Journal of Zhejiang University-SCIENCE A

Cite this as: Dong-ming Yan, Sheng-qian Ruan, Shi-kun Chen, Yi Liu, Ye Tian, Hai-long Wang, Tian-nan Ye, 2021. Effects and mechanisms of surfactants on physical properties and microstructures of metakaolin-based geopolymer. *Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)*, 22(2):130-146. https://doi.org/10.1631/jzus.A2000059

Effects and mechanisms of surfactants on physical properties and microstructures of metakaolin-based geopolymer

Dong-ming YAN[1], Sheng-qian RUAN[1], Shi-kun CHEN[†‡1], Yi LIU[2], Ye TIAN[1], Hai-long WANG[1], Tian-Nan Ye[3]

[1]*School of Civil and Architectural Engineering, Zhejiang University, Hangzhou 310058, China*

[2]*School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China*

[3]*Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.*

[†]E-mail: chen_sk@zju.edu.cn

Key words: Metakaolin-based geopolymer (MKG); Surfactants; Physical properties; Microstructure; Adsorption; Microscopic mechanism

JZUS-A

1 Introduction

- Geopolymers are synthetic materials manufactured using aluminosilicate raw materials with a highly concentrated aqueous alkali hydroxide or silicate solution. Chemical additives used as modifiers have been used to synthesize geopolymers with high quality and good performance.
- Surfactants are widely used in the dispersion of additives for geopolymers. They will also affect the geopolymer through its adsorption onto the surface of raw materials, gels and interphase boundaries. Previous studies have revealed that surfactants can optimize the bubble generation, pore distribution and microstructure of geopolymers.
- The complex effects of surfactants on the microstructure and properties of geopolymers have not been comprehensively studied. Furthermore, the underlying mechanisms have not been discussed, especially in terms of surfactant molecules.

JZUS-A

2 Materials and experimental methods

- The materials including metakaolin, alkaline activator (sodium silicate solution and sodium hydroxide solid), five kinds of surfactants were first mixed in proportion. After molding and curing, various specimens were prepared.
- The experimental methods include viscosity measurement, mercury intrusion porosimetry, scanning electron microscopy, apparent water absorption and compressive strength measurement.

Table 1 Group arrangements with different surfactants

Group	Surfactant	Molecular weight (g/mol)	Manufacturer	pH
SLS	Sodium lauryl sulfonate	273	Meryer (Shanghai) Chemical Technology Co., Ltd.	9.49
APG	Alkyl polyglycoside	348	Karl·Golden (Zhejiang) Biotechnology Co., Ltd.	12.22
BAC	Benzalkonium chloride	354	Titan (Shanghai) Technology Co., Ltd.	8.60
SE	Sucrose fatty acid esters	594	Karl·Golden (Zhejiang) Biotechnology Co., Ltd.	8.15
STA	Stearic acid	284	Dibo (Shanghai) Biotechnology Co., Ltd.	5.92

