Characterization of lithium mining residues for cement applications

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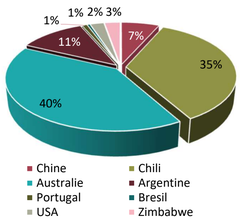
CONTEXT

Lithium production

Lithium application [2]

75-85 % | 5-10 % | Glass & Ceramics ~5 % | 2 %

Global production [1]



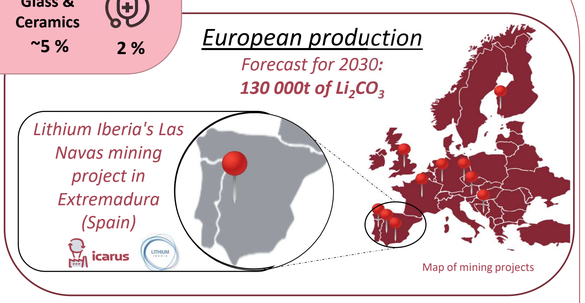
By 2024: ***240 000t of Li_2CO_3*** *Increase threefold over the next few decades*

x3

European production

Forecast for 2030: ***130 000t of Li_2CO_3***

Lithium Iberia's Las Navas mining project in Extremadura (Spain)



Ore

- Spodumene ($LiAl(SiO_3)_2$)
- Feldspars
- Quartz

[3]

Grinding

Treatment

Chemical + Thermal

$CaCO_3$ $CaSO_4 \cdot 2H_2O$

~1050°C [4]

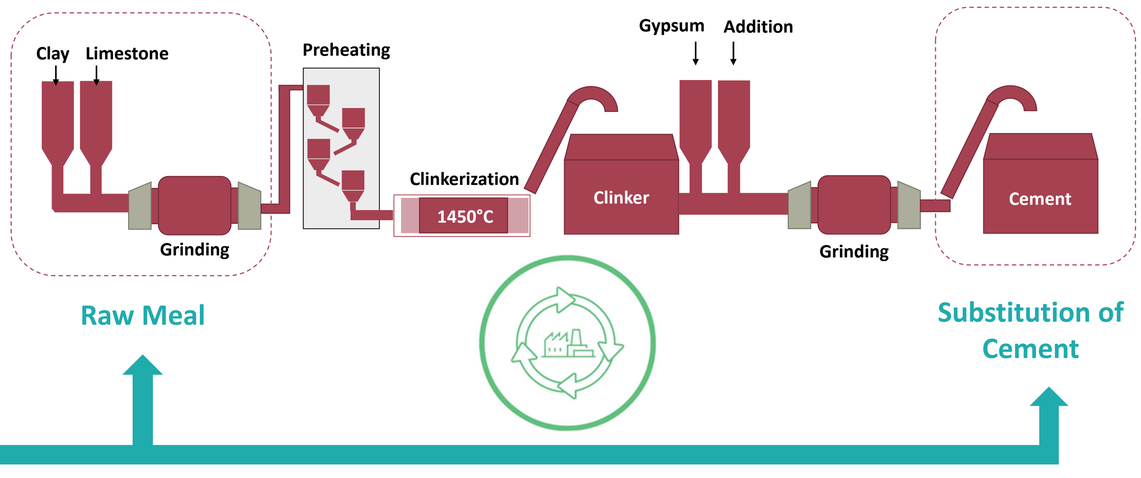
Lithium Extraction

Residues (LAR : Lithium Aluminosilicate Residues)

PRODUCTION OF 1t LITHIUM CARBONATE 10t OF WASTE (LAR) [5]

Cement production

4.1 billion tons of cement are produced every year worldwide [6]



VALORIZATION OF LAR IN CEMENT = REDUCE CONSUMPTION OF NATURAL RESOURCES

Objective: Recover lithium mining waste (LAR), transforming waste into a resource

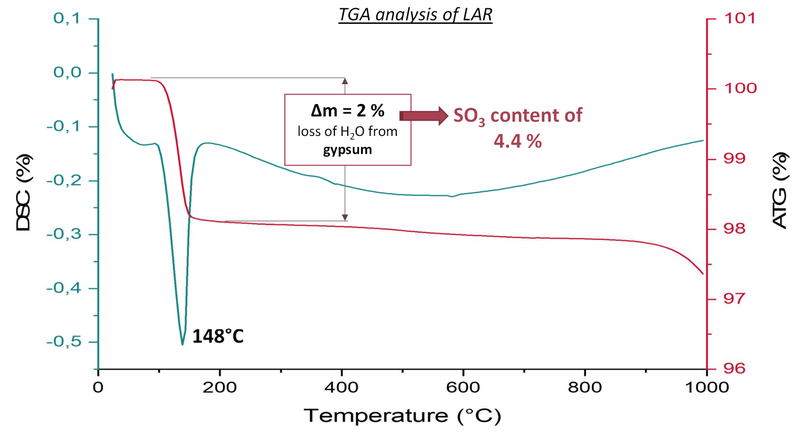
CHARACTERIZATION OF LAR (LITHIUM ALUMINOSILICATE RESIDUES)

