods allow the separation of components and their purification in order to produce products that could be used either in their own processes or in other local industries. Some methods are based on the neutralization of the filtrate with calcium compounds (e.g. calcite CaCO₃) (Turner, 2008). Others focus on reuse and mostly predominate in the full exploitation of the raw material base. They tend to extract cryolite and carbon (Shi, 2012; Cao, 2014) and useful fluoride compounds (Lisbona, 2008, Ntuk, 2015) by dissolving in bases, acids or in solutions of aluminium salts. Some separation techniques use a two-step technique. Other techniques use three-stage separation, namely: water purification, basic and, finally, acidic cleaning (Indurkar, 2014; Shi, 2012, Schönfelder, 2014). Also, flotation is used to physically separate the carbon and brick part (Li, 2010; Holywell 2013; Schönfelder, 2014).

3.3 The results of experimental work

The decision to proof, the technological process on a laboratory scale before further development with different technology providers have been made. Managerial proposal to process the waste in the cement production process was not feasible as cement works experienced a series of operational problems. In addition, this kind of waste has a lower calorific value and is not competitive with some others like preferable wastes tires. The state-of-the-art findings from scientific articles about other treatment technologies were included in the knowledge. Cooperation with people from different departments inside the organization began and, in this way, the exchange of tacit and explicit knowledge followed. Company's experts from the different field of expertise and outsourcing experts were involved.

Firstly, the thermal option was verified, as the goal was to reduce the volume of the waste. Afterwards, chemical testing was performed.

3.3.1 Thermal tests on SPL

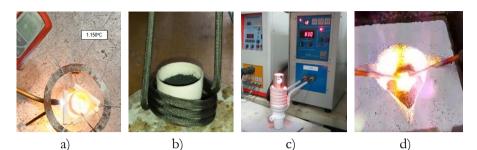
Thermal tests on different thermal devices offered by the equipment providers are usually very expensive. To proof some thermal technology solutions that exist on the market, laboratory tests need to follow. These technologies merely base on gasification processes at a temperature of around 900 °C where the products are syngas and inert residues.

Tests were done with a sample of SPL first cut. Preliminary tests were done with a ceramic crucible, which was exposed to a direct gas burner flame. The waste sample did not ignite until 950 °C. One reason is that the material is supposed to withstand high operating temperatures in electrolysis environment. The other is that the inorganic components like NaF melt and prevent oxygen access to the carbon matrix.

Induction heating with direct coil exposure gave no promising results, as there was no increase in temperature of the granulated waste sample. The opposite was the case of an induction coil wrapped around a bulky sample of first cut SPL sample. The temperature raised but only to 250 °C as low power induction apparatus was used for experimenting (1 kWe). By using stronger power equipment (7 kWe) and indirect heating trough stainless steel the temperature raised quickly to 900 °C and the effect was like the mentioned indirect heating with a gas burner. The problem is the stainless-steel crucible which material is at this elevated temperature rapidly degrade.

In addition, some individual providers of the high-temperature technology of waste treatment (more than 3,000 °C) were reviewed and contacted. The socalled plasma gasification technology has some advantages regarding waste volume decomposition but also shortcomings regarding electricity consumption, high capital costs and in some cases unreliable operation and performance. Some tests were also performed with plasma generating equipment on a first cut SPL sample. The first testing was performed exposing the granulated sample to an arched flame at an electrical power of 2 kW. The result was a molten inorganic form and later also crust that again prevented oxidation of carbon. The next test was performed with a powerful plasma cutter equipment (13.7 kWe). A bulky stone of first cut SPL waste was exposed to a plasma flame. The mass of the missing piece of the bulky stone was measured and residence time and used energy calculated. The calculated result of the test gives a throughput of treated first cut SPL in the size of 2 kg/h at operating cost that would double the existing cost of the SPL destruction.

Testing was also performed within a fluid bed pilot plant technology at operating temperatures up to 800 °C. The test result in the reactor gives the SPL waste and the operating sand material lumped together to form stone like products that completely clog the feed equipment. Even if the waste material was subjected to temperatures up to 1,200 °C, the results of the leaching of fluorides from the residual waste exceeded the legally permitted limit values (Mikša., 2003).



