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VALORIZATION OF TREATED SPENT POTLINING IN CEMENT INDUSTRY

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ABSTRACT

Spent potlining (SPL) is a hazardous waste produced by aluminum smelters. It is classified as a hazardous waste due to its contamination with fluorides and cyanides and its reactivity with water, generating explosive gases. After being industrially and hydrometallurgically treated by the Low Caustic Leaching and Liming (LCL&L) process, the refractory part of SPL becomes an inert, non-hazardous material, called LCLL Ash. The cement industry is a major emitter of greenhouse gases. One of the best options for reducing the carbon footprint of concrete is the use of supplementary cementitious materials or fillers to replace part of the cement in the concrete. This article presents the conditions that make LCLL Ash a suitable and value-added material for the cement industry. The results presented were obtained over the past four years as part of an R&D project at the Ecole de Technologie Superieure (Montreal) and Universite Laval (Quebec), with the support of Rio Tinto and Ciment Quebec.

INTRODUCTION

Spent potlining is a hazardous waste produced in the pot rooms of aluminum smelters. This waste is generated from the internal lining of aluminium (Al) cells consisting of carbon and refractory bricks, which are replaced after five to eight years of service life. SPL is classified as a hazardous waste because of its contamination with fluorides and cyanides and its reactivity with water, generating explosive gases. Therefore, transportation, storage and final disposal of SPL are subject to strict environmental regulations.

Each tonne of aluminum produced generates approximately 22 kg of SPL. Several options to treat SPL exist and were reported in the literature [1,2]. In the early 1990s, Rio Tinto developed the “Low-Caustic Leaching and Liming” hydrometallurgical process (LCL&L) at the Arvida Research and Development Centre (ARDC) in Jonquiere, Quebec. This process leaches fluorides and cyanide compounds out of SPL and produces inert by-products having high valorization potential [3,4]. In 2008, an SPL treatment plant was built in Jonquiere, which processes up to 80 kt of SPL per year [5,6].

During this hydrometallurgical treatment, the refractory part of SPL becomes an inert, non-hazardous material, called LCLL Ash. Due to its chemical and mineral composition, LCLL Ash is attractive for the clinker chemistry and its use as a raw material for cement production will be presented in this paper. LCLL Ash material has also the potential to be used as a supplementary cementitious material (SCM) in the production of concrete and backfill. Cement production is known to generate 4-8% of global carbon emissions [7]. Efforts are being made worldwide to reduce the use of cement in concrete mixes. Many improvements in the cement production process have been made to reduce the energy consumption of cement plants and make them less polluting. However, the production of one tonne of Portland clinker can produce up to one tonne of CO_2, 60 % of which comes from the inevitable decarbonation reaction. The use of a supplementary cementitious material (SCM), to reduce the amount of cement in concrete and its environmental impact, is one of the preferred solutions today. This paper, written in collaboration with the Ecole de Technologie Superieure (ETS, Montreal) and Universite Laval (Quebec), presents the conditions that make LCLL Ash a suitable SCM for applications in concrete. Other valorization options for LCLL Ash, for example in ultrahigh resistance concrete (UHPC), were also studied and summarized in this paper.

THE LCL&L PROCESS

The LCL&L process leaches fluorides and cyanide compounds out of SPL and generates inert by-products, which can be valorized more easily than hazardous waste.