Particle size			Density
d20 = 50µm	d50 = 100µm	d80 = 200µm	2.689 g/cm³

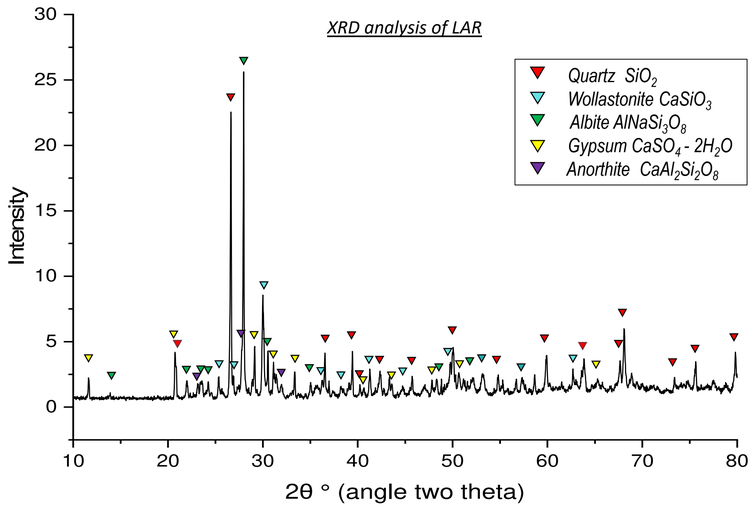
- High sulfur and calcium oxide contents due to the chemical treatment (addition of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$)
- Fineness adapted for incorporation in raw meal but LAR is too coarse for substitution of cement

Chemical composition *(expressed in terms of oxides)*	(% mass)
SiO_2	55.56
Al_2O_3	12.37
Fe_2O_3	0.97
CaO	17.79
SO_3	4.51
Na_2O	2.75
K_2O	1.31
P_2O_5 /TiO_2/MnO/ SrO/ MgO	2
LOI (%) at 950°C	2.4
Sum	99.69

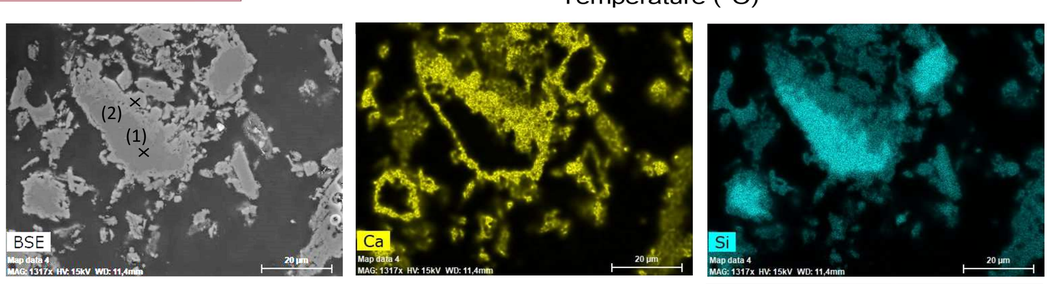
TGA analysis of LAR



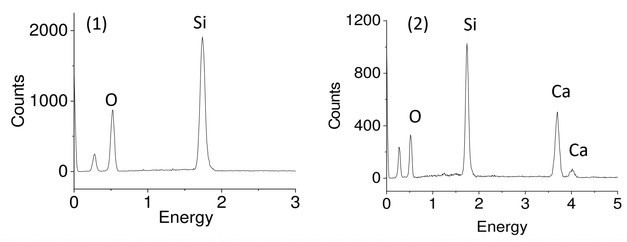
XRD analysis of LAR



- X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) revealed the presence of mainly Quartz (SiO_2) and Feldspars (Albite), as well as Gypsum ($CaSO_4 \cdot 2H_2O$) at ≈ 9.6 % (Thermogravimetric analysis)
- During the treatment of the ore with calcium oxide (CaO) at 1100°C, feldspars and quartz are partially attacked, favoring the formation of new phases (as wollastonite ($CaSiO_3$)) on particle surface.



