SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

北京科技大学
University of Science and Technology Beijing

Recycling of Some Steel Industrial Solid Wastes for High-value Materials Application

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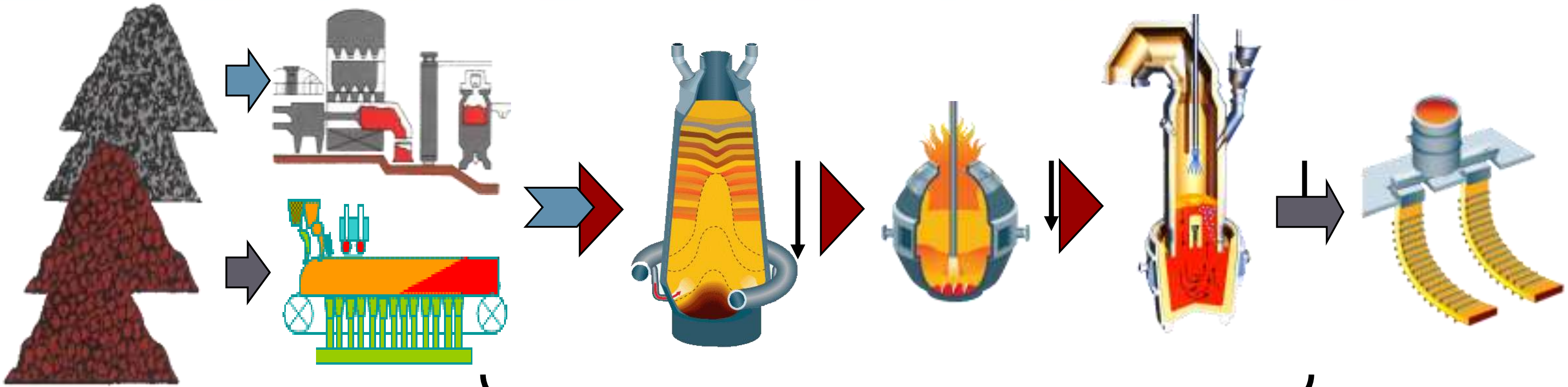
centre

SMART-PRO²

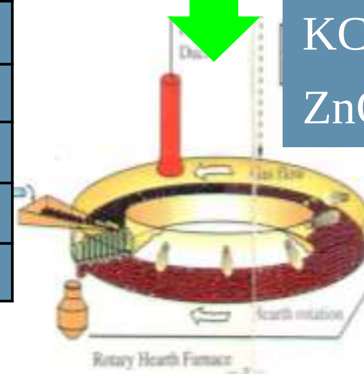
Introduction---problem 1

dust of steel works



dust:
~100 kg/ton steel

	TFe	C	K_2O	Na_2O	Pb	Zn
LD	60.7	1.6	**0. 14**	0.43	0.03	0.11
BF	24.2	33.3	0.07	0.63	0.15	**6.70**
EAF	~36	~2			~4	**~25**
Sinter	23.1	10.0	26. 9	2.24	2.15	0.50

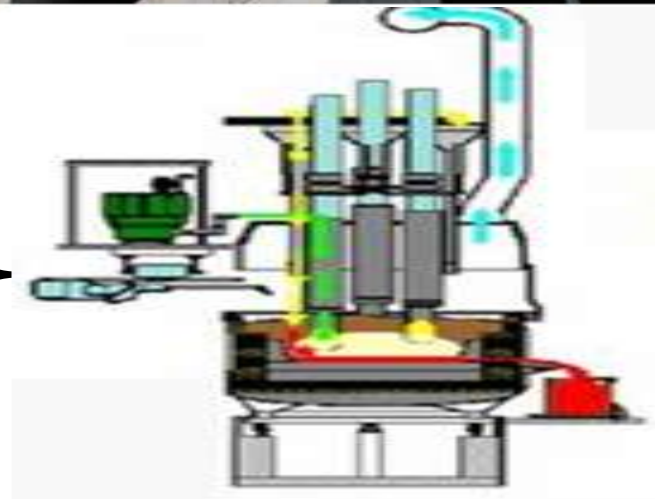


Second fume
~100kg/ton pellet
KCl: 10~20%
ZnO: 30~50%

How to use the sintering dust ?

Introduction---problem 2

dust of Si-Fe alloy works



→ 1000 kg Si-Fe

→ Silica fume ~100 kg/ton Si-Fe

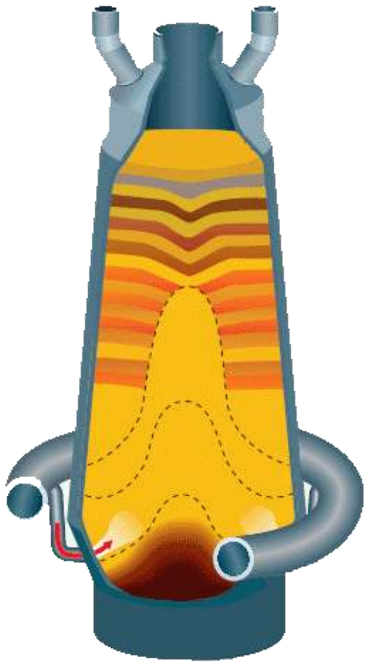
Composition of typical silica fume

Comp.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	S	size
%wt	**86.5**	0.54	3.15	0.73	2.39	3.34	0.56	<0.1	0.24	<1um (80%)

If SiO_2 >90%, silica fume can be used as cement additive.
But generally, SiO_2 <90%, How to use it ?

Introduction---problem 3

slag of steel works



250 kg slag/T hot-metal

water-granulated slag

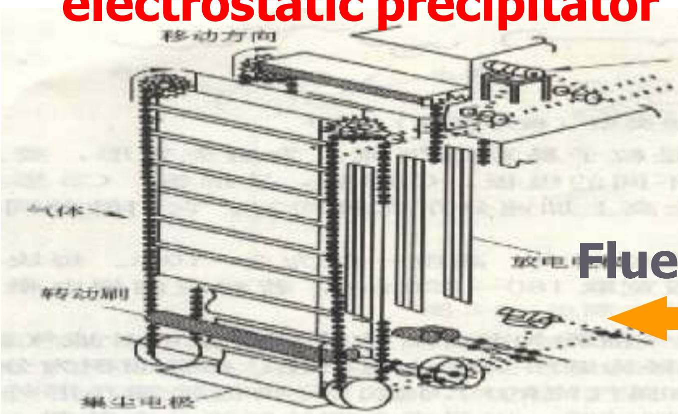
Pore particles

Cement production

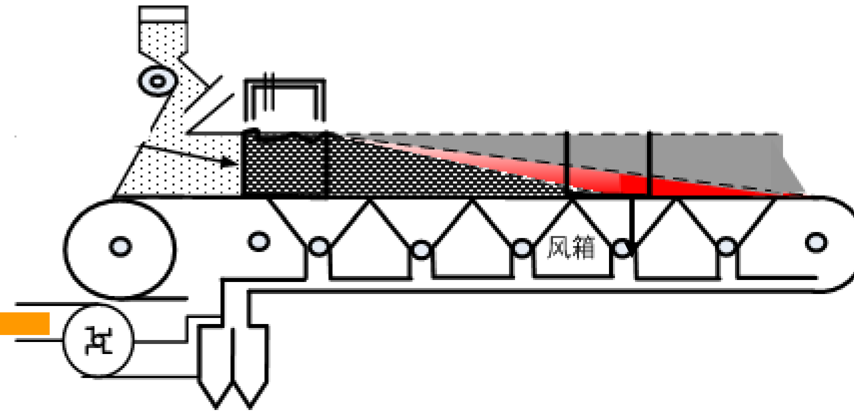
If it is possible to be used as the of other high-value material ?

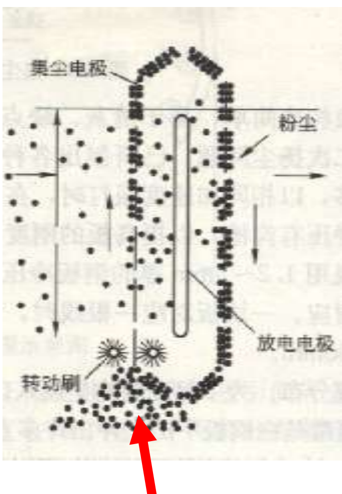
1. Recovery of Potassium Chloride from Sintering Dust of Iron making Works

electrostatic precipitator



Flue gas





Sintering Dust
~4kg/ton sinter

At the sintering temperature:

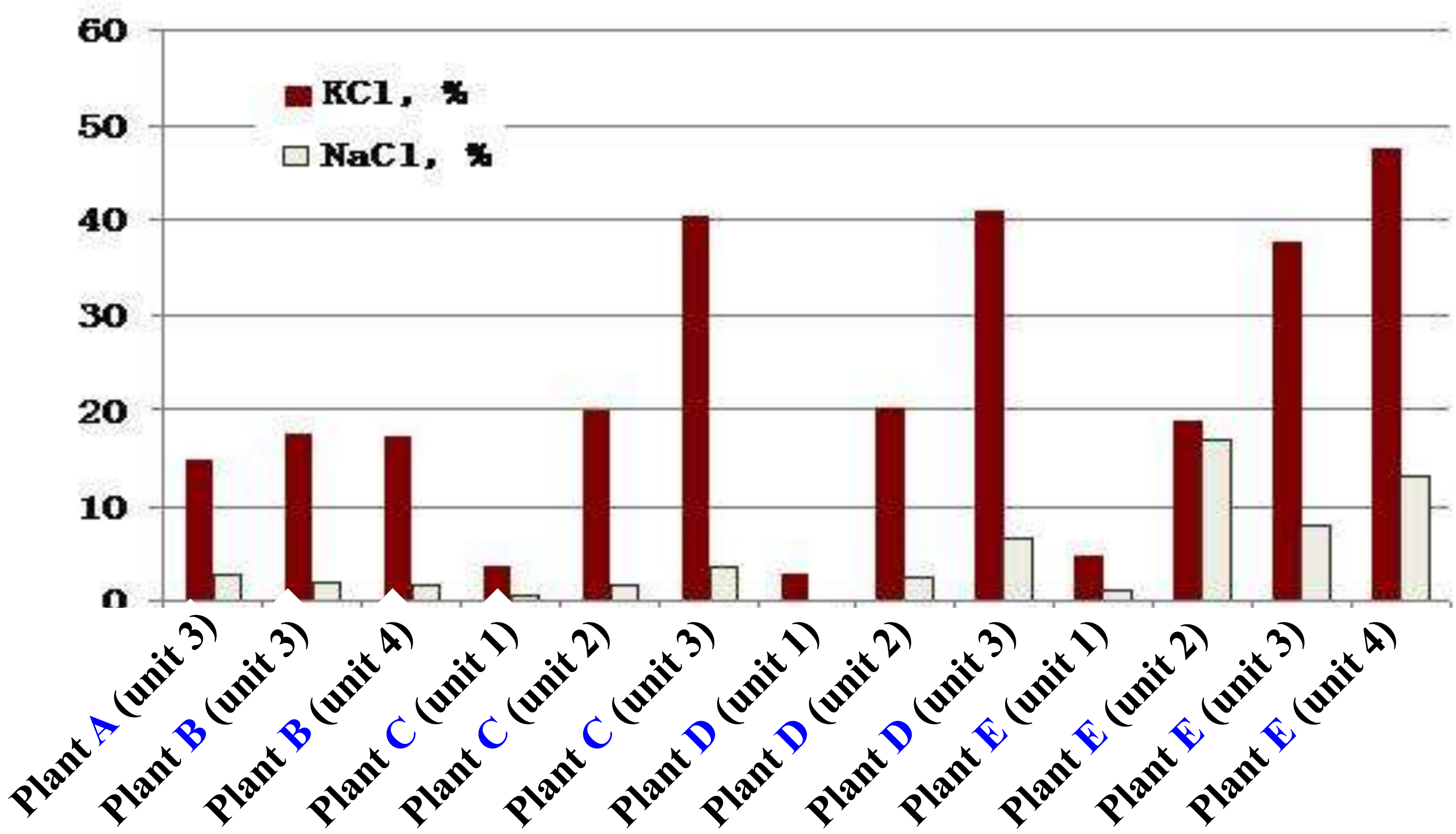
KCl, NaCl (in the raw) $\longrightarrow$ KCl(g), NaCl(g)

At the low temperature:

KCl(g), NaCl(g) (in flue gas) $\longrightarrow$ KCl(s), NaCl(s)

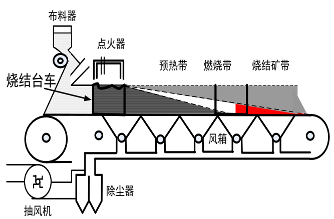
$P_{KCl} > P_{NaCl}$, KCl is more than NaCl in the dust

KCl, NaCl content the sintering dust collected by electrostatic precipitator（5 steel works in China)



Potassium resource estimation

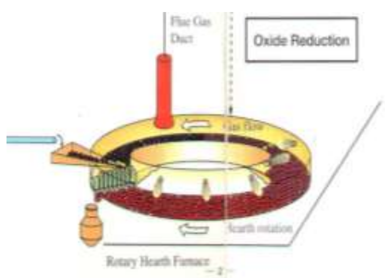
- ✓ **About 800 million tons sinter in China**



- ✓ Sinter fume ~4 kg/ton sinter
- ✓ ~ 3 million tons sinter fume per year
- ✓ If the average KCl is 20% estimated