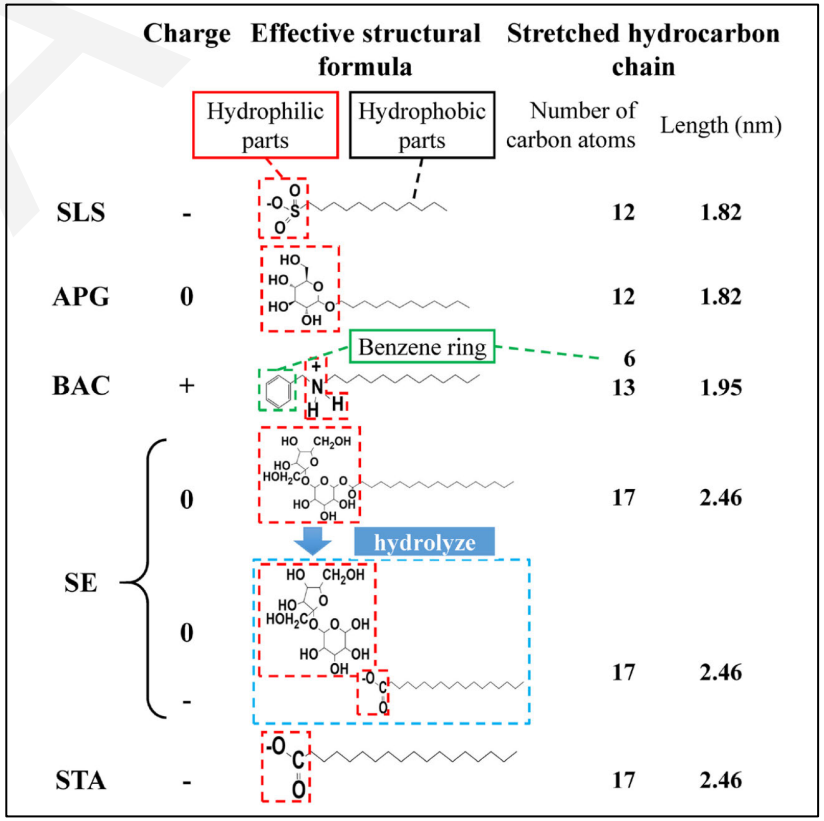

Fig. 1 The effective structural formula, electric charge and length of stretched hydrocarbon chain of different surfactants

