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Effect of Induced Oxidation on the Mechanical Properties of Lignite by using Hydrogen Peroxide in the SCG Method

OAKM Badrul Alam¹, Noritaka Aramaki¹, Shuji Tamamura¹, Akio Ueno¹, Takuma Murakami¹, Satoshi Tamazawa¹, Yoshiaki Fujii², Katsuhiko Kaneko¹ (1. Horonobe Research Institute for the Subsurface Environment, Northern Advancement Center for Science & Technology, Saka-machi, Horonobe-cho, Teshio-gun, Hokkaido, 098-3221, Japan, 2. Rock Mechanics Laboratory, Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, North 13 West 8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan)

The lignite resource of the Tempoku coal field in Hokkaido, Japan is under consideration at our institute for production of biomethane from lignite using the subsurface cultivation and gasification method. The first stage of the method is important and involves dissolved organic carbon (DOC) formation by induced oxidation of lignite using H₂O₂ solution. The subsequent stages involve methanogen cultivation by the organic carbon as substrates to produce biomethane and the last stage is gas recovery. To obtain more insight into the important first stage, changes in mechanical properties of lignite by induced oxidation were investigated in this research. These properties are important from a ground control standpoint. Lignite core specimens 30 mm in diameter and 60 mm in height were immersed into a 1 wt.% H₂O₂ solution having a liquid/solid ratio of 5:1 to induce oxidation at atmospheric pressure and room temperature. P-wave velocity and density were measured before and after immersion. A series of uniaxial compression tests and the Brazilian tests were performed on both the induced-oxidized (H₂O₂-immersed) and unoxidized (H₂O₂-immersed) specimens. Intense oxidation was observed at most parts of the exposed surface of lignite specimens, whereas slight oxidation was expected to occur in inner parts, at the specified experimental condition. The induced oxidation of lignite produced DOC, resulting in a decrease of 1.79% and 0.54% in the average P-wave velocity and average density respectively. The P-wave velocity of lignite showed positive correlations with the strength, static tangent modulus, dynamic Young's modulus, and tensile strength regardless of the oxidation of lignite. Although the P-wave velocity and density decreased slightly in post DOC production by the induced oxidation, the damage of the lignite caused by H₂O₂ can be ignored during the design of SCG reactors at the given experimental condition.
1. Introduction

Conventional energy reserves, such as oil and natural gas, are being depleted due to increased worldwide energy demands. Unconventional energy sources such as oil sand, shale gas, and methane hydrate are being investigated; however, large coal reserves (World Energy Council, 2017) remain underutilized. These reserves could become a valuable source of energy through the development of resource engineering that might avoid challenging mining practices. The Horonobe Research Institute for the Subsurface Environment in Japan (Horonobe-RISE) is developing subsurface cultivation and gasification (SCG) methods for producing biomethane from lignite seams within the Tempoku coal field at Hokkaido, Japan. Tamamura et al. (2016) and Aramaki et al. (2015) found that a solution of H2O2 is useful for producing dissolved organic carbon (DOC) from lignite. The DOCs comprise several types of low-molecular-weight organic acids, and their production is the first stage in the SCG method. Subsequent stages are the methanogen cultivation utilizing the DOCs as substrates (to produce biomethane), and a final gas recovery. The mechanical properties of lignite are changed by its chemical reaction with H2O2. The strength and stiffness of lignite are important factors with regard to ground control, and the influence of cleat on the strength is also important. Many researchers have found the tensile strength of brittle materials to be an important component in the initiation of fractures (Haimson and Comer, 2003; Myer et al., 1992; Stacey 1981; Taponnier and Brace, 1976; Griffith, 1921).

In our research, we investigate the extent to which the mechanical properties of lignite are changed by a chemical reaction with H2O2—after the formation of DOC for methanogen cultivation (performed at atmospheric pressure and room temperature). A series of uniaxial compression and Brazilian tests were carried out on induced-oxidized (H2O2-immersed) and unoxidized (H2O-immersed) specimens.

