



11th GeopolymerCamp 2019

# Geopolymer material high-added-value application: coating, membrane and microsphere

Tutor: Xuemin Cui

Reporter: Xuesen Lyu

Organization : Guangxi University (China), Date : 9<sup>th</sup>, July, 2019





# Guangxi University



Guangxi University was established in 1928, locates in Nanning city(E 108°22', N 22°48), capital of Guangxi Province in China, 9200 KM to Paris, 2040 KM to Peking

**Specialized Major:**

1. Chemical Engineering (Materials)
2. Civil Engineering



Library



University Gate



Biyun Lake



Auditorium

# Group introduction

## Lab head:



Dr. Xuemin Cui

*Welcome to join in our group:  
Postdoctor, Phd. and postgraduate students  
Email:Cui-xm@tsinghua.edu.cn*

## Lab members:



Dr. Leping Liu



Dr. Yan He



Dr. Yuanyuan Ge



Dr. Yaocong Han



Dr. Kaituo Wang

## Research interests:

- 1.Preparation, molecular structure characterization, polymerization mechanism and physical/chemical properties of geopolymer materials.
- 2.Development of microporous and mesoporous materials, new inorganic membrane materials and water treatment technology
- 3.Development and application of engineering protective materials, inorganic coatings, building energy conservating and decorating materials
- 4.Comprehensive utilization of solid waste and development of green building materials.

# Contents of group research works

---

## Research content

1. Exploitation of alkali activated geopolymer materials of different raw material systems
2. Study on depolymerization and condensation polymerization process and influencing factors in activated period: reaction kinetics and thermodynamics
3. Study on the relationship of alkali-activated materials' macroscopic properties with gel (quantity, composition, structure).
4. Development of high-value-added alkali-activated materials

### Exploration of alkali - activated geopolymer materials: Different raw material systems

1. Precursor: kaolin (mekakaolin), slag, fly ash, red mud, volcanic ash, meteorite, electrolytic manganese slag, etc.
2. Activators: sodium hydroxide solution, sodium silicate solution, dry powder sodium silicate, potassium hydroxide solution, potassium silicate solution, dry powder potassium silicate, quick lime etc.
3. Fillers: steel slag, calcium carbonate, quartz sand, etc

# Contents of group research works

metakaoline+sodium silicate solution system	}	Exploration of geopolymerization mechanism Preparation of zeolite molecular sieve
metakaoline+NaOH solution system		
slag+sodium silicate solution system	}	Exploration of polymerization reaction mechanism
slag+NaOH solution system		
slag+fly ash+sodium silicate powder	➡	Powder type alkali-activated cement
slag+red mud+sodium silicate solution system	}	Immobilization and utilization of waste residue
metakaolin+manganese slag+sodium silicate system		
slag+manganese slag+sodium silicate system		
meteorite +alkaline activators	}	Near 0-water demand geopolymer cement
volcanic ash+alkaline activators		
slag(metakaolin)+volcanic ash+sodium silicate solution	➡	Composites materials, 3D printing
slag+steel slag+sodium silicate+foamer	➡	Thermal insulation material
Slag(metakaolin)+sodium silicate solution	➡	Filtration and adsorption porous materials
slag(metakaolin)+sodium silicate powder	➡	Geopolymer coatings

slag: ground granulated blast furnace slag

# Application 1: geopolymer coating



Geopolymer coating manufacture line

We established a geopolymer coating factory in 2017, production of 3000t/year each line the manufactured coating has been used in engineering

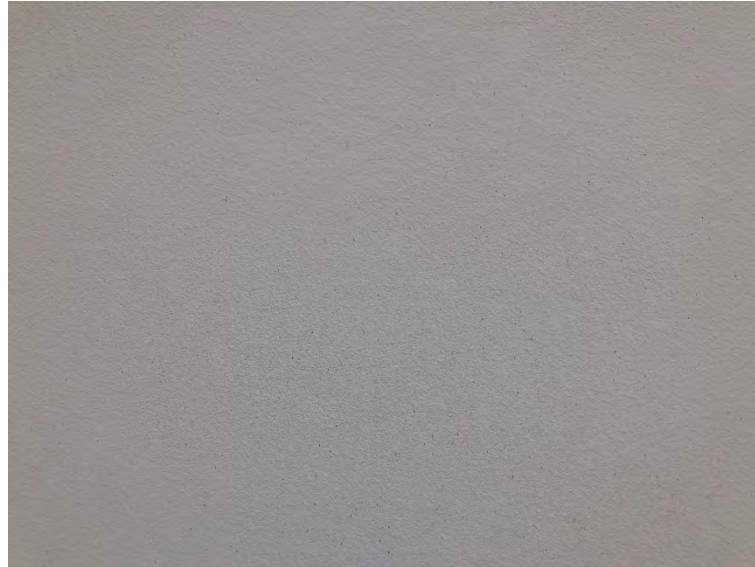
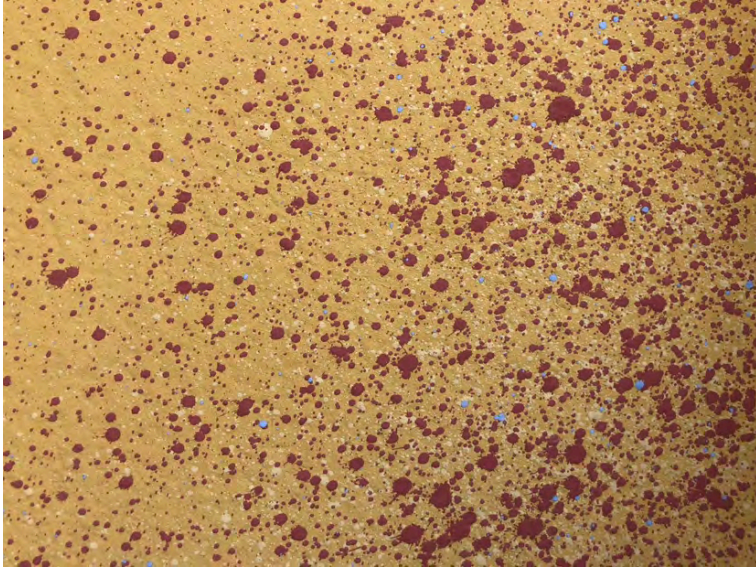


