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NORTH CHINA ELECTRIC POWER UNIVERSITY

Supercritical CO_2 coupled with mechanical force to enhance carbonation of fly ash, stabilization of mercury and other heavy metals in lab and a pilot

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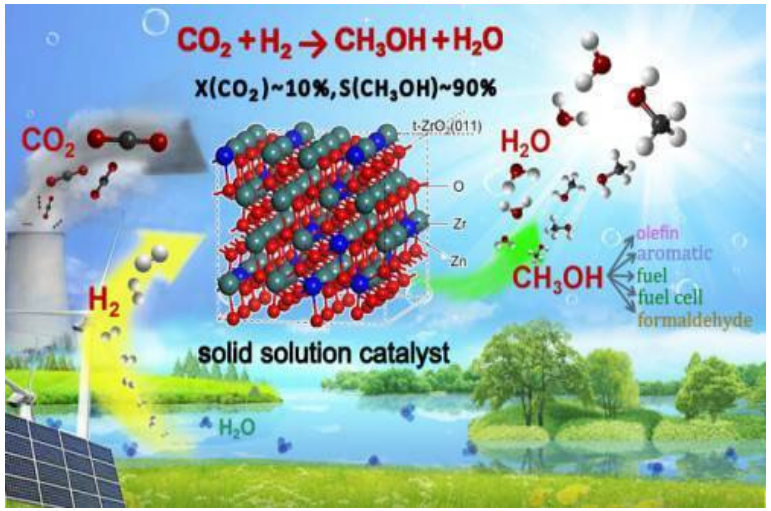
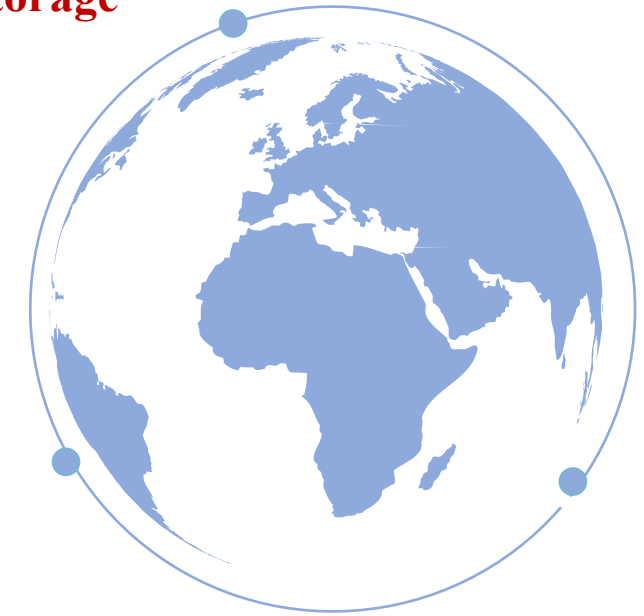
Challenge 1- Greenhouse gas

CO_2 is the largest contributor to greenhouse gases, and coal-fired power plants(CFPP) are the largest source of CO_2 emissions.



Geological storage *onshore, offshore, and oceanic*

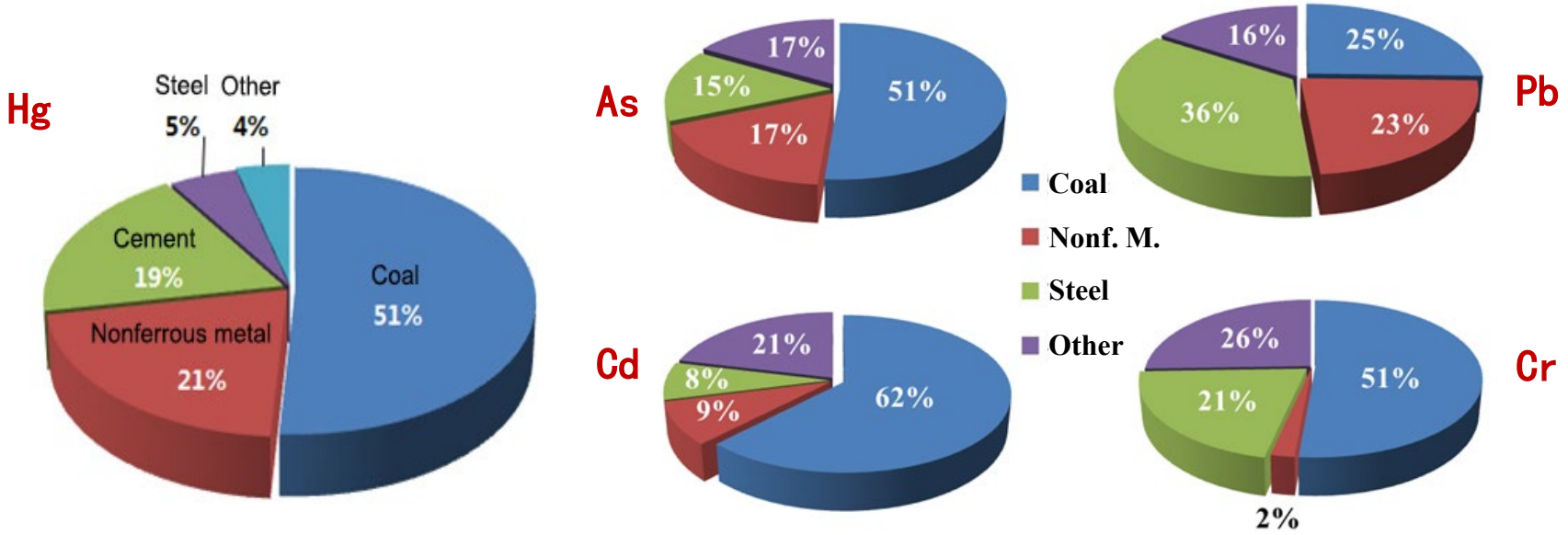


Carbonation storage *Natural mineral processes: slow reaction, even for thousands of years*

Conversion and utilization

Storage

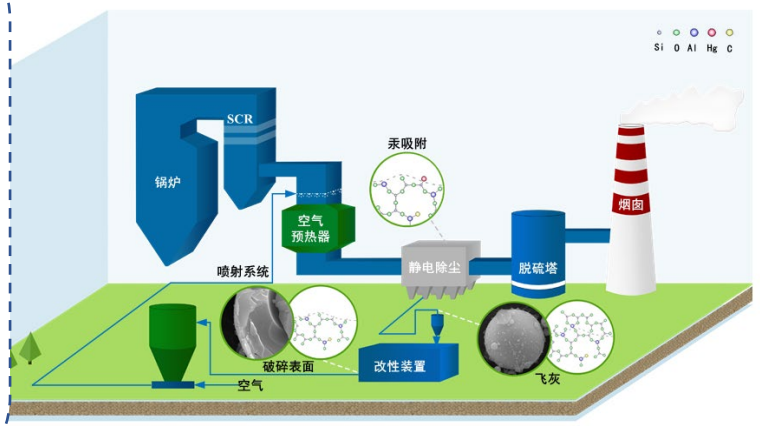
Challenge 2- Heavy metals pollution

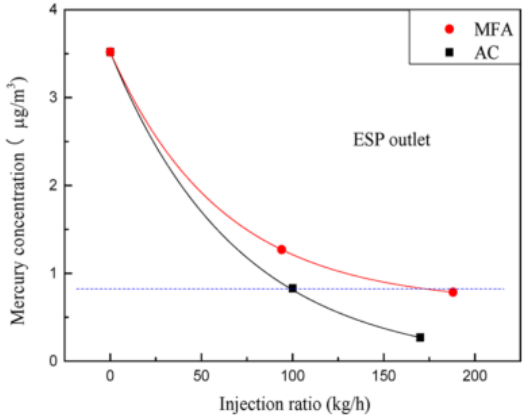


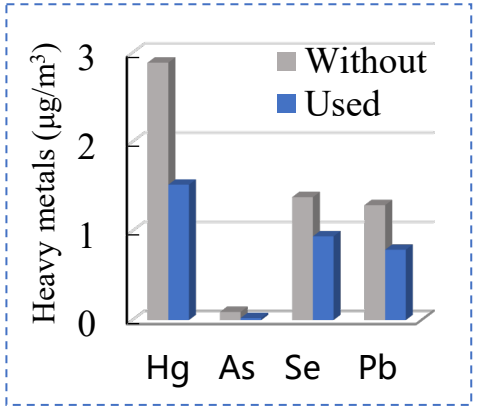
- The total amount of Hg emitted into the atmosphere by human activities worldwide was approximately 2500 ±500tons
- The emissions of Hg, As, Cd, Cr, etc. from coal-fired flue gas account for over 50% of China's atmospheric emissions
- Hg and other heavy metals in flue gas transport over long distances and spread over a larger area

