AL18 - Valorization of Treated Spent Pot Lining By-Product in Concrete

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Abstract

About 20 kt Spent Pot Lining (SPL) is generated by Rio Tinto in Québec each year from aluminum electrolysis cells and listed as industrial hazardous waste. After treatment by the Low Caustic Leaching and Liming (LCL&L) process, the refractory SPL becomes an inert non-hazardous material, called LCLL ash.

The project discussed aims to valorize this by-product into safe supplementary cementitious materials (SCM). This article evaluates the potential of LCLL ash as a supplementary cementitious material with isothermal calorimetry. The expected results of the research project are expected to greatly contribute to the potential for reuse of LCLL ash as part of sustainable concrete, which addresses an important issue for the sustainable development of the combined aluminium, cement and concrete sectors.

Keywords: Primary aluminum production, low caustic leaching liming (LCLL), spent pot lining (SPL) treatment, supplementary cementitious materials, calorimetry, sustainable development, LCLL ash.

1. Introduction

Each tonne of aluminum produced generates approximately 22 kg of spent pot lining (SPL). For Rio Tinto in Québec, nearly 20 000 tonnes of SPL is generated per year. SPL is listed as industrial hazardous waste because it contains significant concentrations of toxic and leachable constituents (cyanide and fluoride) [1]. After treatment in the Low Caustic Leaching and Liming (LCLL) process used in the SPL treatment plant in Jonquière (Quebec), the refractory part of SPL (also called Second Cut) becomes an inert non-hazardous material. This material can be reused and is called LCLL ash. Due to its chemical composition, this industrial by-product has the potential to become supplementary cementitious materials (SCM), which can then be used in the concrete industry to reduce the carbon footprint [2]. Replacing parts of Portland cement by materials that does not require clinkering at high temperature can lead to a significant reduction of CO_2 emissions that is caused by the limestone transformation to CaO and the heating process. Commonly used SCM materials are fly ash from coal combustion and granulated blast furnace slag, a by-product from pig iron production. However, these common SCM materials are becoming less available and they can require long distances for transportation, which impacts the sustainability of its use. Therefore, there is a need to identify new sources of SCM according to local/regional economic activities, which then also becomes a demonstration of a circular economy where the by-products from one industry feed into another industrial sector.

Isothermal calorimetry measures the rate of heat production during cement hydration over time and it is used to assess the reactivity of SCM [3]. This is an exothermic process and the cement clinker is formed of tricalcium silicate (C_3S in cement notation, $3CaO.SiO_2$ in chemical notation), dicalcium silicate (C_2S in cement notation, $2CaO.SiO_2$ in chemical notation), tricalcium aluminate (C_3A in cement notation, $3CaO.Al_2O_3$ in chemical notation) and tetracalcium ferroaluminate (C_4AF, or $4CaO.Al_2O_3Fe_2O_3$) [4]. A small percentage of gypsum ($CaSO_4.2H_2O$) is added to control the aluminate reaction. The heat flow curve developed during the first 20 hours is characterized first by a silicate reaction peak and then a sulfate depletion peak [5]. The C3A dissolution is visible in the sulfate depletion peak, which is indicative of the aluminum reaction in the hydration process.

The project aims to valorize the refractory part of SPL after it is treated by the LCLL process at the Rio Tinto treatment plant into safe supplementary cementitious materials (SCM) called LCLL ash. The innovation is to identify the conditions for safe and optimized use of LCLL ash into Portland cement and to develop new industry expertise. The first step is to identify the effect of the LCLL ash on cement hydration. In this study, we studied the effect that particle size and proportion of LCLL ash have on cement hydration. We compared LCLL ash with both fly ash and limestone filler. Quartz was also selected as a comparative inert material. This assessment will help guide potential end users to the optimum conditions to include LCLL ash into sustainable concrete.

2. Materials and Methods

2.1. Materials

In this study, the main raw material considered is LCLL ash is produced at the Rio Tinto treatment plant located in Jonquière, QC, Canada. On average 10 000 tonnes per year of LCLL ash are produced in this plant. A standard type Portland cement (Type GU, Ciment Quebec, St Basile, QC, Canada) was used in the calorimetry tests. The LCLL ash was compared to fly ash, CV (Class F fly ash, Ciment Quebec, Laval, QC, Canada). Furthermore, two inert materials were used, a limestone filler, FC (Pulverized limestone, Ciment Québec, St Basile, QC, Canada) and a quartz powder Q made by grinding graded Ottawa sand. These materials were chosen to access a potential pozzolanic reactivity of LCLL ash by comparing it to the heat released of reactive and inert SCMs. The LCLL ash was calcined by placing 10 g of LCLL ash in an alumina crucible at 1000 °C for 1 h in a muffle furnace. The chemical composition of cement used for the blended mixes and SCM was measured by X-ray fluorescence (XRF) bed fusion and the results are shown in Table 1.

