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Cyclic Carbonation Properties of Calcium-Based Industrial Wastes during Calcium Looping Cycle

Yingjie Li Ph.D

School of Energy and Power Engineering
Shandong University, China

Calcium-based solid industrial wastes

- Every year, lots of calcium-based solid industrial wastes such as carbide slag and lime mud are produced which contain $Ca(OH)_2$ and $CaCO_3$, respectively.
- About 70% of the ethyne gas (C_2H_2), which is the raw material of polyvinyl chloride (PVC), is produced from calcium carbide in China.
- About 1.5-1.9 tons of carbide slag are obtained in the production of 1 ton of PVC in a chlor-alkali plant.
- It is estimated that about 0.47 m^3 of lime mud is generated to produce 1 ton of pulp in a paper mill.
- Carbide slag and lime mud are ordinarily landfilled outside the plants, resulting in land occupation, waste of calcium resources and environmental pollution.

Carbide slag from chlor-alkali plants

Lime mud from paper mill

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + 3C \rightarrow CaC_2 + CO$$

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 \text{ (carbide slag)}$$

$$\text{white liquor (NaOH) + cellulosic material} \rightarrow \text{black liquor + paper pulp product}$$

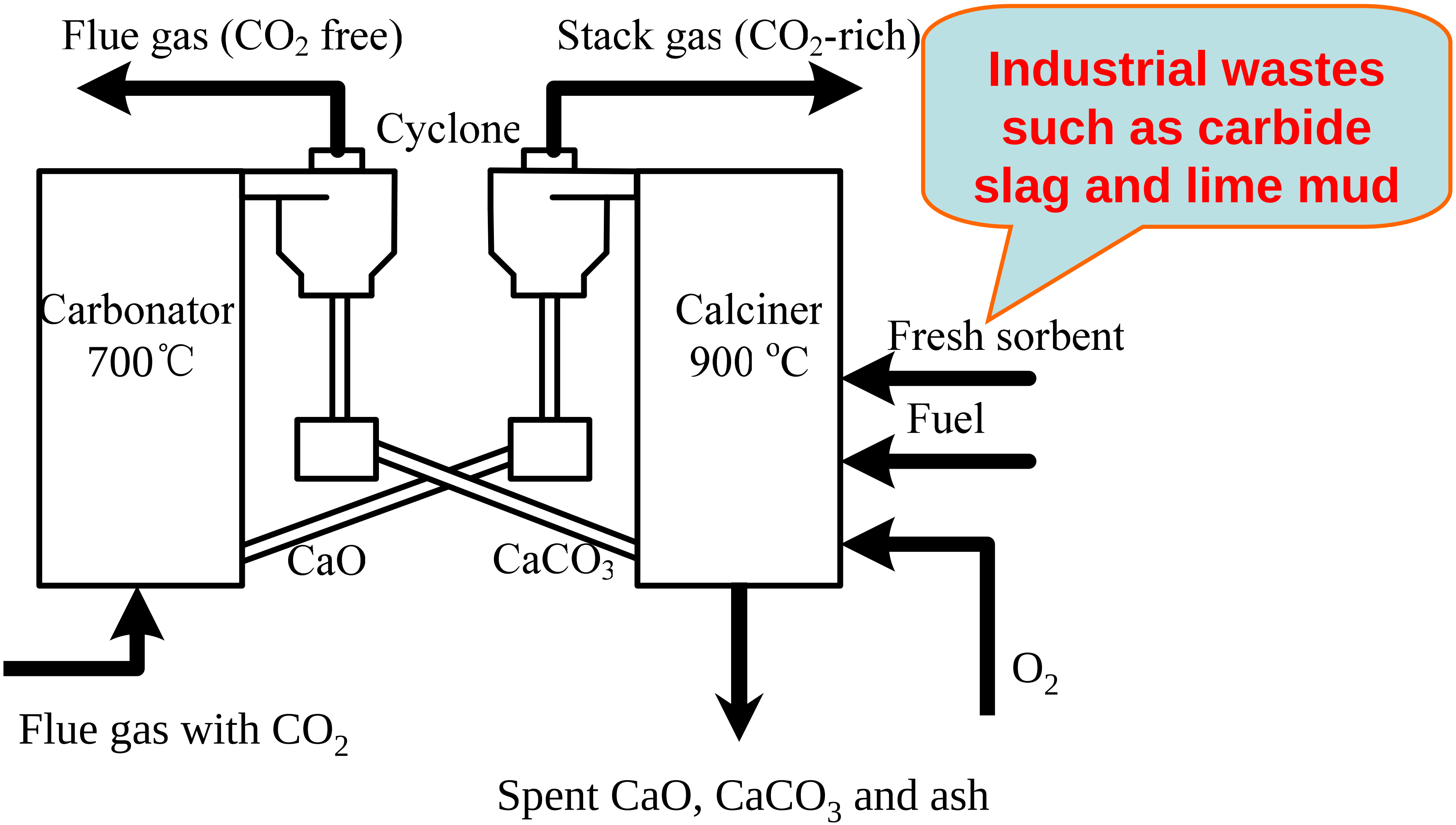
$$\text{black liquor} \xrightarrow{\text{in recovery furnace}} \text{green liquor } (Na_2CO_3)$$

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3 \text{ (lime mud)} \downarrow$$

How to recycle these industrial wastes

As sorbents for CO_2 capture in calcium looping technology **?**

Calcium-based industrial wastes as CO_2 sorbent in calcium looping process (CLP)