Online modified fly ash and adsorption heavy metals in CFPP

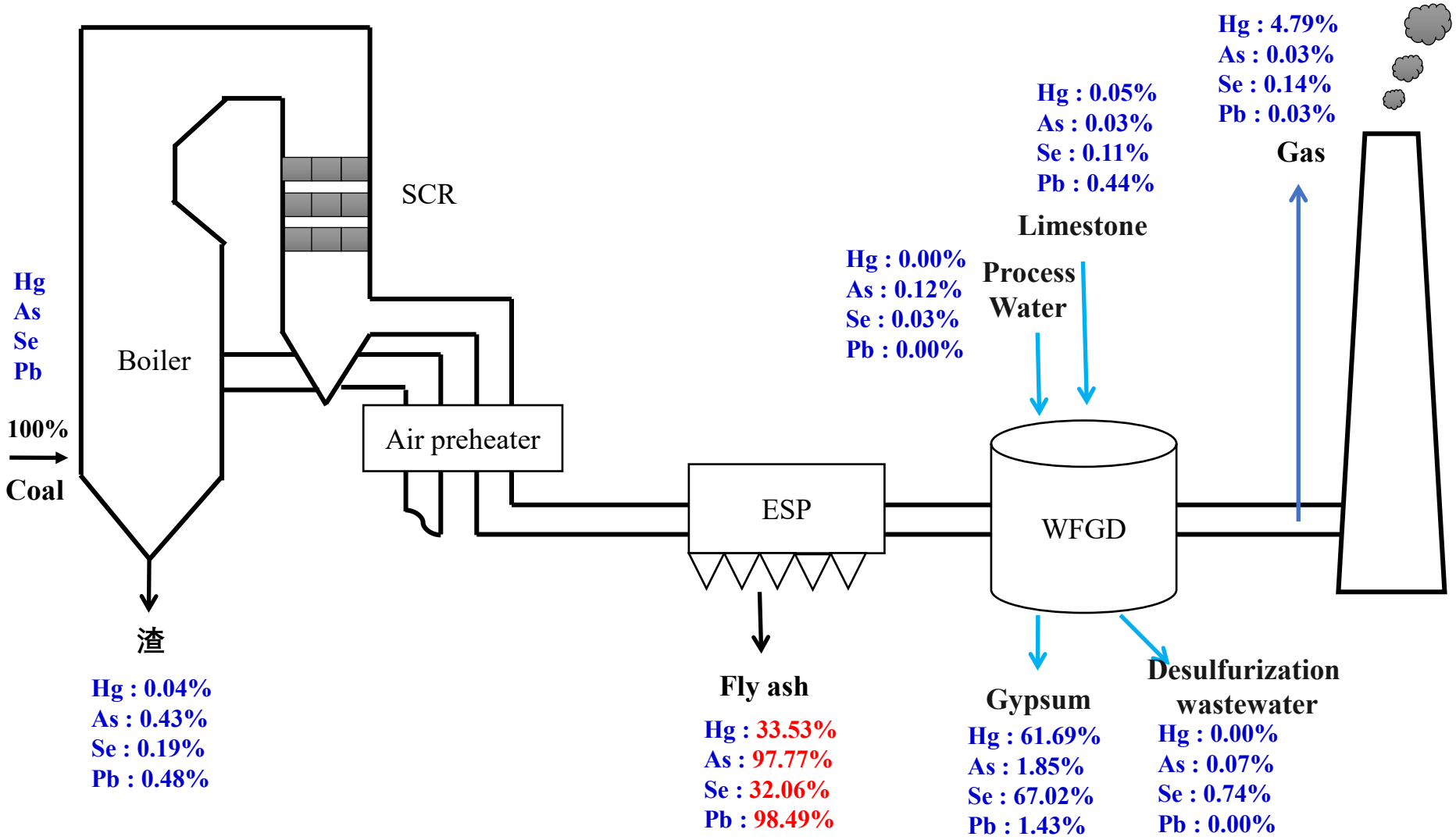
- Developed the first set of mechanochemical modified equipment, achieved demonstrations in 300MW supercritical (2015) and 1000MW ultra supercritical (2017) CFPP
- Comprehensive removal efficiency over 90%, and the cost is only 15-20% of the activated carbon adsorption mercury removal technology







Distribution of heavy metals in CFPP



Fly ash + CO_2 carbonation and heavy metals stabilization

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Main elements in fly ash

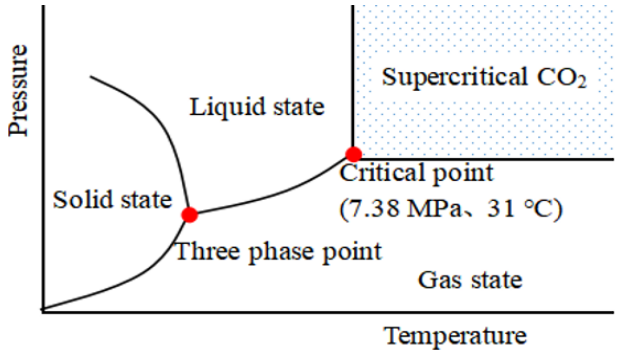
	YN	HB	SX	SF
CaO (%)	25.83	11.74	10.51	16.22
Al_2O_3 (%)	8.90	19.57	32.13	18.78
Fe_2O_3 (%)	6.73	7.25	9.64	8.97
MgO (%)	2.17	0.84	1.14	1.11
SiO_2 (%)	43.37	46.60	34.69	41.46

Carbonation

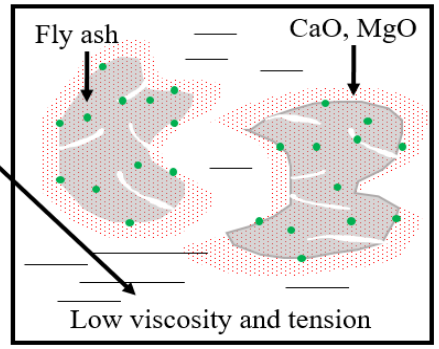
Natural processes:
slow reaction time

Technical ideas:
fast reaction time

Higher diffusion coefficient

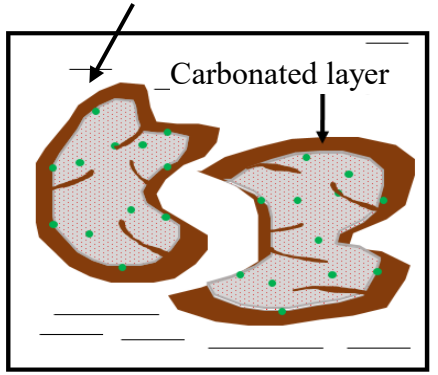


More fresh reaction surface



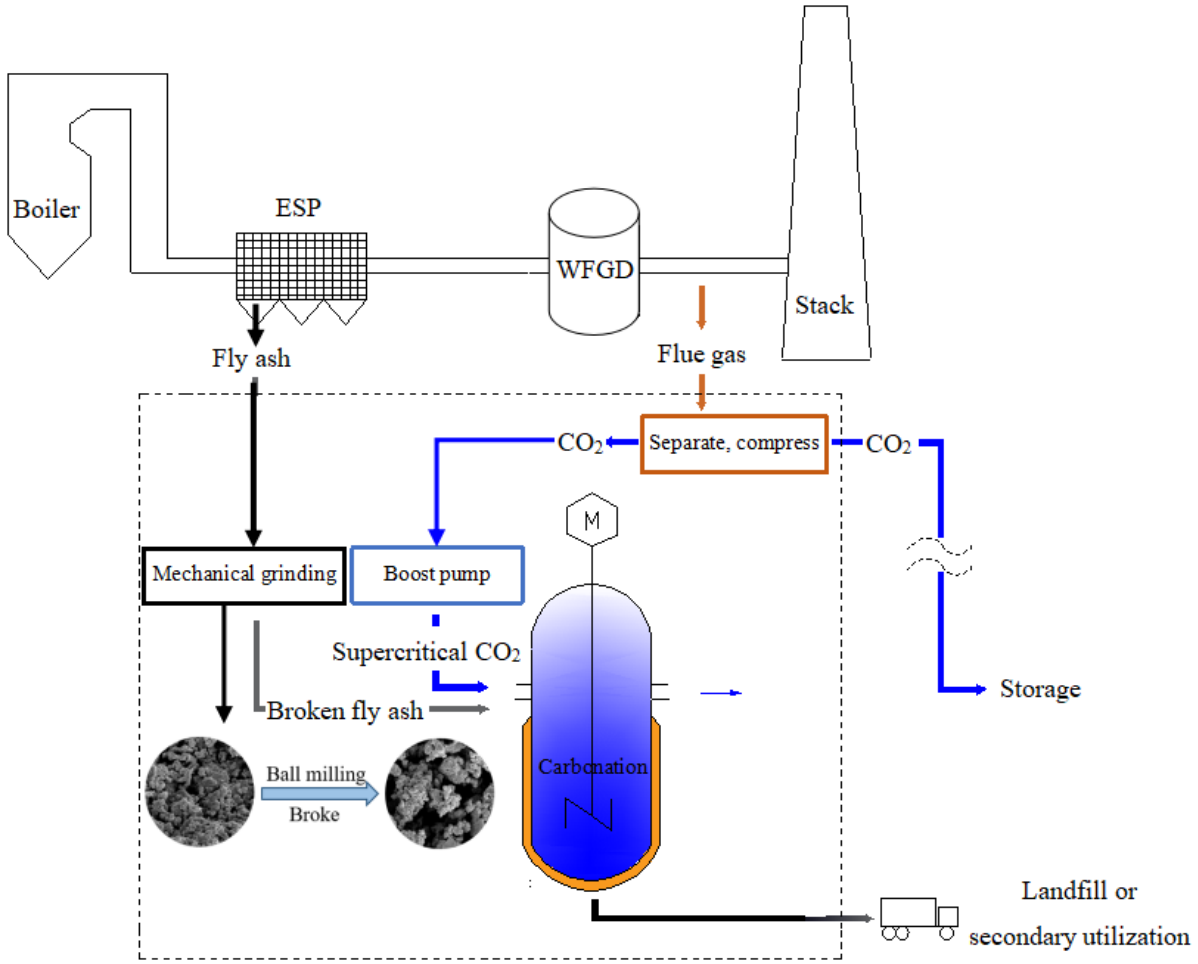
Carbonation

Reduce heavy metal release to environment



Supercritical CO_2 coupled with mechanical force to enhance fly ash carbonation

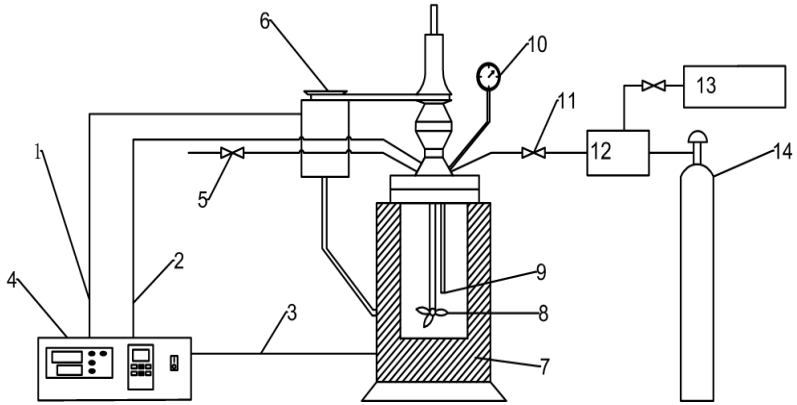
Mechanochemical technical route for CFPP