For each material, the particle size distribution (PSD) was measured using Malvern Mastersizer\E by laser diffraction granulometry with isopropanol as the dispersant. The particle size distributions are presented in Figure 1. To study the effect of the PSD of LCLL ash on cement, three granulometries were studied: G0 (ungrounded), G1 and G2 ground with a planetary grinder to reach a d50 of 7.5 µm and 4 µm respectively.

Table 1. Chemical composition of cement and SCMs.

Oxide	Percentage in weight (wt%)					
	OPC	**FC**	**Raw LCLL ash**	**Calcined LCLL ash**	**Q**	**CV**
SiO_2	19.17	2.21	37.18	38.83	91.40	58.53
Al_2O_3	4.69	0.37	36.29	36.57	4.94	19.64
Fe_2O_3	3.61	0.14	7.36	8.59	1.72	5.89
CaO	61.52	53.57	3.04	4.00	0.55	5.54
MgO	2.40	0.51	0.38	0.39	0.04	2.01
SO_3	3.98	0.10	0.06	0.12	0.00	0.21
K_2O	1.06	0.13	0.77	0.79	0.10	1.91
Na_2O	0.25	0.02	8.23	8.03	1.09	1.03
TiO_2	0.25	0.01	0.75	0.78	0.10	0.82
P_2O_5	0.14	0.01	0.12	0.10	0.01	0.58
V_2O_5	0.01	0.00	0.03	0.03	0.01	0.04
LOI at 1000° C	2.62	42.89	5.72	1.11	0.00	3.63

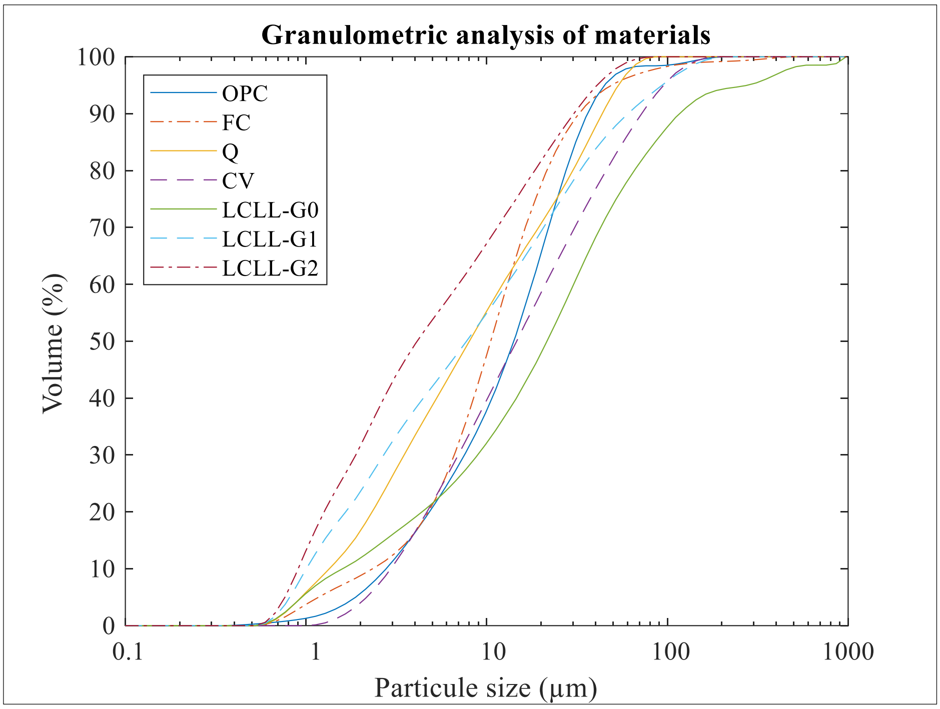

Figure 1. Granulometry of OPC, LCLLs and SCMs.

2.2. Methods

Isothermal calorimetry was performed with a TAM Air isothermal calorimeter from TA Instruments. The calorimeter was set to 23 °C followed by calibration of the heat flow channels. The sealed reference flasks were inserted into the calorimeter and the system was left to stabilize. The reference ampoule consisted of 16 g of Ottawa sand to match with the thermal capacity of the sample about ± 20 %. The baseline heat flows (both initial and final) of each channel were determined at the timestamp 30 minutes after the stabilization of the calorimeter. For each sample, 4.44 g ± 0.02 g of cement or blended cement was mixed with 2.00 g ± 0.02 g of deionized water inside the ampoule and stirred for 2 minutes. The heat release was recorded until 2 days, as most of the reaction occurs within 48 h. The total heat was calculated from 45 minutes after the introduction of the sample ampoule in the calorimeter.