Pure KCl resource is 60×10^3 tons

About 50 million tons general dust



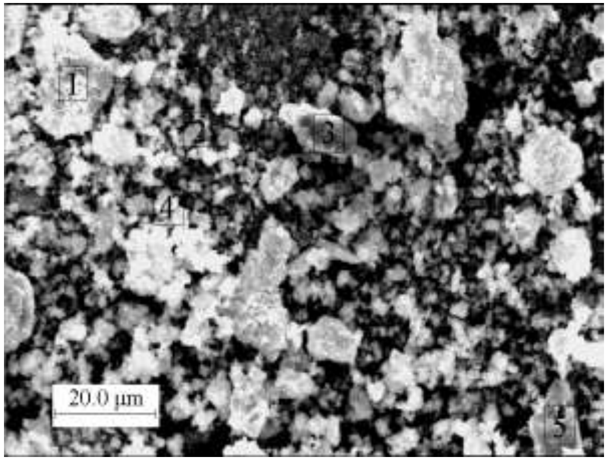
- ✓ if 60% of dusts treated by RHF in the futer
- ✓ ~100 kg fume generated again to treat one ton dust
- ✓ ~3 million tons fume per year
- ✓ If the average KCl is 20% estimated

Pure KCl resource is 60×10^3 tons

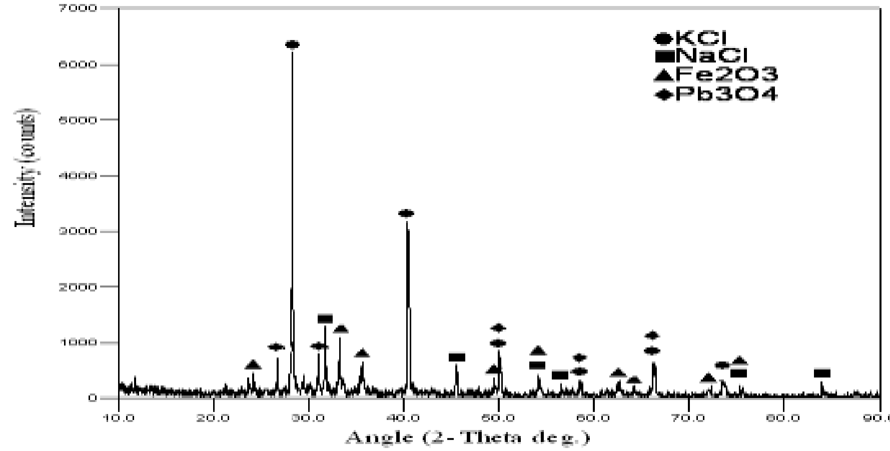
1.5 million tons potassium fertilizer production

About 50% of Chinese potassium fertilizer output in present

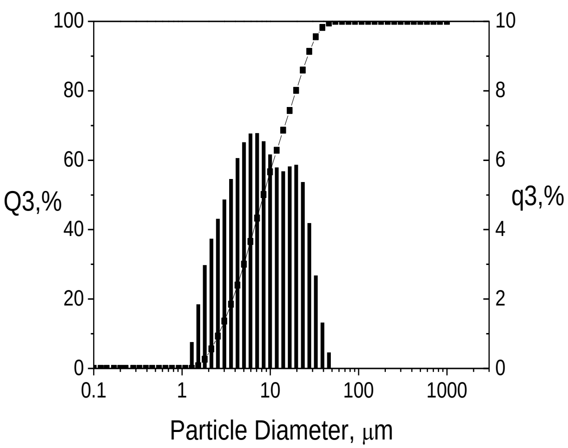
Properties of sintering fume



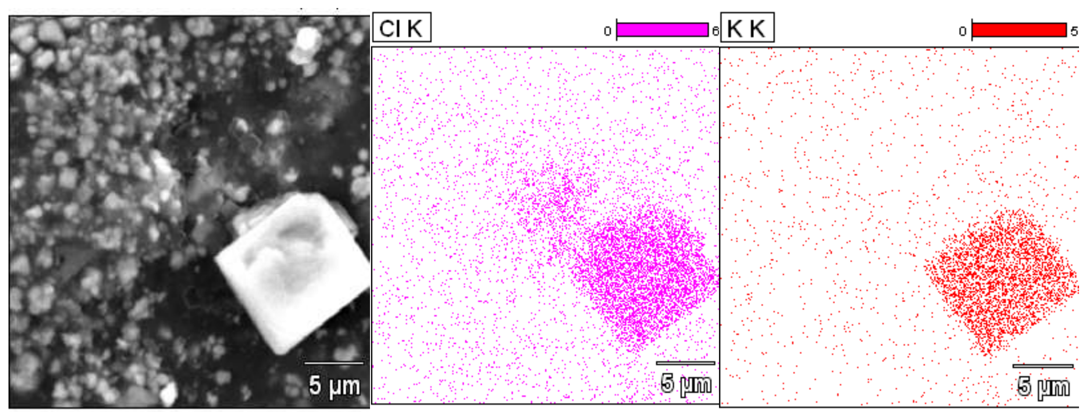
SEM of sintering fume



XRD pattern of as-received fume

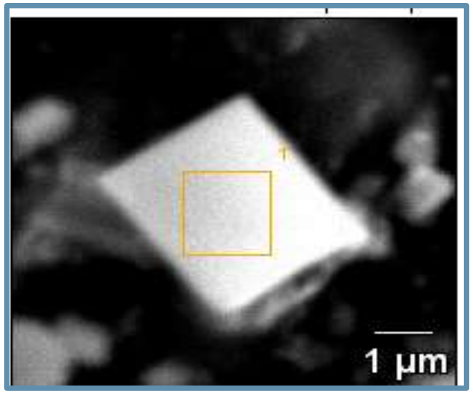


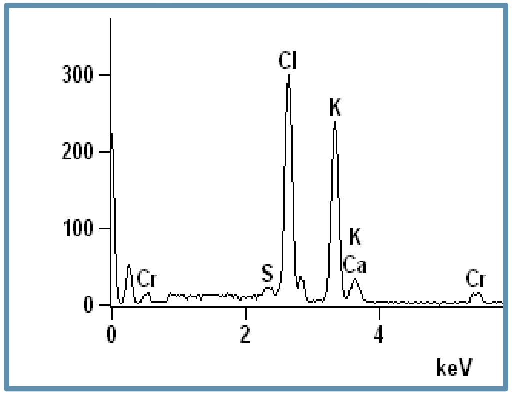
Granulometric distribution of sintering fume



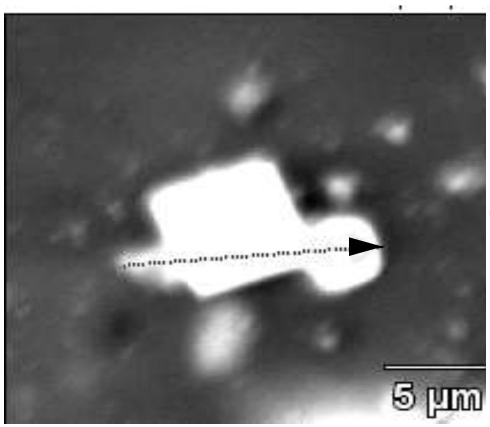
SEM EDS mapping of Cl and K for an fume particle (magnification×20000)

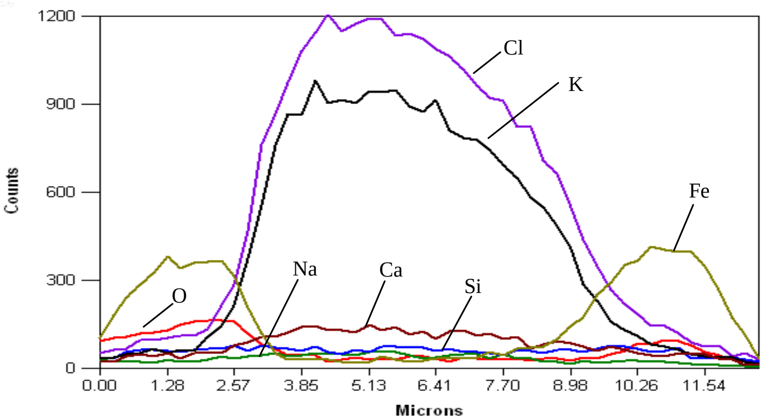
Properties of sintering fume





element	S	Cl	K	Ca
% atom	1.42	43.95	46.25	3.76





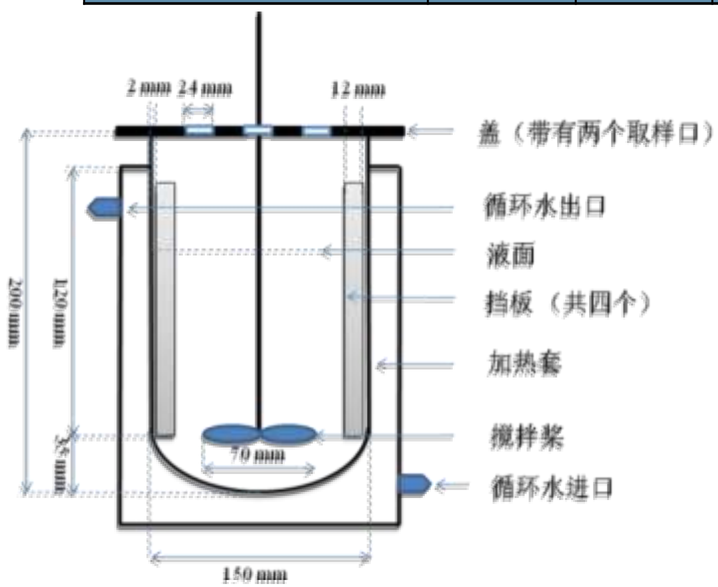
SEM and EDS for an KCl particle in fume

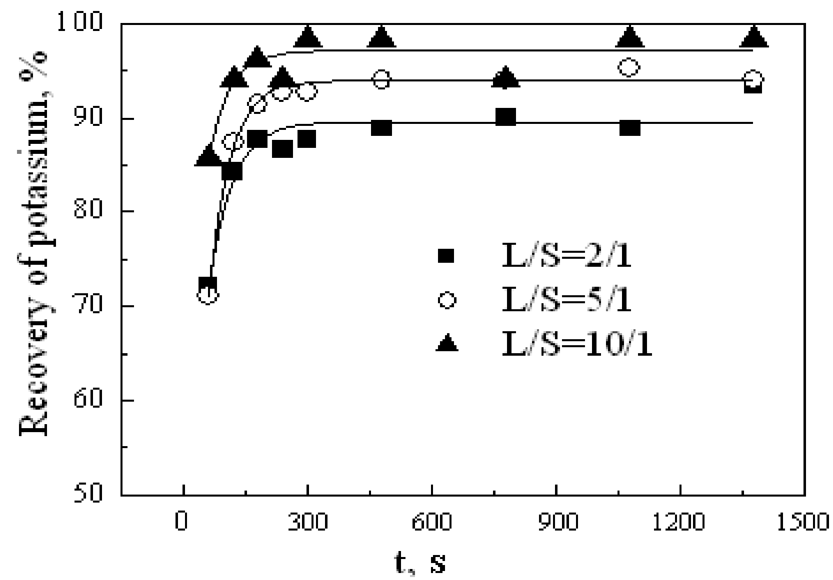
How to separate KCl ?

Step 1---leaching

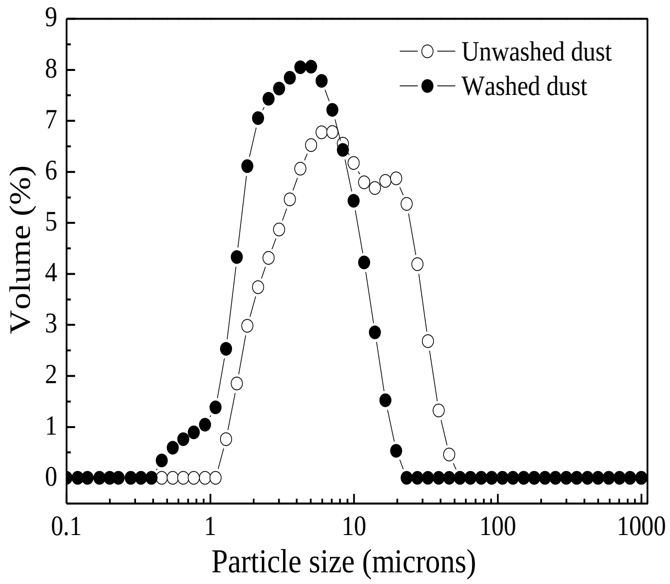
Composition of the fume used in the experiment

Elements	K	Na	Ca	Mg	Zn	Pb	Fe	C
Composition,wt%	11.50	1.48	6.71	1.002	0.20	0.885	21.73	2.76
Elements	Si	S	Al	Cu	Mn	Ti	P	Ni
Composition,wt%	1.762	1.21	4.56	0.041	0.132	0.060	0.065	/



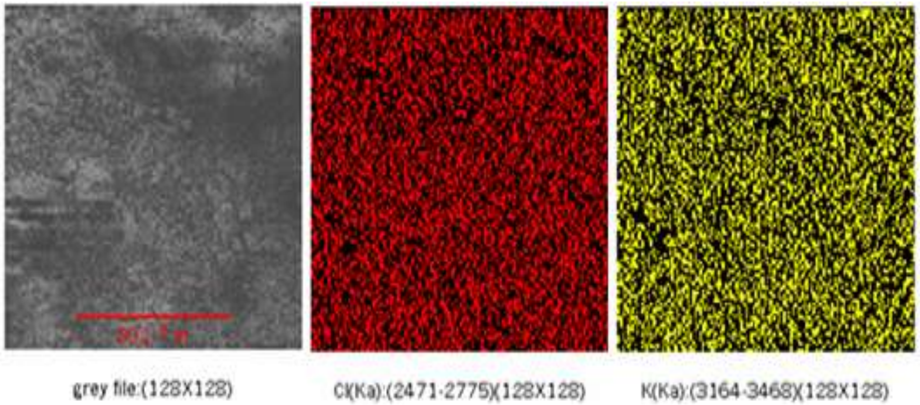


Effect of L/S ratio on leaching rate of K element at 303 K with particle size of 8.297μm and stirring speed of 550 rad/min