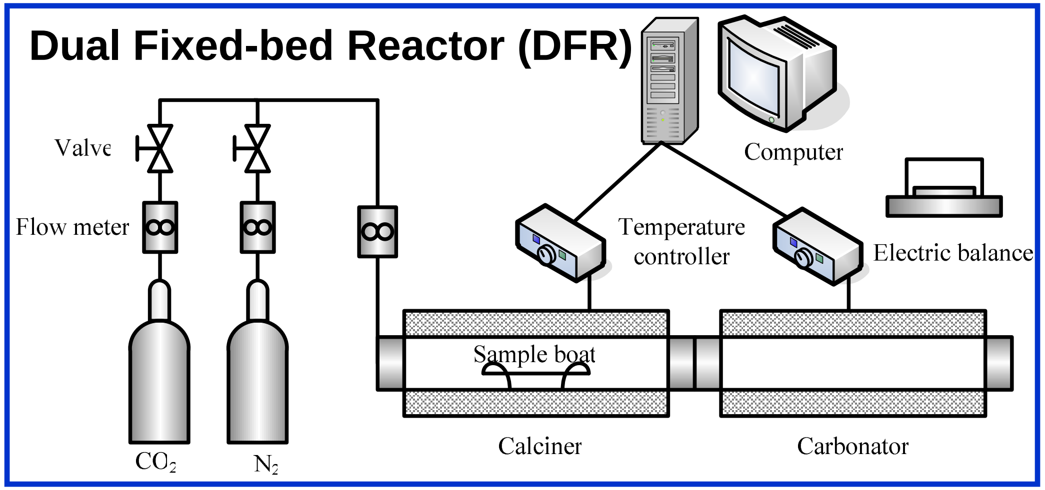


Difference between calcium-based industrial waste and natural limestone in chemical component

Sample	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	Na_2O	TiO_2	Others	LOI
Carbide slag	61.96	0.12	3.38	0.18	3.44	0.03	0.49	1.88	28.52
Limestone	52.08	1.32	3.32	0.03	0.53	0.02	-	0.47	42.23

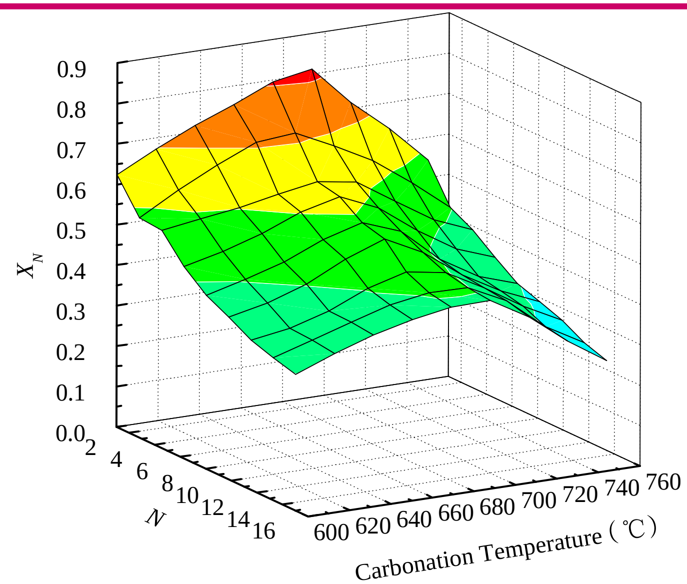
Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	TiO_2	K_2O	Na_2O	Cl	others	LOI
Lime mud	52.39	0.7	2.52	1.49	0.29	0.31	0.056	0.013	0.14	0.88	0.049	41.16
limestone	52.08	1.32	3.32	0.53	0.03	-	-	-	0.02	-	0.47	42.23

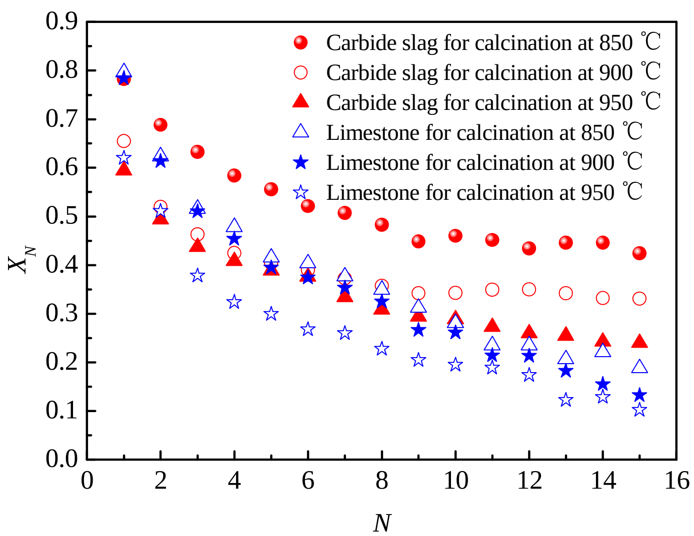
CO_2 capture behavior of calcium-based industrial wastes in CLP

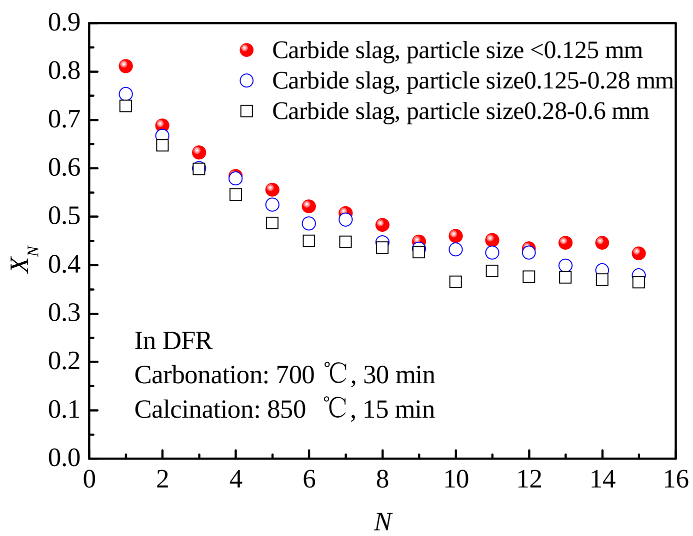


- CO_2 capture capacity of calcium-based wastes is depicted by "X_N" , i.e. carbonation conversion.
- X_N denotes conversion of CaO in the calcined waste to $CaCO_3$ after N calcination/carbonation cycles.
- X_N was calculated according to change of mass of sample after calcination and carbonation reactions.