3. Results and Discussion

Using isothermal calorimetry measurements, a first assessment is made of the effect of LCLL ash on cement hydration. LCLL ash decreases total heat of hydration and retards the string time by retarding the initial peaks of hydration heat (Figure 2). The granulometry G1 and G2 showed a higher peak of hydration, which means that the finer LCLL is more reactive. However, the heat released stay below the values of the OPC reference. Moreover, the G1 and G2 granulometry did not show strong difference in terms of total heat, that suggest LCLL G1 is sufficient to be used in cement and decrease the grinding energy consumption. For the rest of this study, only G1 granulometry will be studied.

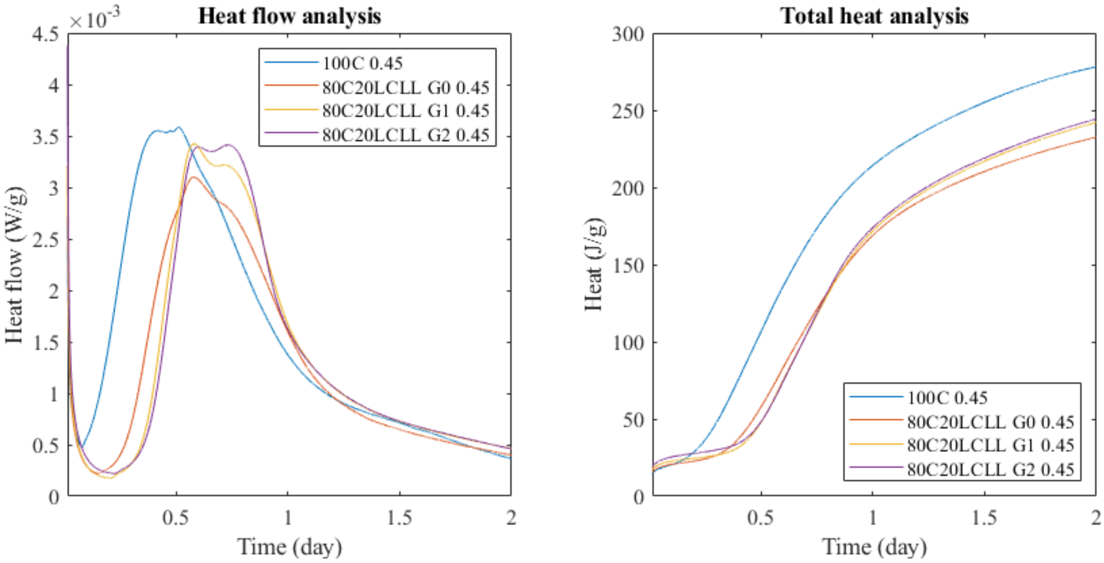

Figure 2. Calorimetry for three fineness of LCLL ash at 20 % cement replacement compared with 100 % cement.

Figure 3 shows the heat flow and the total heat released in function of LCLL ash replacement in cement at 0 %, 10 %, 20 % and 30 % respectively the curves red, black, blue, and pink. Adding more LCLL ash caused more retardation in the hydration and a perturbation of aluminate peaks, the second peak. With more LCLL ash present there the total heat available is less, which means that the aluminum in the LCLL ash is not directly available for cement hydration. Figure 4 compares LCLL ash and calcined LCLL ash with others SCMs. The behavior of LCLL ash is similar to quartz powder and lime with a retarder effect. Even if mixed with a lime filler, strong retard is observed, which means that it is a mineral retarding admixture promoting a slower setting of concrete. The hydration of cement mixed with calcined LCLL ash also compares to a fly ash, which tends to indicate a possible pozzolanic reactivity. This is due to the reaction between portlandite and amorphous silica which tends to precipitate more C-S-H. The aluminium becomes more available to cement hydration after the calcination of LCLL ash.