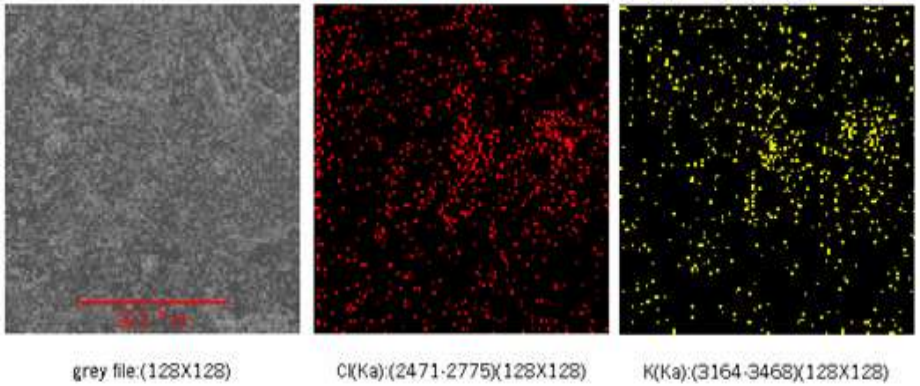


Sizing analyses of un-washed and washed dust

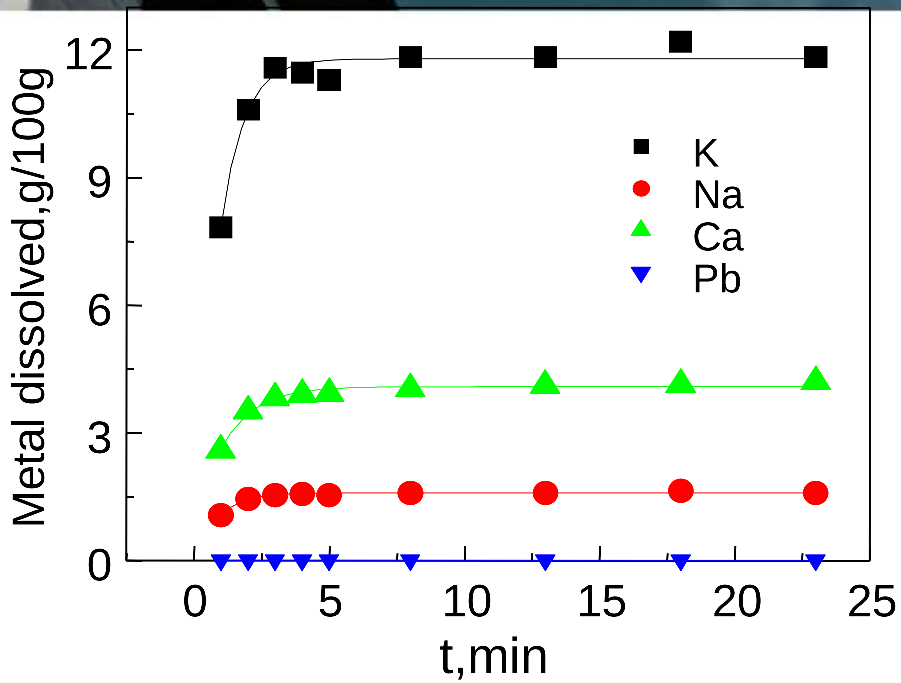
EDS map for an Cl and K the received dust



EDS map for an Cl and K the washed dust



Comparison of available leaching content of potassium, calcium, sodium and lead as a function of leaching time

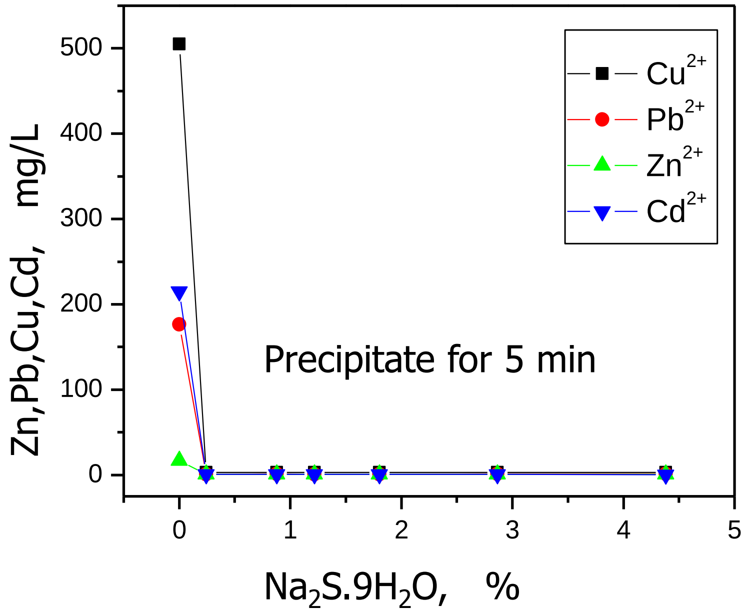


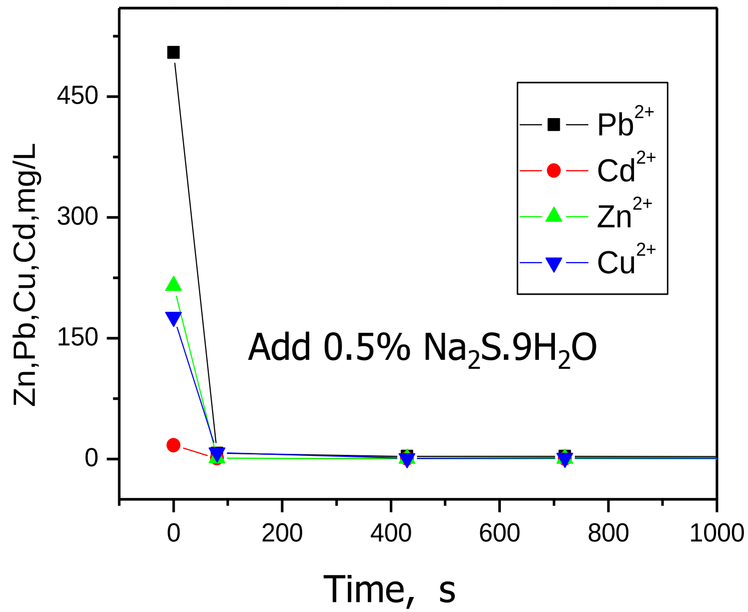
Comparison of ion concentration in the leach liquor with L/S ratio of 1/1 and that after sulfide precipitation

Constituents	KCl, g/L	NaCl, g/L	$CaCl_2$, g/L	Pb, ppm	Zn, ppm	Cu, ppm	Cd, ppm
Concentration in the leach liquor	206	46	24.7	504.9	176.6	215.1	16.8

Step 2---impurities removal

Sodium sulfide can be used to precipitate the heavy metals

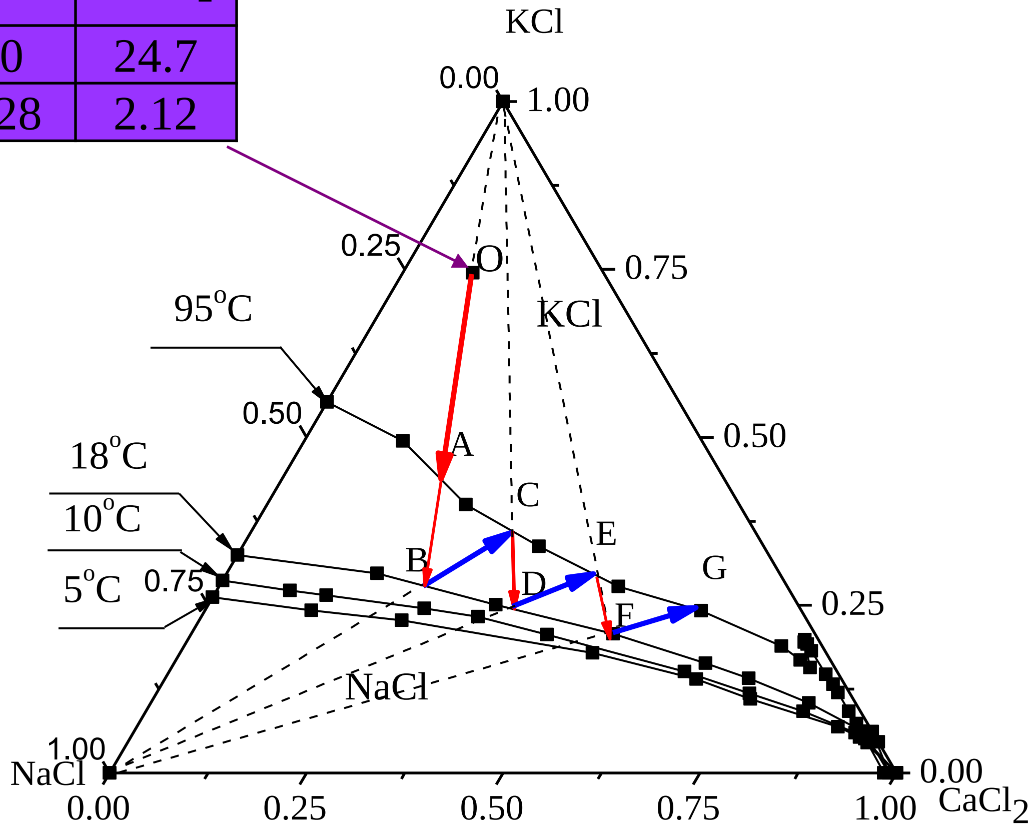




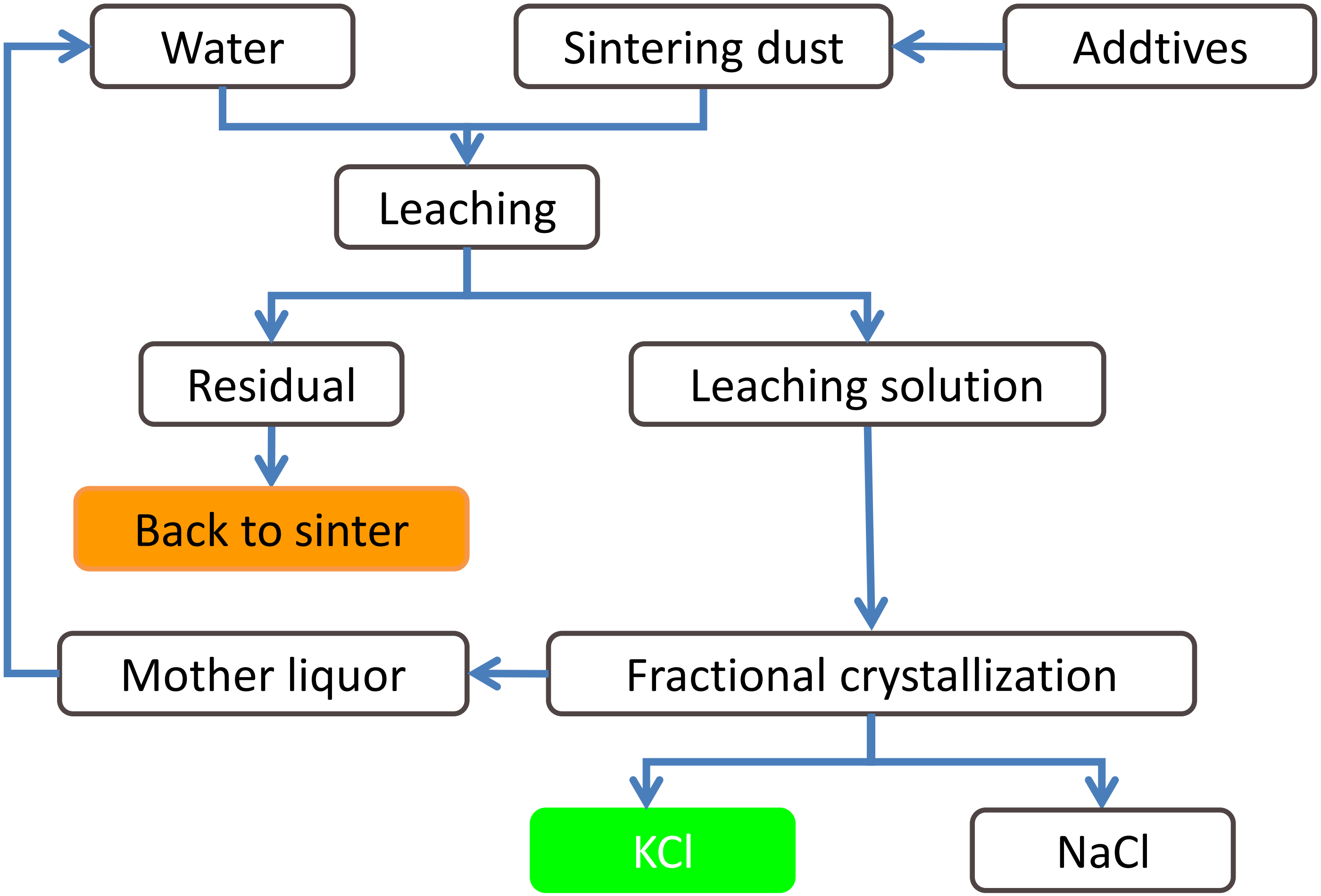
Constituents	KCl, g/L	NaCl, g/L	$CaCl_2$, g/L	Pb^{2+}, mg/L	Zn^{2+}, mg/L	Cu^{2+}, mg/L	Cd^{2+}, mg/L
leach liquor	206	46	24.7	504.9	176.6	215.1	16.8
after sulfide precipitation	205	51	2.45	2.9	0.9	0.3	0.2