Application of geopolymer coating in engineering  
Nanning city, China, 2018

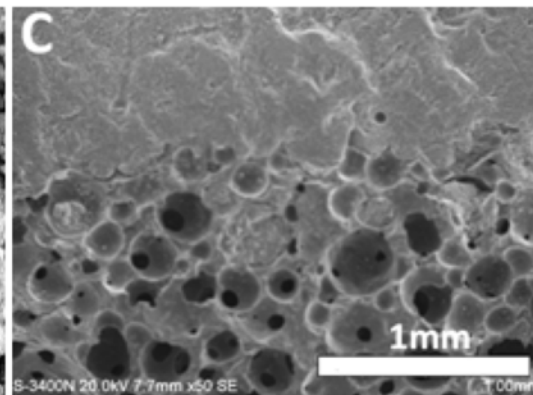
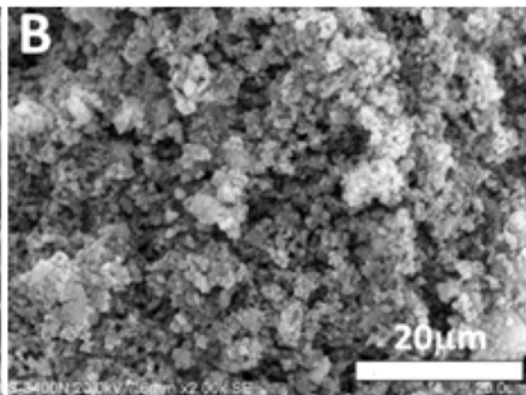
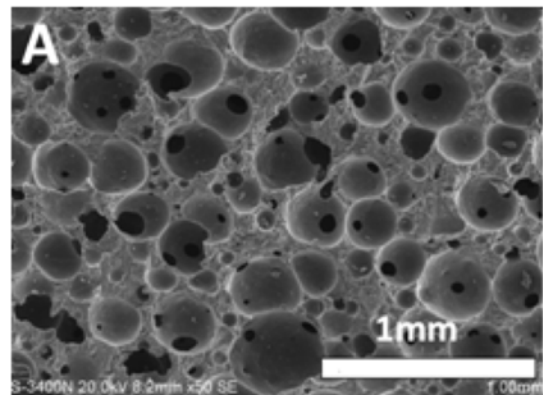
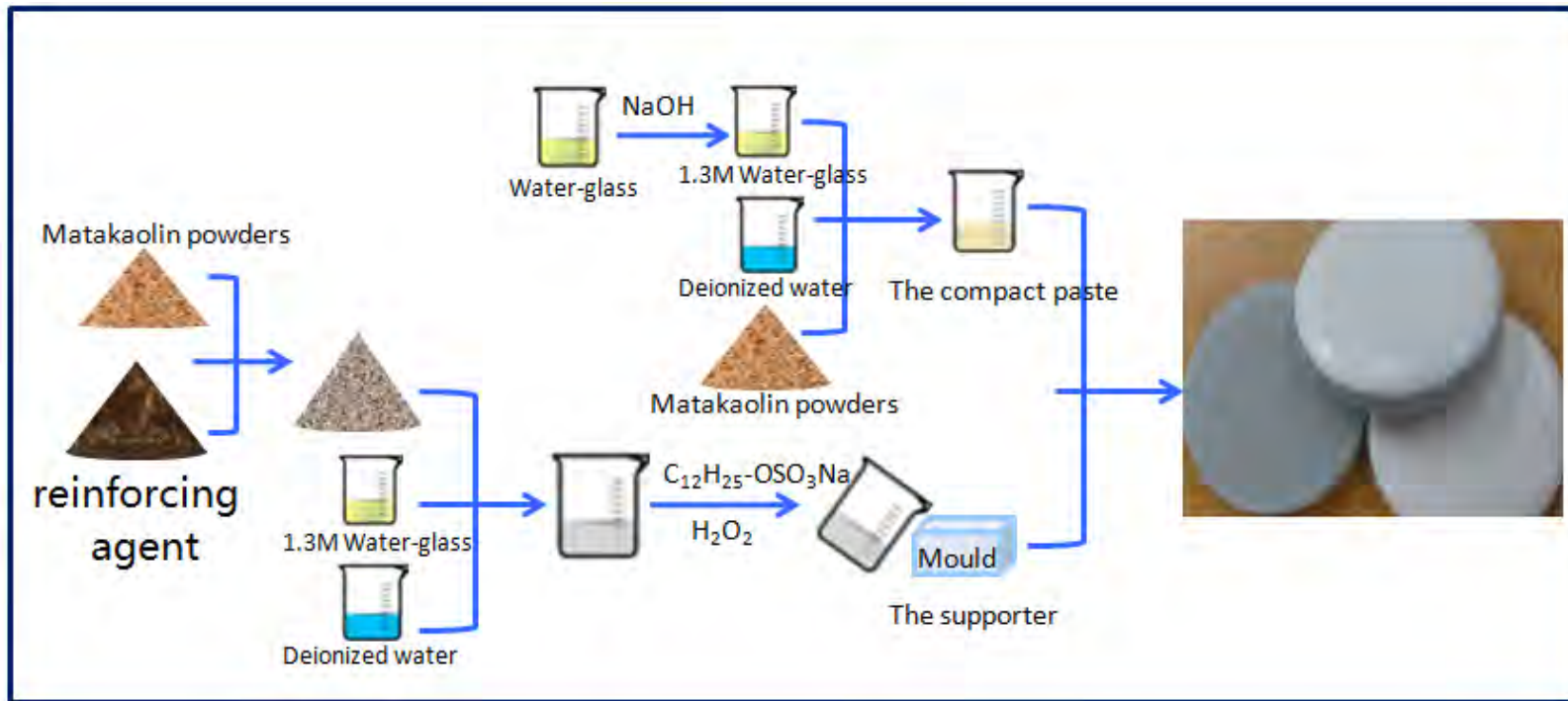


Geopolymer coating used in emergency repair engineering  
Nanning city, China, 2019

# Application 1: geopolymer coating

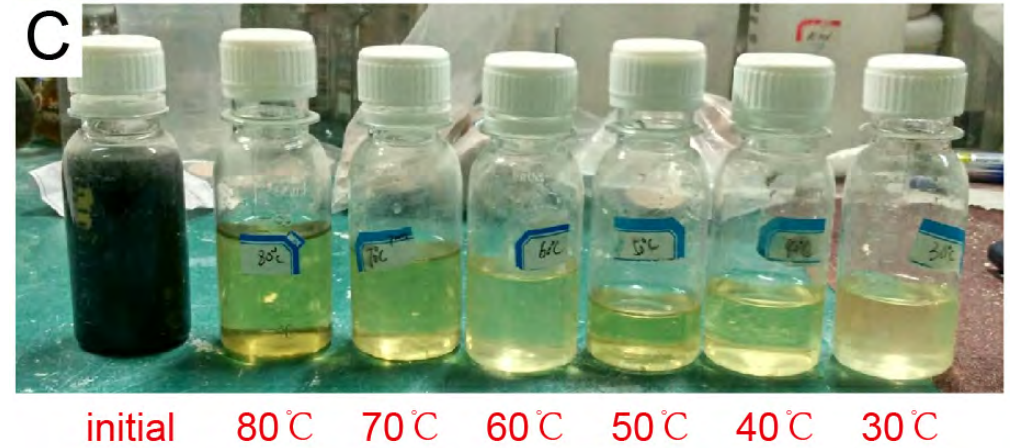
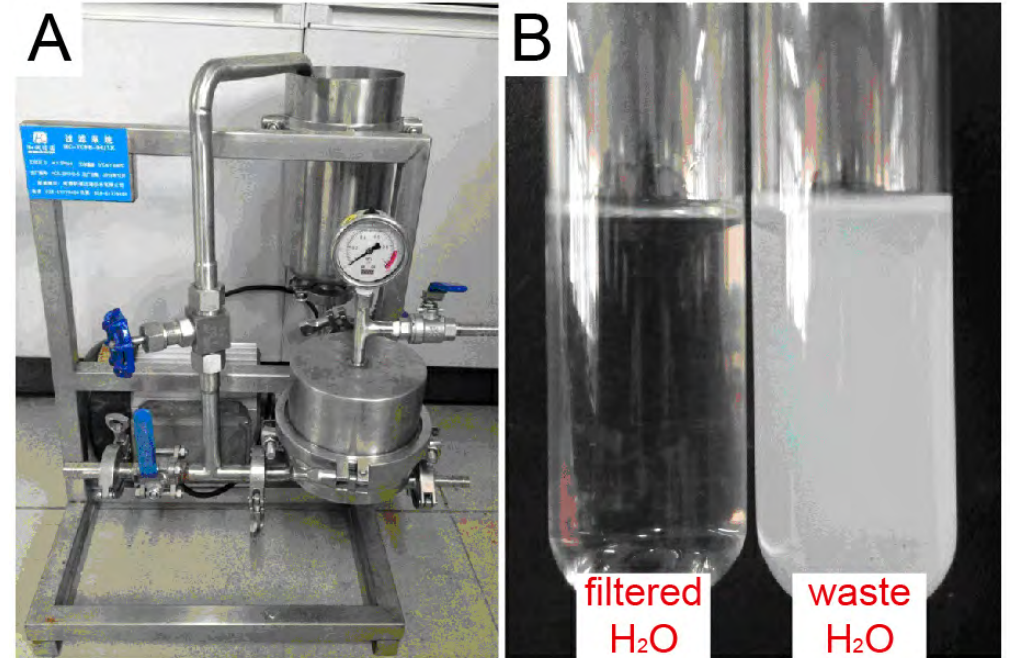
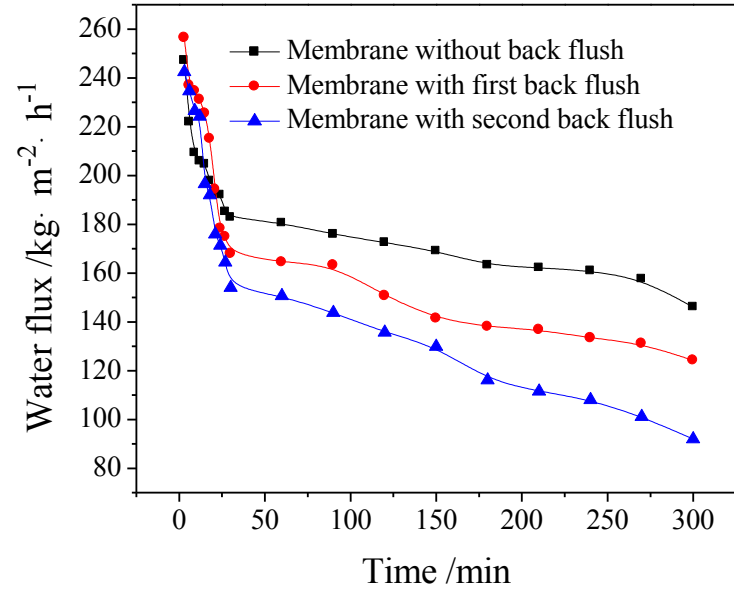