S-CO_2 coupled with mechanical force to enhance fly ash carbonation reaction

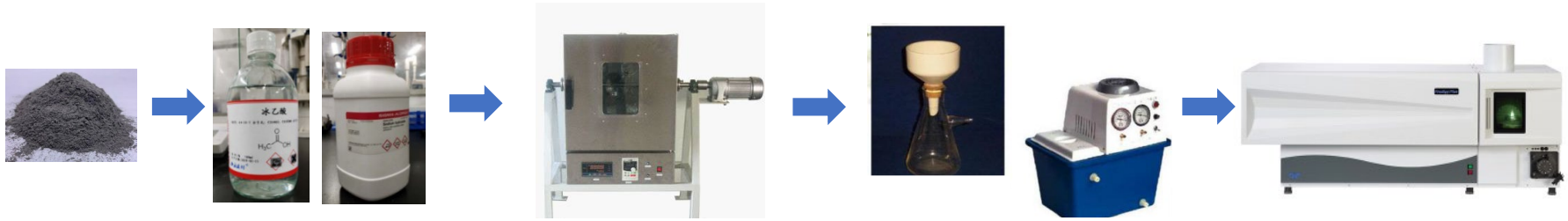
Experimental methods in lab

Planetary ball mill- Mechanical force



1: speed control; 2: temperature control; 3: heating control; 4: operation panel; 5: exhaust valve;
6: stirring motor; 7: heating jacket; 8: stirrer; 9: thermocouple; 10: pressure gauge; 11: intake valve;
12: booster pump; 13: compressed air; 14: CO_2 gas source

s-CO_2 carbonation reaction system

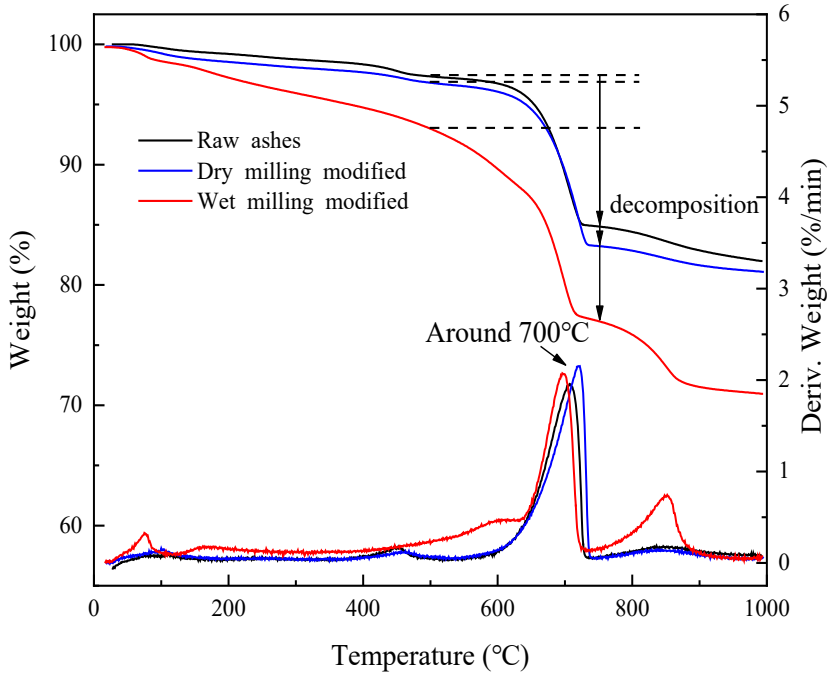


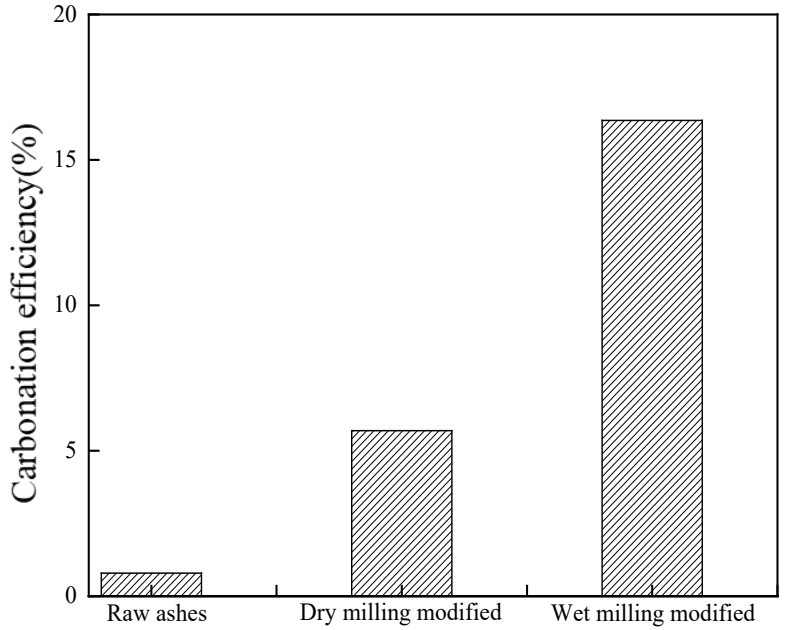
Samples → Extraction → Inversion oscillation → Suction filtration → Measurement

TCLP standard leaching method - Heavy metal toxic leaching

Mechanical force enhance carbonation

Fly ash

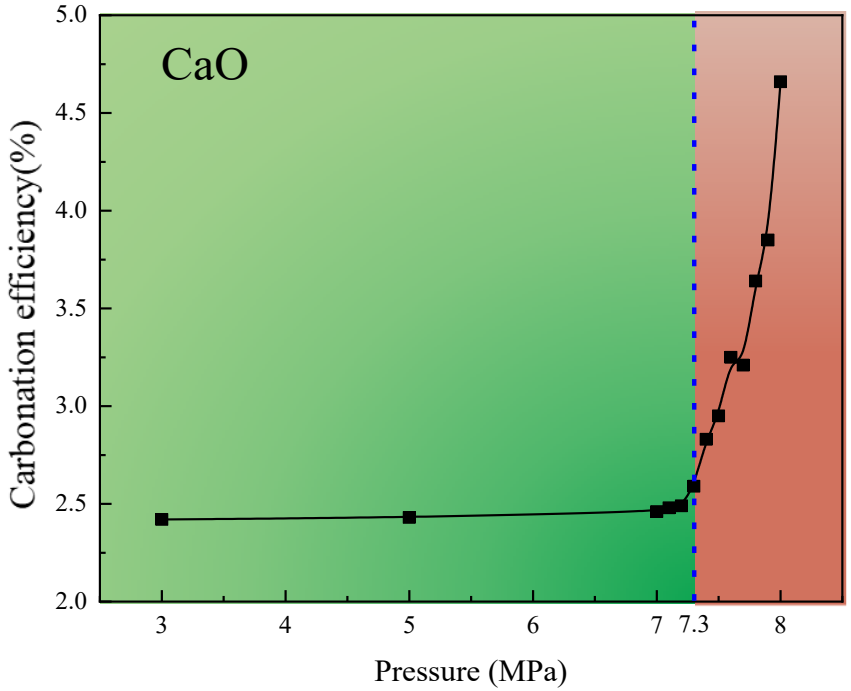




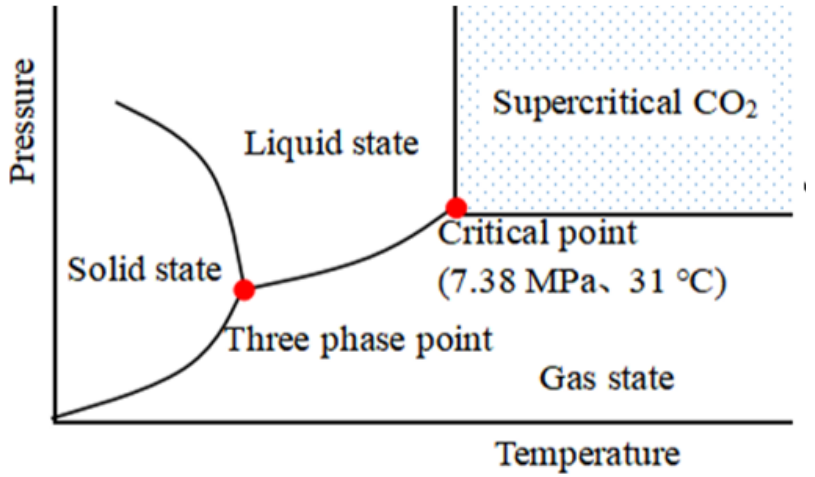
Mechanical force enhance the carbonation characteristics, compared with dry milling, wet milling has a more good performance

Carbonation characteristics in transcritical processes

In order to eliminate the influence of other substances of fly ash, dry and wet carbonation experiments were carried out with CaO