Step 3---evaporating and cooling crystallization

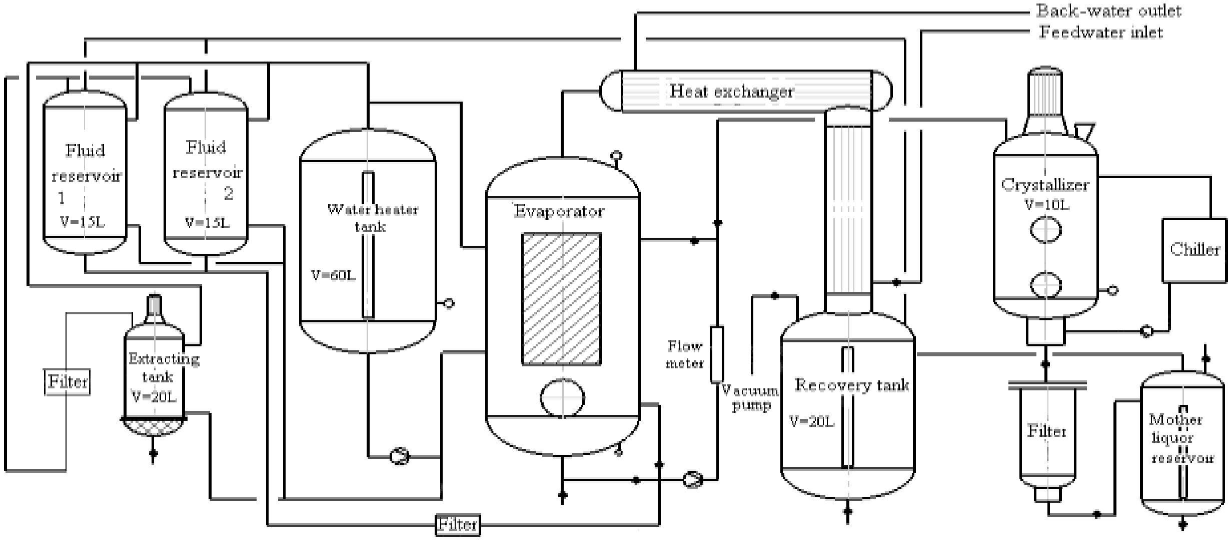
	KCl	NaCl	$CaCl_2$
g/L	206	50	24.7
wt%	17.65	4.28	2.12



Schematic diagram of recovery KCl from the sintering dust



pilot test



purity
96.5%

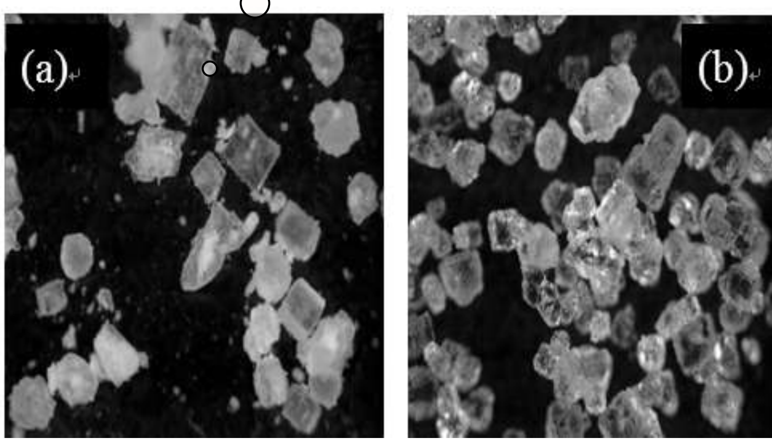
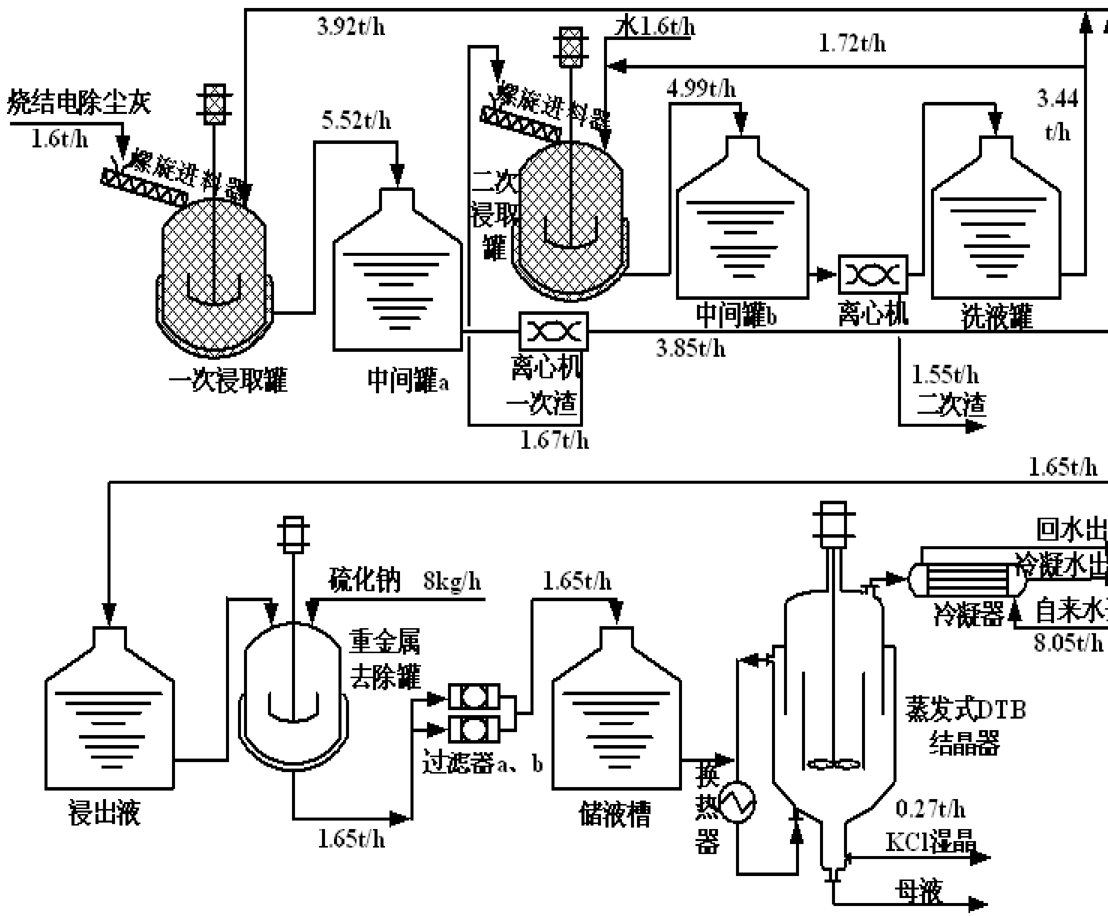
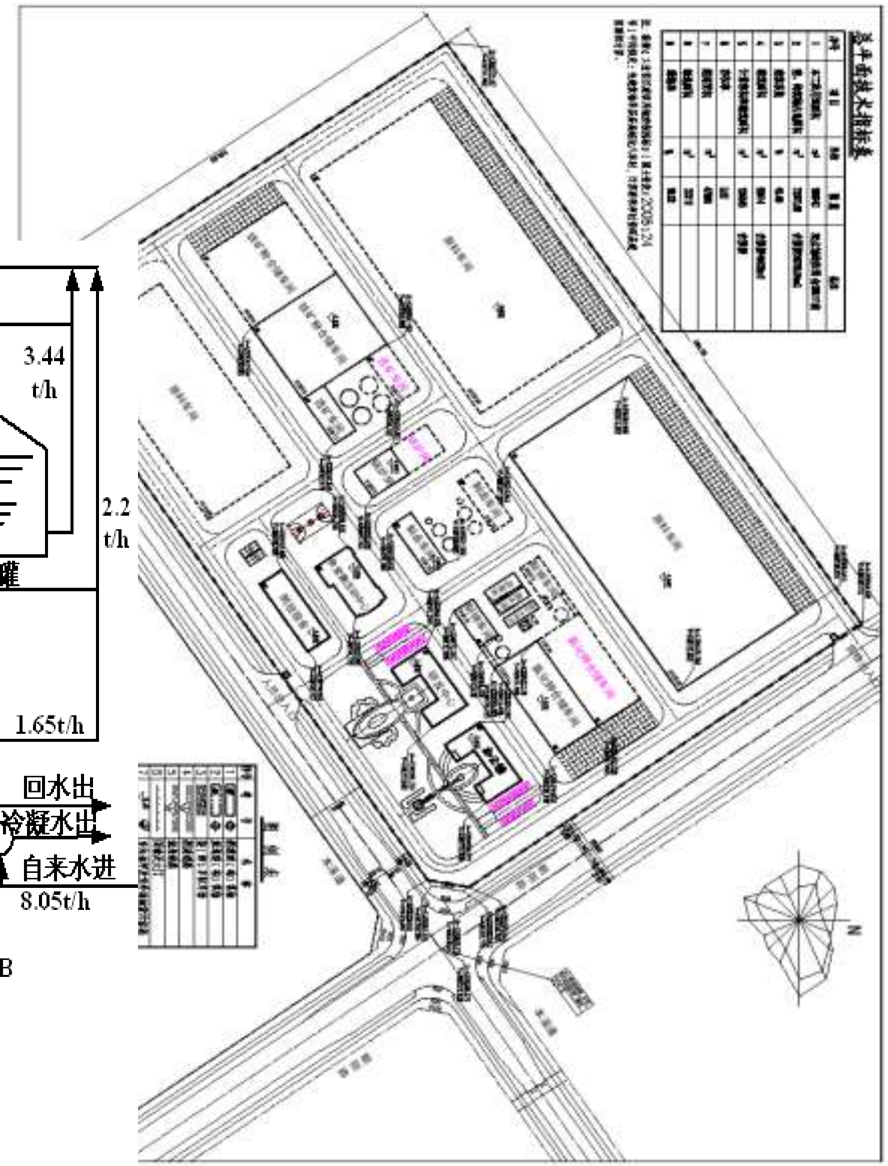


Photo of KCl product recovered from the sintering dust

A industrial plant will be set up in Dangshan

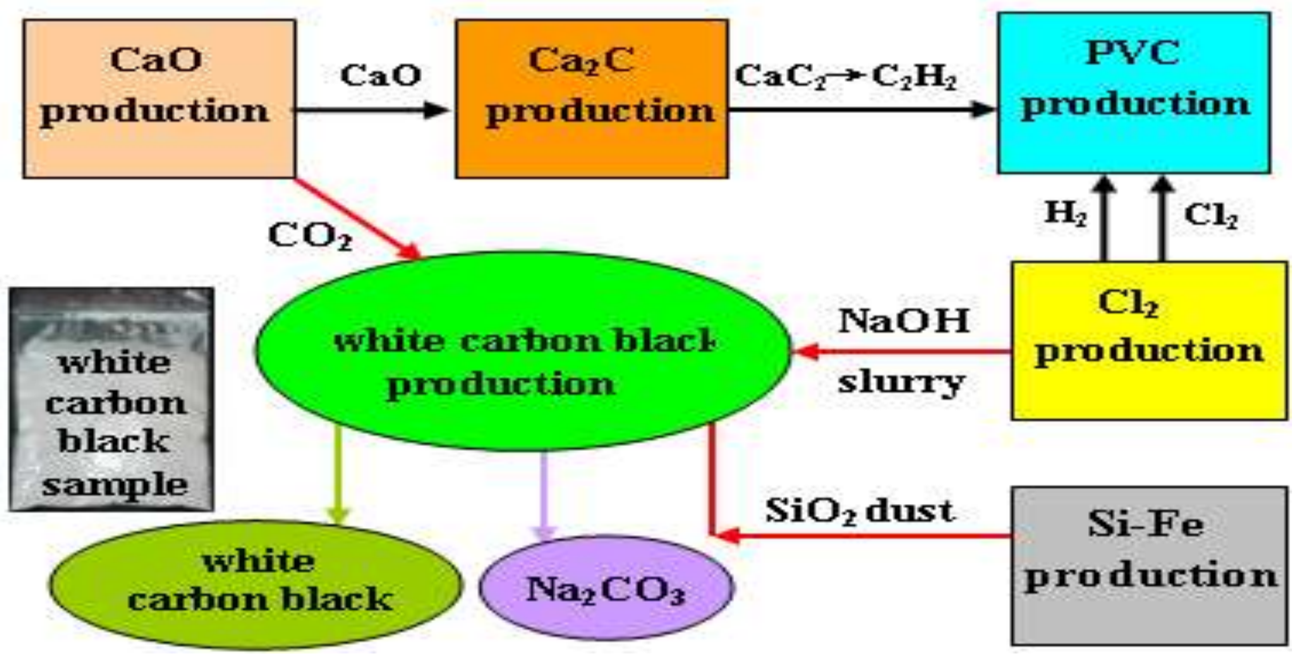
100×10^3ton dust/year
2×10^3 ton KCl/year around





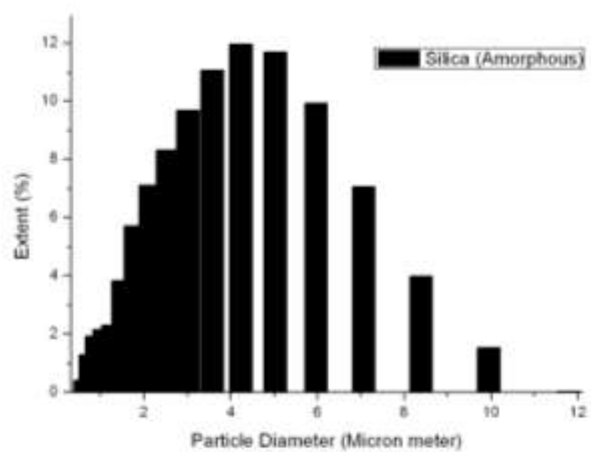
2. White Carbon Black Preparation from the Dust of Ferrosilicon Plant

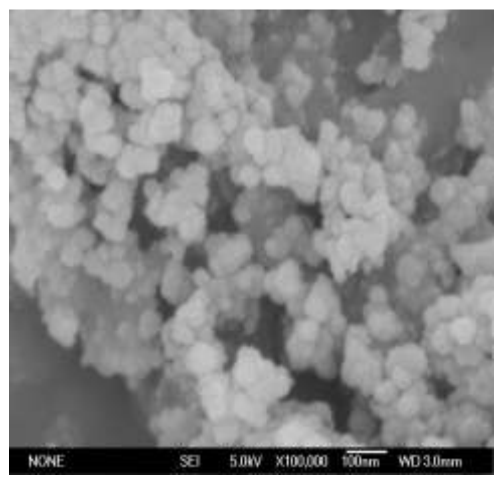
White Carbon Black: A kind of mic-nano size SiO_2
Used as rubber additives
Produced by precipitation of sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) solution with acid (HCl or H_2SO_4)