# Application 2. geopolymer membrane for water treatment

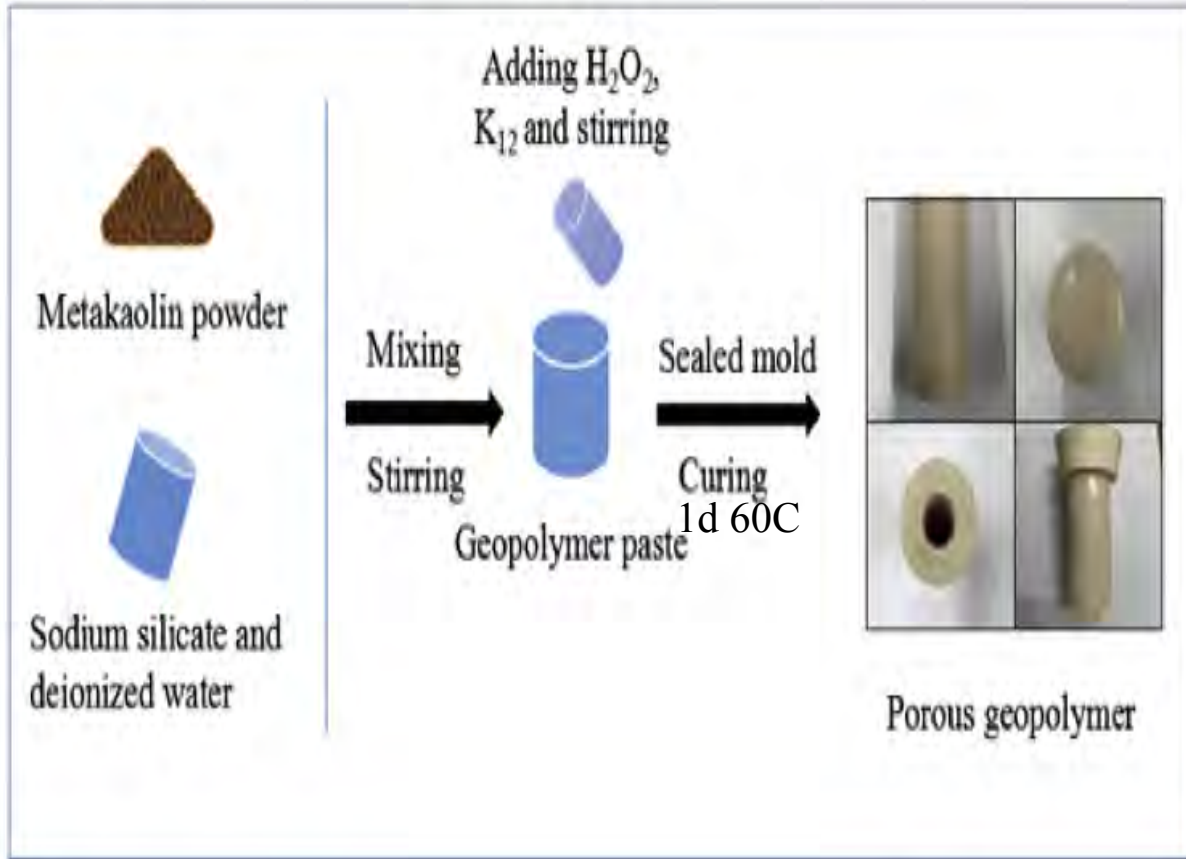




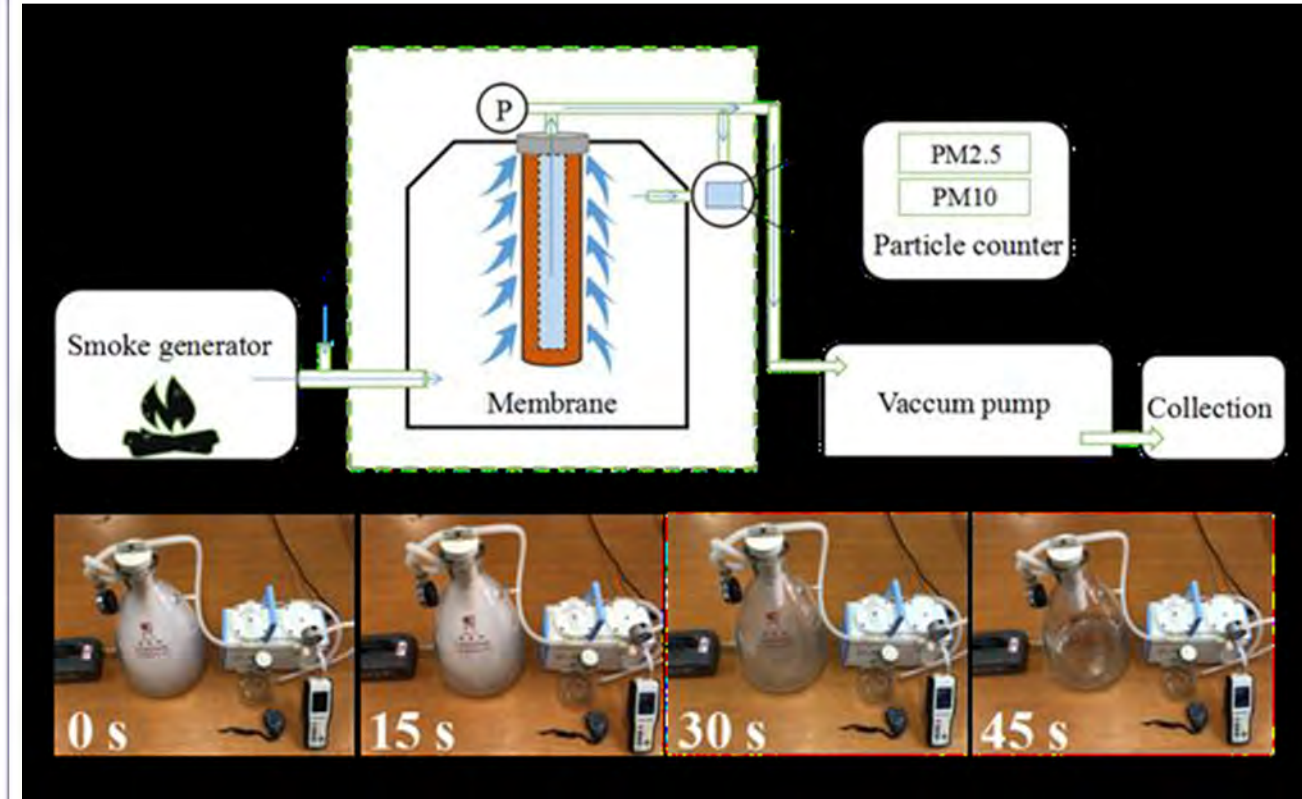
# Application 2. geopolymer membrane for water treatment



# Application 2. geopolymer membrane for gas treatment

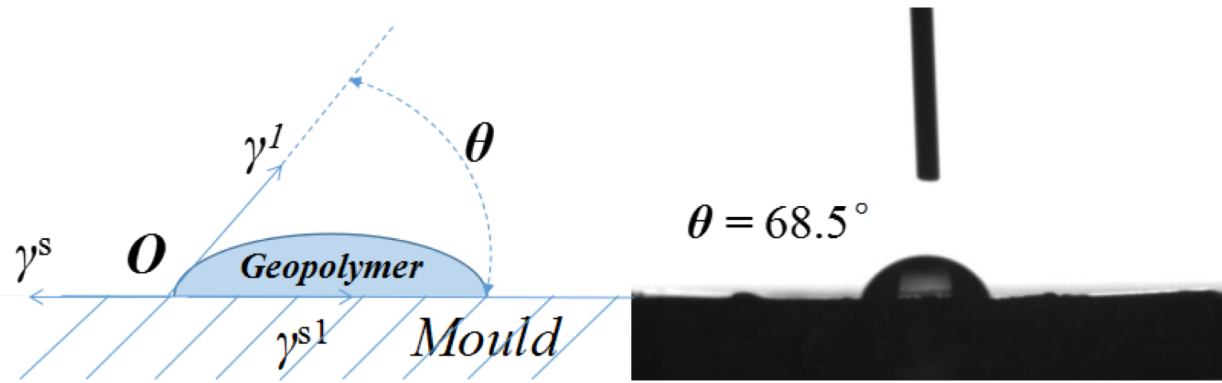


Fabrication process of micro porous geopolymer-based membrane.



Filtration process of PM2.5/10 simulate realistic filtration process.

# Application 2. geopolymer membrane for gas treatment

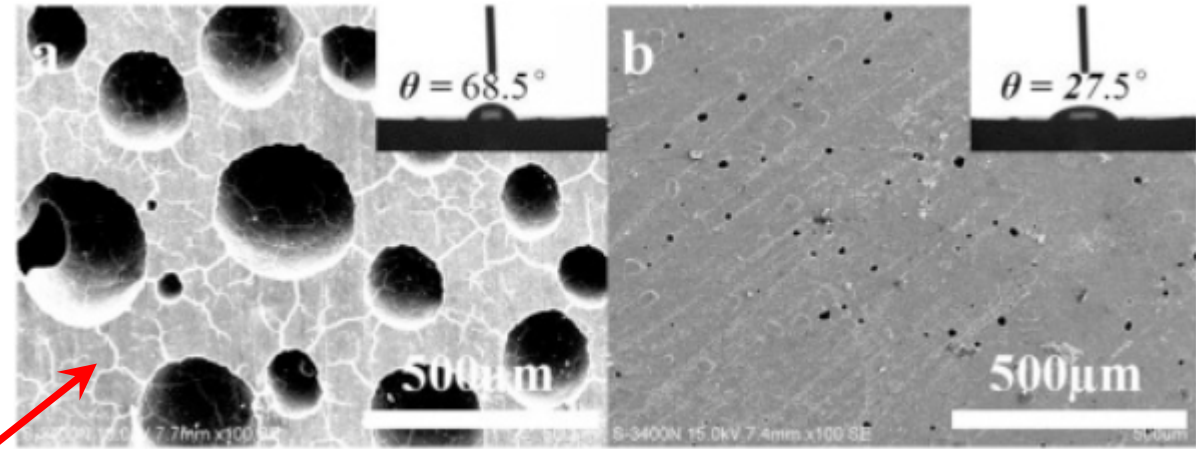


Young equation:

$$\gamma^s = \gamma^{sl} + \gamma^l \cos\theta$$

1. If  $\theta$  is too high: bubbles diffuse from inside up only

2. If  $\theta$  is too low: mold surface will be stuck by the paste and lost the compact layer with small pores.

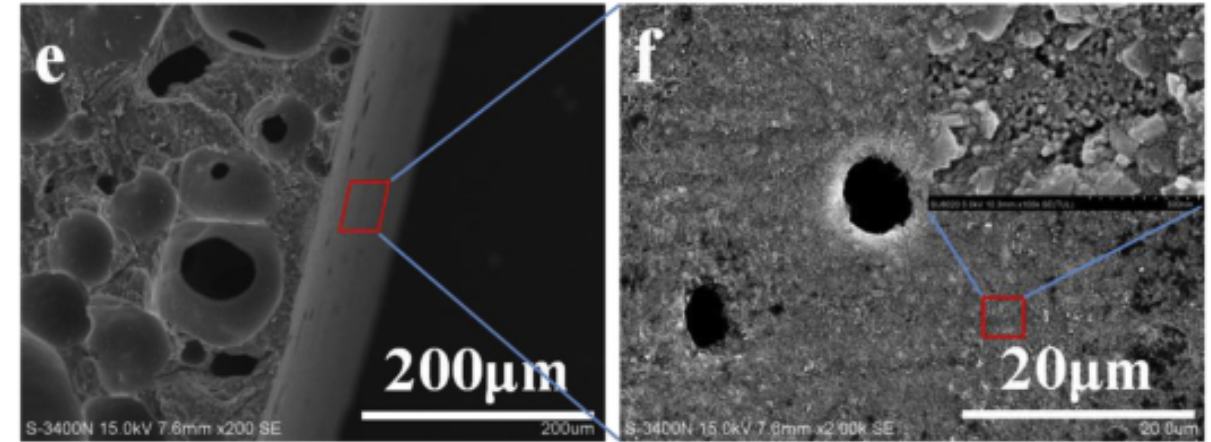
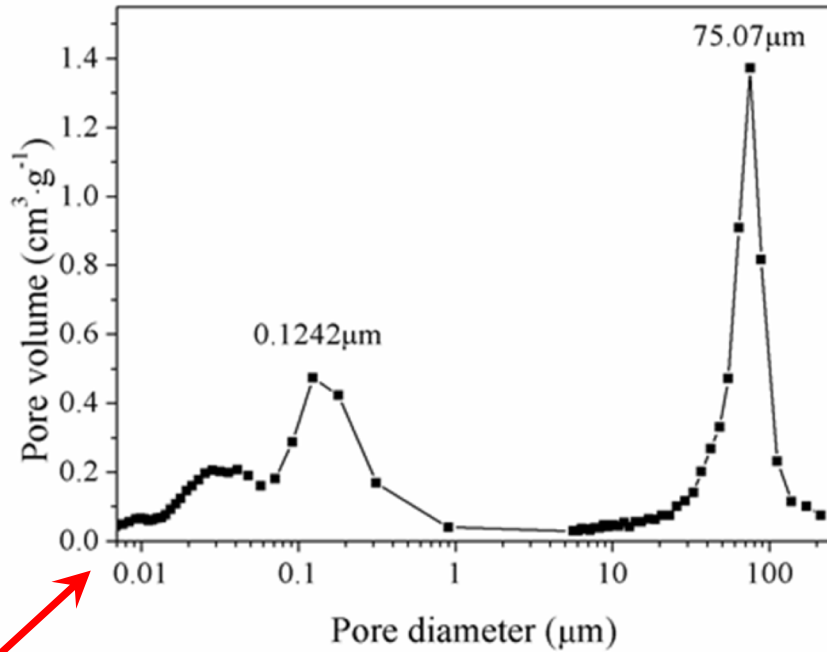


$\theta = 68.5^\circ$ ,  
membrane with  
large open cells

$\theta = 27.5^\circ$ ,  
compact layer  
with small pores

Surfactant K12 was used to adjusted the  $\theta$ , thus the geopolymer paste can maintain complete contact with the surface of the mold, a porous gradient structure was fabricated.

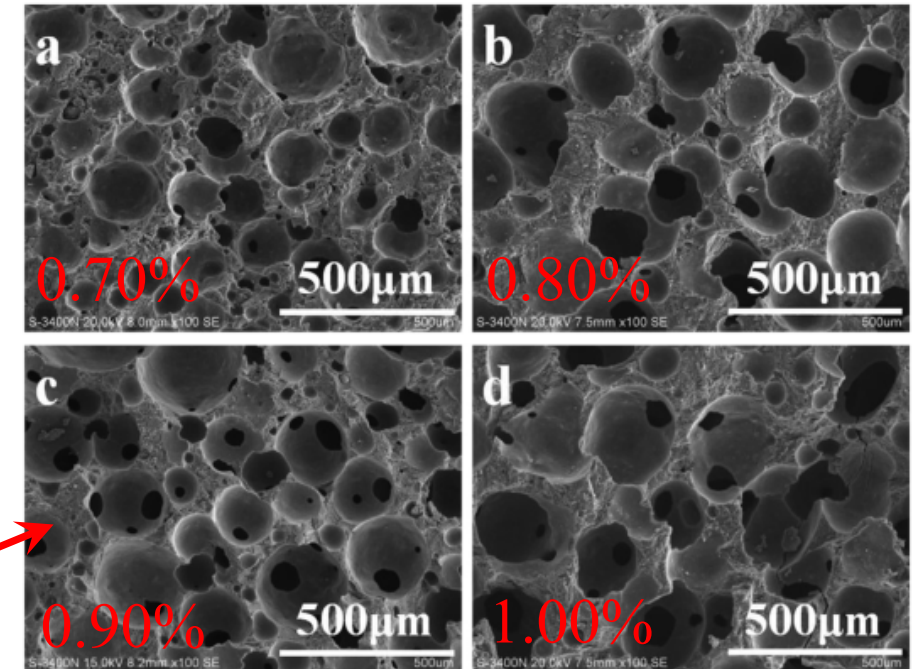
# Application 2. geopolymer membrane for gas treatment



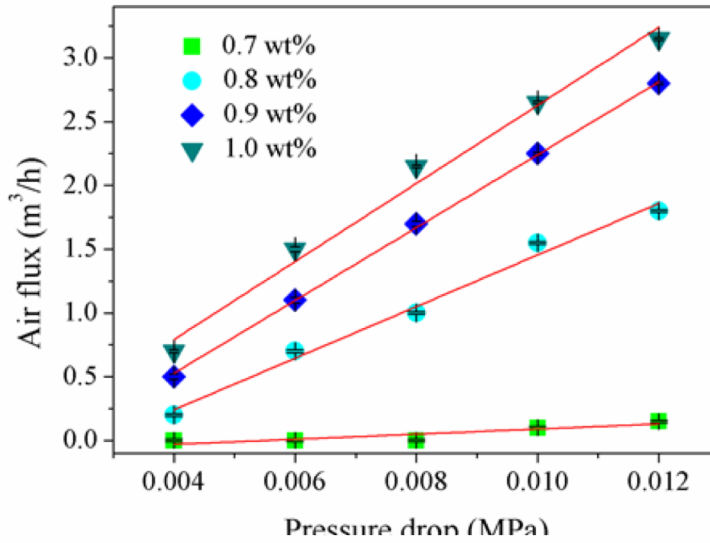
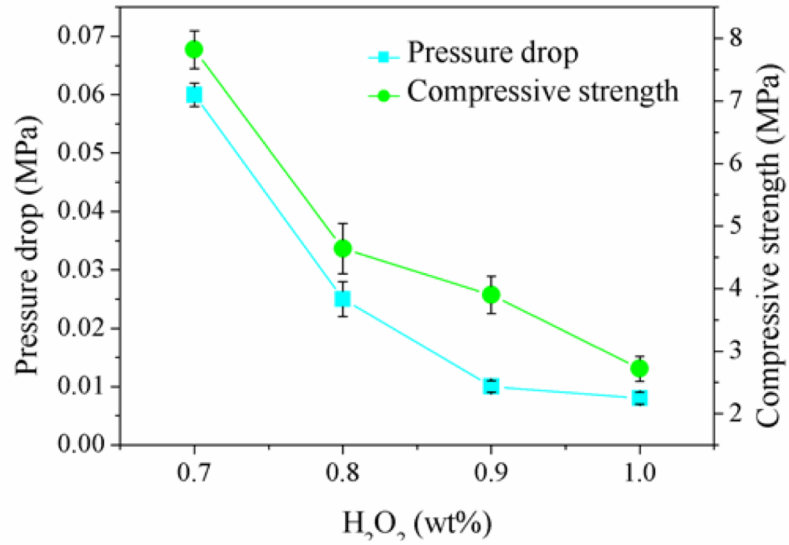
Porous body of cross-section combined with compact surface

0.12 μm pore of compact surface results from water evaporation and 10 -100 μm pore of internal structure  
Nano porous structure of the surface ensured the interception of particles, and the near millimeter-sized porous structure of the membrane body ensured high permeability.