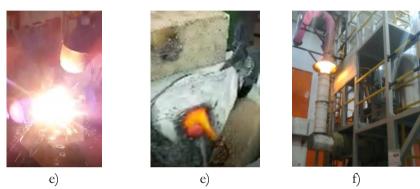


Figure 5: Thermal laboratory testing of SPL waste decomposition:

- Induction heating of waste sample with ceramic (a) and stainless steel crucible (b)
- Gas burner indirect heating of SPL (c)
- Thermal arc plasma of SPL (d) and plasma cutting with resulted bulk SPL piece (e)
- fluid bed reactor pilot plant test (f)

3.3.2 Conclusion of laboratory thermal testing on SPL

The laboratory thermal tests imply that this kind of treatment need high temperature and energy demand, uses large quantities of oxygen and requires complex equipment maintenance as the process operates in a corrosive environment. The results of thermal laboratory tests of SPL waste were unsatisfactory even after exposure to very high temperatures. The general problem of the results without adequate mixing is contact with oxygen. Carbon in the SPL does not get enough oxygen because molten inorganic waste fraction, which liquefies at temperatures around 900 °C overflow the SPL particle. To proceed with thermal testing, the inorganic fraction of waste needs to be

removed. Namely, as thermal testing on water-washed SPL sample give sample ignition at a substantially lower temperature (750 °C) and burned later independently without disturbance caused by mentioned impurities.

3.3.3 Chemical leaching tests

As the results from thermal tests were negative, the decision to continue with chemical treatment on laboratory tests seems to be logical. To enable the thermal test results some major impurities must be removed first. A review of existing technology solutions was performed, some of them are still at the stage of laboratory development, while others are already close to commercial scale. This kind of technologies differs in process steps and types of products at output like cryolite, carbon and aluminium fluorides.

In the first step, water-soluble salts extraction gives best results also in combination of soluble cyanide degradation. Insoluble salts, like cryolite, can only be extracted by chemical reaction, a combination of reactive extraction offer an optimal solution of the problem. Flotation can be used to separate mixed SPL into silicate (chamotte) part and a carbon one. For all three procedures, water leaching, reactive extraction, and flotation, introductory tests were carried out to test the promise of basic results. The testing procedure was divided into three phases. Reactive extraction of insoluble salts or cryolite represented the 1st phase. Based on 1st phase tests, optimum parameters for the dissolution of the cryolite were obtained and represent an input for the second phase. In a 2nd phase followed in optimized reactive extraction is combined to separate carbonaceous parts from Chamotte ones. The carbon part was subsequently subjected to the optimal conditions obtained from the 2nd phase of reactive extraction of the First Cut sample.

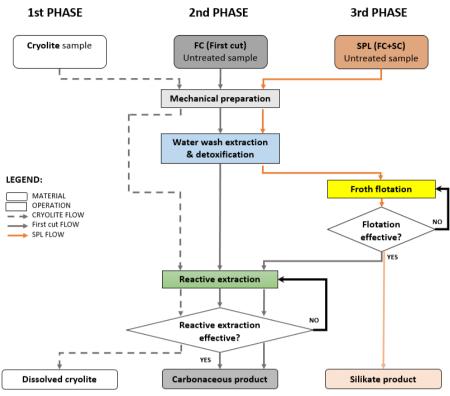


Figure 6: A model of laboratory scale testing of SPL waste recovery.

The first test was intended to separate impurities which are soluble in water. Sodium fluoride dissolves quickly in water and therefore leach quickly. A variety of test was performed to define optimal parameters for dissolution time, liquidsolid (L/S) ratio and the number of water extraction repetitions or equilibrium data at different L/S conditions. Such basic parameters are crucial for further process design.

Review of the flotation was performed with two types of commercially available mixtures of flotation reagents. Promising results give 95 % separation efficiency, enough for most application of the separated material.

Further experiments with the extraction of most water-insoluble inorganic impurities follow some information about basic, acid (Shi, 2012) and Al³⁺ [Lisbona, 2008] reactive leaching. To simplify preparation of samples all experiments were performed with the mechanical separated first material. Initial

water leaching tests remove water-soluble components (NaF and Na₂O all around 10 %), dissolve most of the cyanides and rise carbon content to approx. 72 %. Reactive components like small amounts of carbides (less than 0.5 %) react to form methane gas. The inert and insoluble material still contain fluorine, sodium salts (cryolite, calcium fluoride; more than 10 %), sodium silicates and sodium components of alumina (diaoyudaoite and alumina). Further reactive leaching can be directed toward removal of all fluorine and sodium or same sodium alumina components and calcium fluoride can be left. Important results on rising carbon content are achieved by NaOH reactive leaching where no additional ionic species is introduced in the system. Carbon content rises to 83 % what can be, together with useful remaining (mainly CaF₂, and some parts of sodium silicate and alumina components), an acceptable composition for some metallurgical applications. Next level of carbon content close to 90 % is reached only with acid or Al3+ leaching but enormous complications with new ionic species (chlorine or sulphate) appear at final recycling of extract. This is not the case in sodium hydroxide extraction where almost complete reuse of chemicals is possible.