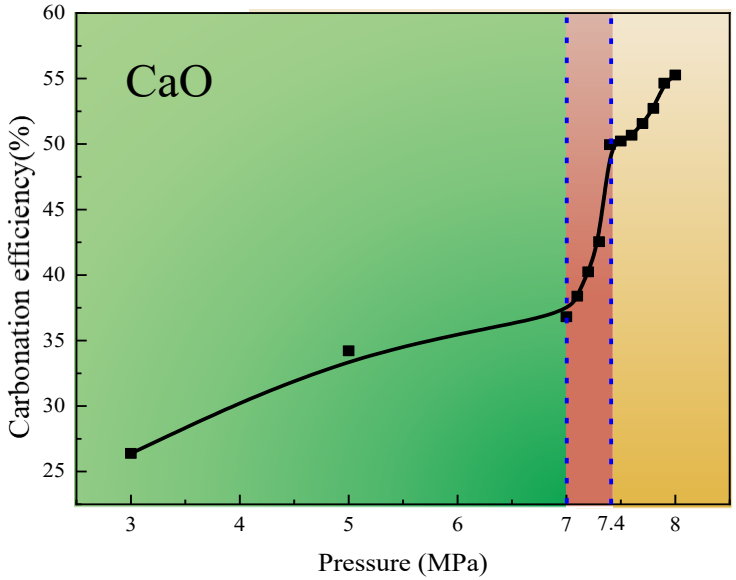


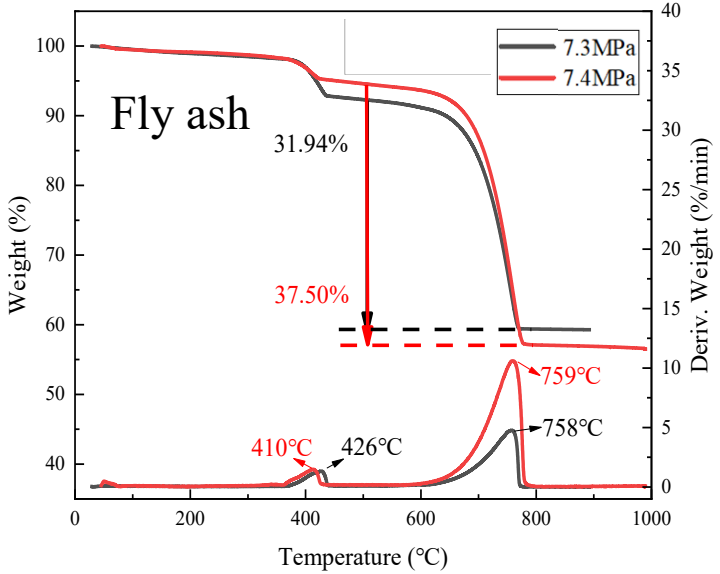
Dry carbonation



As the pressure increases, the carbonation efficiency of the process is divided into two stages: first a slow increase, then a rapid increase during transcritical

Carbonation characteristics in transcritical processes

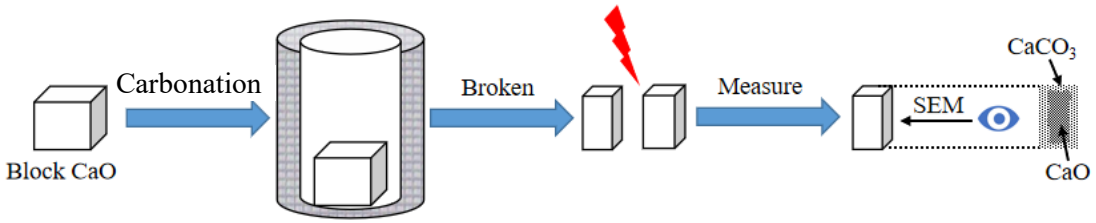




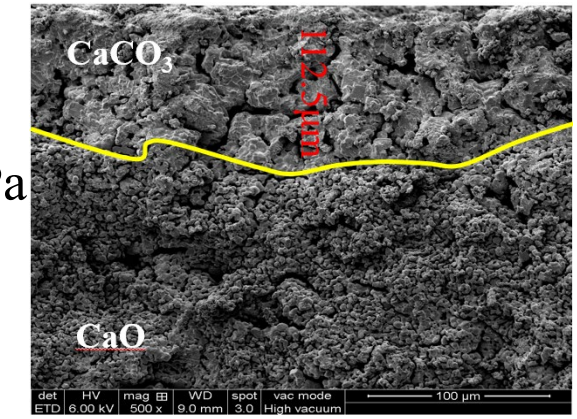
Wet carbonation

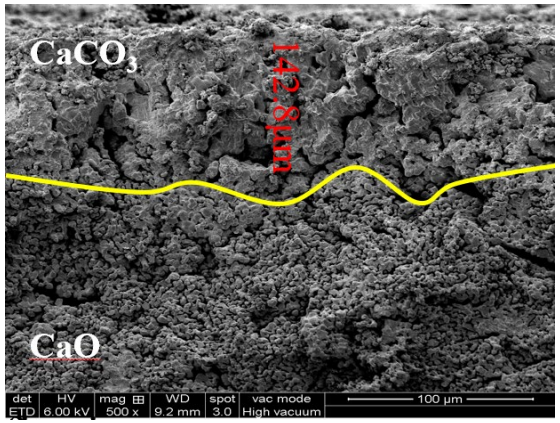
- As the pressure increases, the efficiency of the process changes in three stages, first a slow increase, then a fastest increase, and finally another fast increase
- Supercritical can effectively improve carbonation efficiency