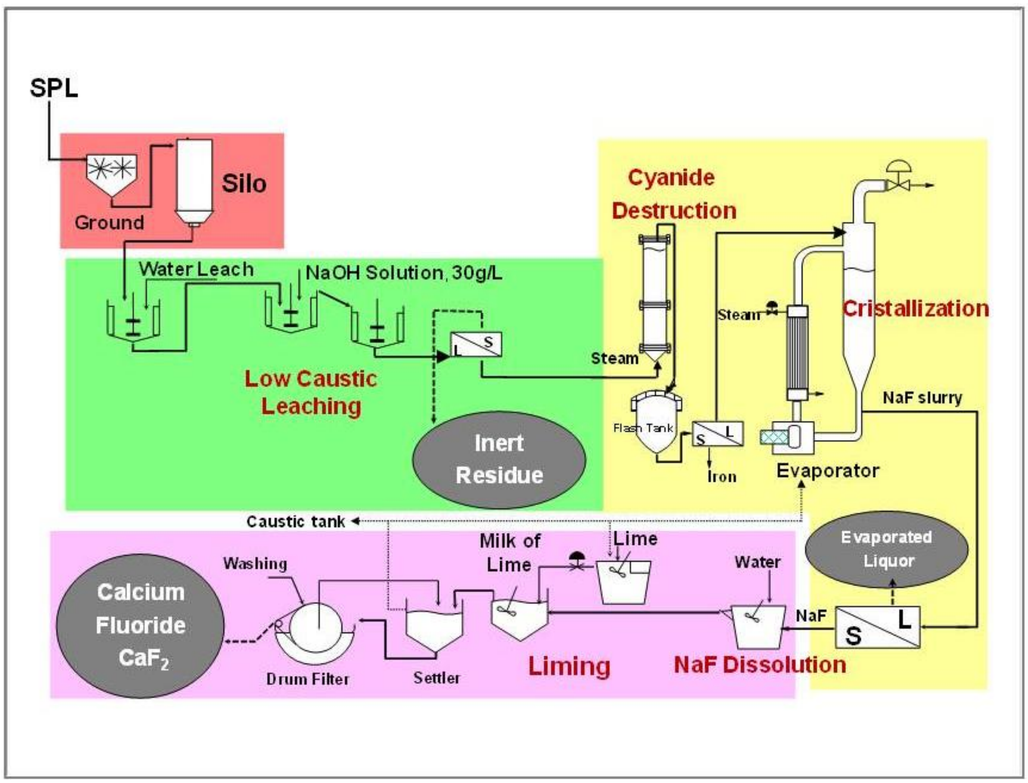

Figure 1. LCL&L process flow diagram.

As shown in Figure 1, two separate sectors (one wet and one dry) are needed to treat SPL. The dry sector includes unloading, handling and storage of SPL containers, SPL grinding (less than 300 microns) and ground SPL storage. The wet sector consists of low-caustic serial leaching steps to extract soluble fluorides and cyanide compounds. These inert residues are called carbonaceous by-products (CBPs). Cyanide compounds, contained in the leachate, are subsequently destroyed in pressurized reactors using high temperature hydrolysis, while fluorides are precipitated as inert calcium fluoride after reaction with lime. More details on the recent development of the LCL&L process are available in [8].

VALORIZATION OPTIONS FOR CARBON BY-PRODUCTS (CBPs)

Figure 2 presents the different options for CBP valorization. Since the start-up of the SPL treatment plant, approximately 800 kt of SPL has been treated, half of which comes from SPL stored in warehouses from mid 80s until the start-up of the plant in 2008. Due to this latter mixed composition (carbon and refractory lining), the produced CBP contains approximately 30-40% of carbon (on a dry basis) and 60-70% of inert materials (mainly SiO_2 and Al_2O_3). All this mixed CBP production has been valorized as a low-density (1250 kg/m^3) civil engineering construction material (called LCLL Geotek) for the construction of dams, at the Rio Tinto bauxite residue disposal site.