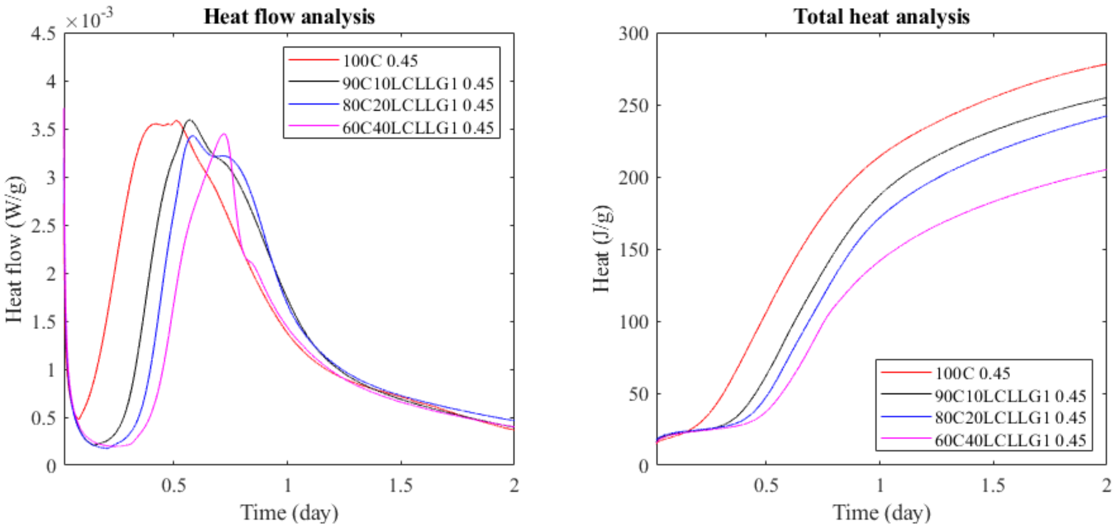

Figure 3. Calorimetry results for three cement replacement percentages of LCLL ash with 0 %, 10 %, 20 % and 40 % replacement of cement.

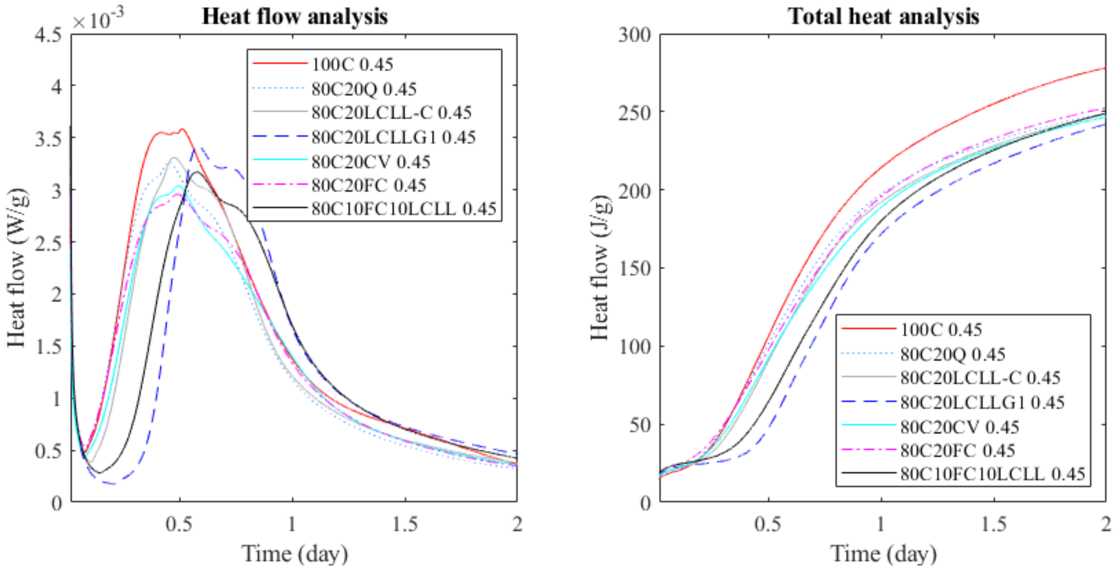

Figure 4. Comparison of LCLL ash with other mineral admixtures using isothermal calorimetry, with the reference at 0 % replacement (red solid line) and with 20 % replacement.

4. Conclusion

LCLL ash is a useful byproduct from the LCLL SPL treatment process. In this paper is presented a first assessment from using isothermal calorimetry on mixtures of LCLL ash and standard SCMs in cement. The results show that LCLL ash behaves as a mineral retarder in cement hydration with the potential to reduce the heat of hydration. Furthermore, calcined LCLL ash behaves more like a standard fly ash and has the potential to be used as a reactive supplementary cementitious material in concrete. Overall, LCLL ash is a promising new raw material in cement with properties that make the use of cement more sustainable and environmentally friendly.

5. References

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