Lime carbonation in dolomitic refractory

Influence of stabilizer on the reactivity of calcium oxide before and after use in steel industry

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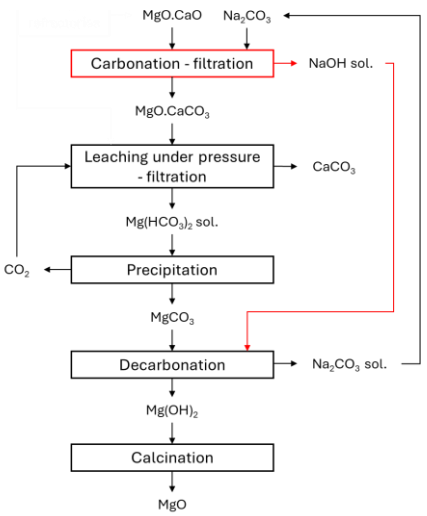
Context

Magnesium is a critical raw material largely produced in China from dolomite ($Mg.Ca(CO_3)_2$), with Europe importing 97% of its supply. The conventional Pidgeon process extracts magnesium by vacuum reduction but has major drawbacks, notably the use of ferrosilicon to separate calcium and magnesium.

An alternative under study is the bicarbonate process which produces MgO, a key intermediate for magnesium metal production, by selectively dissolving magnesium. Since calcium can also dissolve, a preliminary carbonation step is applied to convert lime into calcium carbonate, limiting calcium contamination during magnesium dissolution.

Bicarbonate process



Lime carbonation :

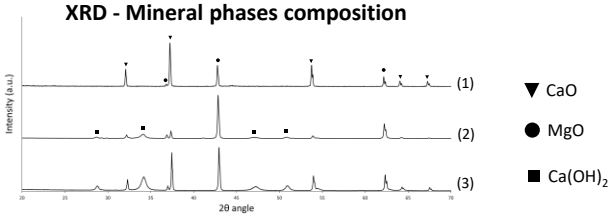
$$MgO.CaO + H_2O + {CO_3}^{2-} \leftrightarrow MgO.CaCO_3 + 2\,OH^-$$

Refractories Characterisation

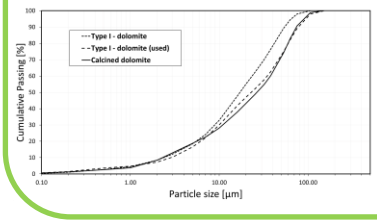
XRF - Chemical composition (%wt)

	MgO	CaO	Fe_2O_3	SiO_2	Al_2O_3
(1) Calcined dolomite	41.0	56.6	0.6	0.1	0.0
(2) Type I dolomitic	35.9	60.1	0.4	0.3	0.4
(3)Type I dolomitic (used)	59.6	34.9	0.8	1.9	1.7

XRD - Mineral phases composition



Particle size distribution – Specific surface area



	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)	SSA (m^2/g)
Calcined dolomite	2.3	26.5	73.7	6.85
Type I	2.4	17.1	54.2	0.17
Type I (used)	2.9	22.9	76.8	1.28

Lime carbonation results

Operating conditions :

- Solid/liquid ratio : 20%wt
- Ca content : [21.5;42.5]%wt
- Na2CO3/CaO ratio : 1
- Stirring speed: 350 RPM

Titration methodology :

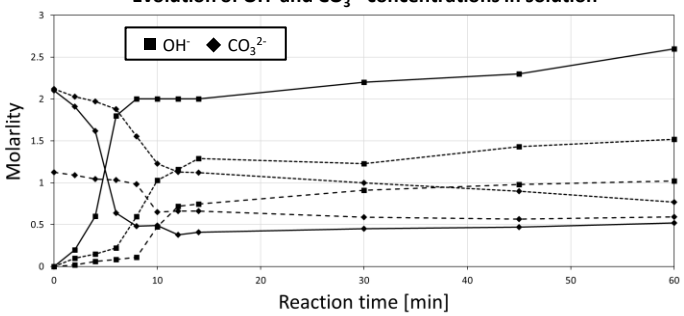
An acid-base titration was used to determine the OH^- and CO_3^{2-} concentrations in the filtrate through two coloured indicators (phenolphthalein and methyl orange)

Main conclusions :

- **The lime carbonation is kinetically controlled by the SSA**
- **CaO stabilizer in type I refractory doesn't influence its carbonation**
- **Ion's concentration doesn't correlate carbon content evolution**

" Further experiments needs to be conducted on other dolomitic refractory to compare their carbonation behaviour and to improve lime carbonation as well as titration method "

Evolution of OH^- and CO_3^{2-} concentrations in solution



After 1h of carbonation	Carbon content (%wt)	Carbonation rate (%)
Calcined dolomite	6.8	79.6
Type I	4.9	55.9
Type I (used)	3.6	67.2