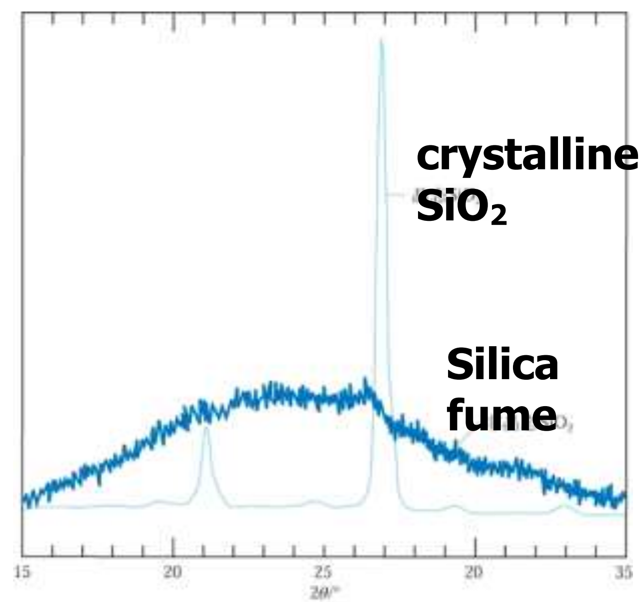
Composition of typical silica fume

Comp.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	S	size
%wt	**86.5**	0.54	3.15	0.73	2.39	3.34	0.56	<0.1	0.24	<1um (80%)





SEM of silica fume

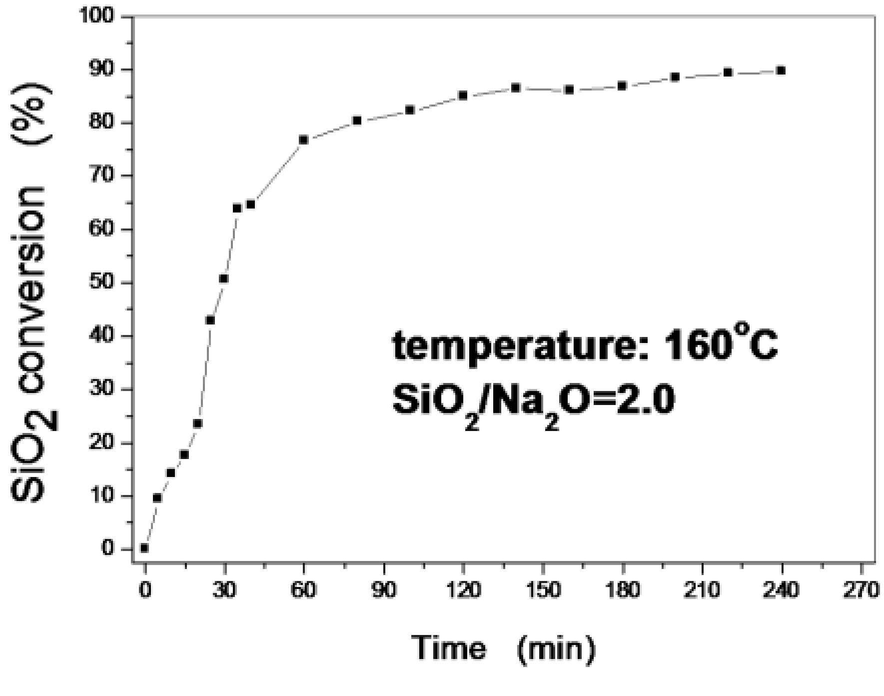


XRD of silica fume

How to make white carbon black ?

Step 1--- prepare sodium silicate solution

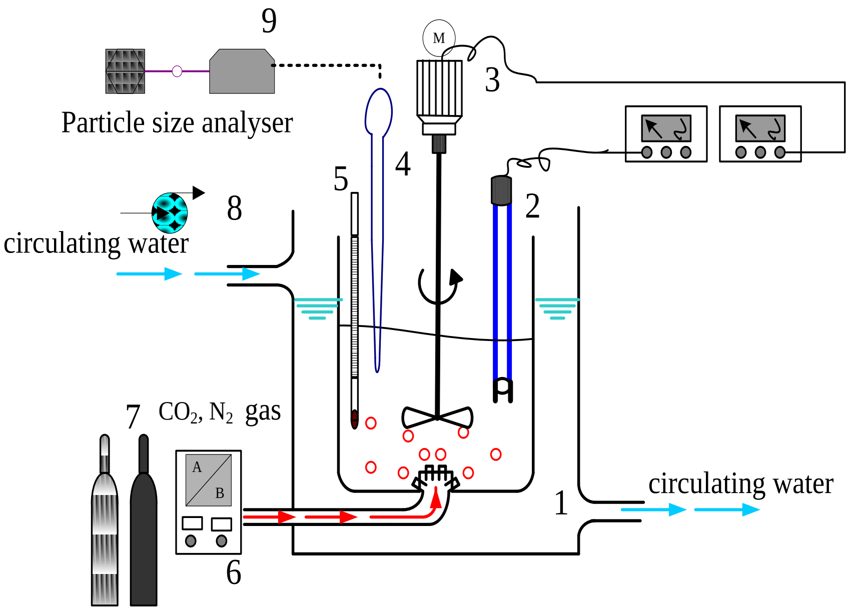
$$2NaOH + nSiO_2 = Na_2O.nSiO_2 + H_2O$$



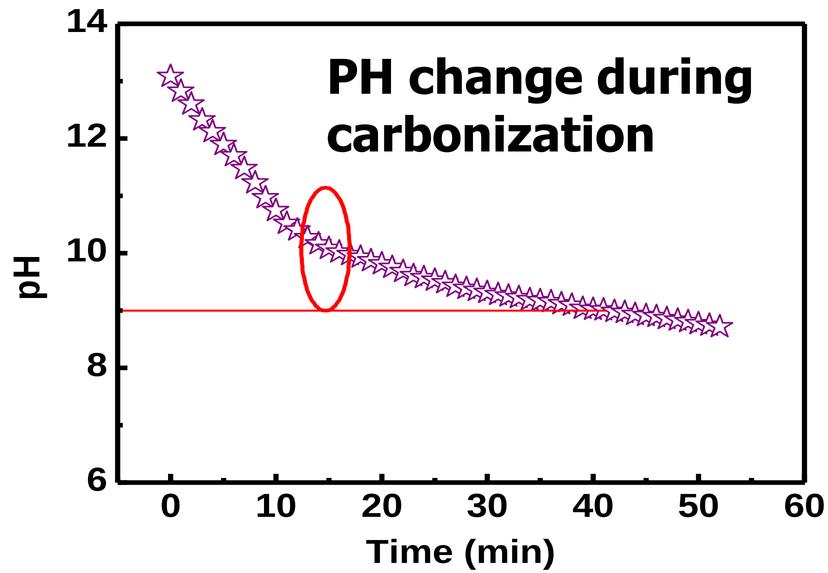
Step 2--- Preparation of silica particles by CO_2

$$Na_2SiO_3+CO_2+H_2O \rightarrow Na_2CO_3+H_2SiO_3\downarrow$$

$$H_2SiO_3\rightarrow SiO_2.nH2O\downarrow$$



1—碳化恒温反应器；2—pH计；3—增力搅拌器；4取样吸管；
5—温度计；6—气路控制柜；7—CO_2、N_2钢瓶；
8—恒温循环水；9—粒度分析系统



feasible conditions:

Na_2SiO_3: 20-80 g/L

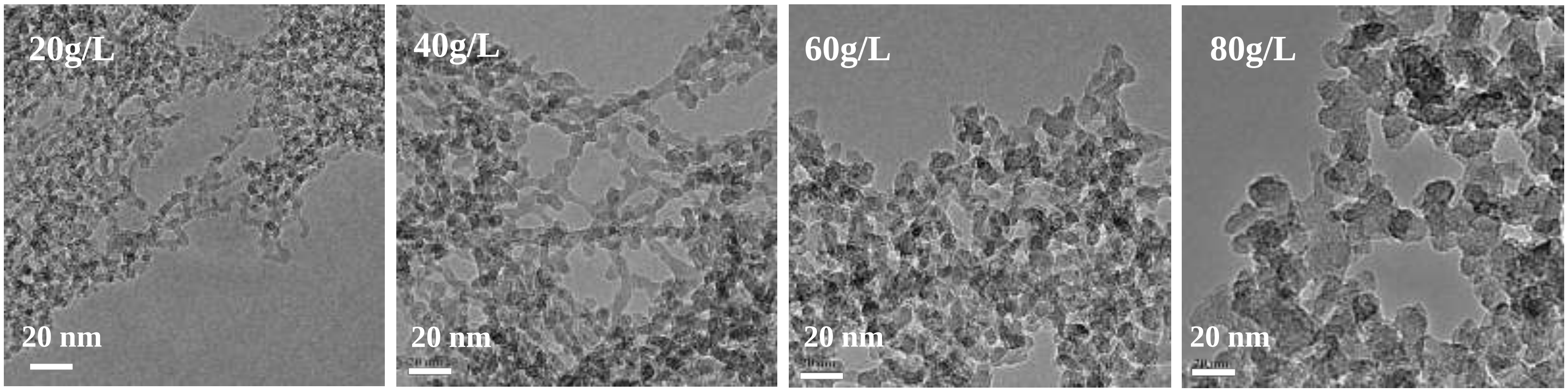
Temperature: 50-95 ℃

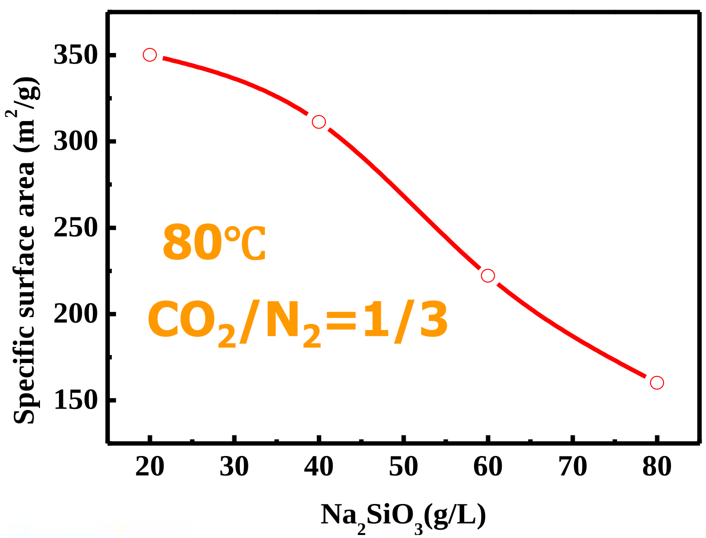
CO_2: 10-40 %

Experimental Results

Effect of Na_2SiO_3 content on SiO_2 partical size

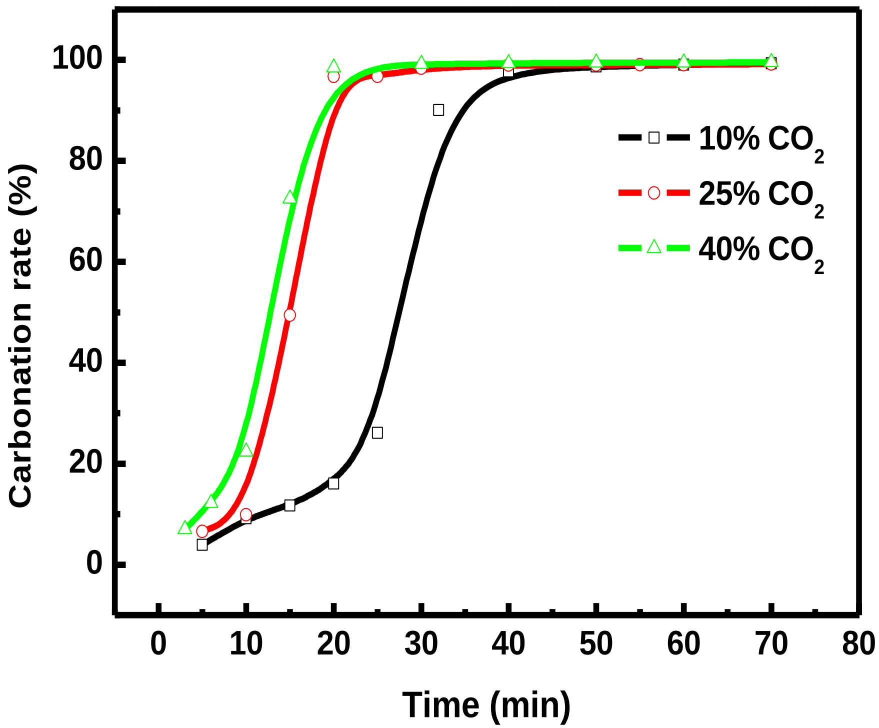
TEM ×100,000



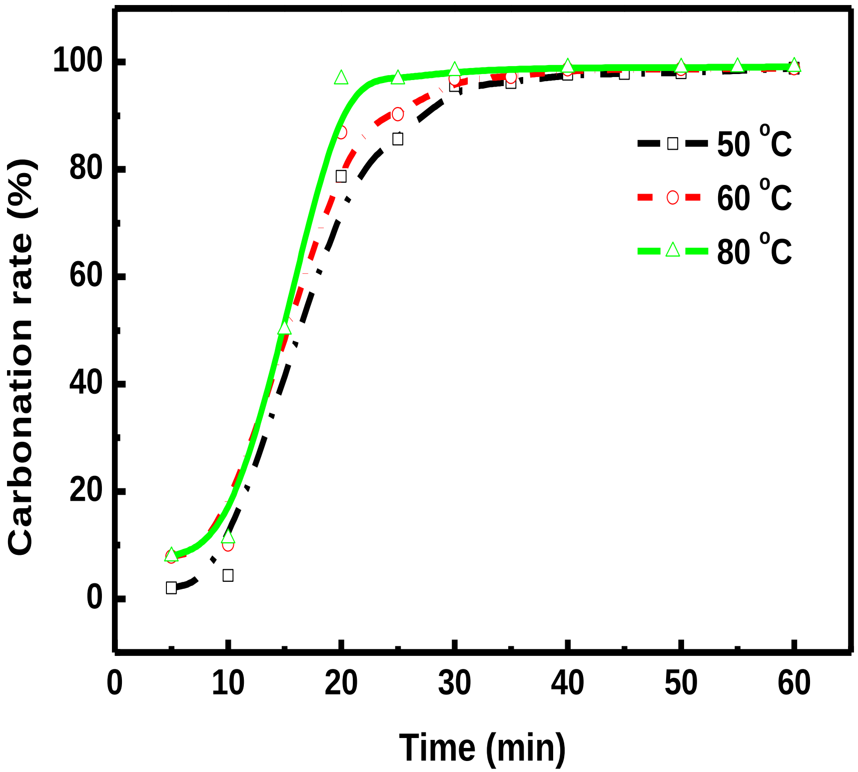


The size of white carbon black particle increase with Na_2SiO_3 content,

and BET surface decreases with Na_2SiO_3

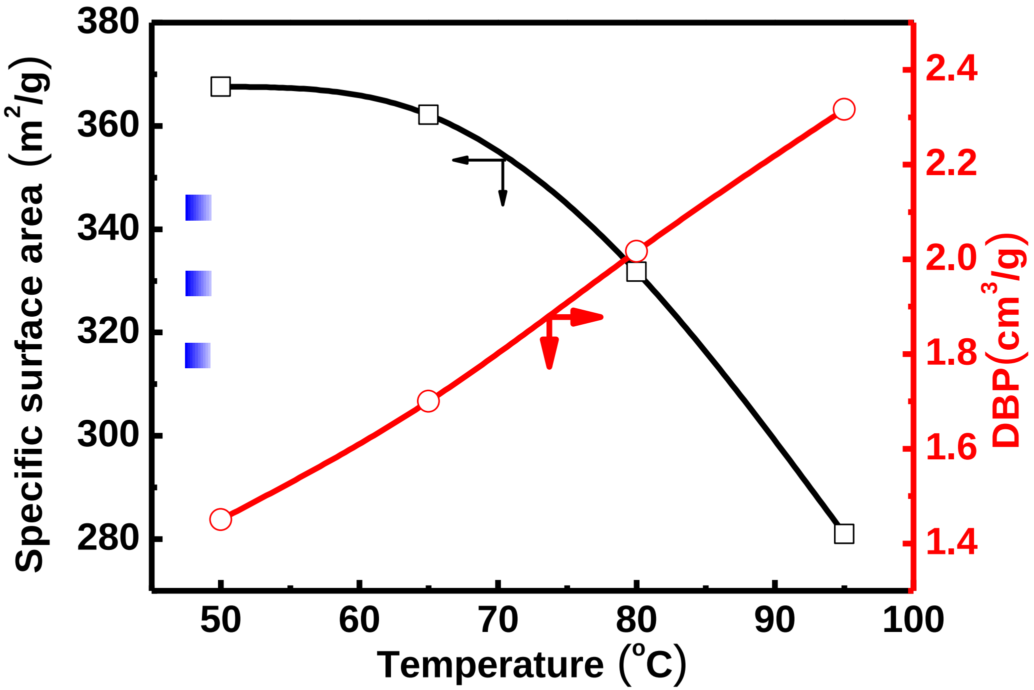


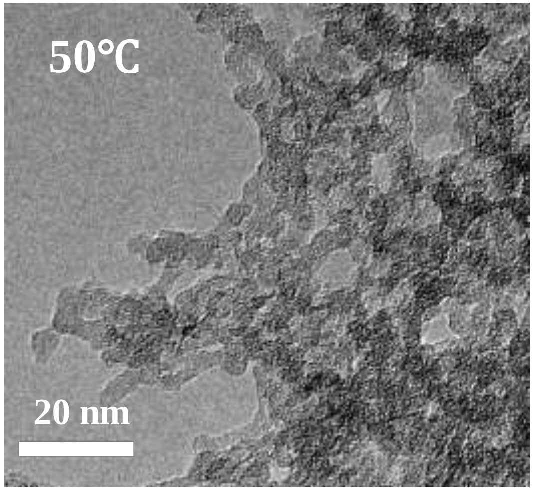
Effect of CO_2 content on carbonation rate