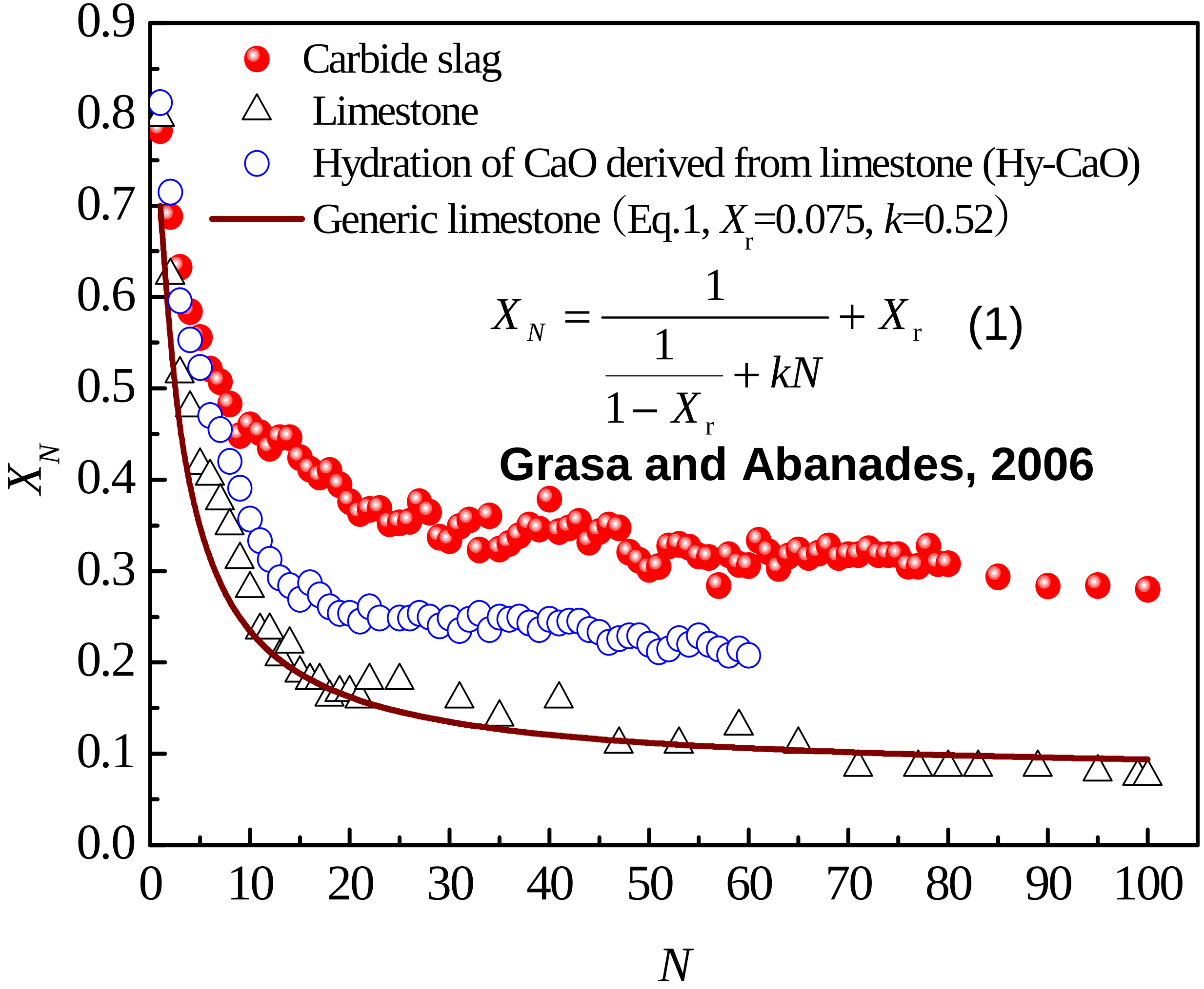
Cyclic CO_2 capture of carbide slag in CLP





