Valorization of Treated Spend Pot Lining Byproduct from the Primary Aluminum Production as Supplementary Cementitious Materials

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Abstract

About 22 kg of spent pot lining (SPL) is generated per tonne of aluminium from electrolysis cells and listed as industrial hazardous waste. After the hydrometallurgical treatment in the Low Caustic Leaching and Liming (LCL&L) process, the refractory part of SPL is separated and becomes an inert non-hazardous material, called LCLL ash. This article presents the conditions for LCLL ash to be a suitable supplementary cementitious material (SCM) for use in the production of concrete. Multiple tests, including Frattini test, Rilem R3 and XRD, are used to evaluate the reactivity of LCLL ash and calcined LCLL ash. The rheology and mechanical properties of concrete with LCLL ash as SCM were determined for the optimum conditions. The results also showed that the utilization of LCLL ash is feasible to use in ultrahigh performance concrete with acceptable flow and strength. In addition, the LCLL ash can potentially be also used in mine backfill production. This makes that LCLL ash, a by-product from primary aluminum production, has several promising valorization avenues in the applications of cement and concrete.

Keywords: Aluminum primary production, Low Caustic Leaching & Liming, Treated spent pot lining (SPL), Calcination, Supplementary cementitious materials (SCM), Ultra-high-performance concrete (UHPC).

1. Introduction

The production of primary aluminium generates about 22 kg of spent pot lining (SPL) per tonne of aluminium from electrolysis cells. Because of its nature and properties SPL is listed as industrial hazardous waste and has to be treated in a special process such as the LCLL process developed by Rio Tinto. During the hydrometallurgical treatment by the Low Caustic Leaching and Liming (LCL&L) process, the refractory part of SPL becomes an inert non-hazardous material, called LCLL ash. This LCLL ash material has the potential to be used as supplementary cementitious materials (SCM) in the production of concrete and backfill. Cement production is known to generate 4-8% of global carbon emissions [1]. Globally endeavors are taking place to reduce the use of cement in concrete mixes. This article presents the conditions for LCLL ash to be a suitable SCM for applications in concrete, ultrahigh resistance concrete (UHPC), and mining backfill. The summary of the results to evaluate the reactivity of LCLL ash and calcined LCLL ash is explained. More details are found in a recent article [2]. The compressive strength and the flow table values of the designed UHPC mixtures were measured to find the optimum dosage of LCLL ash. First recipes of LCLL ash were tested for cemented paste backfill for mining.

2. Materials and methods

2.1 Materials

In this study, the LCLL Ash comes from the Rio Tinto SPL treatment plant based in Jonquière, QC, Canada. For the rest of the paper, LCLL will refer to LCLL Ash. Different materials were used for this study: plain Portland cement (OPC), two fly ashes type F (FA-E and FA-PA), slag from blast furnaces (GGBS), blue silica fume (SF), limestone filler (FC) and quartz powder (Q). The chemical composition of the materials tested, was measured in anhydrous conditions by X-ray fluorescence (XRF), see results in Table 1.

Table 1. Chemical composition of cement and SCMs used.

Oxide	Percentage in weight (wt%)								
	OPC	FC	SF	LCLL ash	Calcined LCLL ash	Q	FA-E	FA-PA	GGBS
SiO_2	19.17	2.21	96.48	37.18	38.83	91.40	58.53	58.54	38.64
Al_2O_3	4.69	0.37	0.48	36.29	36.57	4.94	19.64	20.91	10.28
Fe_2O_3	3.61	0.14	0.45	7.36	8.59	1.72	5.89	7.23	2.13
CaO	61.52	53.57	0.35	3.04	4.00	0.55	5.54	3.60	35.69
MgO	2.40	0.51	0.41	0.38	0.39	0.04	2.01	1.96	8.82
SO_3	3.98	0.10	0.08	0.06	0.12	0.00	0.21	0.14	2.08
K_2O	1.06	0.13	0.66	0.77	0.79	0.10	1.91	2.35	0.78
Na_2O	0.25	0.02	0.11	8.23	8.03	1.09	1.03	1.10	0.43
TiO_2	0.25	0.01	0.00	0.75	0.78	0.10	0.82	0.90	0.56
P_2O_5	0.14	0.01	0.10	0.12	0.10	0.01	0.58	0.21	0.04
V_2O_5	0.01	0.00	0.00	0.03	0.03	0.01	0.04	0.69	0.11
LOI at 1000° C	2.62	42.89	0.56	5.72	1.11	0.00	3.63	2.89	0.13