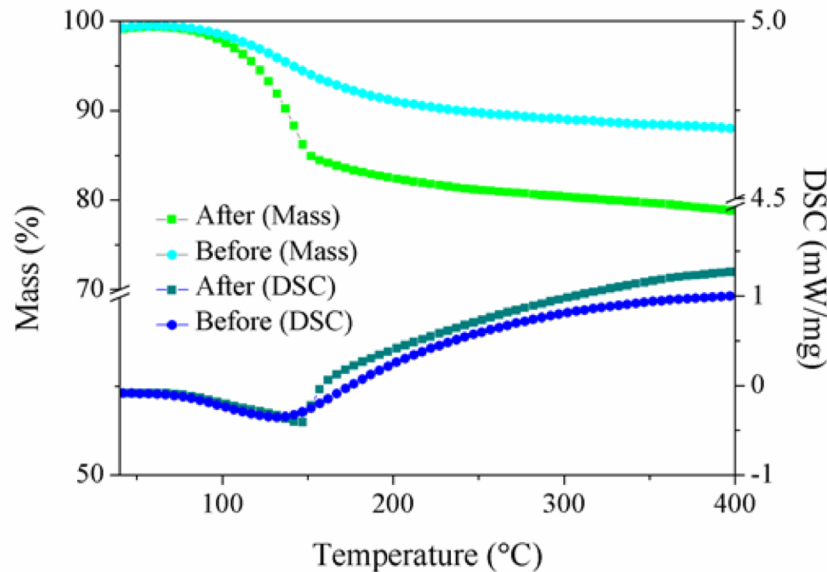
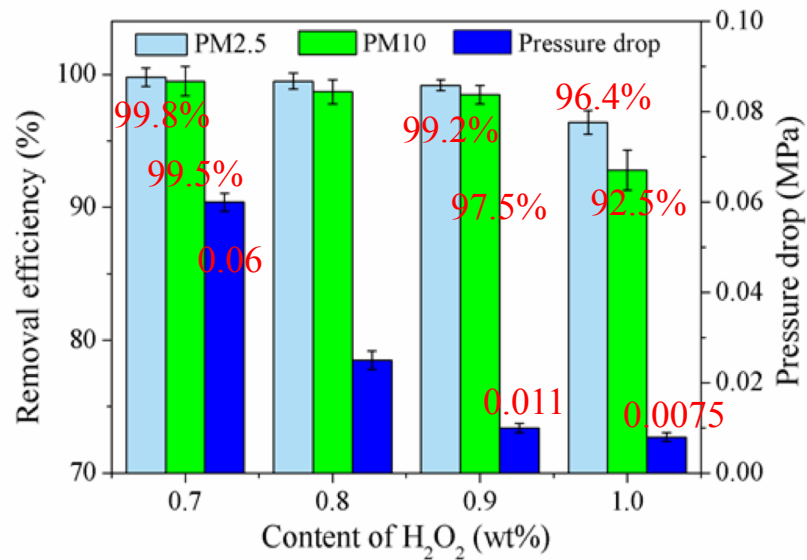
Randomly distributed millimeter-sized open pore giving the high permeability. Pores size increased with the H<sub>2</sub>O<sub>2</sub> addition



# Application 2. geopolymer membrane for gas treatment

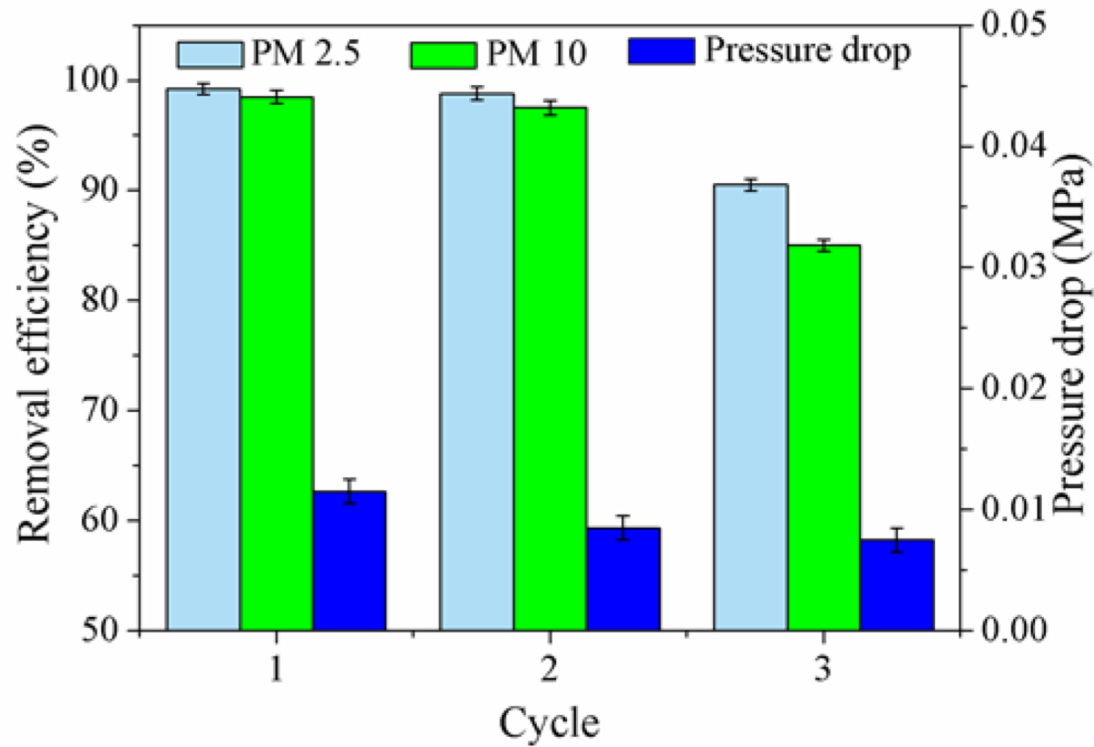


1. Pressure drop and compressive strength decrease with the increase of foaming agent.
2. Air flux improve with the increase of Pressure.
3. Permeability can be controlled by foam agent.

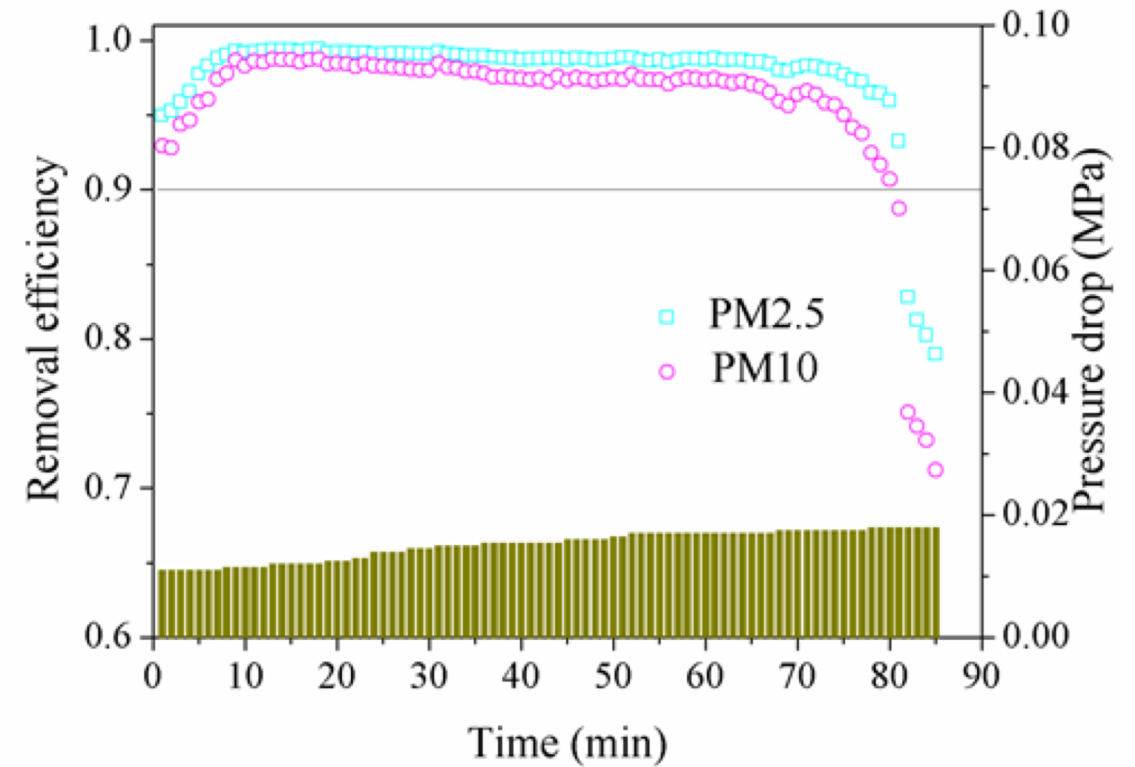


1. Membrane with 0.9% foam agent shows PM<sub>10</sub> and PM<sub>5</sub> removal efficiency of 99.2% and 97.5%.
2. After 90 min filtration, about 9 wt% PM matter was filter in membrane.