2. Experiments

Lignite blocks were collected from a stream-side outcrop at the Tempoku coalfield, in Hokkaido, Japan (Fig. 1a). Core samples of 30 mm diameter (Fig. 1c) were prepared from the blocks, with the core ends cut and polished to flatness within 0.02 mm at a height of approximately 60 mm (for uniaxial compression tests) and a thickness of 11–30 mm (for Brazilian tests).

![Fig. 1 (a) Location of lignite deposit and core specimens; (b) streamside outcrop at Horonobe, Hokkaido, Japan; and (c) core specimens.](image)

The DOC and H2O2 concentrations of core immersed 1 wt.% H2O2 solution were measured at arbitrary time intervals along with the values of pH and Eh. The core specimens were immersed into the solution at a liquid:solid ratio of 5:1 at atmospheric pressure, and at a temperature of 25±1°C. Ultrasonic velocity measurement was performed by a Sonic Viewer-SX (Oyo corporation-Model 5251C) with a lower limit frequency of 10 kHz ± 2 kHz, an upper limit frequency of 1000 kHz ± 200 kHz, and a cut off frequency of 200 ± 40 kHz to measure the P-wave velocity of the lignite specimens. Temporal change in density and P-wave velocity were measured for saturated core specimens (30 mm in diameter and 60 mm in height) that had been immersed into the H2O2 solution (H2O2-immersed) or into H2O (H2O-immersed). The measurements were made at arbitrary time intervals.

A series of uniaxial compression and Brazilian tests were carried out by MTS 815 on both induced-oxidized (H2O2-immersed) and unoxidized (H2O-immersed) lignite specimens at a strain rate of 10^-5 s^-1 (0.036 mm/min). The applied load in the uniaxial compression test was parallel or perpendicular, whereas for Brazilian test it was perpendicular to face cleat. Uniaxial compressive strength tests of parallel and perpendicular to the face cleat was carried out to evaluate the effects of anisotropy on the strength of the lignite.
3. Results

3.1 Induced oxidation

DOC and H$_2$O$_2$ concentrations along with the pH and $E_h$ of a 1 wt.% H$_2$O$_2$ concentrated solution were measured, in which a core specimen was immersed at a liquid:solid ratio of 5:1, at atmospheric pressure and room temperature. The measurements were conducted at arbitrary time intervals until the H$_2$O$_2$ concentration became zero. As shown in Fig. 2a, H$_2$O$_2$ concentrations gradually decreased with time, reaching zero on the 21st day. The DOC concentration gradually increased with time (as the concentration of H$_2$O$_2$ decreased) reaching a value of 740 mg/L when the H$_2$O$_2$ concentration had become zero. The initial pH of 6.06 decreased with time, reaching a value of 2.83. The initial $E_h$ of 515 mV increased, and subsequently decreased to 440 mV on the 21st day (at the end of the chemical reaction, as seen in Fig. 2b). Intense oxidation was observed on the exposed surface of the lignite by the induced oxidation (in atmospheric pressure and room temperature at 25 ± 1 °C, Fig. 3a). This is also seen in naturally oxidized samples collected from an outcrop of the stream site (Figs. 3b).

![Fig. 2 Changes in the concentration of H$_2$O$_2$, dissolved organic carbon (DOC), and chemical indices of immersion solution with time. (a) H$_2$O$_2$ concentration and DOC; (b) pH and $E_h$.](image)

![Fig. 3 Induced-oxidized and naturally-oxidized lignite. (a) Induced oxidized core specimen by H$_2$O$_2$; (b) Naturally oxidized lignite from outcrop.](image)

3.2 Change in density and P-wave velocity

The change in density and P-wave velocity of immersed lignite core specimens (H$_2$O$_2$ and H$_2$O) were measured with time (Fig. 4). The density of the specimen immersed into H$_2$O$_2$ solution was 1.342 g/cm$^3$ before immersion, which slightly increased to 1.343 g/cm$^3$ within 2 days, and then gradually decreased to 1.338 g/cm$^3$ (Fig. 4a.)