3 Results

◆ Viscosity

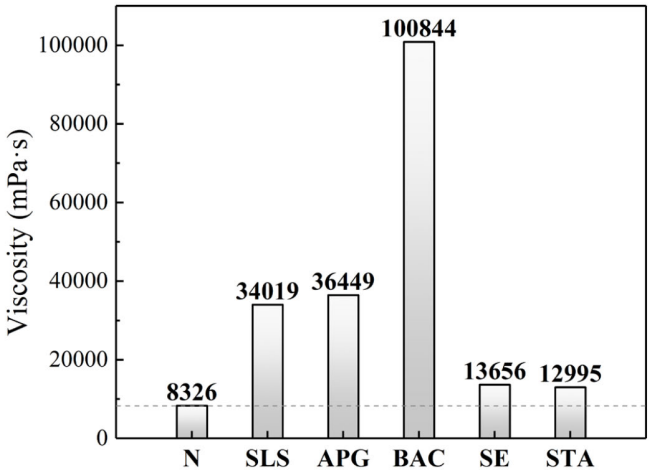

Fig. 2 The dynamic viscosity of MKG slurry after mixing

◆ Compressive strength

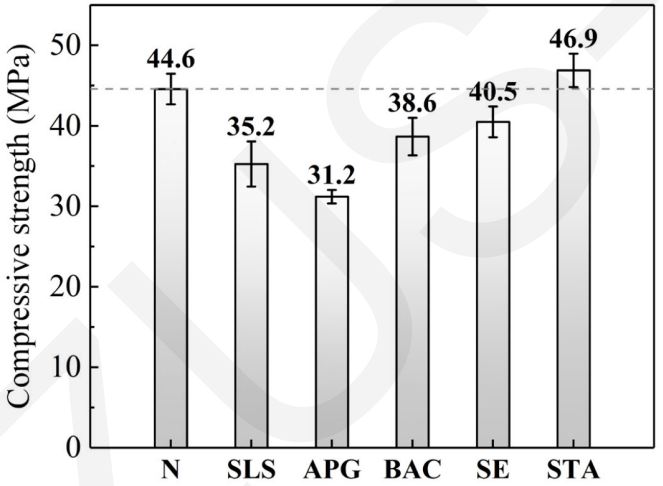

Fig. 3 Compressive strength measured by the universal testing machine

◆ Apparent water absorption

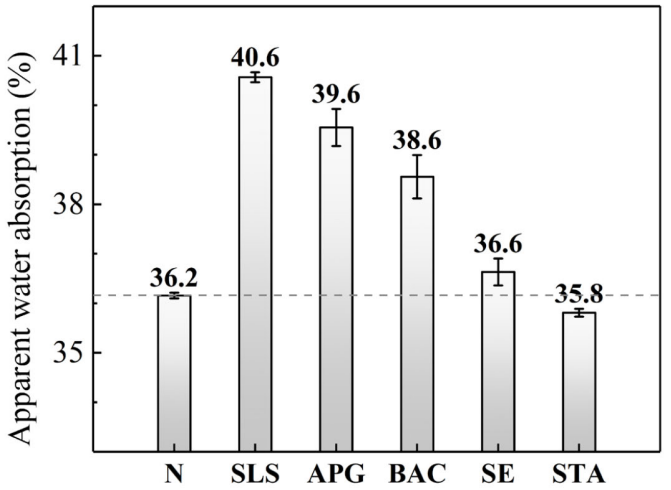

Fig. 4 Apparent water absorption tested by water saturation method

JZUSCA

3 Results

◆ Microstructure analyses

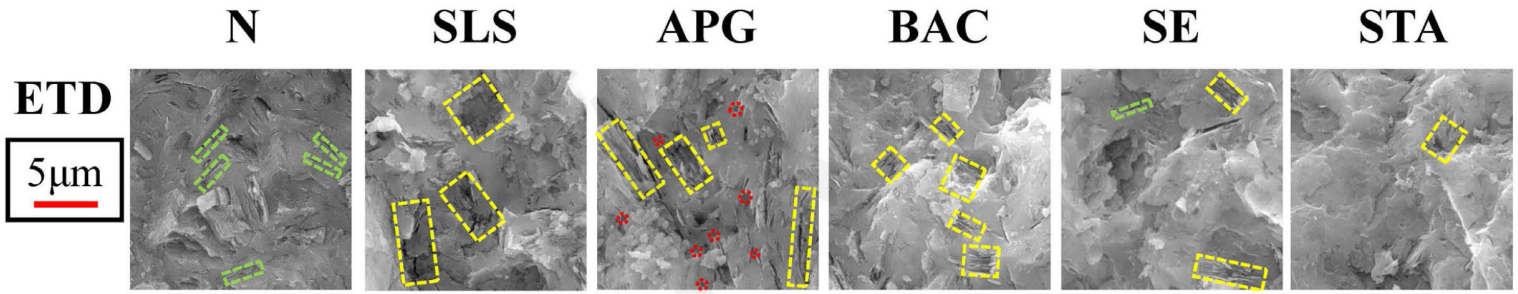

Fig. 5 ETD images of the microstructures observed using SEM
The ETD images show the micron-scale microstructure 20,000X-magnified of samples from the different groups. Green boxes indicate the micro-cracks; yellow boxes indicate defects of unreacted metakaolin; red boxes indicate unconnected global bubble pores.

◆ Porosity characterization

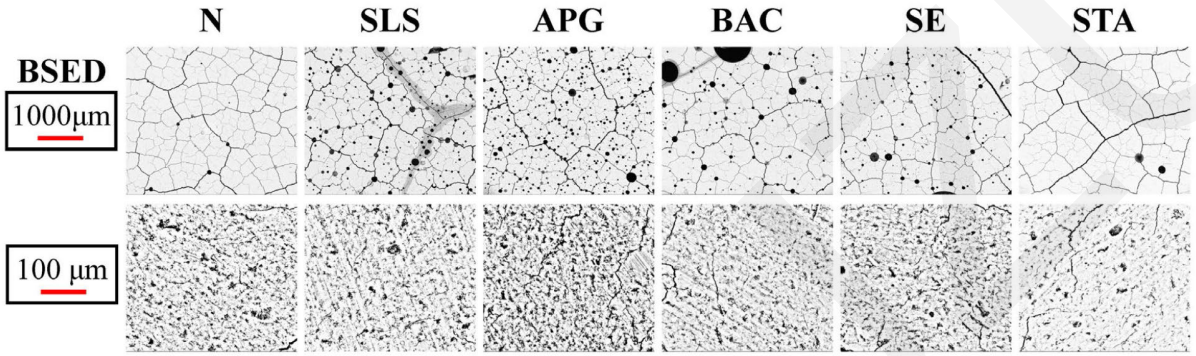

Fig. 6 BSED images of large- and medium-sized pores observed by SEM
The first row of BSED images were 100X-magnified, and bubble pores larger than 20 μm can be counted. The second row of BSED images were 2000X-magnified, and pores with a diameter from 150 nm to 20 μm can be counted.