# Application 2. geopolymer membrane for gas treatment



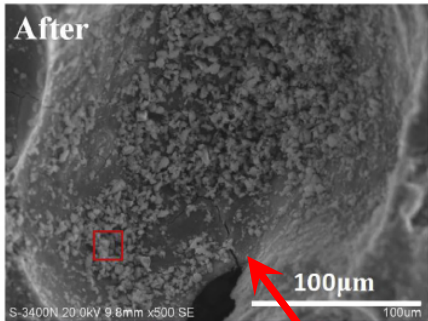
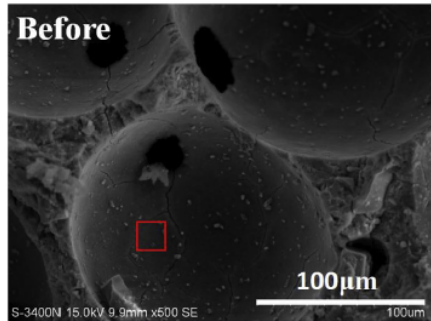
After 90 min filtration, PM2.5 and PM10 removal efficiencies of 98.5% and 99.3%, pressure drop from 0.011 to 0.018 Mpa.  
After recycling, PM2.5/10 removal efficiency of still as high as 90%/85%.



3 stages of filtration:

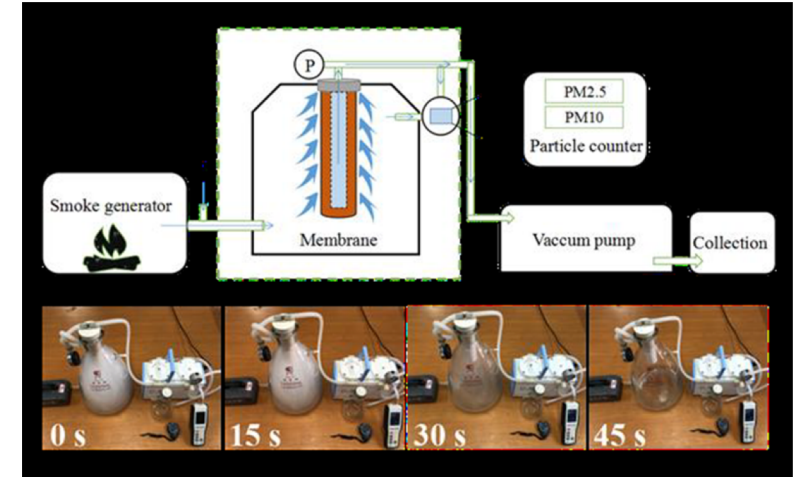
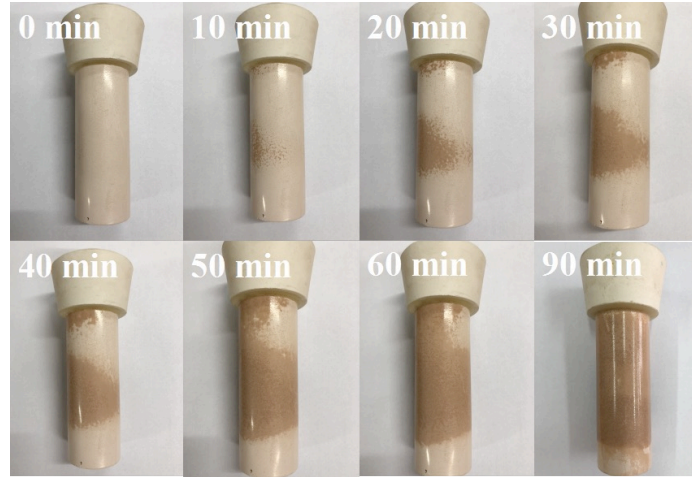
- 1st, removal efficiency increase, forming cake layer
- 2nd, keeping stable removal efficiency
- 3rd, removal efficiency decrease, adsorption saturation.

# Application 2. geopolymer membrane for gas treatment



Element	Wt%	At%
CK	02.94	04.66
OK	59.40	70.55
NaK	04.62	03.82
AlK	08.87	06.25
SiK	16.18	10.95
CaK	07.99	03.79
Matrix	Correction	ZAF

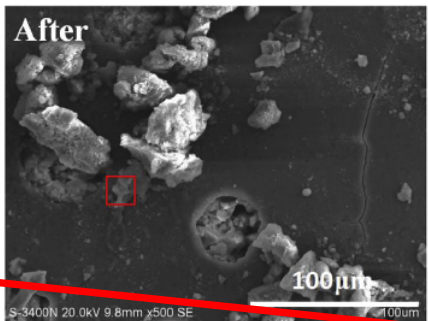
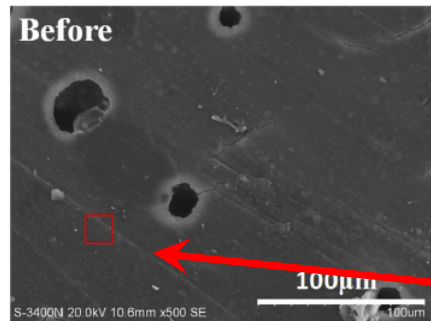
Element	Wt%	At%
CK	08.85	13.52
OK	54.88	62.90
NaK	06.55	05.22
AlK	08.29	05.63
SiK	14.95	09.76
CaK	06.49	02.97
Matrix	Correction	ZAF



After 90 min, membrane completed the filtration

large PM was rejected on the surface

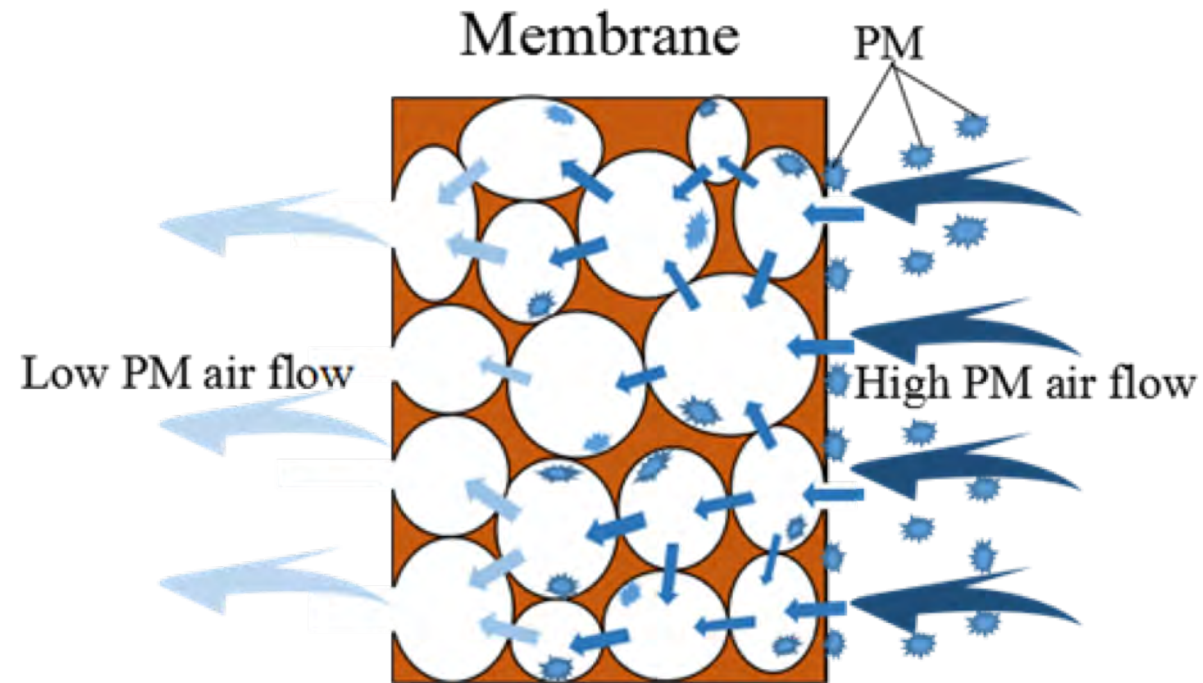
surface compact layer intercepted extremely small particulate matter.