LCLL ash was provided by Rio Tinto Quebec. To increase the LCLL ash reactivity, an additional treatment was made by calcination of the LCLL ash at 1050°C for 2h in an alumina crucible. For UHPC testing, LCLL ash was ground as fineness of cement and was used as a cement substitution by 0 %, 6 % and 12 % by weight.

2.2 Reactivity testing of SCM

The procedure to evaluate the reactivity of the LCLL ash required to be used as supplementary cementitious materials is summarized in the figure 1. Frattini test was carried out to evaluate the pozzolanic reactivity, following the procedures in [3], [4]. This test evaluates the reactivity of SCM alumino-silicate phases with the portlandite to precipitates more hydrates. R^3 tests are based on a mix that recreates the chemical behavior of limestone cement, without cement particles [5]. The heat generated by the precipitation of hydrates was measured by isothermal calorimetry and the consumption of portlandite was measured by thermogravimetrically analysis (ATG). The pastes were measured by X-Ray diffraction after the R^3 tests. The Finally, the reactivity of LCLL ash, calcined LCLL ash and the others SCMs were tested by measuring the compressive strength of mortar containing 20 % in weight of SCMs. After this level of testing, the LCLL ash was calcined to measure the improvement in reactivity with the same procedure.

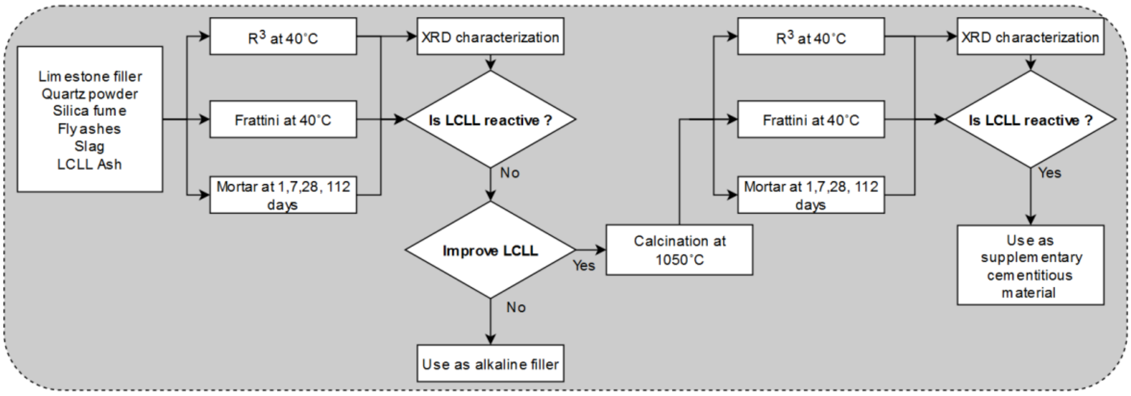

Figure 1. Schematic of the experimental plan to evaluate the reactivity of LCLL ash.

2.3 UHPC testing

The flow characteristic of all mixtures was measured by means of a flow table test based on ASTM C1437. The mixtures were cast into the 50 x 50 x 50 mm^3 cubes for compressive strength test according to ASTM C39/C39 M 2010. The compressive strength of UHPC mixtures was determined as the average of three measurements at 7 and 28 days.

2.4 Mine backfill

The potential of LCLL ash use in mining backfill was evaluated with compressive strength test at 3, 7, 28, and 56 days. These tests were carried out according to the ASTM C109.