Surface morphology of CaO



3MPa

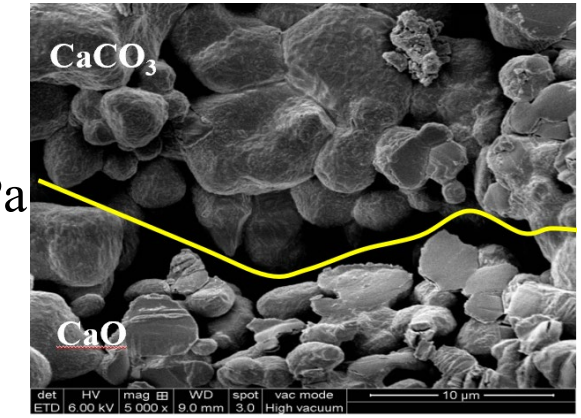


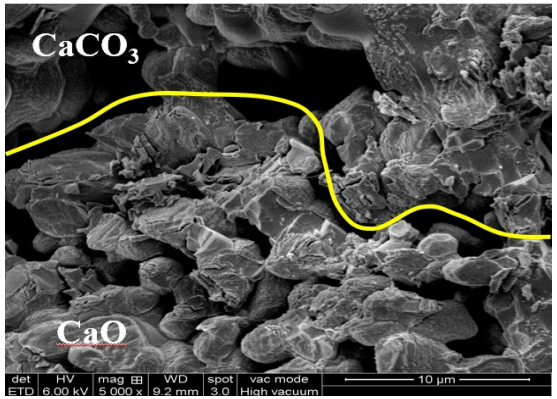


8MPa

500 magnification

3MPa

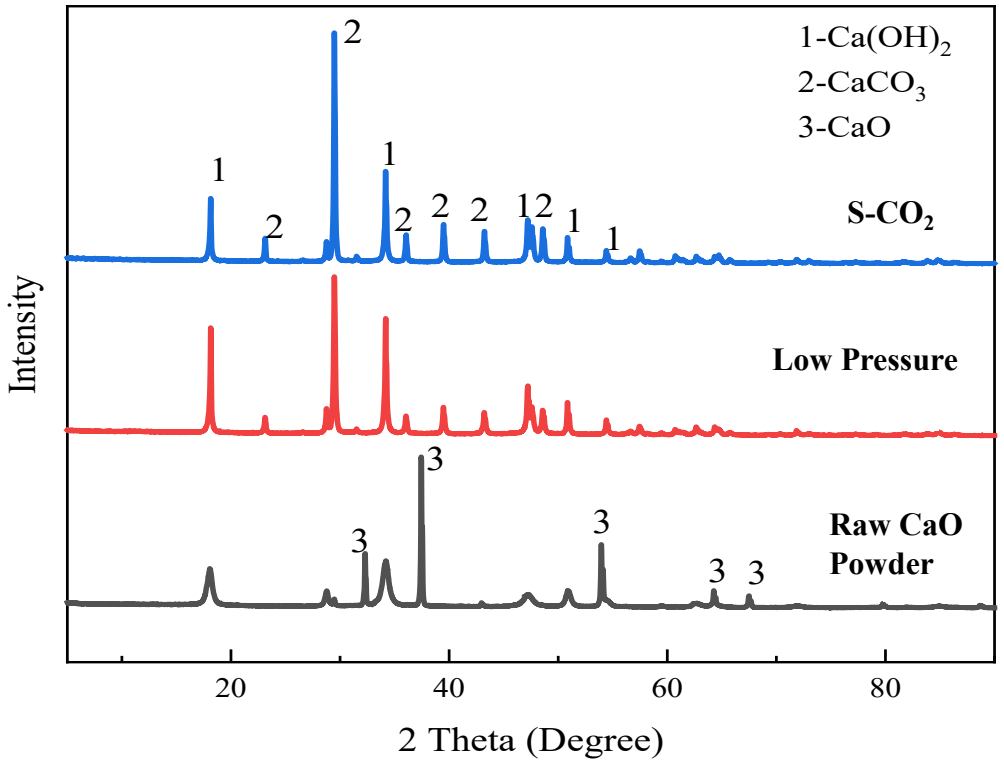




8MPa

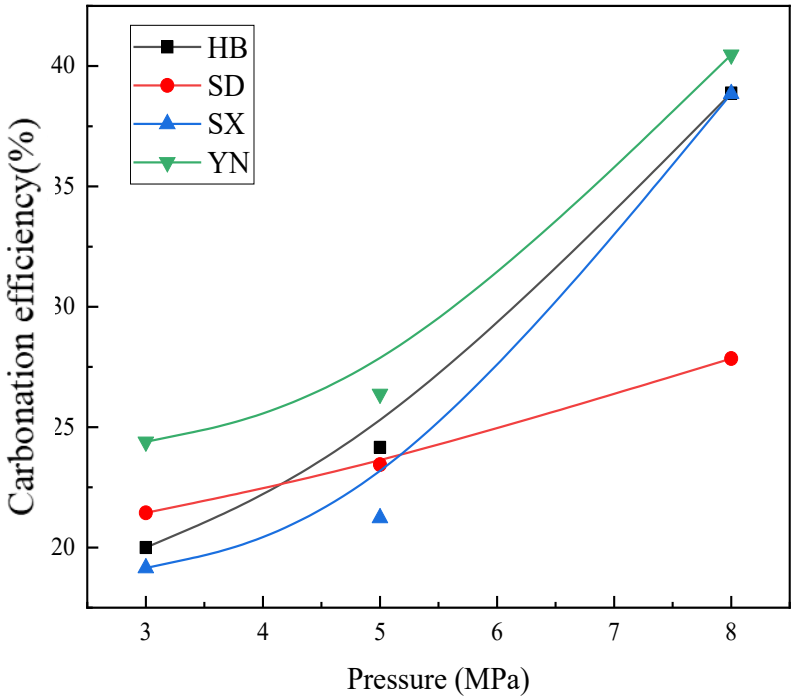
5000 magnification

Mineral analysis



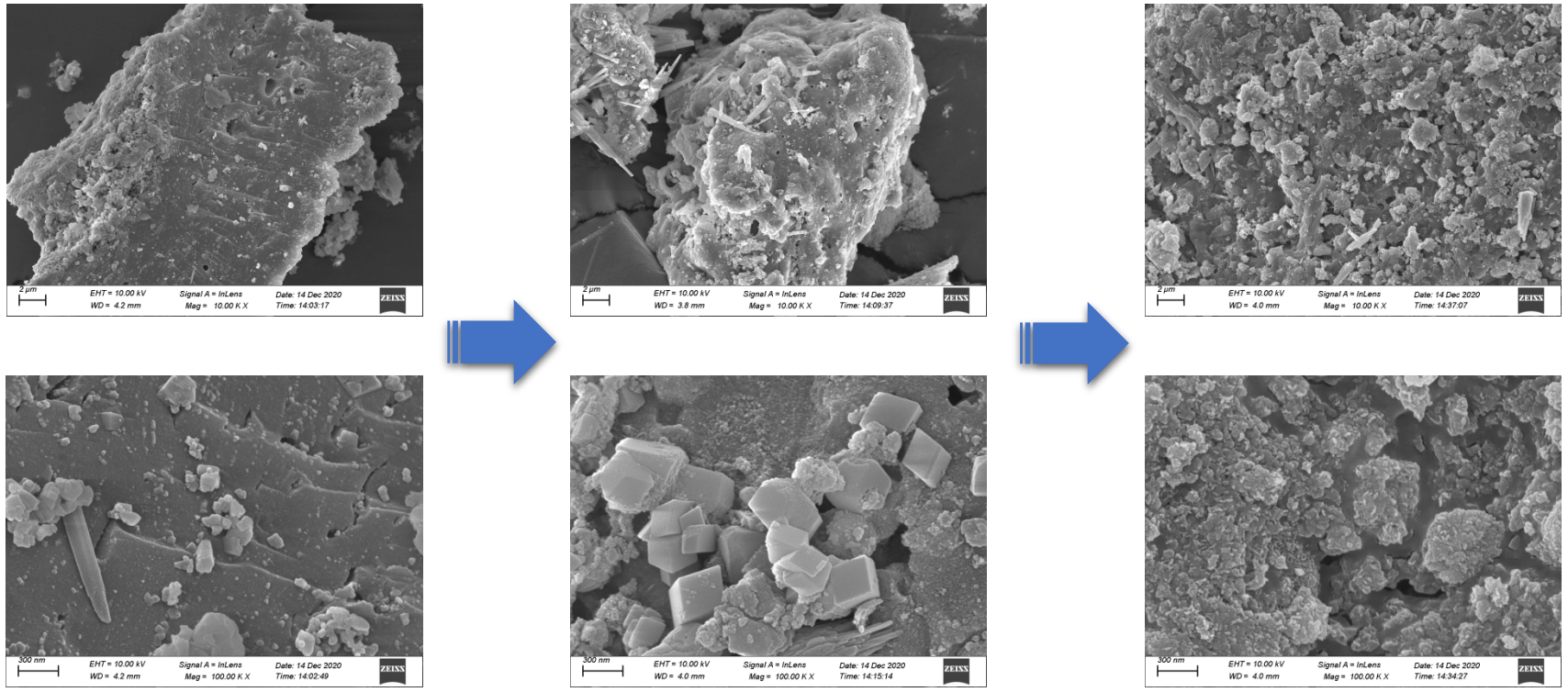
After carbonation, the intensity of the $CaCO_3$ peak increases, the CaO peak decreases, especially under s-CO_2 conditions

Different fly ash carbonation



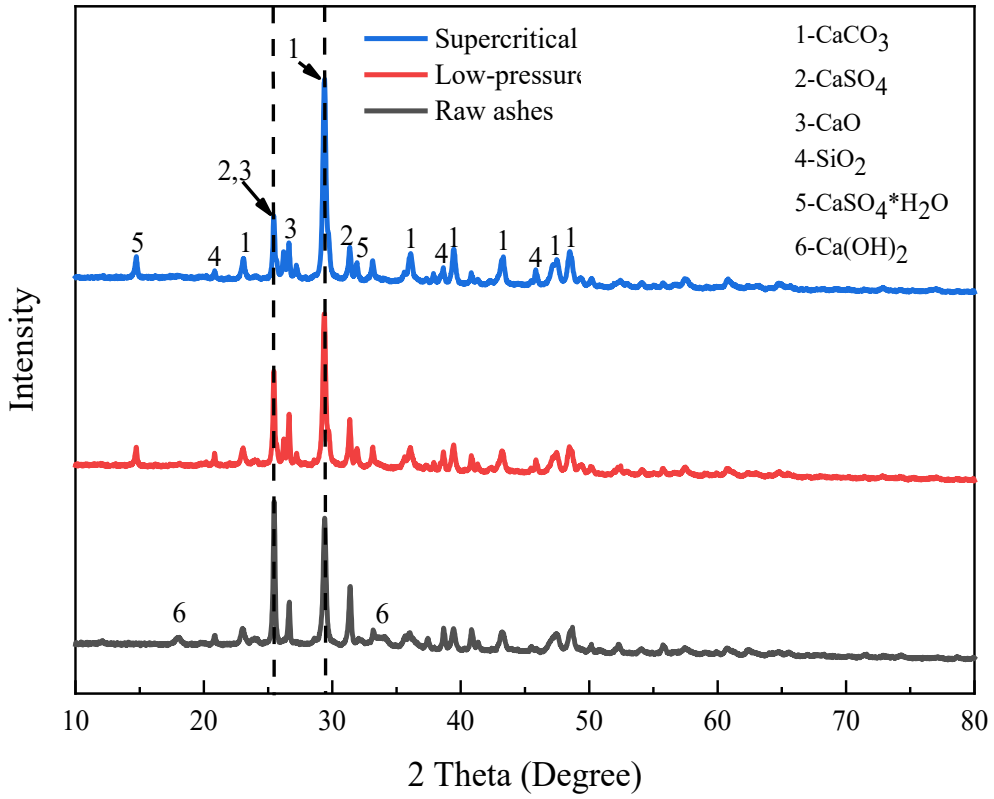
	YN	HB	SX	SD
Specific surface area(m^2/g)	21.68	9.32	19.47	10.71
Pore volume(mm^3/g)	0.082	0.023	0.094	0.025
Aperture (nm)	15.20	10.024	19.25	9.40
Al_2O_3 (%)	8.90	19.57	32.13	13.33
CaO (%)	25.83	11.74	10.51	6.03
Fe_2O_3 (%)	6.73	7.25	9.64	5.69
K_2O (%)	0.54	2.62	2.22	14.64
MgO (%)	2.17	0.84	1.14	0.24
Na_2O (%)	0.12	2.27	0.38	1.12
P_2O_5 (%)	0.02	0.53	2.15	ND
SiO_2 (%)	43.37	46.60	34.69	68.75
TiO_2 (%)	0.39	0.82	1.50	1.08
SO_3 (%)	1.12	0.54	0.68	0.02

Surface morphology of fly ash



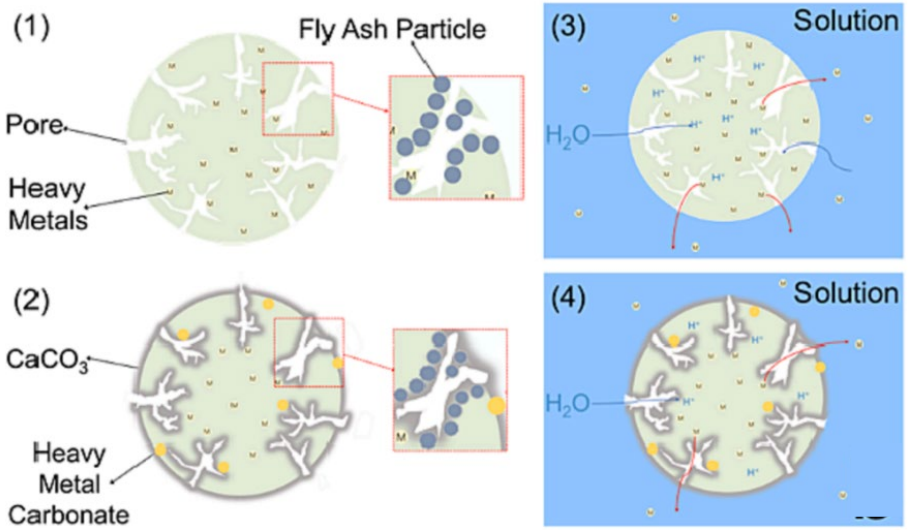
Raw ash　　Low pressure carbonation　　s-CO_2 carbonation