Element	Wt%	At%
CK	02.86	04.90
OK	46.59	59.99
NaK	04.01	03.59
AlK	10.69	08.16
SiK	22.48	16.49
CaK	13.37	06.87
Matrix	Correction	ZAF

Element	Wt%	At%
CK	11.22	18.12
OK	44.32	53.76
NaK	03.92	03.31
AlK	07.30	05.25
SiK	16.71	11.55
CaK	16.52	08.00
Matrix	Correction	ZAF

## Application 2. geopolymer membrane for gas treatment



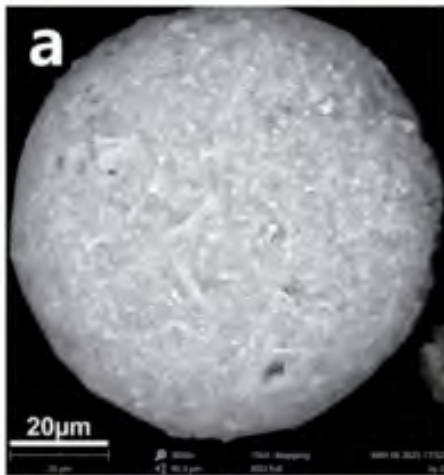
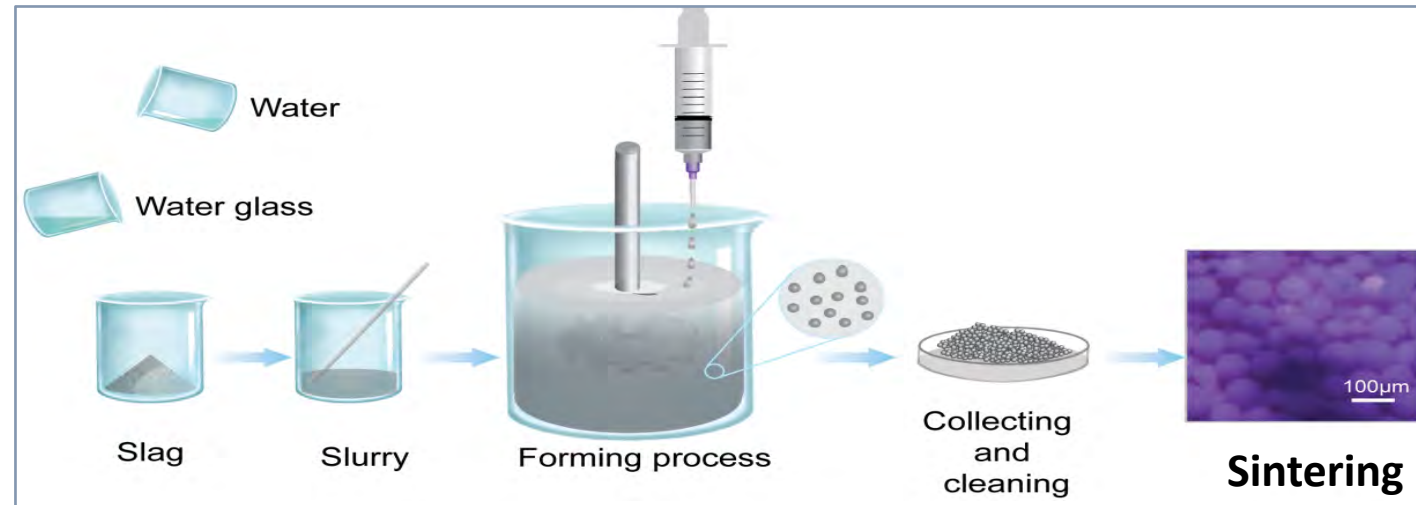
*Filtration mechanism of membrane for PM:*

Majority of PM were absorbed and removed by the large surface area of the membrane body. Nano-size PM were filtered by near-nanoporous surface of the membrane,

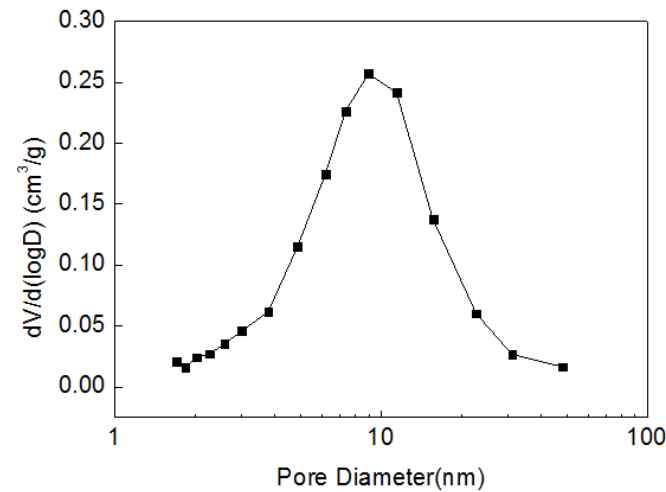




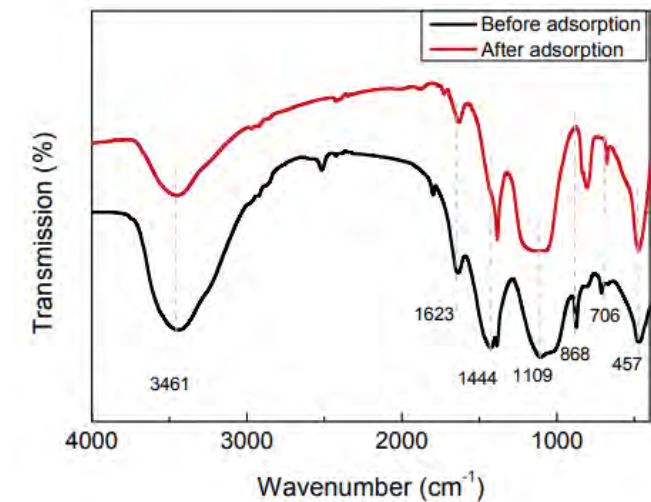
# Application 3. geopolymer microsphere for heavy metal ions removal



Geopolymer microsphere

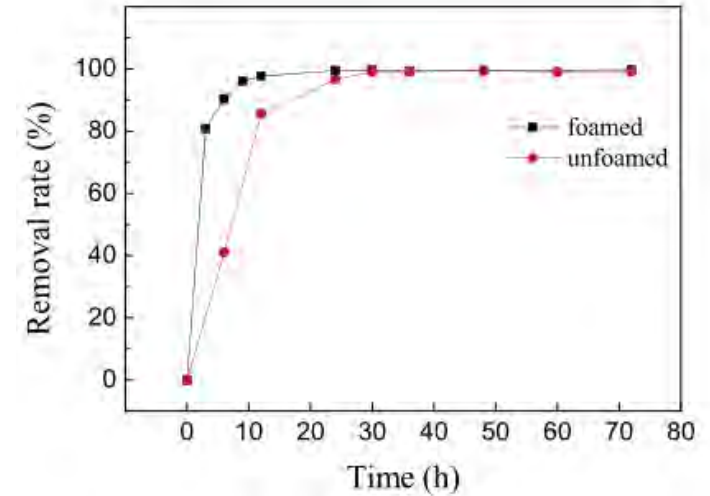
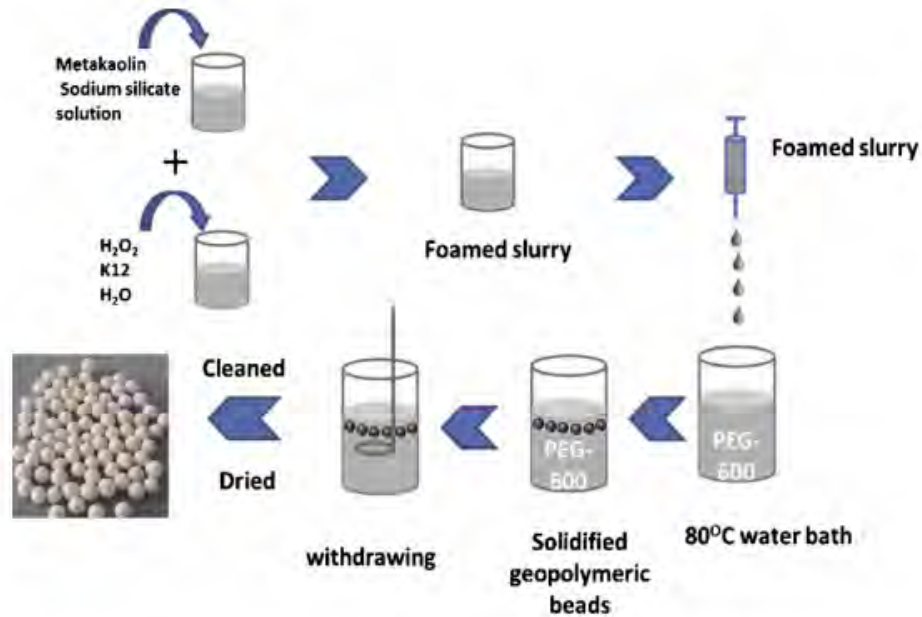


