### Research Advances

# New Discovery on Supercritical CO<sub>2</sub>-H<sub>2</sub>O Treated Coal: Pore Structure and Methane Adsorption

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# **Objective**

Nowadays, the governments and worldwide energy and environmental scientists have been focusing on  $\mathrm{CO}_2$  enhanced coalbed methane recovery ( $\mathrm{CO}_2\text{-ECBM}$ ) to reduce greenhouse gas emissions and to increment coalbed methane production. Previous researches have confirmed that  $\mathrm{CO}_2$  can react with minerals in coal seams to transform the permeability of coal. However, few studies have paid attention to the influence of the reaction of  $\mathrm{CO}_2$  with minerals on the pore distribution and methane adsorption of coals.

### **Methods**

This work conducted physical experiments to simulate the treatment between supercritical  $\rm CO_2\text{-}H_2O$  and coals in a high-pressure reactor under the conditions of 35°C and 9.0 MPa for 168 hours.

The morphologies of pores were imaged by a scanning

electron microscope, and the pore structures were determined using a mercury intrusion porosimetry. The amount of major elements was determined by X-ray fluorescence (XRF) analysis. In addition, methane isothermal adsorption on samples was measured using a Laboratory Isotherm Adsorption System on an IS-300 adsorption system.

#### Results

By comparing the physical properties of the raw and supercritical CO<sub>2</sub>-H<sub>2</sub>O treated coals, the results of mercury intrusion porosimetry show that the treatment with supercritical CO<sub>2</sub>-H<sub>2</sub>O enlarges the size and increases the amount of pores (Fig. 1). The scanning electron microscope images of raw and supercritical CO<sub>2</sub>-H<sub>2</sub>O treated coals indicate that the pore size enlarging and number increasing effects mainly occur on the surface of pores and fissures. The XRF analysis shows that the changes of pore structures are mostly caused by the

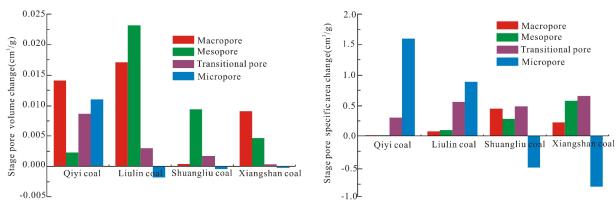


Fig. 1. Changes of pore distribution of supercritical CO<sub>2</sub>-H<sub>2</sub>O treated coals.

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dissolution of carbonate, sulfate and sulfide minerals, while the dissolution of minerals containing silicates and oxides have negligible effect.

Methane adsorption results show that the treatment of supercritical CO<sub>2</sub>-H<sub>2</sub>O and coal petrography change the methane adsorption ability on coal. Data statistical analysis of methane adsorption and pore structure suggests that the change in methane adsorption volume is proportional to the change in micropore specific surface area, further confirming that pore surfaces are the critical sites for methane adsorption (Fig. 2).

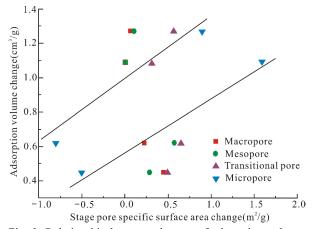


Fig. 2. Relationship between changes of adsorption volume and stage pore specific surface area.

#### **Conclusions**

- (1) The treatment of supercritical CO<sub>2</sub>-H<sub>2</sub>O and coal petrography has pore size enlarging and number increasing effects. In addition, supercritical CO<sub>2</sub>-H<sub>2</sub>O treatment with coal is influenced by the pores and fissures existing in the raw coals.
- (2) The changes of pore structures are mostly caused by the dissolution of carbonate, sulfate and sulfide minerals by the acid of supercritical CO<sub>2</sub>-H<sub>2</sub>O, and the dissolution of minerals containing silicates and oxides has a negligible effect on the changes of pore structures.
- (3) The treatment of supercritical CO<sub>2</sub>-H<sub>2</sub>O and coal petrography change the methane adsorption ability on coal, and there is a positive relationship between the changes in methane adsorption volume and micropore specific surface area.

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