Figure 7: Chemical laboratory testing of SPL waste recovery (A mixing, B vacuum filtration, pH and conductivity measurements)

3.3.4 Conclusion of laboratory chemical tests on SPL

Results of chemical testing, in comparison to thermal techniques, open totally new perspectives in a direction of material recycling and reuse in the local economy. There are several advantages: operating at normal environmental conditions, low maintenance of equipment, low operating costs, promising products and no residues.

Undoubtedly, the direction toward preparation of SPL with reactive extraction seems to be a most permissible path toward reuse and material recycling of still now a toxic waste burden. Such a path of research and development toward acquiring sustainable solutions to remain waste problems in primary aluminium production can lead to sustainable waste-free and low carbon local economy.

4 Conclusion

Comparison of results/products by the standard approach and by the innovative method are presented in the following tables.

What's new?	Details	More explanation and examples
Comprehensive & interdisciplinary approach	Review of available technology	Mechanical, Physical, Thermal, Chemical BAT treatment techniques; Peer- review
Local tacit knowledge	Experiences with technology, and providers Examples of good practices	Thermal treatment Local Cement works, waste companies
Laboratory verification	of technology advantages of products of by-products	Thermal tests: point of ignition, energy balance, residues after incineration Chemical tests: equilibrium states by the method of multi-stage extraction, dissolving the contained weakly soluble structures (cryolite, CaF2, aluminates) and gaining useful products (AIF2OH, separated cryolite, etc.)
A solution for the local environment	Waste is processed at the location it generates Products are consumed at the treatment plant or/and at local industries	SPL is processed at or near electrolysis plant NaOH is consumed in the waste process, CaF ₂ in metallurgy

Table 1: New developments achieved with the introduction of the innovative method

The benefits	Details	More explanation and examples
Determinate the best available technology (BAT)	for the given environmental issue	The solution refers to waste originating worn out electrolysis cathode
The closed circle of local waste treatment and product usage	No residue as resulted products are marketable, and by-products are used in the proposed treatment technology	The solution is especially intended for the local environment as there are restrictions regarding transportation legislation and transportation costs
Low CAPEX & OPEX	Comparing to the thermal solution and best chemical solutions	by-products (NaOH) reuse no acid usage – high operating costs no acid formation – corrosiveness and high maintenance no residue
Complete material utilization	No residues Material instead of energy harvest	The left impurities in carbon are not disturbing the quality of material flow in the metallurgy industry. By-products: NaOH Products: Semigrahitised carbon and Fluorspar CaF ₂
Marketable products	Semigraphitized carbon, NaOH caustic solutions, Fluorspar CaF ₂	Metallurgy industry (carbon, CaF ₂) Chemical industry (NaOH)
The possibility of marketing the knowledge	Adopted Basic engineering Technological solutions	Creating offers to industries with the same waste issue
Knowledge collection and skills upgrade	Building your team s competences and skills	Raising the potential for solving technological problems

Table 2: The benefits of the innovative method

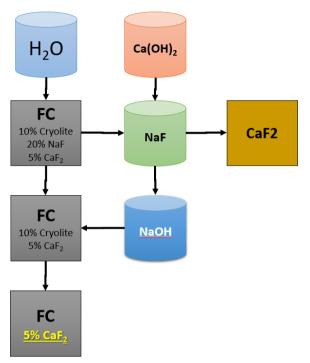


Figure 8: The proposed solution diagram for SPL treatment.

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References

- Balasubramanian G., Nimje M. T., Kutumbarao V. V., 2000. Conversion of aluminium industry wastes into glass-ceramic products, Trav. Com. Int. Etude Bauxites, Alumine, Alum. (13th Int. Symp. of ICSOBA, 2000), 27 (2000), 396-402.
- Black Phil, 2015. Innovation in SPL Transformation the Industrial Ecology Way Regain, 2015 - LIGHT METAL AGE
- BREF Non Ferrous Metals Industries, 2014. Final Draft 10, NFM 2014 EC directorategeneral JRC
- Cao Xiao-zhou, SHI Yuan-yuan, Zhao Shung, Xue Xiang-Xin, 2014. Recovery of Valuable Components from Spent Pot Lining of Aluminium electrolytic Reduction Cells, Journal of Northeastern University (Natural Science), Vol. 35, No. 12