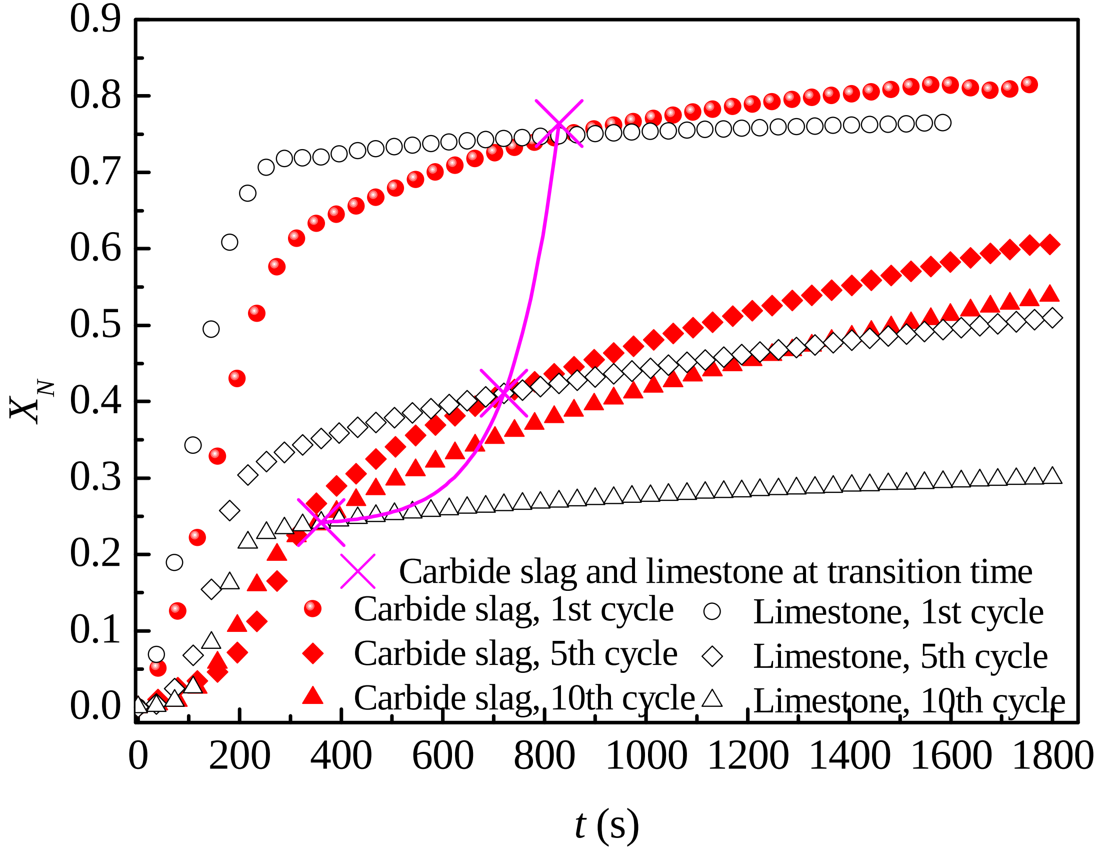


Comparison of carbide slag and limestone in calcium looping cycles



Carbonation: 700 ℃, 30 min; Calcination: 850 ℃, 15 min; Particle size: <0.125 mm

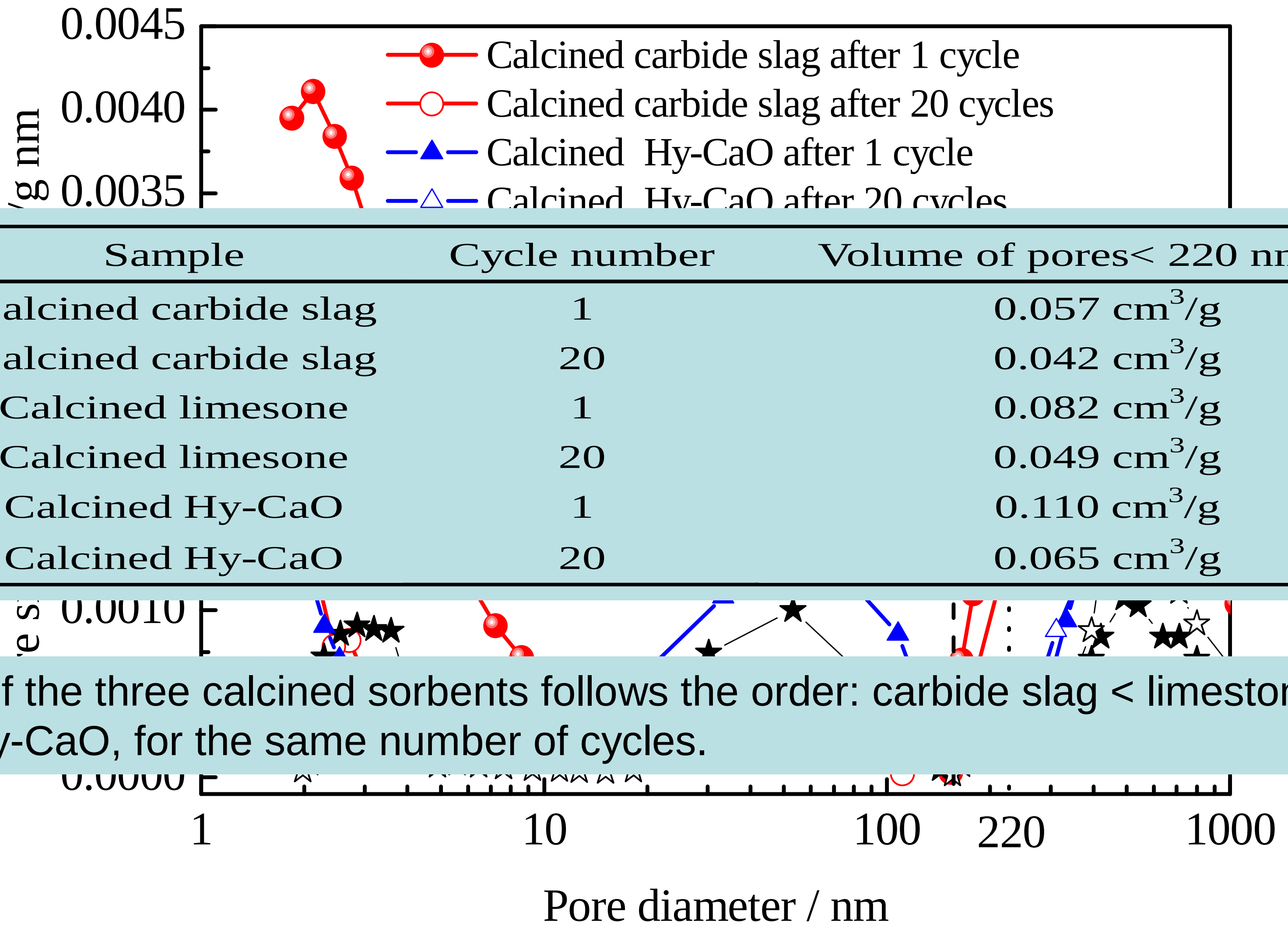
Cyclic carbonation kinetics of carbide slag



In TGA; Carbonation: 700 ℃; Calcination: 850 ℃; Particle size: <0.125 mm

For the same number of cycles, the carbonation conversion of the carbide slag is lower than that of the limestone before a certain time called the transition time; however, the carbide slag achieves higher conversion than the limestone after the transition time. Moreover, the transition time is shortened with the number of cycles.