3. Results

3.1 LCLL ash as SCM

The testing on the reactivity of LCLL ash in cement in Frattini and compressive mortar (Figure 2) showed a behavior similar to filler materials like quartz powder and limestone filler. However, in the R^3 conditions, LCLL ash generated more heat and consumed more portlandite, due to its hydroreactivity which generated expansion in the paste. XRD tests on LCLL ash R^3 paste also confirm this observation with new peaks between 10 and 11° 2θ attributed to monosulfoaluminate and hemicarboaluminate phases, which contain reactive alumina. For calcined LCLL ash, a better reactivity was observed in Frattini test with a higher calcium removal, close to fly ashes observations. The same trend was observed on mortar (Figure 2), with a relative compressive strength close to fly ashes and slag values. This trend was also confirmed by the R^3 tests showing a higher heat released, a higher portlandite consumption and the presence of new hydrates, identified by XRD, like monocarboaluminate. The behavior of the calcined LCLL ash is closer to one of supplementary cementitious materials.

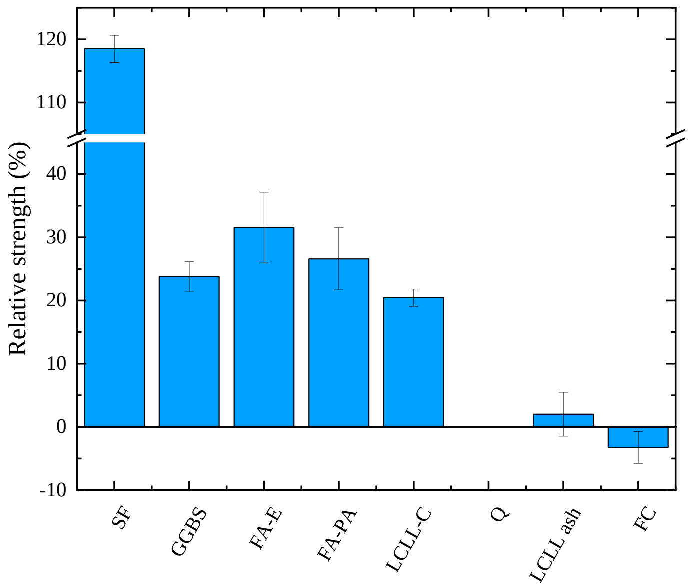

Figure 2. Relatives strength of mortar containing 20 % SCMs in weight at 112 days (data were normalized to quartz values).

3.2 LCLL ash for UHPC

Figure 3 shows the result of the compressive strength, and the flow table values of the designed UHPC mixtures. The flowability of the mixture is an important parameter of the ease to place concrete. LCLL ash particles reduced the flowability of the mixtures. The spread flow value of L6 and L12 decrease by 4.3% and 13 %, respectively, compared to the reference. This can be explained by the high content of alumina and silica of LCLL ash that absorbs more water from the total added water, thus reducing the flowability similar to what was observed by others [6]. The compressive strength of the 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. It means that LCLL ash can replace cement up to 12 % with only a minimal effect on acceptable strength and flowability.