SEM coupled with EDX analysis of LAR sample



VALORIZATION

LAR as Raw Meal

The proportion of each component in the raw meal is obtained according to criteria that produce a clinker with a specific chemical composition

LSF: Lime Saturation Factor = $\frac{CaO}{2.80 \times SiO_2 + 1.18 \times Al_2O_3 + 0.65 \times Fe_2O_3}$

	Acceptance limit
LSF	*0.93 – 0.98*
SR	*2.2 – 3.3*
AF	*1.4 – 2.2*
% SO_3	*< 1.5 %*

SR: Silica Ratio = $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$

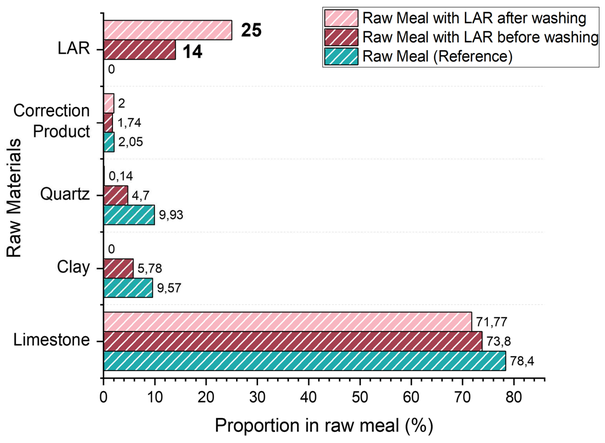
AF: Aluminate Ferrite Ratio = $\frac{Al_2O_3}{Fe_2O_3}$

% SO_3: Sulfur Content

Because of the sulphate content the use of LAR in raw meal is limited at ***14 %.***

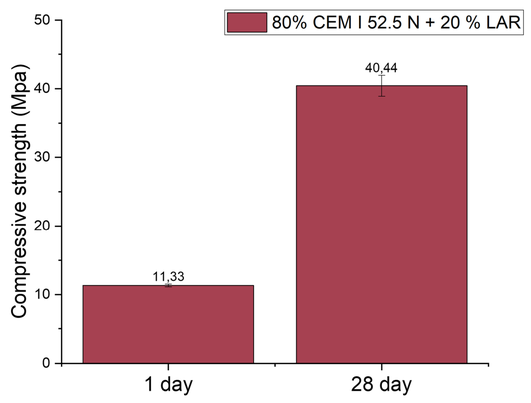
If the LAR is washed to remove excessive sulfur content, there is less sulfate and therefore a higher percentage of LAR in the clinker (25 %).

The proportion of components in the raw meal was optimized in order to use the maximum proportion of LAR in the raw meal



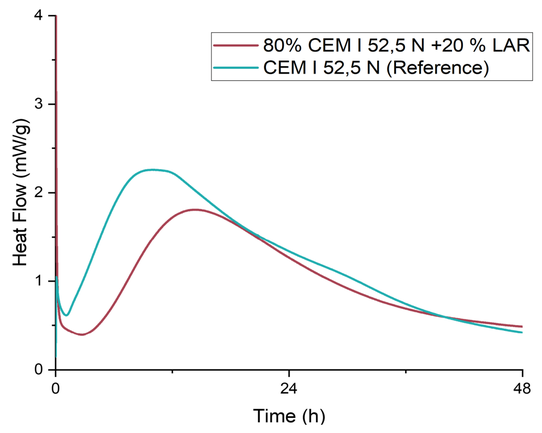
LAR as replacement of Cement (20 %)

Compressive strength of standard mortars (EN 196-1)



Compressive strength of mortar with 20% of cement replaced by LAR is equivalent to a cement strength class 32.5 (EN 197-1).

Microcalorimetry analysis



80% CEM I 52.5 N +20 % LAR, shifts and reduces heat flow compared to reference

PERSPECTIVES

Potential addition to the raw meal even without treatment (14 %)
LAR could reduces the consumption of natural resources (clays, quartz, limestone)

- Following the phase formation and crystalography to analyse the influence of LAR on burnability
- Understanding the impact of minor elements on clinker formation

For addition in cement or concrete, untreated LAR is not suitable (high gypsum content and low hydraulic or pozzolanic properties) → upcycling is necessary

- Understanding the long term effects: the reactivity of the phases (Wollastonite and Sulfate) present in the LAR ?
- How to upcycle the LAR (grinding, washing, etc.) ?

[1] A. Alessia and all "Challenges for sustainable lithium supply: A critical review", *J. Clean. Prod.*, 2021
[2] B. Swain, "Recovery and recycling of lithium: A review ", *Sep. Purif. Technol* 2017
[3] Robert M. Lavinsky, Walnut Hill Pegmatite Prospect, Huntington, Hampshire County, Massachusetts, USA
[4] P. Meshram and all, "Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review"
[5] X. Wang, "Comprehensive utilization of waste residue from lithium extraction process of spodumene" Miner. Eng, août 2021
[6] "Ciment-chiffres: 2023-2024" France-ciment.fr

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