Fly ash mineral analysis

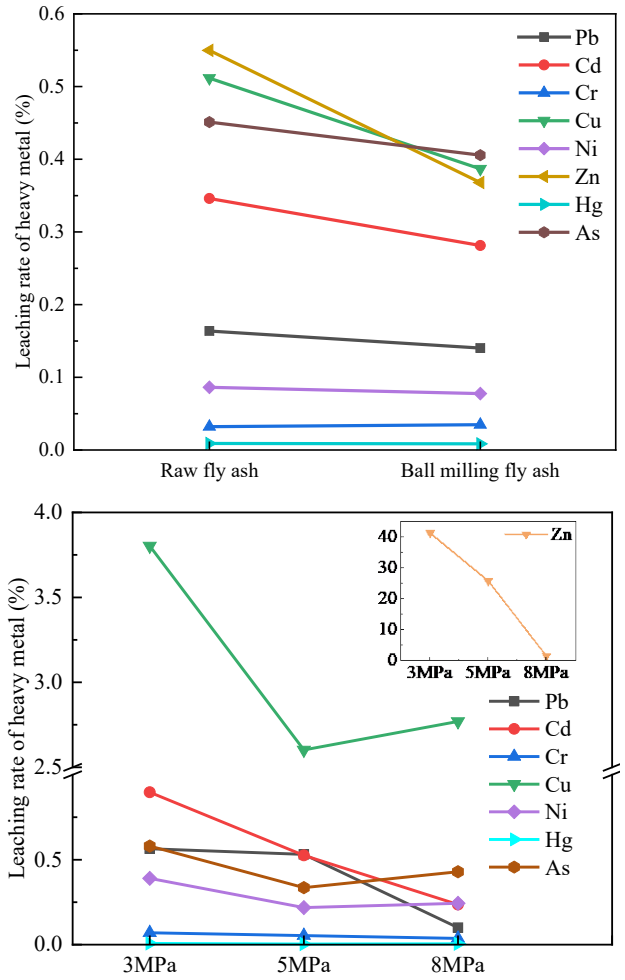


- After carbonation, the intensity of the $CaCO_3$ peak increases, the CaO peak decreases, and the $Ca(OH)_2$ peak disappears, especially under s-CO_2 conditions
- CO_2 may react with heavy metal oxides in the fly ash to generate corresponding carbonates or basic carbonates

Stabilization of heavy metals in fly ash



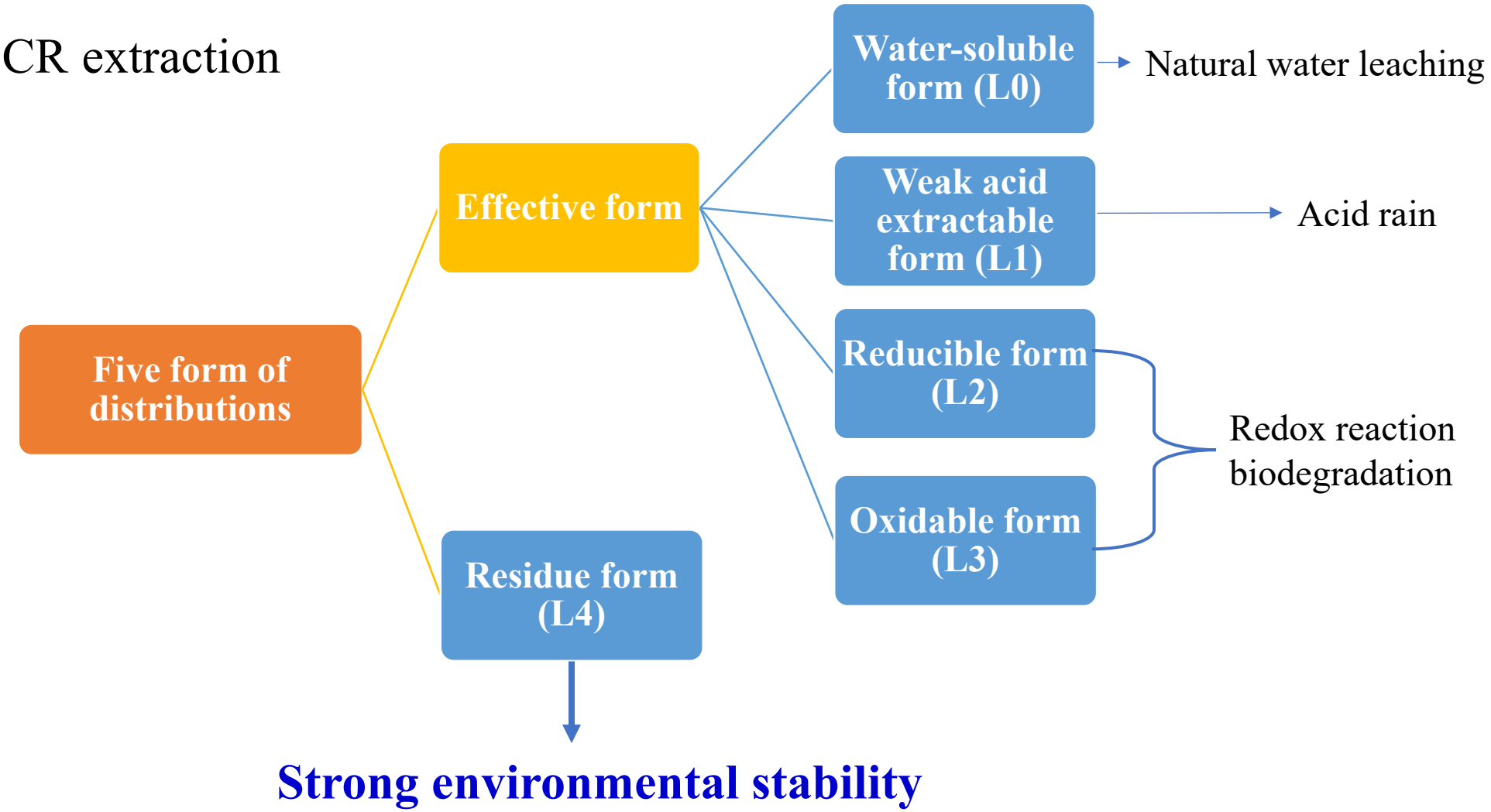
carbonation and leaching model



Compared with the raw ash, Hg leaching concentration decreased by 47.06%, Pb by 38.65%, Cd by 31.66%, and As by 4.91% under supercritical conditions.