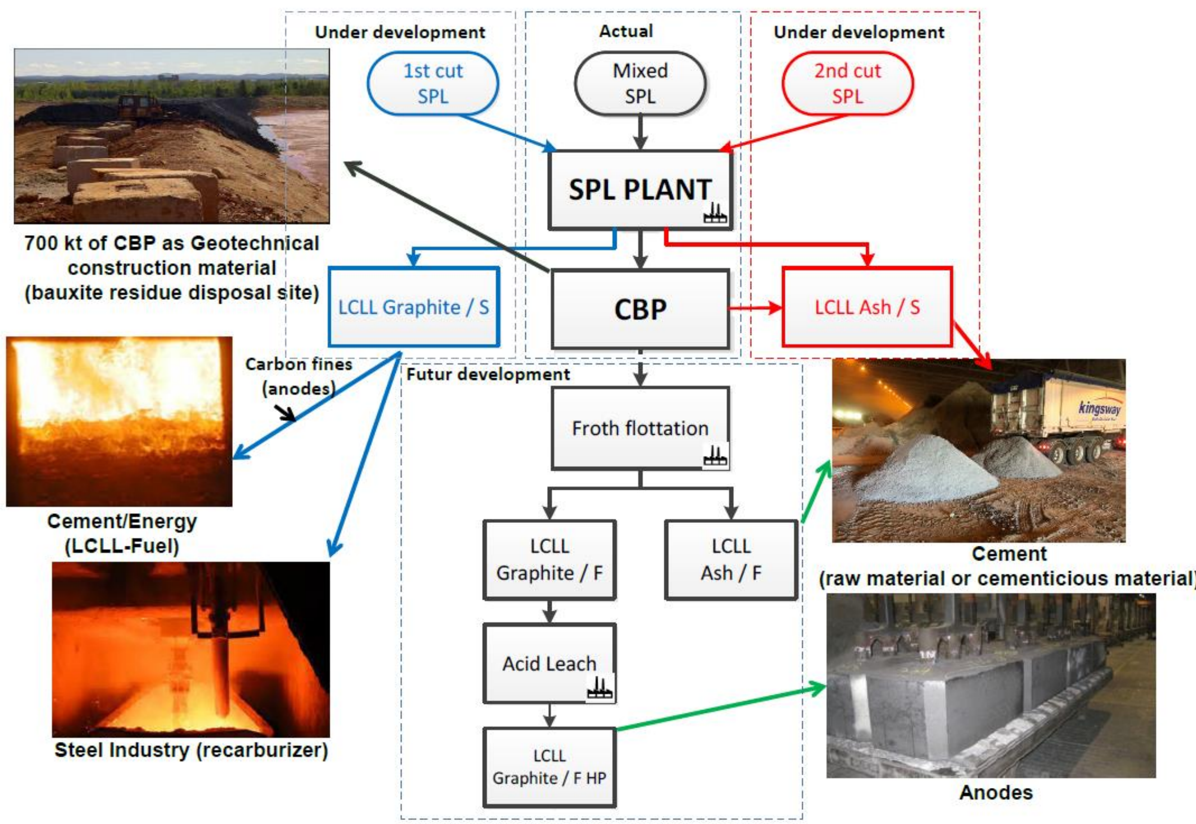

Figure 2. Valorization options for the carbon by-products (CBPs)

Since 2006, Rio Tinto has developed an intensive R&D program to find alternative valorizations for CBP. Due to its mixed nature (carbon and refractory compounds), CBP is essentially limited to be used as alternative fuel and raw material for clinker production in the cement industry. Carbon is attractive for its energy content (approx. 13 GJ/t), while the inert material is attractive for its mineral composition (rich in aluminosilicates), which is very close to that of the clinker chemistry. Depending on the use of CBP in the cement process, it is more interesting to separate the carbon fraction from the refractory fraction. The first cut (SPL fraction above the collector bars, mainly carbon) and the second cut (SPL fraction below the collector bars, mainly refractory brick) can be separated when dismantling electrolysis pots. The carbon concentrate from the first cut treatment is called LCLL graphite, and the refractory concentrate from the second cut treatment is called LCLL Ash (C <10%).

VALORIZATION OF LCLL ASH IN CEMENT INDUSTRY

LCLL Ash as raw material for clinker production

The cement industry as well as some other industrial pyrometallurgical processes can use SPL as generated, without any pretreatment [2]. However, strict restrictions on the sodium and fluoride content in the final product limit the amount of SPL that can be added to these processes. Nowadays, environmental regulations are also stricter, and it becomes difficult for these industries to accept unprocessed SPL. LCLL ash is attractive for the clinker chemistry due to its mineral composition and can be used as raw material. Compared to the direct valorization of SPL in the cement industry, LCLL Ash contains ten times less total fluorides and lower alkalis (sodium), which enables a higher dosage in the kiln.

Since 2018, Rio Tinto, Geocycle Canada and Lafarge Canada have been working together to reuse LCLL Ash as raw material for clinker production. To meet their specifications, Geocycle Canada and Rio Tinto have developed a new product called Alextra, made from LCLL Ash with additions of alumina or refractory waste materials coming from the aluminum industry. Alextra is the result of years of research and development, aimed at finding new ways to deliver sustainable outcomes and value from used potlining. Alextra is a good alternative to raw materials such as alumina and silica, which are commonly refined or mined for use in the cement industry. This leads us to also develop new products based on treated mixed SPL and other industrial wastes as sources of silica or iron to meet customer needs.

LCLL Ash as Supplementary Cementitious Material (SCM)

In 2017, an intensive R&D program, for the potential use of LCLL Ash as SCM, was initiated in collaboration with the Ecole de Technologie Superieure (ETS, Montréal), Universite Laval and Ciment Quebec. The aim of this project was to identify the conditions that make LCLL Ash a suitable supplementary cementitious material (SCM) for concrete production.