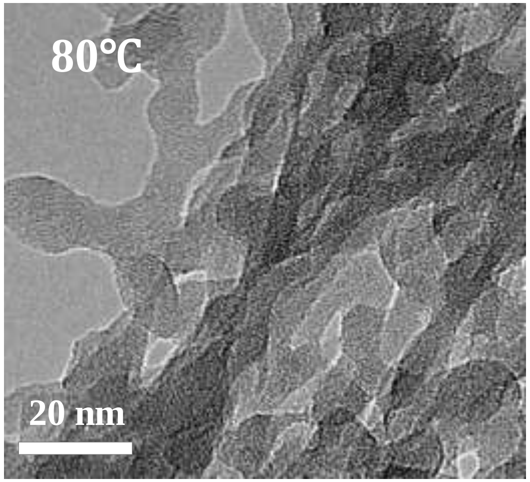


Effect of temperature on carbonation rate

Effect of temperature on properties of the product

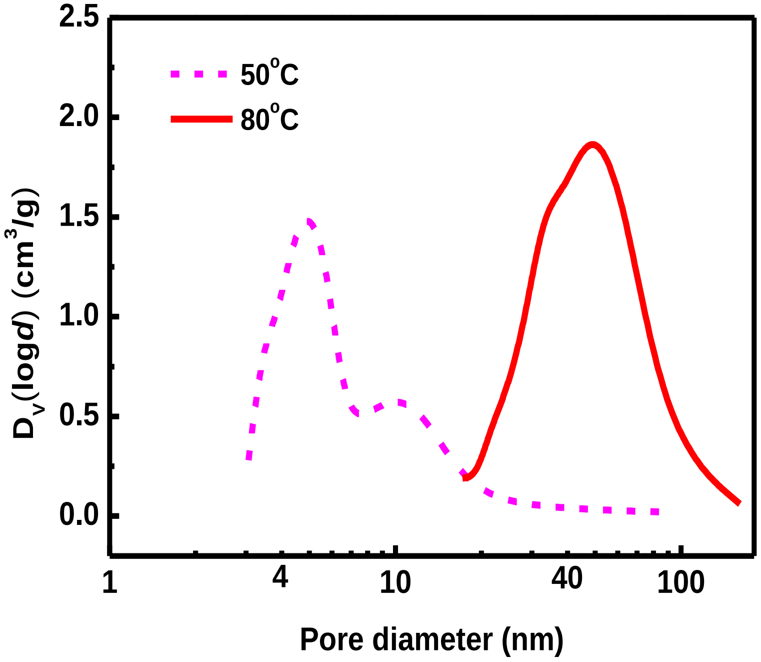


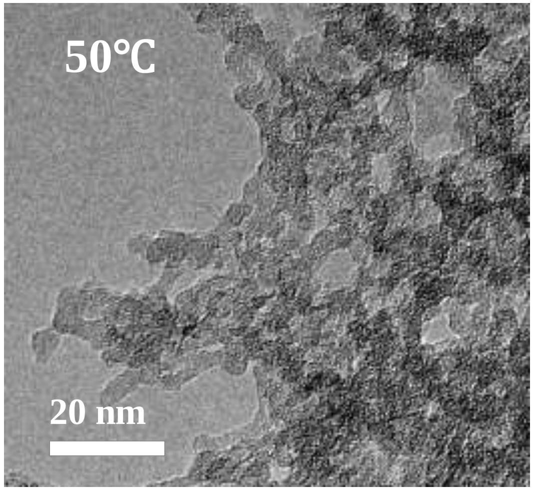


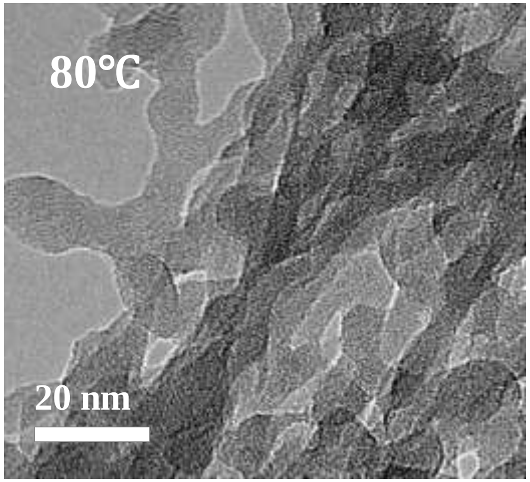


T ↑ d ↑ BET ↓ DBP ↑

pore size distribution of the product

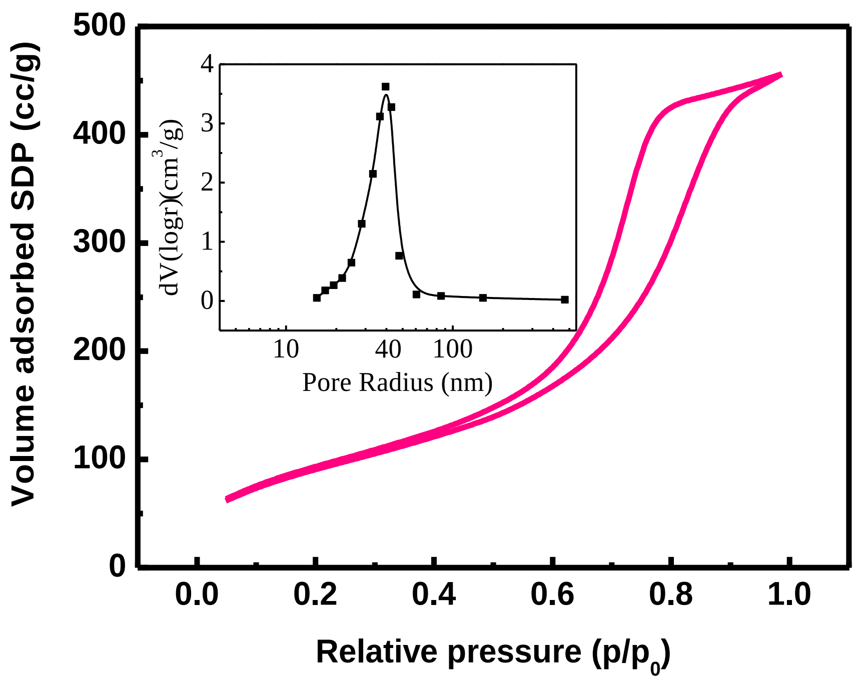


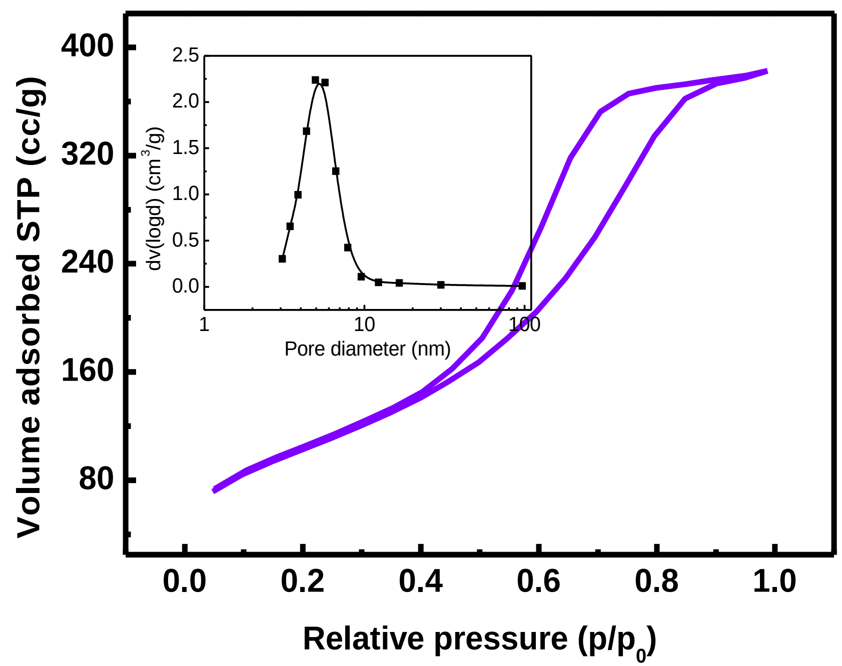




Effect of temperature on pore size distribution

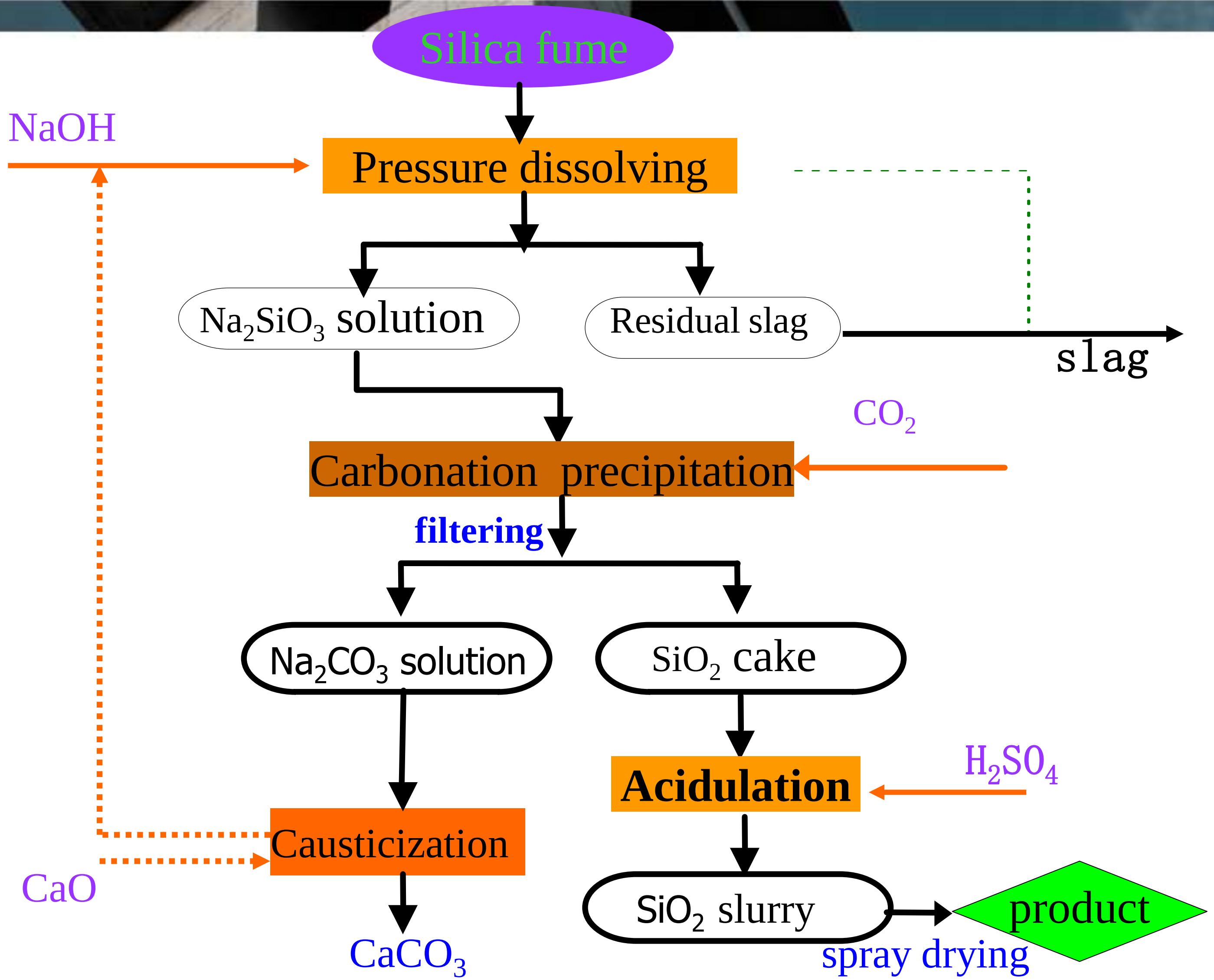
Comparison between CO_2 precipitation and H_2SO_4 precipitation



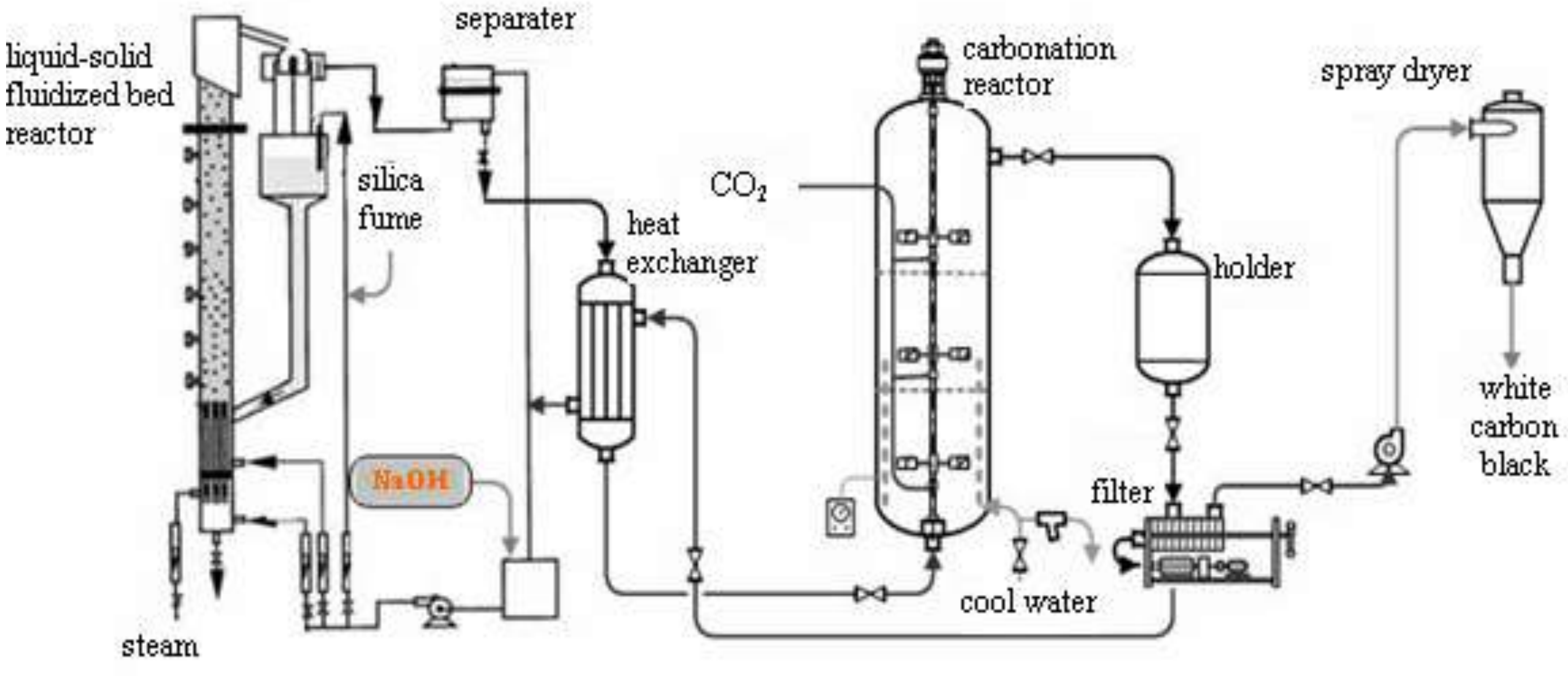


The white carbon black with more pore and larger pore diameter can be obtained by carbonization precipitation than acid precipitation.

Schematic diagram of white carbon black production by silica fume with NaOH and CO2

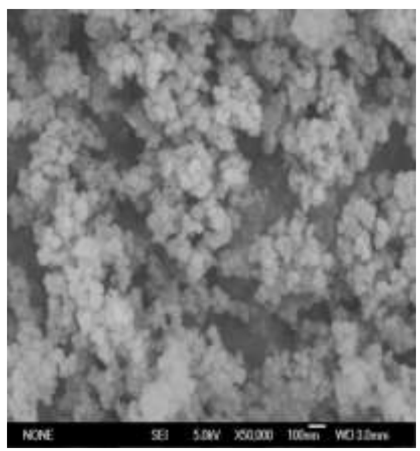


Schematic diagram of white carbon black production by silica fume with NaOH and CO2

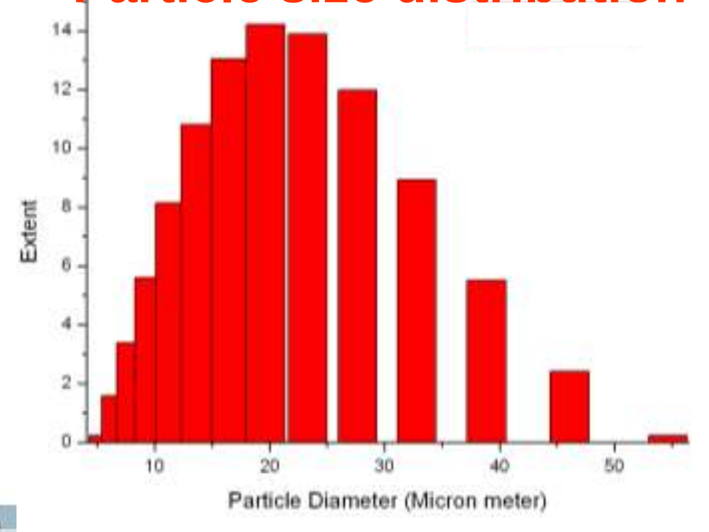


dissolving reaction	Carbonation reaction	hydrolyzation reaction
$2NaOH+SiO_2 \rightarrow Na_2SiO_3 + H_2O$	$Na_2SiO_3+CO_2+H_2O \rightarrow Na_2CO_3+H_2SiO_3\downarrow$	$H_2SiO_3 \rightarrow SiO_2.nH_2O\downarrow$

Pilot plant test: 1500 tons/year of white carbon black product



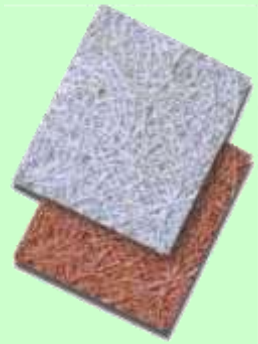
Particle size distribution



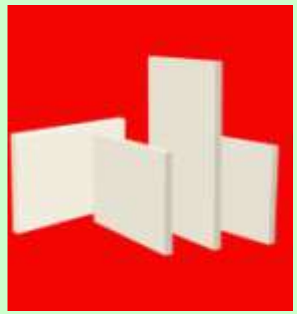
The plant of industrial scale with 10000 ton/year will be set up.