Microstructure of calcined carbide slag in CLP

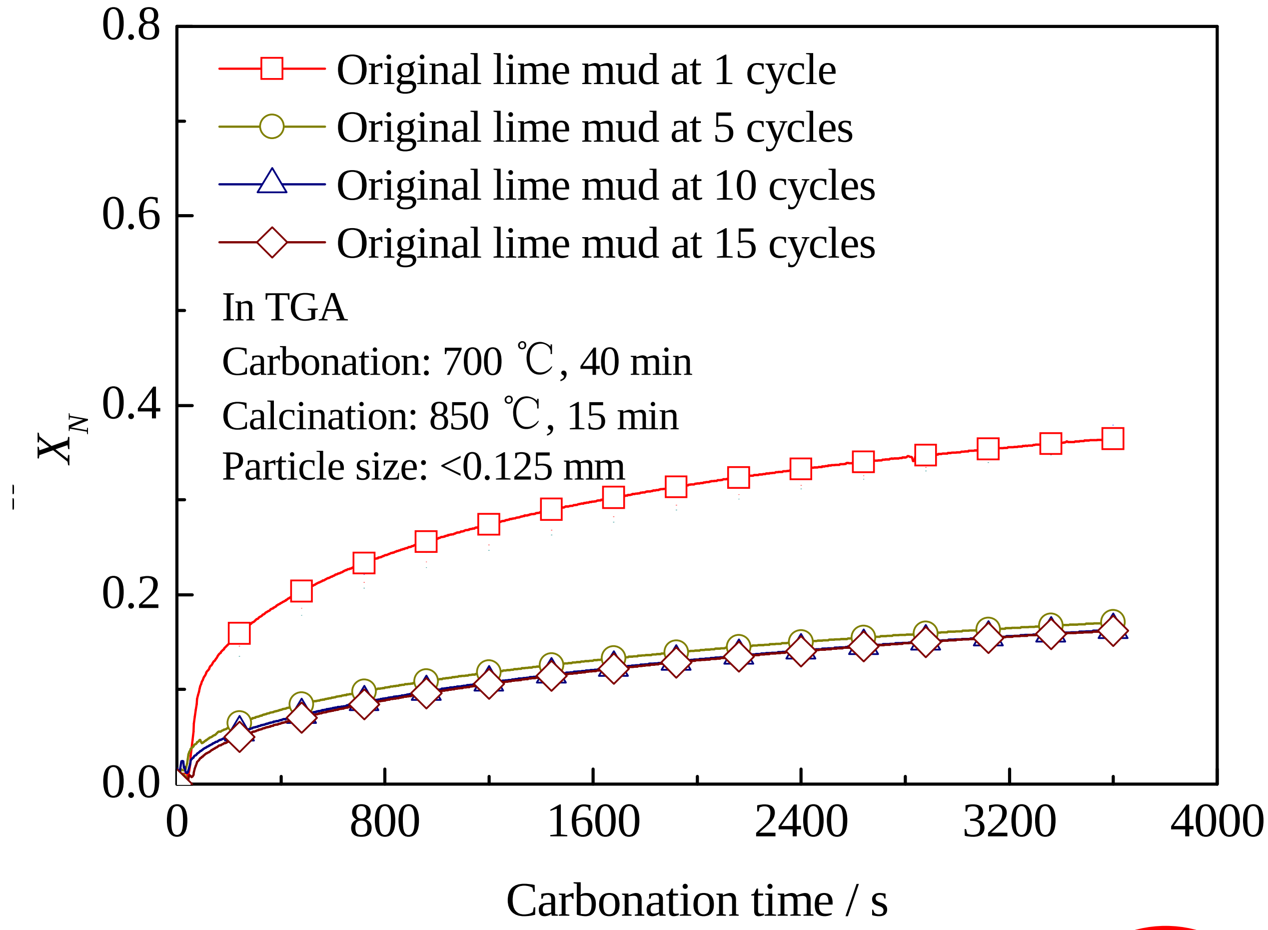


Sample	Cycle number	Volume of pores< 220 nm (V_1)
Calcined carbide slag	1	0.057 cm^3/g
Calcined carbide slag	20	0.042 cm^3/g
Calcined limesone	1	0.082 cm^3/g
Calcined limesone	20	0.049 cm^3/g
Calcined Hy-CaO	1	0.110 cm^3/g
Calcined Hy-CaO	20	0.065 cm^3/g

V_1 of the three calcined sorbents follows the order: carbide slag < limestone < Hy-CaO, for the same number of cycles.

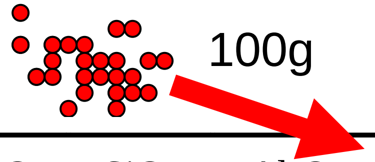
The fast stage of carbonation of CaO was determined by the volume of pores < 220 nm in diameter (Sun et al., 2007)