The procedure for evaluating the reactivity of LCLL Ash for use as a supplementary cementitious material is summarized in Figure 3. A Frattini test, following the procedures in [9], [10],.was carried out to evaluate the pozzolanic reactivity of LCLL Ash. This test evaluates the reactivity of SCM aluminosilicate phases with portlandite to precipitate more hydrates. R^3 tests are based on a mix that recreates the chemical behavior of limestone cement, without cement particles [11]. The heat generated by the precipitation of hydrates was measured by isothermal calorimetry, and the consumption of portlandite was measured by thermogravimetrically analysis. The pastes were measured by X-ray diffraction after the R^3 tests. The reactivity of LCLL Ash (with and without calcination) as well as the other SCMs were tested by measuring the compressive strength of mortar containing 20 wt% SCMs.

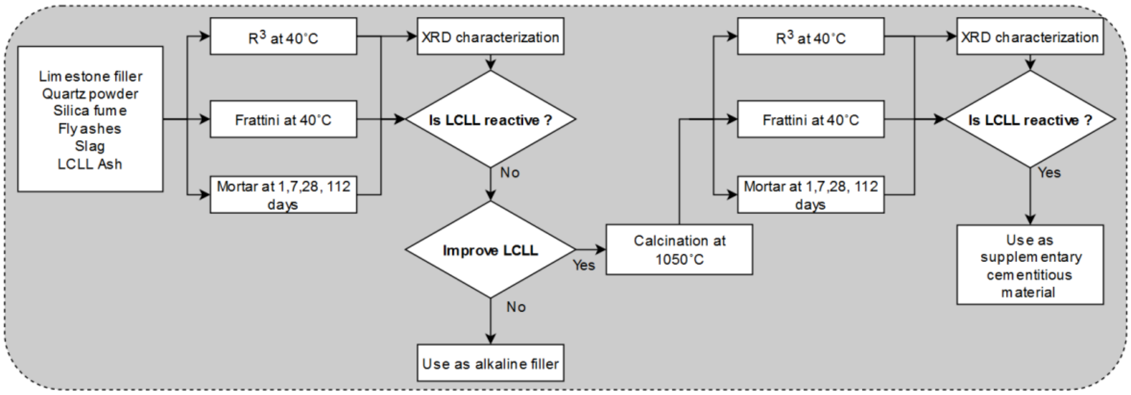

Figure 3. Schematic of the experimental plan to evaluate the reactivity of LCLL Ash [12].

As shown in Figure 4, tests on the reactivity of LCLL ash in cement in Frattini and compressive mortar [12] showed similar behaviors to that of fillers such as quartz powder (Q) and limestone filler (FC). For LCLL Ash calcined at 1050 °C, referred to as LCLL-C in Figure 4, improved reactivity was observed during the Frattini test with higher calcium removal, close to what was observed for fly ash. The same trend was observed on the mortar (Figure 4) with a relative compressive strength close to that of fly ash (FA) and slag (GGBS) values. This trend was also confirmed by R^3 tests showing higher heat release, higher portlandite consumption and the presence of new hydrates, identified by XRD, such as monocarboaluminate. The behavior of calcined LCLL Ash is closer to that of supplementary cementitious materials.

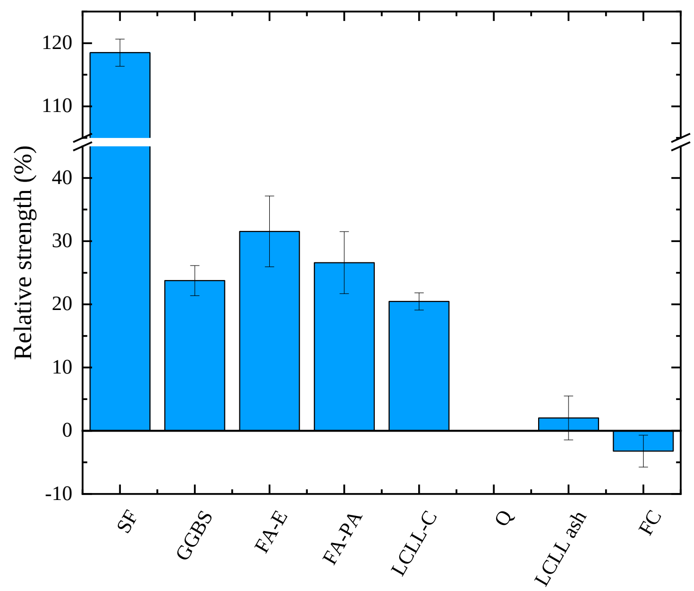

Figure 4. Relative strength of mortar containing 20 wt% SCMs at 112 days (data normalized to quartz values).