3. Sound-absorbing Material preparation from Iron-making Slag

sound absorbing material



wood fiberboard



organic fiberboard

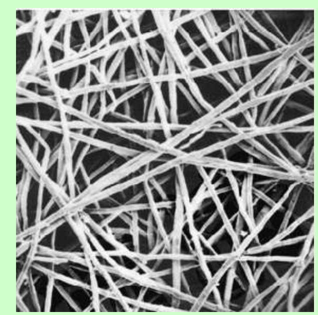
micropunch plate

plant fiber board

argil board

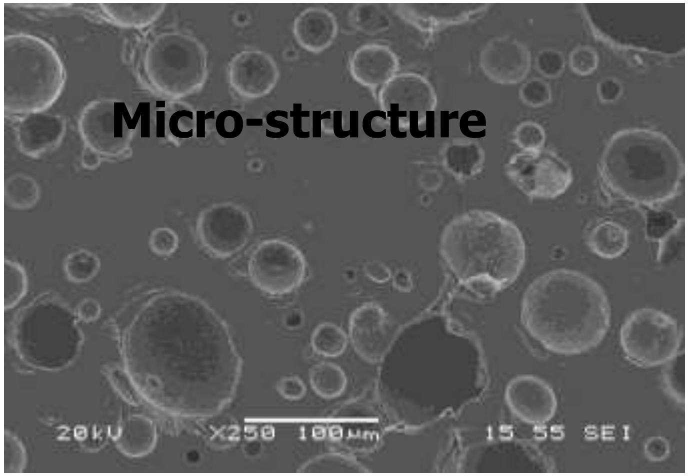
perlite brick

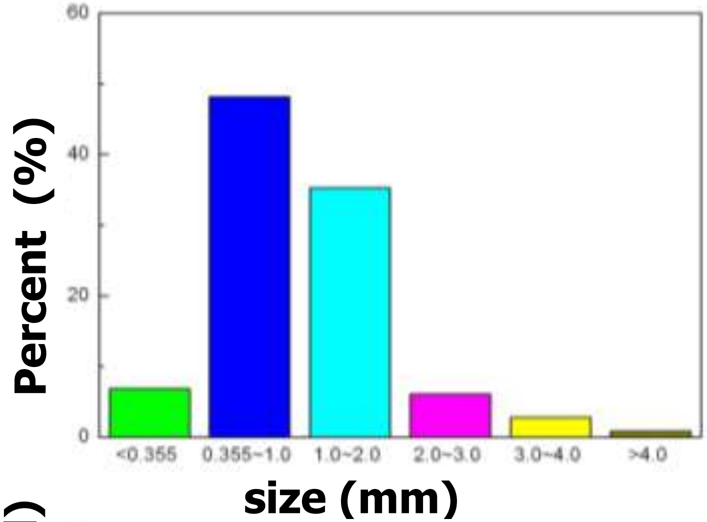
foamed aluminium

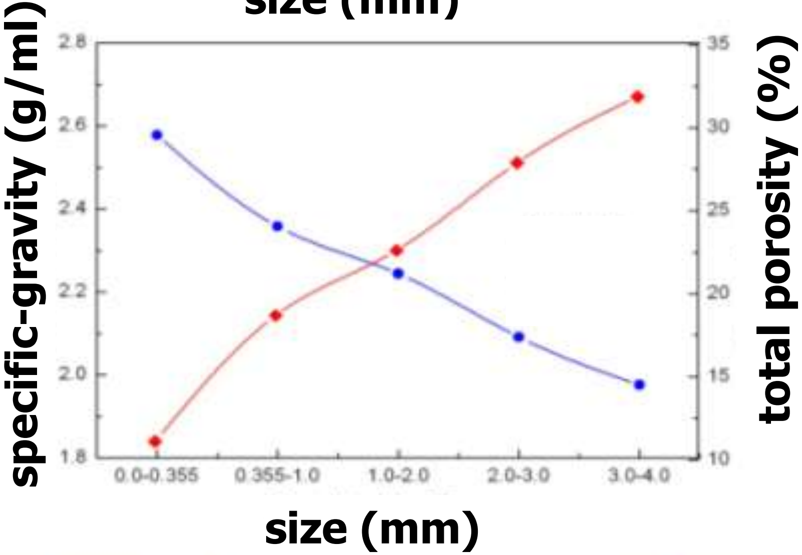


metallic fibres sinter

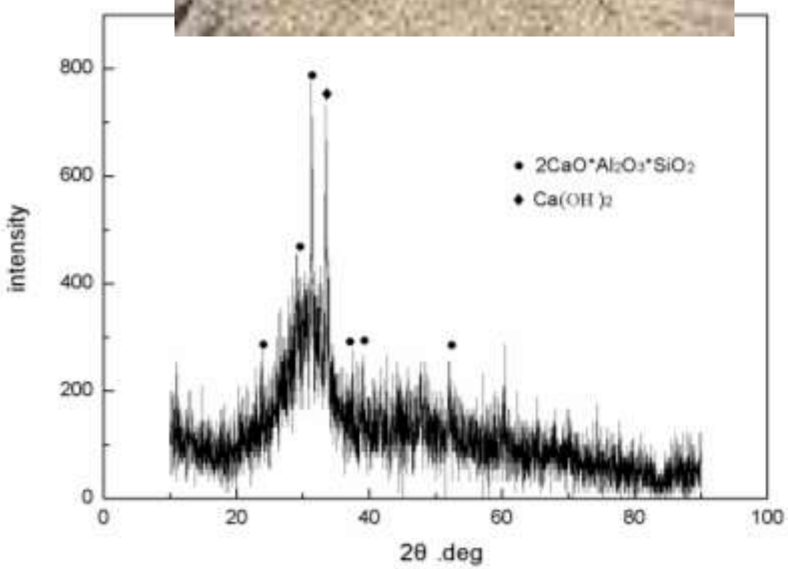
Properties of the water-granulated slag



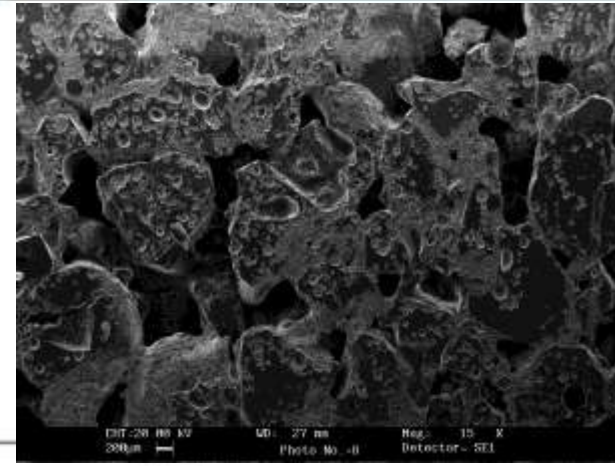


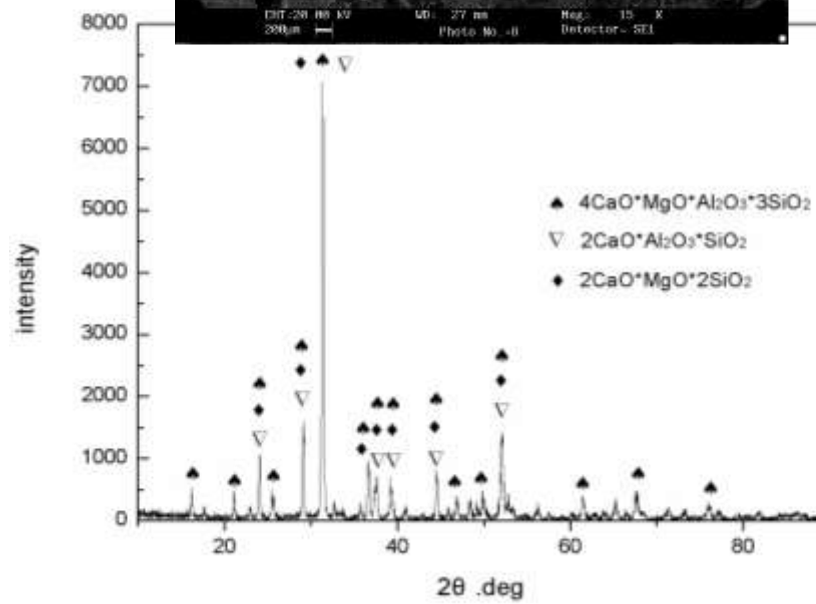


Properties of the water-granulated slag



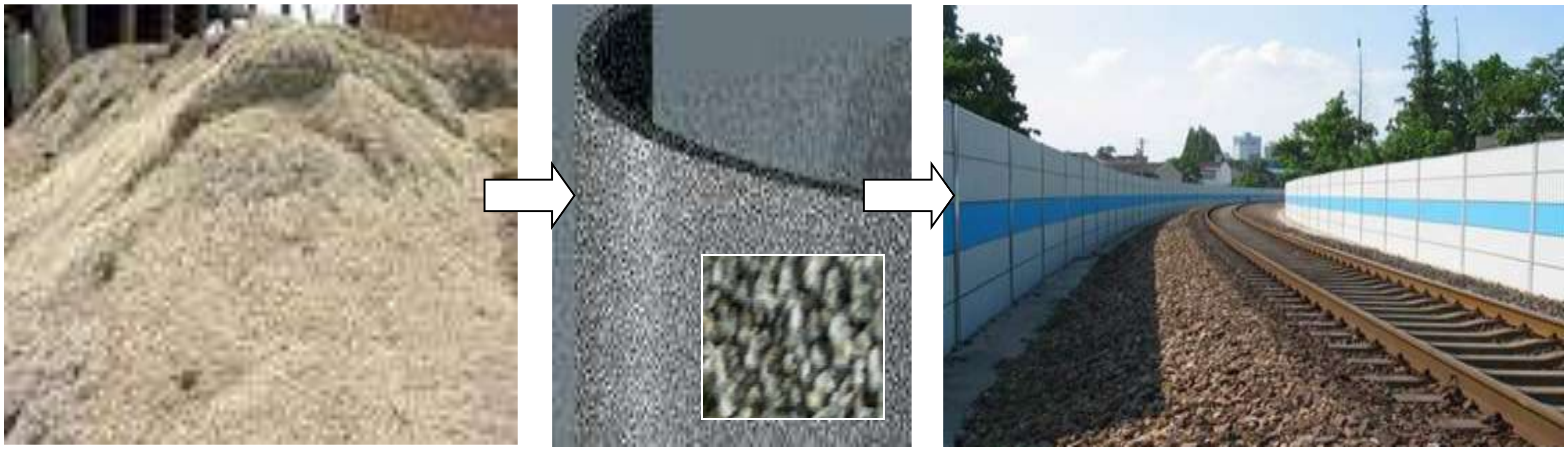
XRD of the original slag

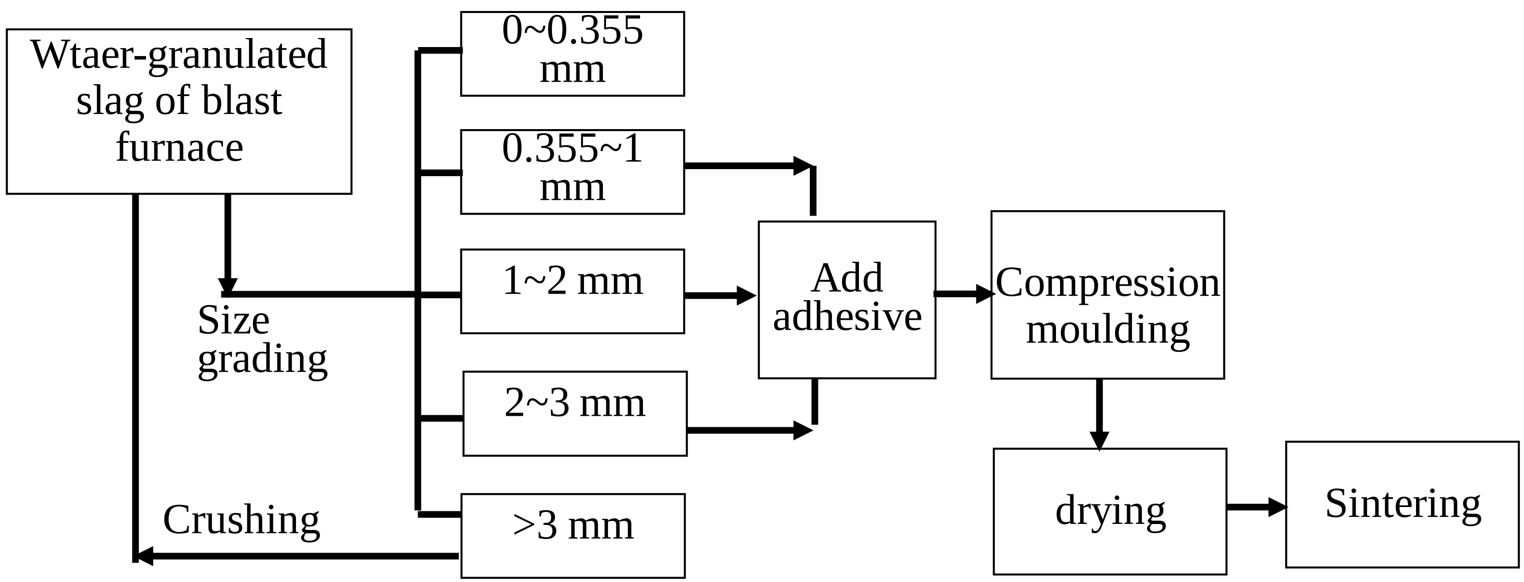


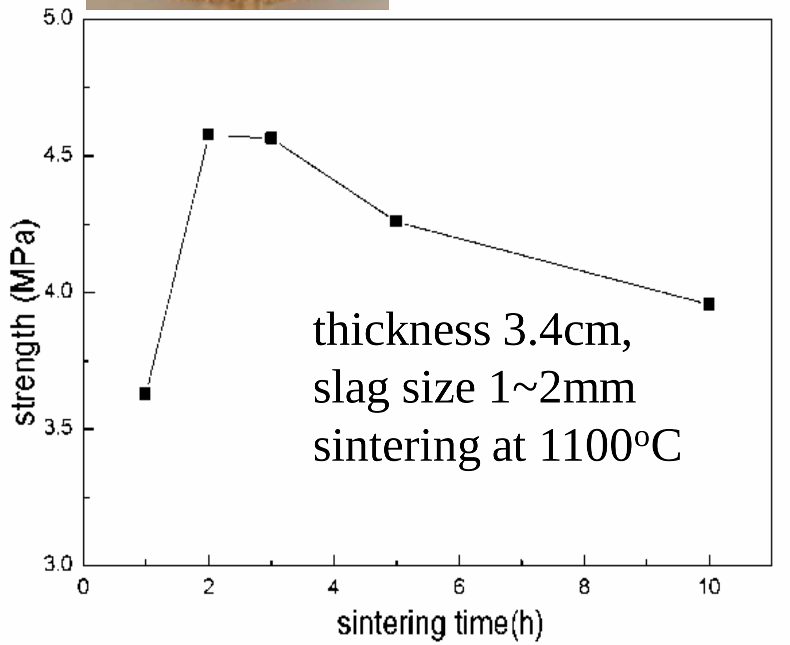


XRD after sintered at 1100^{o}C for 2h

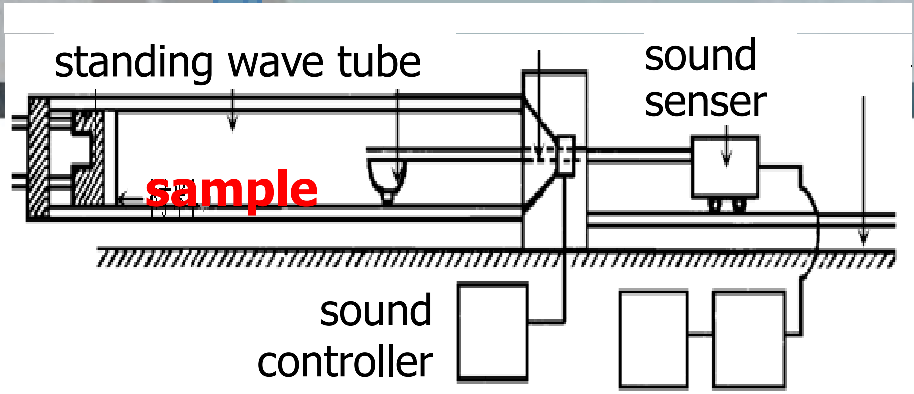
Schematic diagram of sound-absorbing material made from Iron-making slag

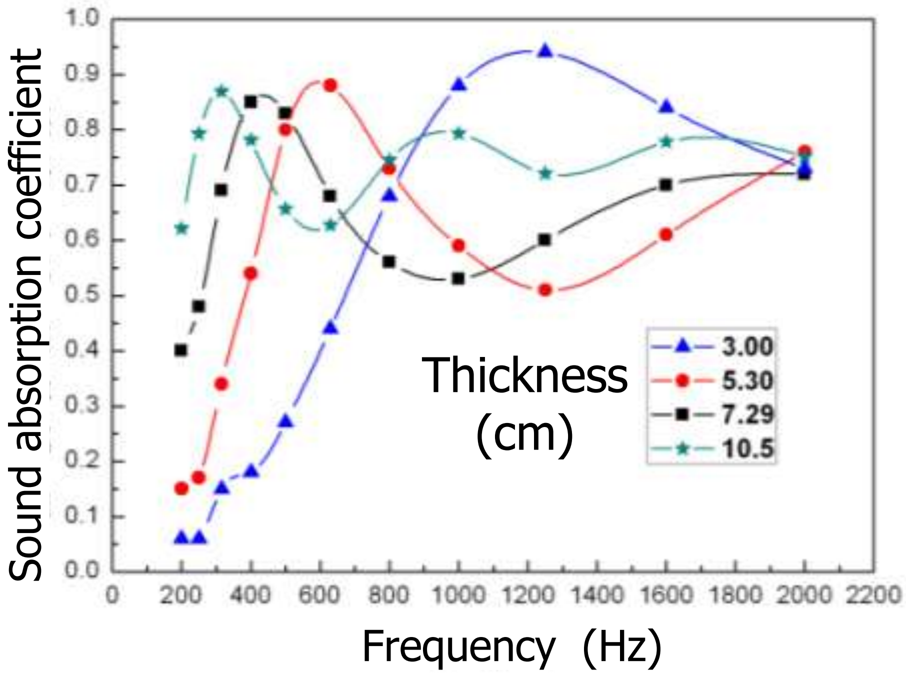






Effect of sintering time on strength





Effect of sample thickness on sound absorption

Conclusions

◆Due to the rich pores and good sintering property of the water-granulated slag of ironmaking, it is possible to be used to produce sound-absorption plate.

◆Due to the high activity property of silica fume, it can be used to produce white carbon black.

◆The sintering fume in steel industry contain high content potassium chloride. It can be used to produce potassium chloride by hydro-process.

Welcome to The Lab. of Ecologic and Recycle Metallurgy, USTB

- Recycle of the second recourses of metallurgy
- Utilization of the social wastes in metallurgy
- Technologies for utilization of the poor or complex iron ores