CO_2 capture of lime mud in CLP



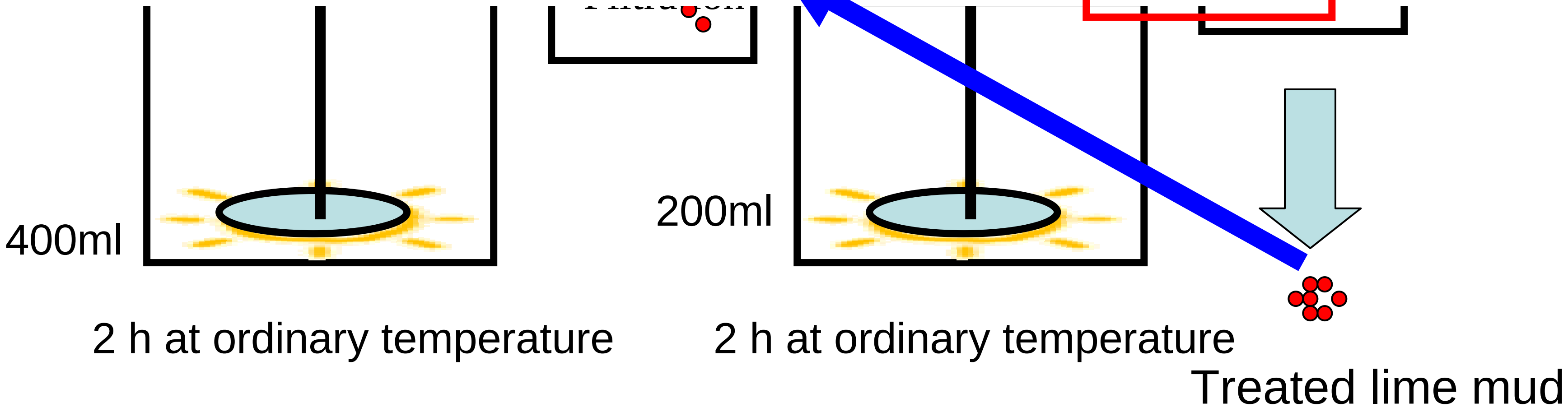
Sample	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	TiO_2	K_2O	Na_2O	Cl	others	LOI
Lime mud	52.39	0.7	2.52	1.49	0.29	0.31	0.056	0.013	0.14	0.88	0.049	41.1[illegible]
limestone	52.08	1.32	3.32	0.53	0.03	-	-	-	0.02	-	0.47	42.2[illegible]

Original lime mud was pre-washed with distilled water

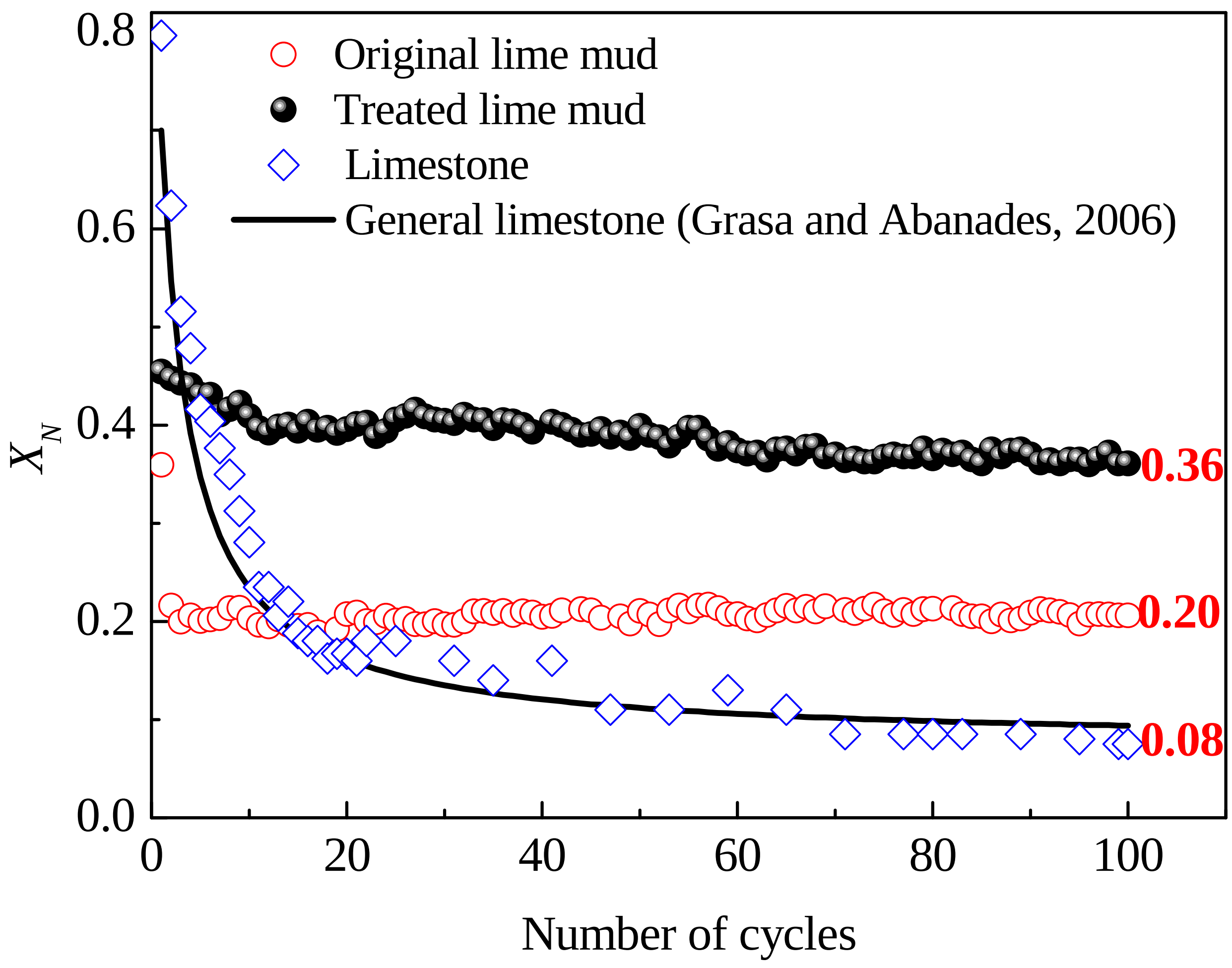


CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Ti_2O	K_2O	Na_2O	Cl	others	LOI
52.39	0.7	2.52	1.49	0.29	0.31	0.056	0.013	0.14	0.88	0.049	41.16

CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Ti_2O	K_2O	Na_2O	Cl	others	LOI
52.52	0.73	2.64	1.71	0.27	0.30	0.066	0.013	0.044	0.30	0.051	41.36