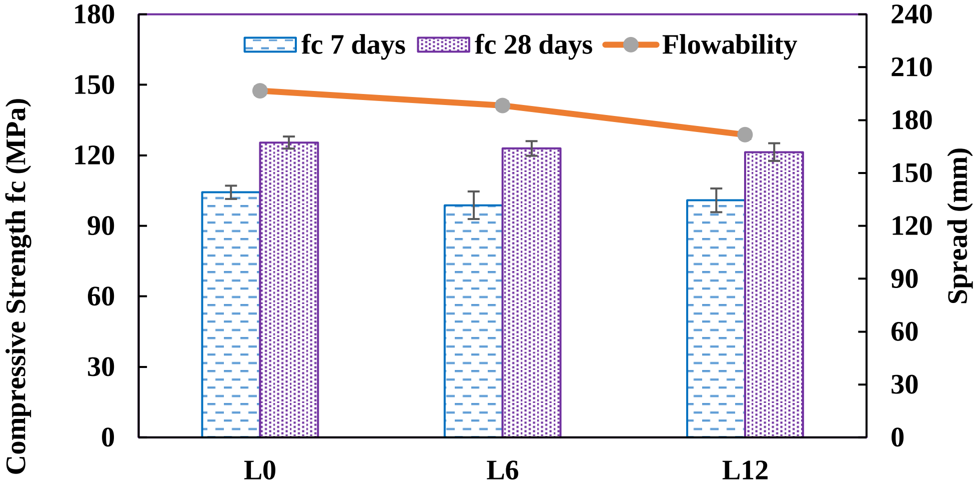

Figure 3. Compressive strength versus flowability with the standard derivation.

3.3 LCLL ash for mine backfilling

Figure 4 shows the mechanical behavior of cemented paste backfill produced with LCLL ash and without it. By applying a normal compressive stress on the sample, the maximum strength is 950 kPa for 80S+20GU, 537 kPa for 60S+20LCLLash+20GU and lower at 405 kPa for 100 GU. The mix with LCLL ash is better than only general use cement, but still not as good as the mix with only slag and cement. More research is better to improve the mix design.

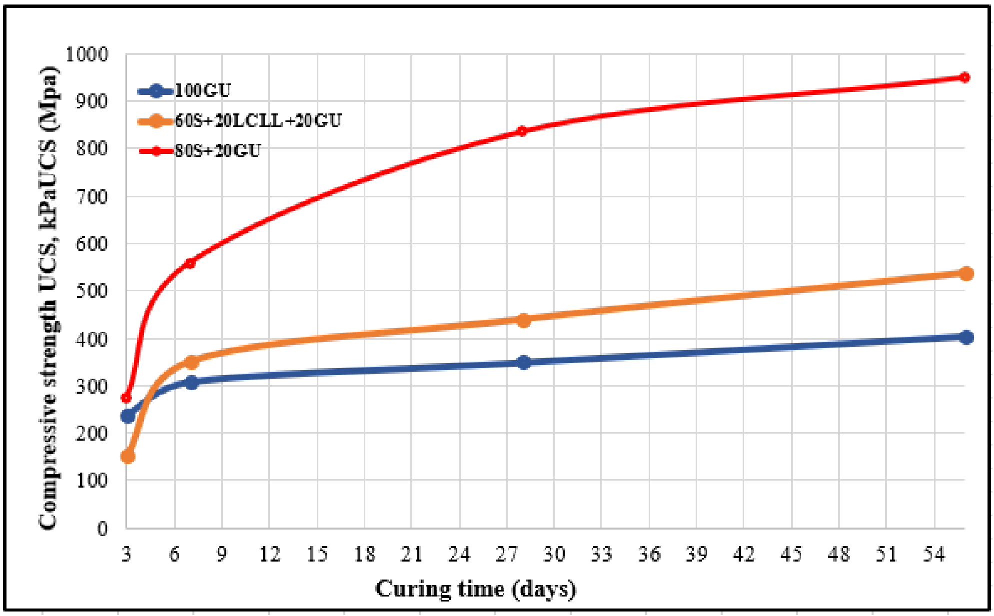

Figure 4. Measurement of uniaxial stresses of samples

4. Conclusion

In summary, the LCLL ash that is generated from the LCLL process for treatment spent pot lining from primary aluminum production, is lightly reactive. Calcination of the material improves its reactivity and that makes it potentially a suitable cementitious material to replace Portland cement in concrete. In ultrahigh performance concrete, LCLL ash can replace cement up to 12 % with no detrimental effect on acceptable strength and flowability. A mix design of cemented paste backfill with LCLL is still under investigation to find the optimum dosage. For this application there is no firm conclusion yet.

5. Acknowledgements

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