Specific surface 79.80 m<sup>2</sup> /g  
Mean pore 7 nm

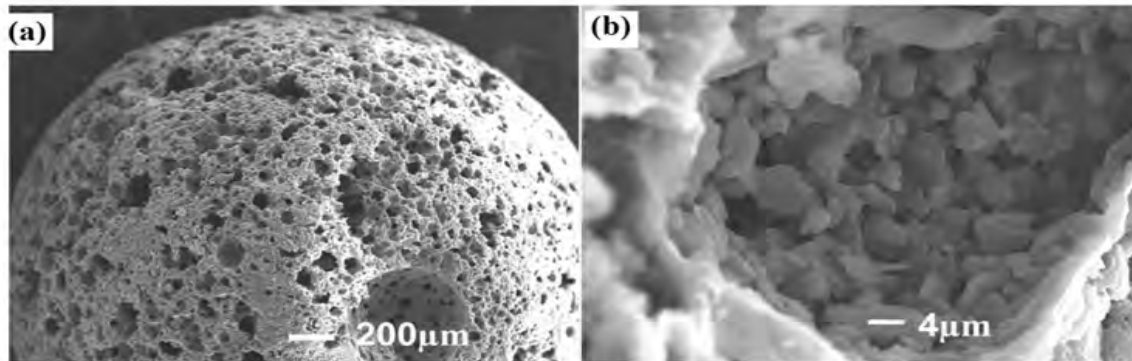


Si-O-Si shift to lower number  
Pb<sup>2+</sup> adsorb in geopolymer

# Application 3. geopolymer porous microsphere

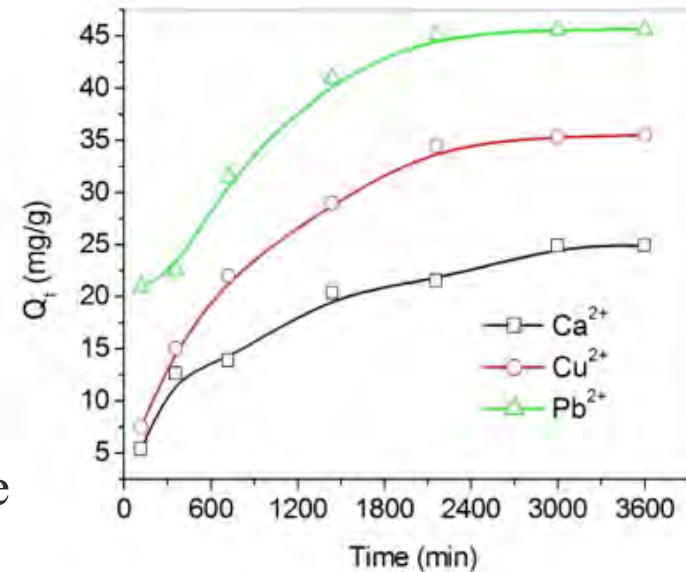


Active sites and surface area increase, after foaming



Surface of microsphere

Cross-section of microsphere



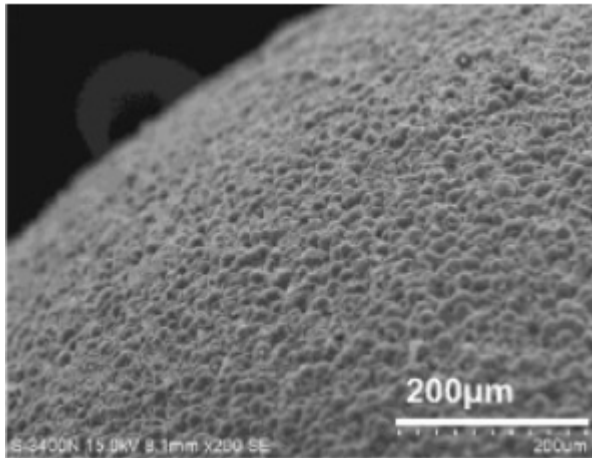
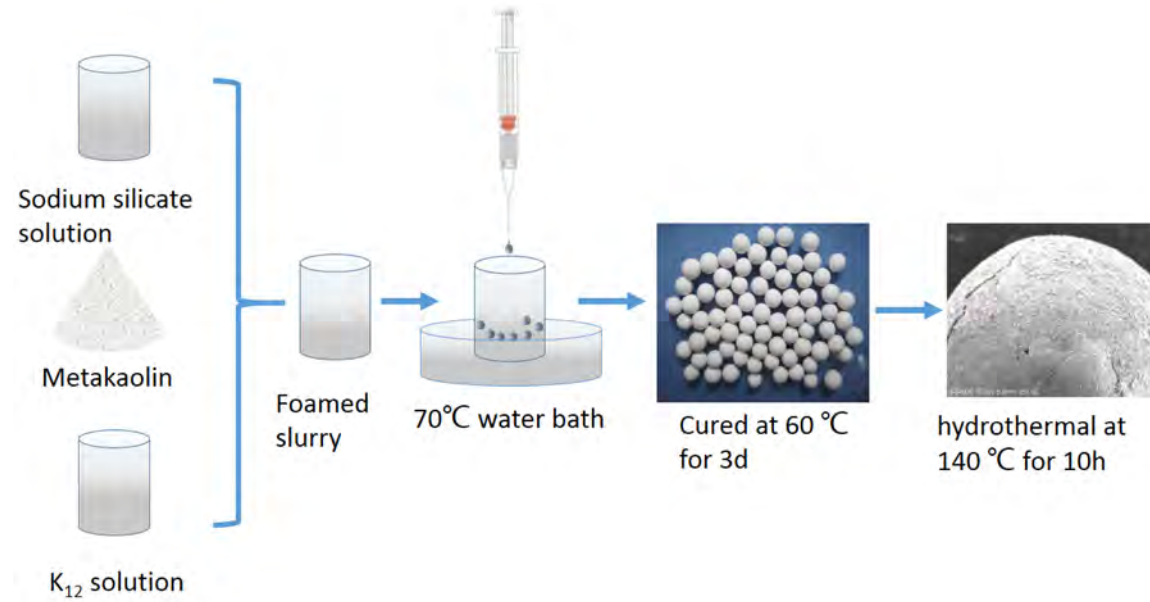
Adsorption capacity of metal ions:  
Pb>Cu>Ca

# Application 3. geopolymer microsphere for heavy metal ions removal

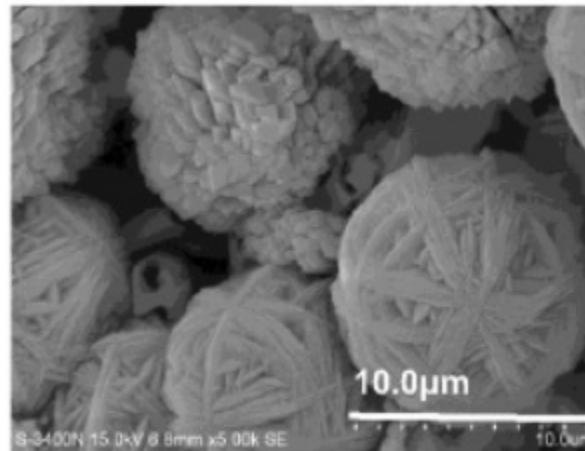
Number	Adsorbent	Type	BET surface (m <sup>2</sup> /g)	Heavy metal	pH	Temperature (° C)	Qm (mg/g)
1	Fly ash-based geopolymer	Powder	/	Pb <sup>2+</sup>	5	25	134.95
2		Powder	/	Cu <sup>2+</sup>	6	25	96.80
3	Metakaolin-based geopolymer	Particle	65.7	Pb <sup>2+</sup> , Cu <sup>2+</sup>	4	25	100.00
				Cr <sup>3+</sup> , Cd <sup>2+</sup>			54.54
4		Membrane	39.66	Ni <sup>2+</sup>	5	25	10.15
5		Powder	9.65	Cu <sup>2+</sup>	5	25	75.74

Porous geopolymer microspheres present an adsorption capacity 4–5 times larger than similar geopolymer materials

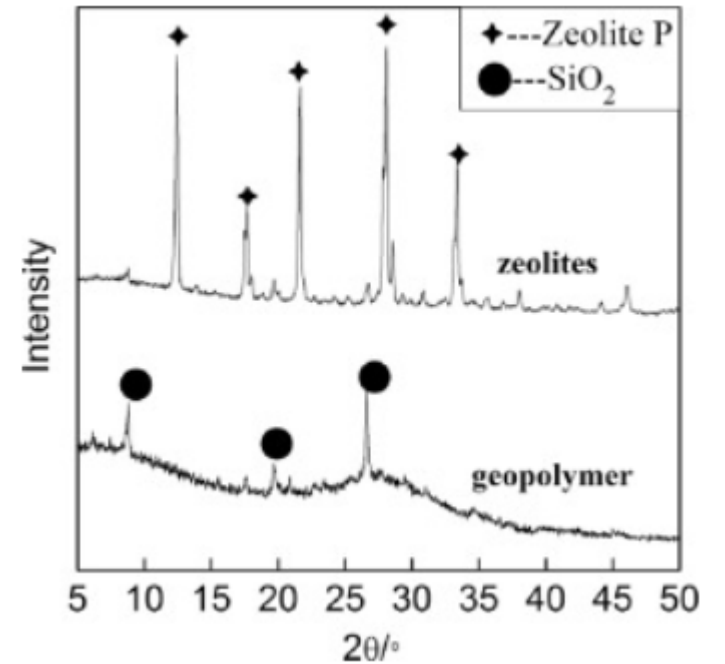
# Application 3. geopolymer P-type zeolite microsphere



Surface of zeolite sphere



Cross-section of zeolite sphere



Zeolite P ( $Na_{3.6}Al_{3.6}Si_{12.4}O_{32} \cdot 14H_2O$  transition)

That's all of my presentation,  
thanks for listening!