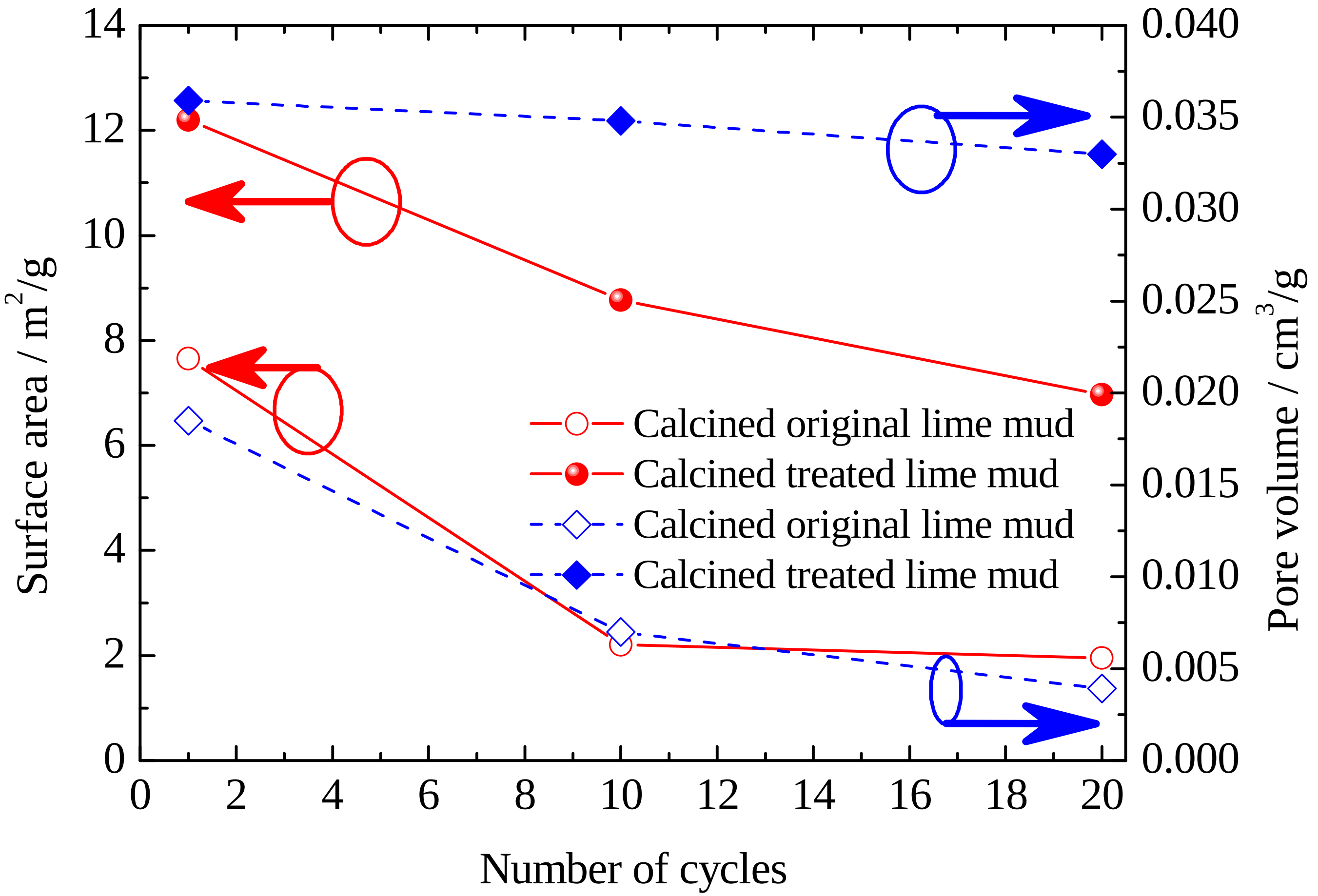


X_N of original and treated lime mud in CLP



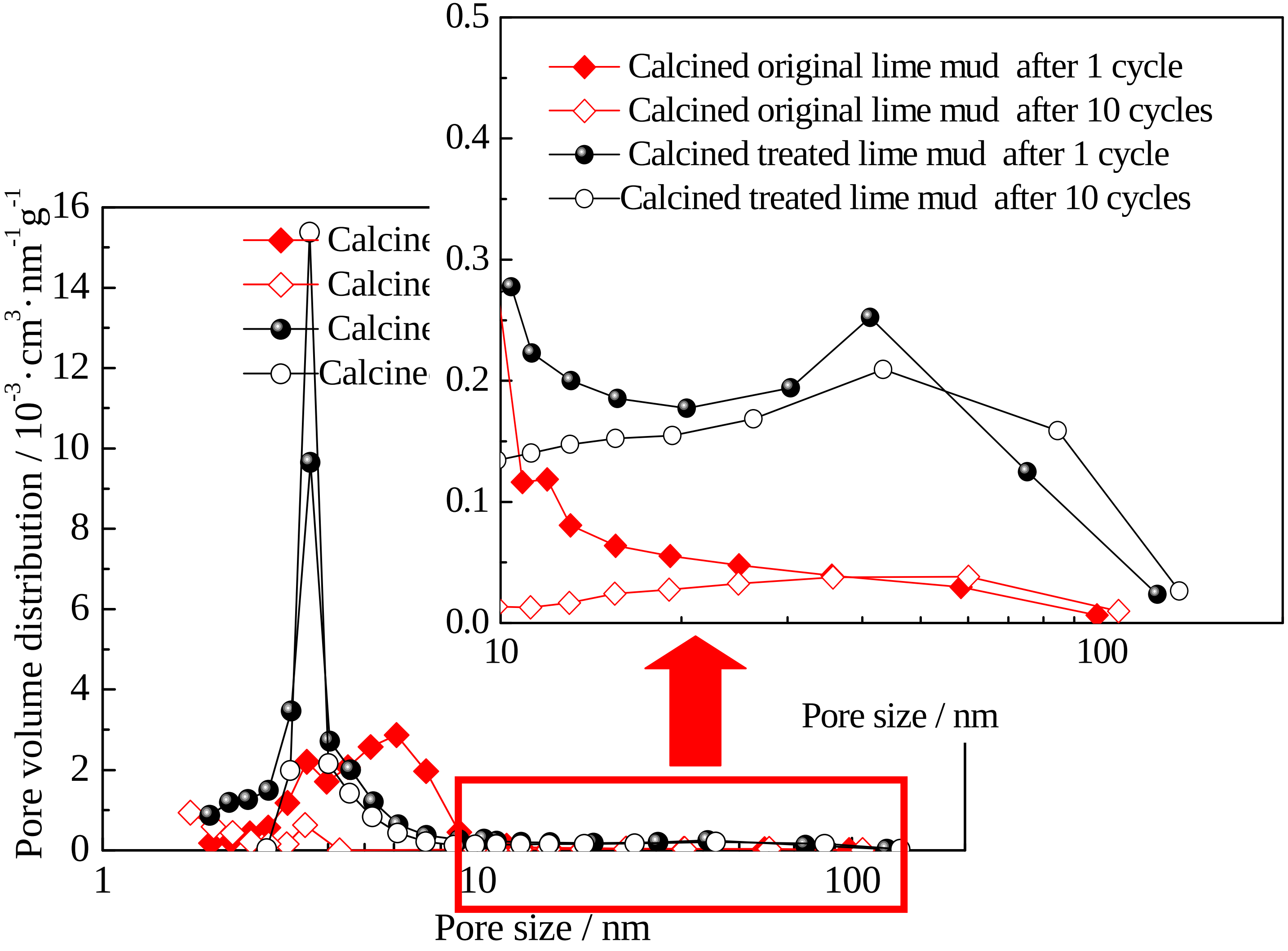
Microstructure analysis of original and treated mud in CLP

Surface area and pore volume with number of cycles

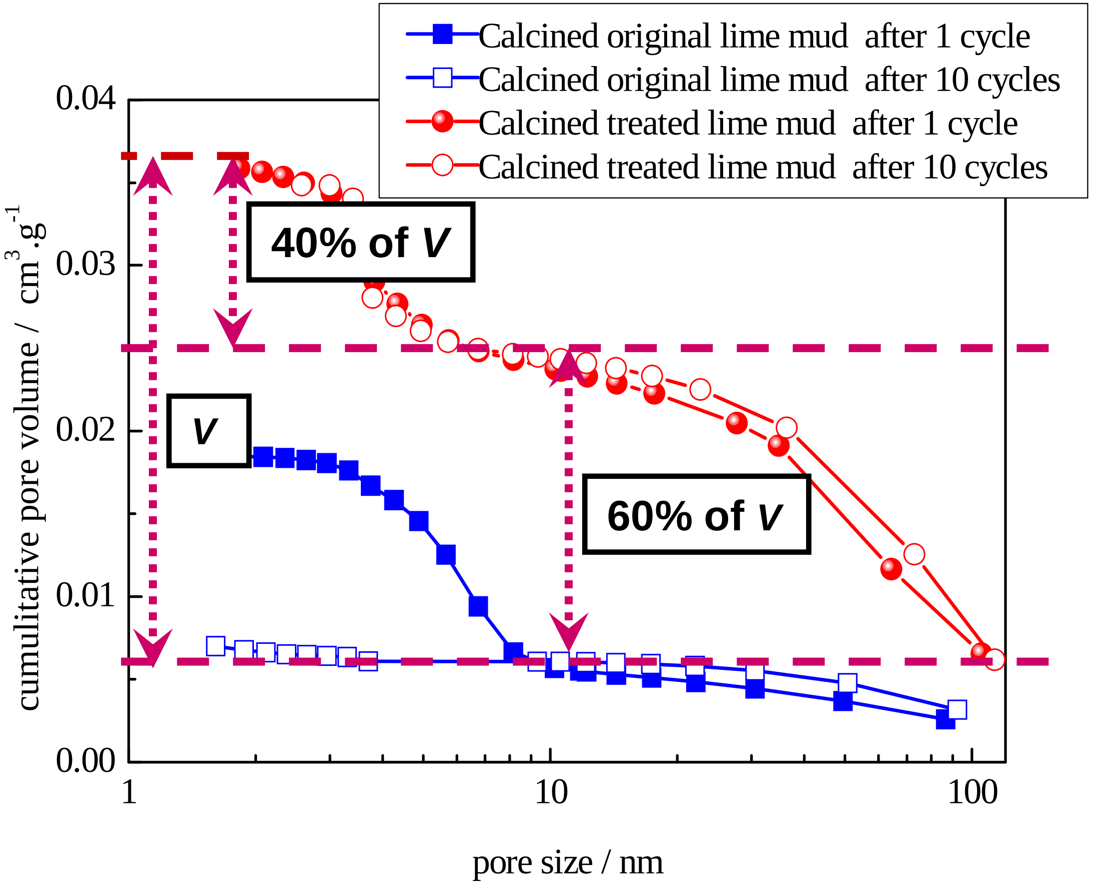


From DFR; Carbonation: 700 ℃, 40 min; Calcination: 850 ℃, 15min; Particle size: <0.125 mm

Pore size distribution with number of cycles



Cumulative pore volume with number of cycles



The pre-washed treatment improves obviously volume of pores in 10-112 nm in diameter.

Future work

- Cyclic CO_2 capture of calcium-based industrial sorbent in a dual fluidized bed reactor
- Particle attrition of calcium calcium-based industrial sorbent
- Pelletization of calcium-based industrial sorbent

Acknowledgment

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Thank you for your attention!