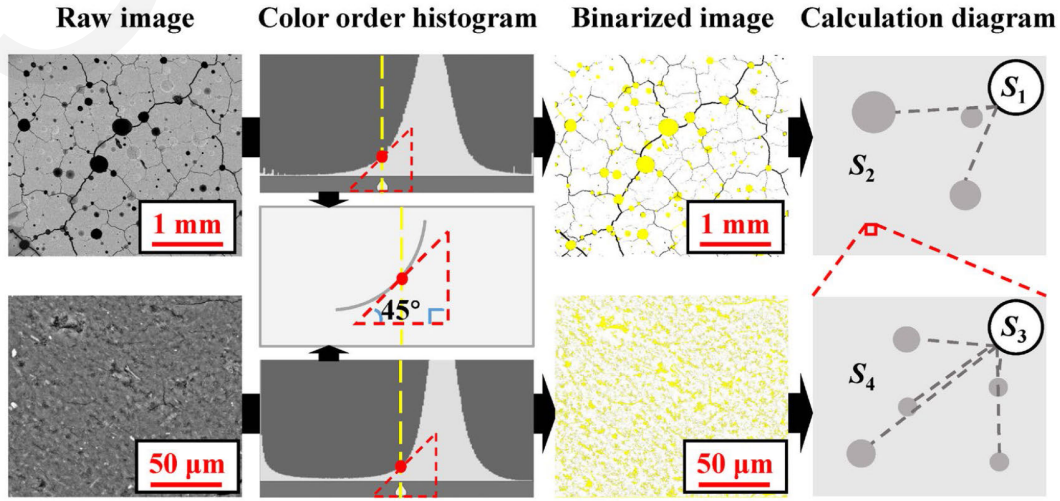

Fig. 7 Illustrative diagram of BSED image analysis and the porosity calculation process in different diameter ranges
Pores and defects of different diameter ranges observed by SEM in raw images. Based on color order histogram analysis and image binarization, pore distribution and porosity can be calculated using pixels.