LCLL Ash for ultrahigh resistance concrete (UHPC)

This work aimed at developing UHPC mixtures with LCLL Ash powder using their mineral filler effect to improve the competitiveness of UHPC in terms of cost and carbon footprint. More specifically, the effect of partially replacing the cement in UHPC mixtures by LCLL Ash was studied in terms of workability, hydration kinetic, autogenous shrinkage, mechanical properties, and microstructure morphology [13].

Figure 5 shows the compressive strength results and flow table values of the designed UHPC mixtures. The flowability of the mixture is an important parameter enabling the pouring of concrete. LCLL Ash particles reduced the flowability of the mixtures. The spread flow value of samples with 6% LCLL Ash (L6) and 12% LCLL Ash (L12) decreased by 4.3% and 13 %, respectively, compared to the reference (L0) without LCLL Ash. This can be explained by the high alumina and silica content of LCLL Ash, which absorbs more water from the total water added, thus reducing the flowability as observed by others [14]. The compressive strength of samples with 6 % and 12 % of LCLL Ash is comparable to the reference, which reached up to 120 MPa at 28 days of normal curing. This means that 12 % of the cement in concrete can be replaced by LCLL Ash with minimal effects on strength and flowability.

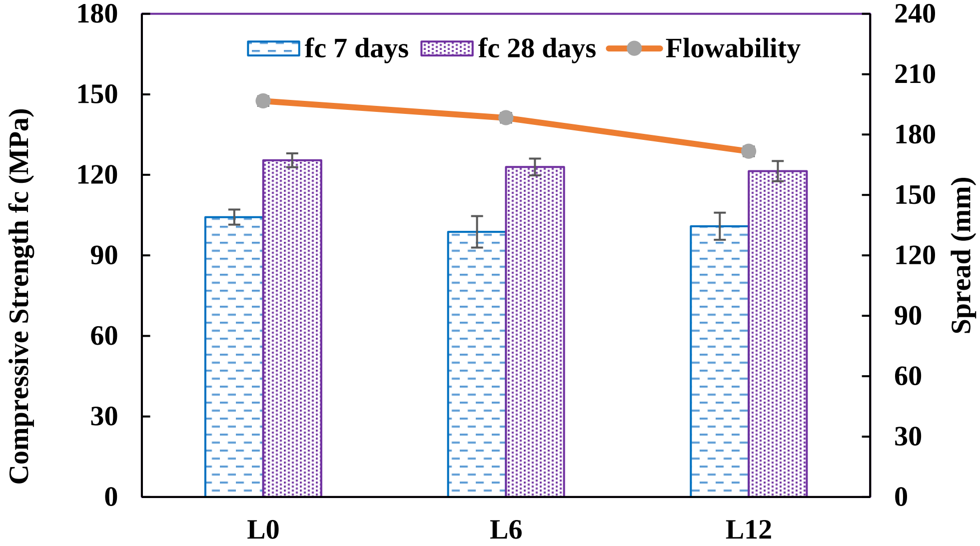

Figure 5. Compressive strength versus flowability with the standard derivation.

SUMMARY

The LCL&L process was developed by Rio Tinto to treat fresh and stored spent potlining generated by the aluminum industry in a sustainable way. It is a proven and robust technology with approximately 800 kt of different types of SPL treated to date. Today, less than 300 kt of SPL remains stored.

Meanwhile, R&D work has been undertaken to develop and implement different ways to valorize LCL&L by-products. As regards the refractory part of SPL (second cut) treated by the LCL&L process, called LCLL Ash, the extensive R&D work carried out over the last five years has enabled great progress to be made in understanding and using this by-product in the cement industry.

For the past two years, LCLL Ash has been used as raw material to produce a manufactured product called Alextra, which is used by Lafarge for clinker production. Regarding the use of LCLL Ash as SCM, R&D studies conducted by ETS have shown that without thermal treatment, the LCLL Ash has low reactivity. However, after further calcination at 1050 °C, LCLL Ash showed a significant improvement of its reactivity in cement, and transforms into a pozzolanic material, similar to fly ash. In addition, due to the high availability of reactive alumina in calcined LCLL Ash, new hydrated phases may precipitate, such as carboaluminate phases. Calcining the material improves its reactivity and makes it potentially a suitable cementitious material to replace Portland cement in concrete. Replacing a portion of the cement with calcined LCLL Ash could reduce the environmental and energetic impacts of blended cement for local use.

For ultrahigh performance concrete, R&D studies conducted by Universite Laval showed that 12 % of the cement used in UHPC concrete can be replaced by LCLL Ash without greatly affecting strength and flowability.

Acknowledgements

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