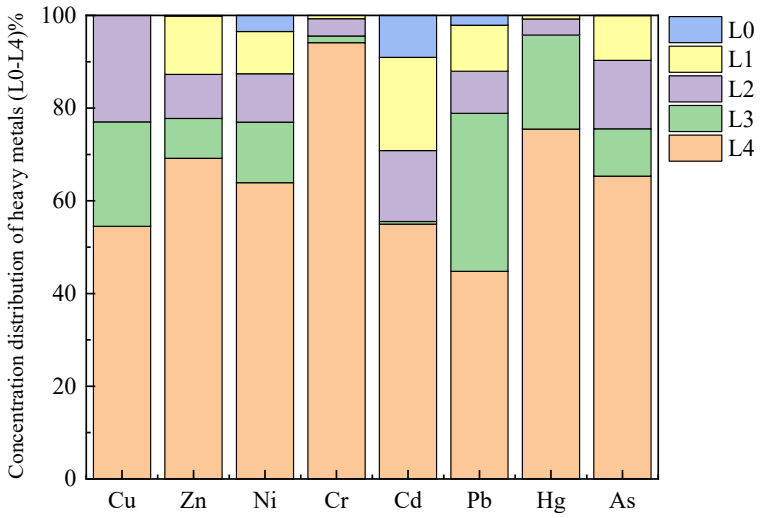
Analysis of speciation

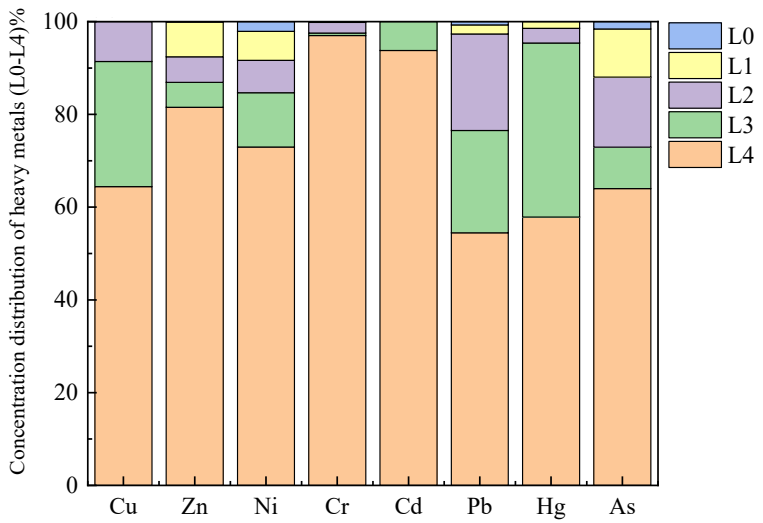
BCR extraction



Strong environmental stability

Analysis of speciation



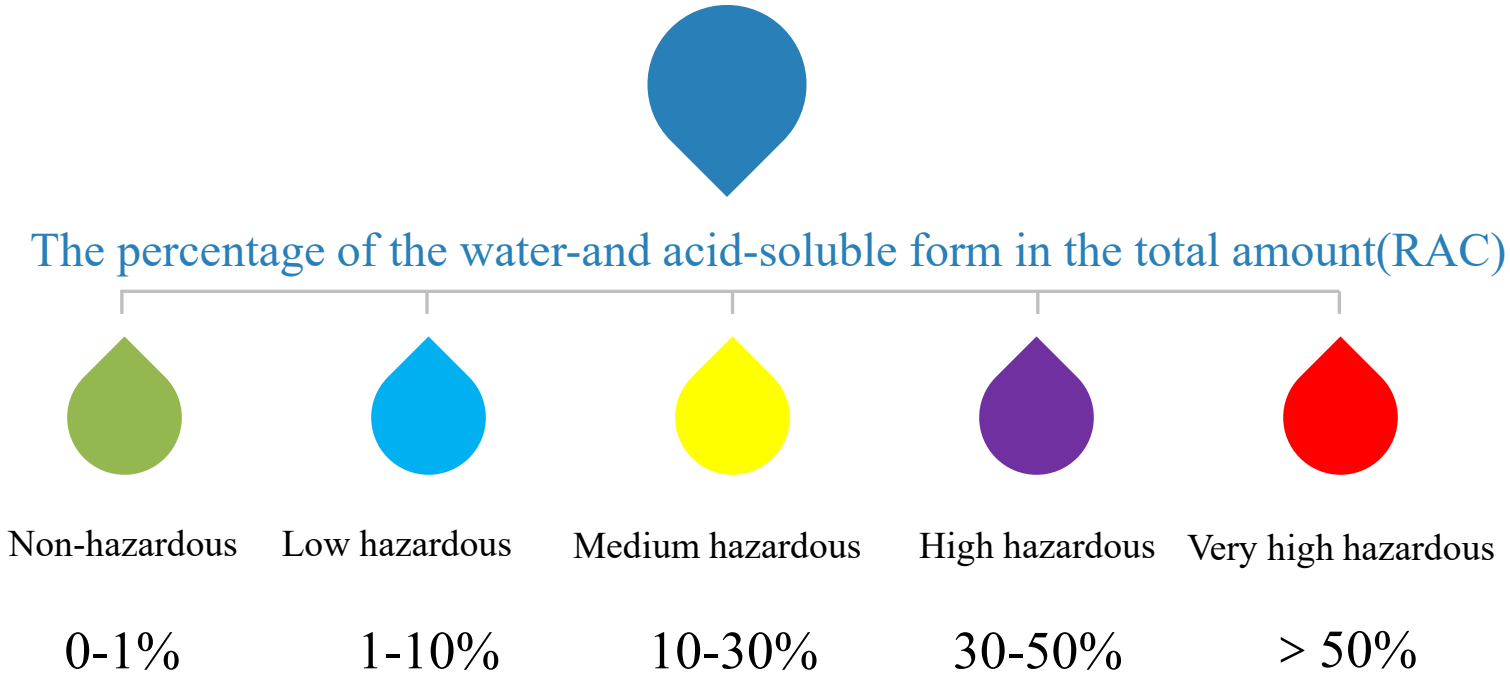


Before carbonation After carbonation

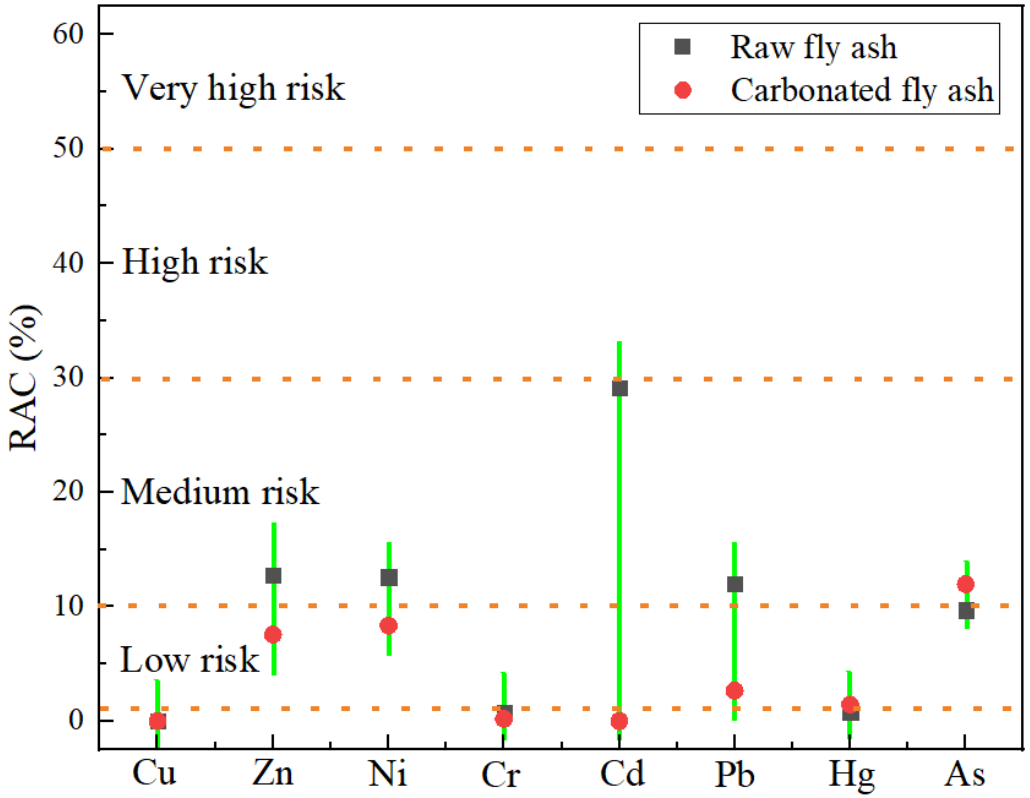
Distribution of different heavy metal form

After carbonation, most heavy metal stability is improved except Hg and As.

Risk assessment code(RAC) criteria



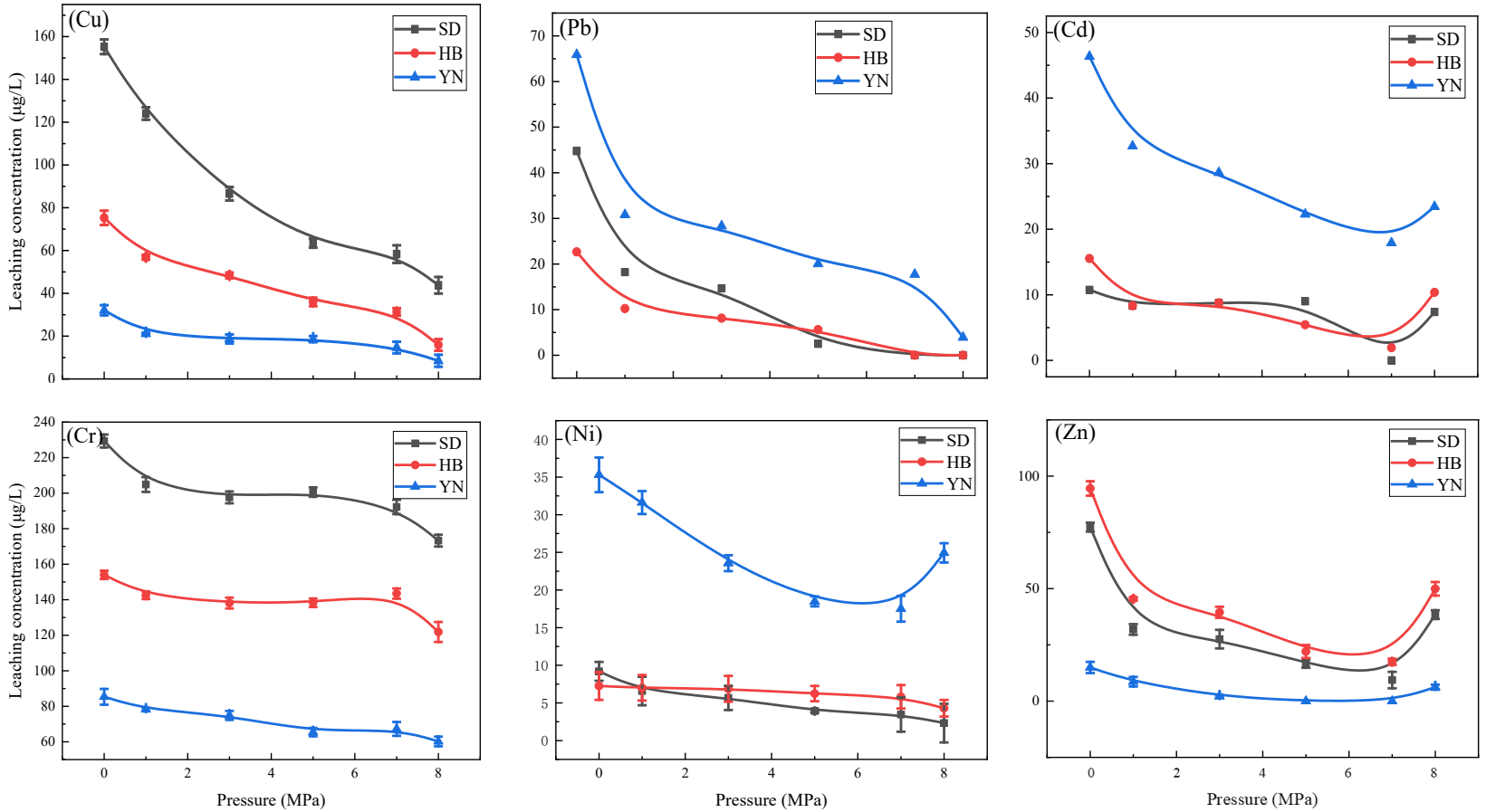
RAC assessment



RACs of heavy metals in fly ash

- The RACs of most heavy metal of the carbonated fly ash decrease.
- Generally, mechanochemical is good for heavy metal stabilization.