3 Results

◆ Porosity characterization

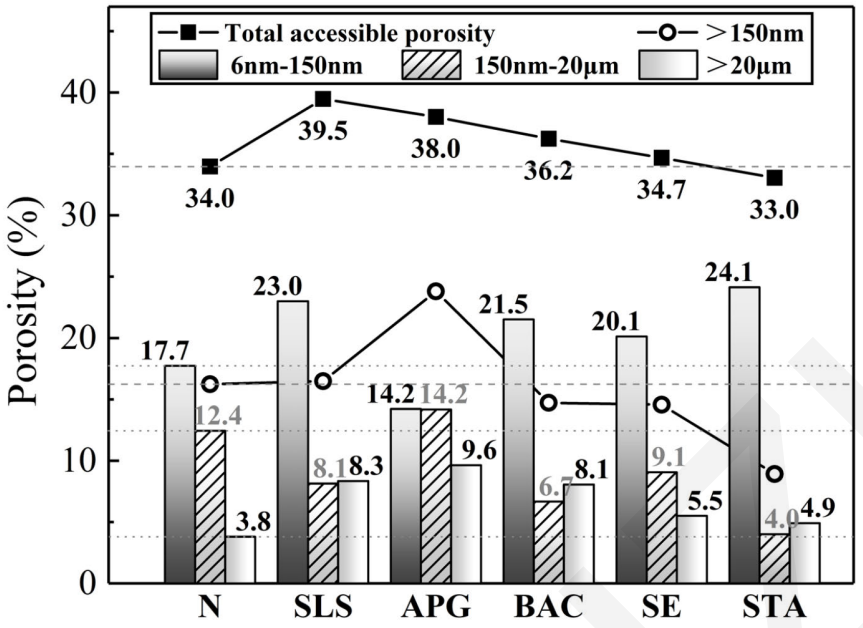

Fig. 8 Porosity of different diameter ranges characterized by SEM and MIP

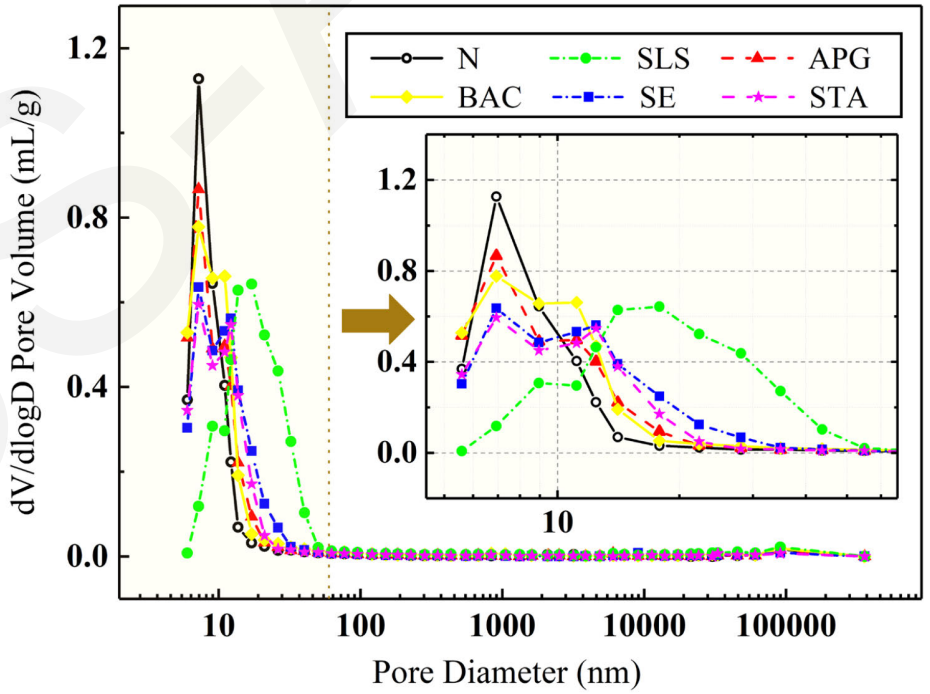

Fig. 9 Pore distribution obtained by MIP
The distribution of pores with diameters within the range from 5 to 60 nm are shown in the chart inset on the right

4 Discussion

◆ Surfactant adsorption capacities

surfactants with different molecular structures can adsorb onto the surface of metakaolin particles in various configurations. Adsorption is different for ionic and nonionic surfactants. For ionic surfactants, adsorption behavior is governed by the charge of the surface and counter ions present in the electrolytes. For nonionic surfactants, it can be driven by hydrogen bonding of the polar moieties (hydrophilic heads).

◆ Microstructure effects

The geopolymerization and microstructure of MKGs are affected by different surfactant adsorption capacities. the five kinds of surfactants were adsorbed onto the surface of metakaolin particles to variable degrees, and could be divided into two types based on their looser or denser microstructure.

◆ Bubble formation

Adsorbed surfactants result in a lowering of surface tension, so less energy is needed to generate stable bubbles. Surfactants adsorbing on both sides of a water film also cause steric interactions, making bubbles repel each other, resulting in large pores in MKGs

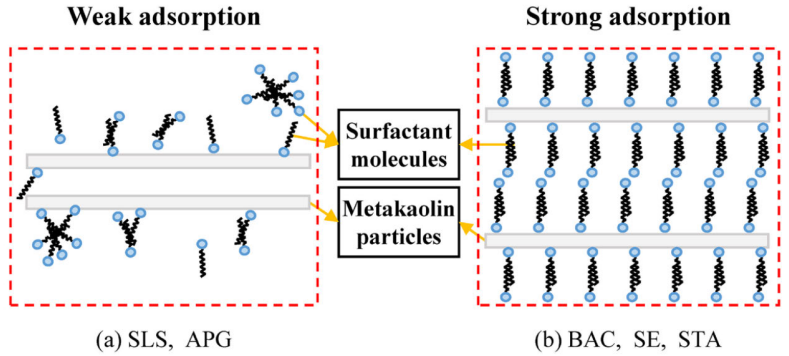

Fig. 15 Schematic representation of the connection between surfactant molecules and metakaolin particles
It is harder for molecules of SLS and APG to adsorb onto the surface of metakaolin, but they self-associate into micelles, making it harder for them to enter the gaps between metakaolin particles. BAC, SE and STA molecules are more easily adsorbed onto the surface of metakaolin, and effectively disperse metakaolin particles.

5 Conclusions

- Surfactants with specific molecular configurations affect the physical properties and microstructure of MKGs. All surfactants can increase the slurry viscosity and promote the generation of bubbles. BAC has the strongest capacity to increase viscosity, and APG the strongest capacity to produce bubbles. The trends of density, water absorption and compressive strength are related to the total intrusion porosity, which reflects the consistency of the microscopic and macroscopic, external and internal structures of MKGs.

- SLS and APG lead to higher porosity, a looser microstructure and more micro-defects for the clustered molecules due to their weaker adsorption.
- BAC, SE and STA lead to a relatively lower porosity and denser microstructure for better geopolymerization, resulting from the stronger adsorption.
- Based on the experimental results, the mechanisms underlying surfactant adsorption on the surface of metakaolin are proposed, and suggest that stronger adsorption leads to a denser microstructure.

JZUSA