- Chen Xiping, Li Wangxing, 2007. Research on Crushing Character of Spent Cathode; Light Metals 2007
- Courbariaux Y., 2001.Thermal treatment of spent potliners in an internal circulating fluidized bed using natural gas burner, Proc. 16th Int. Conf. Fluid Bed Combustion, 1174-1190.
- CSIR, 2002. Environmental Impact Assessment for the proposed Aluminium Pechiney melter within the Coega Industrial Zone, Port Elizabeth, South Africa- Elsevier Energy Conversion and Management, CSIR Report reference: ENV-S-C 2002-092(B)
- Holywell, G., Breault, R., 2013. An overview of useful methods to treat, recover, or recycle spent potlining. Jom 65, 1441–1451. https://doi.org/10.1007/s11837-013-0769-y
- HOP J., A. STØRE, T. FOOSNÆS, and H.A. ØYE, 2004. Chemical and physical changes of cathode carbon by aluminium electrolysis, VII International Conference on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy, 775-782
- Indurkar D. Pankaj, 2014. Optimization in the treatment of Spent pot Lining A Hazardous Waste Made Safe, M. TECH THESIS, Chemical Engineering at National Institute of Technology
- Krüger Paulo, 2011. USE OF SPENT POTLINING (SPL) IN FERRO SILICO MANGANESE SMELTING, Light Metals, 2011, 275-280
- Lisbona, D.F., Steel, K.M., 2008. Recovery of fluoride values from spent pot-lining: Precipitation of an aluminium hydroxyfluoride hydrate product. Sep. Purif. Technol. 61, 182–192. https://doi.org/10.1016/j.seppur.2007.10.012.
- Meirelles Bruna, Santos, H., 2014. Economic and Environmental Alternative for Destination of Spent Pot Lining from Primary Aluminum Production, Light Metals 2014, doi: 10.1002/9781118888438.ch96, ISBN 9781118888438
- Mele Jernej, SPL gasification, Bosio report, 2015
- Mikša, D., Homšak, M., Samec, N., 2003. Spent potlining utilisation possibilities. Waste Manag. Res. 21, 467–473. https://doi.org/10.1177/0734242X0302100509
- Nonaka, I., Konno, N., 1998. The Concept of Ba: Building A Foundation for Knowledge Creation. Calif. Manage. Rev. 43, 1–15.
- Ntuk Ubong, Stephan Tait, Edward T.White, Karen M. Steel, 2015. The precipitation and solubility of aluminium hydroxyfluoride hydrate between 30 and 70 °C, Hydrometallurgy 155, 79–87
- Oliveira D. Goncalves, 2000. Hot processing of spent refractory linings from aluminium electrowinning cells, BR patent 00,004,425 (Appl. date 4 August 2000)
- Pawlek P.Rudolf, Spent Potlining: An update, Light Metals 2012, 1313-1317
- Personnet B. Pierre, 2013. Treatment and reuse of Spent Pot Lining, an Industrial Application in Cement Kiln. Light Metals 2016, doi: 10.1007/978-3-319-48200-2, ISBN 978-3-319-48577-5
- Rahman A., Rasul M. G., Khan M. M.K., Sharma S., 2015. Recent development on the uses of alternative fuels in cement manufacturing process Fuel DOI: 10.1016/j.fuel.2014.12.029, ISBN 0016-2361
- Raymond, C.M., Fazey, I., Reed, M.S., Stringer, L.C., Robinson, G.M., Evely, A.C., 2010. Integrating local and scientific knowledge for environmental management. J. Environ. Manage. 91, 1766–1777. https://doi.org/10.1016/j.jenvman.2010.03.023.

- Renó Maria Luiza Grillo, 2013.Exergy analyses in cement production applying waste fuel and mineralizer, - Elsevier Energy Conversion and Management
- Saxena, S. C., Jotshi, C. K., 1994. Fluidized-bed incineration of waste materials. Progress in Energy and Combustion Science Journal, doi 10.1016/0360-1285(94)90012-4, ISBN 0360-1285
- Schönfelder, I., Gock, E., Tochtrop, E., Rieder, S., n.d., 2014. Recycling von Elektrolyseausbruch (SPL) aus der Primäraluminiumgewinnung 385–404.
- SHI, Z., LI, W., HU, X., REN, B., GAO, B., WANG, Z., 2012. Recovery of carbon and cryolite from spent pot lining of aluminium reduction cells by chemical leaching. Trans. Nonferrous Met. Soc. China 22, 222–227. https://doi.org/10.1016/S1003-6326(11)61164-3
- Soerlie Morten, Oeye A. Harald, 1994. Cathodes in aluminium electrolysis, Aluminium-Verlag 2nd Edition, Düsseldorf
- Turner D. Brett, Philip J. Binning, Scott W. Sloan, 2008, A calcite permeable reactive barrier for the remediation of Fluoride from spent potliner (SPL) contaminated groundwater, Journal of Contaminant Hydrology 95, 110–120.