Heavy metals leaching characteristics of carbonated fly ash

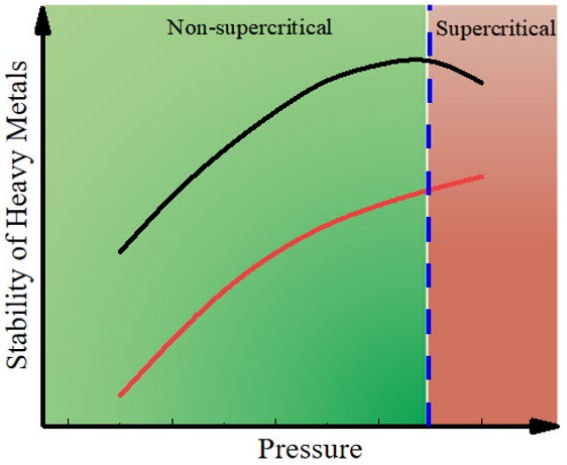


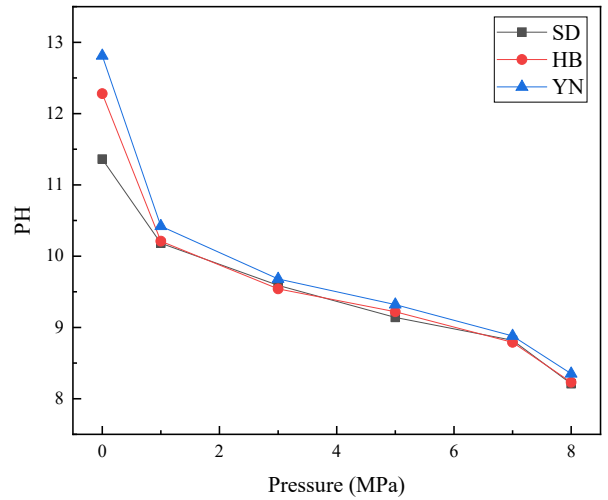
- In most case, leaching concentration decrease with pressure increase.
- Some heavy metal leaching concentration increase in super-critical situation.

Effect of carbonation on heavy metals

Influences on leaching in the transition from non-supercritical to supercritical

Mechanism	Pb	Zn	Cu	Cd	Cr	Ni
Adsorption precipitation	↓	↓	↓	-	-	-
Chemical reaction	↓	↓	↓	-	-	-
Physical encapsulation	↓	↓	↓	↓	↓	↓
Speciation transformation	↓	↓ ↑	-	- ↑	-	- ↑





The solubility of s-CO_2 in water increase, leading to the system pH decrease, some heavy metals will dissolve again.

One trend is gradual enhancement of stability, the other trend is initial increase then decrease.

Pilot test (1 t/d)

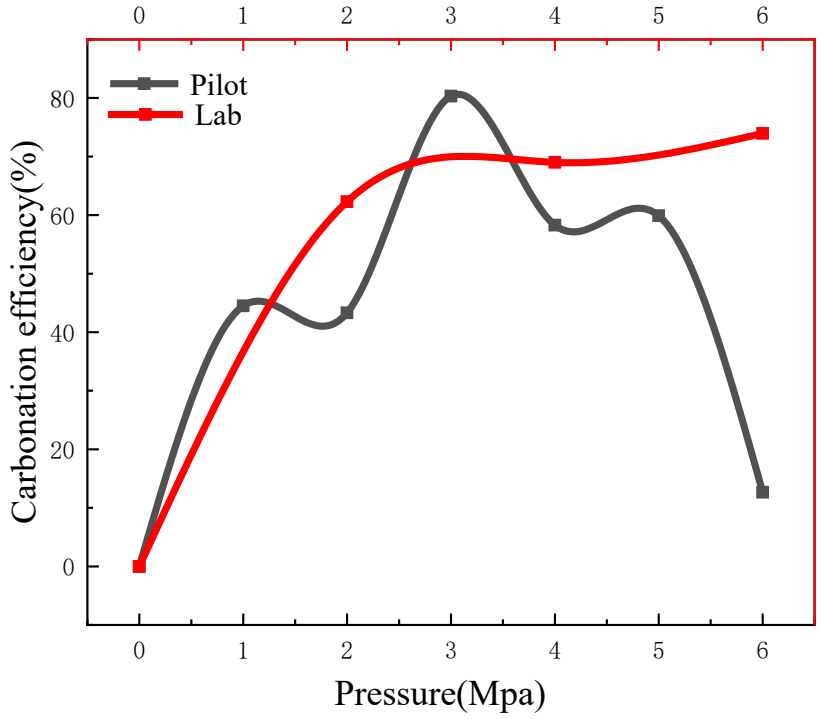
Fly ash milling facility

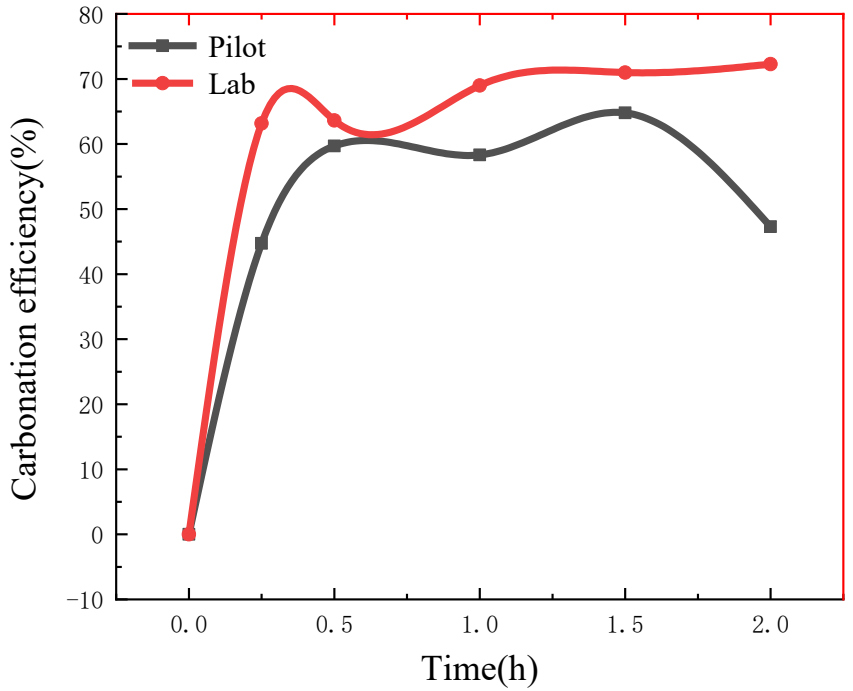
Carbonation facility

Installation

Pilot test platform

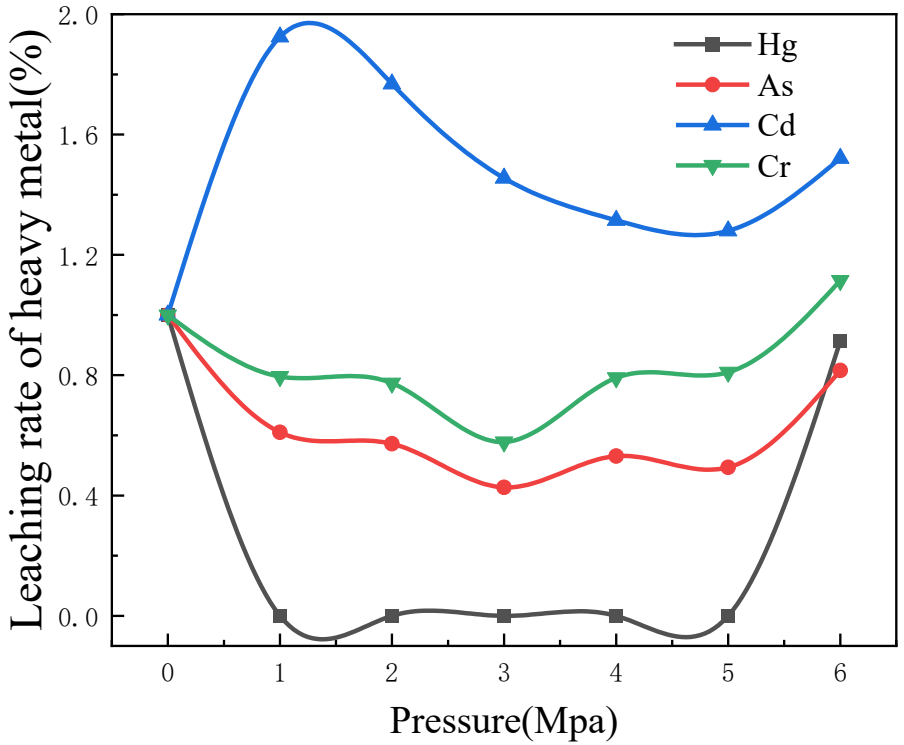
Carbonation characteristics





In the pilot experiment, its carbonation efficiency can reach 81.3%. Compared with the laboratory experiment, there are great different for its carbonation under different pressure.

Heavy metal leaching



Compared with the laboratory experiment, there are also great different for its heavy metal leaching under different pressure.

Conclusions

- Developed a mechanochemical modified fly ash carbonation and stabilize heavy metals technology
- Generally, mechanical force and supercritical conditions can effectively promote carbonation and stabilize heavy metals
- The stability of heavy metals in fly ash is influenced by multiple mechanisms, and its exhibits different characteristics under different conditions

Thanks!