![Fig. 4 Example of changes in (a) density (b) P-wave velocity as of induced oxidation of lignite (H$_2$O$_2$-immersed) with time.](image)
In water, the density was constant at 1.348 g/cm³. Before H₂O immersion, the P-wave velocity was 2318 m/s, which then decreased to 2280 m/s at the 10th day (a reduction of 1.64%, as seen in Fig. 4b). In H₂O, the velocity was the same at 2326 m/s.

Changes in P-wave velocity and density as a result of induced oxidation were observed for 12 specimens. The P-wave velocity range before oxidation equaled 2.22–2.38 km/s, with an average of 2.30 km/s. After oxidation, this range was 2.19–2.31 km/s with an average of 2.26 km/s (Fig. 5a). Before oxidation, the sample densities ranged from 1.304 to 1.354 g/cm³, with an average of 1.336 g/cm³. After oxidation, densities were 1.304–1.346 g/cm³, with an average of 1.329 g/cm³ (Fig. 5b). After H₂O₂ oxidation, the average P-wave velocity decrease equaled 1.79 ± 0.89% and the average density decrease equaled 0.54 ± 0.28% (Fig. 5c).

Fig. 5 Changes in P-wave velocity and density due to induced oxidation. (a) Average P-wave velocity; (b) Average density; (c) Decrease in P-wave velocity and density.

### 3.3 Uniaxial compressive strength

A series of uniaxial compression tests was performed on several unoxidized (H₂O-immersed) and induced-oxidized (H₂O₂-immersed) specimens. Axial cracking and spalling occurred (Fig. 6a) as coal is brittle due to its glassy, strained, and crosslinked molecular system (Larsen et al., 1997). Specimens having longer fractures before the test showed lower strength regardless of the H₂O₂ immersion (Fig. 6b). Unoxidized lignite showed an average uniaxial compressive strength (UCS) of 16.6 ± 9.46 MPa with an average P-wave velocity of 2.26 ± 0.04 km/s. Induced-oxidized lignite showed an average UCS of 20.4 ± 8.28 MPa with an average P-wave velocity of 2.29 ± 0.03 km/s (Figs. 7a and 7b). UCS showed a positive correlation with P-wave velocity (Fig. 7c), which could be expressed as follows:

\[
\text{UCS} = 177.2 \left( V_p - 2.172 \right) 
\]  

where UCS is in MPa, and \( V_p \) is the P-wave velocity in km/s.

Fig. 6 (a) Examples of specimens before and after compression; (b) Stress-strain curves of unoxidized (H₂O-immersed) and induced-oxidized (H₂O₂-immersed) specimens.
Moduli of elasticity

For unoxidized (H$_2$O-immersed) lignite, the average static tangent modulus (STM) equaled 2.50 ± 0.50 GPa, with the average dynamic Young’s modulus (DYM) equaling 3.24 ± 0.39 GPa (Figs. 8a and 9a). Induced-oxidized (H$_2$O$_2$-immersed) lignite displayed an average STM of 2.75 ± 0.23 GPa and an average DYM of 3.51 ± 0.22 GPa. STM and DYM values displayed positive correlations with P-wave velocity (Figs. 8b and 9b), which could be expressed as follows:

\[
STM = 7.22 \left( V_p - 1.902 \right) \tag{2}
\]
\[
DYM = 7.89 \left( V_p - 1.838 \right) \tag{3}
\]

where STM and DYM are in GPa, and $V_p$ is in km/s.

Anisotropy

Anisotropy in uniaxial compressive strength of the unoxidized (H$_2$O-immersed) and induced-oxidized (H$_2$O$_2$-immersed) lignite was evaluated using specimens for which direction was in parallel or perpendicular to the face cleat. In case of cores parallel to the face cleat, unoxidized lignite displayed an average UCS of 26.8 MPa with an average P-wave velocity of 2.30 km/s. Induced-oxidized lignite displayed an average UCS of 28.9 MPa (Fig. 10a).
with an average P-wave velocity of 2.30 km/s (Fig. 10b). For cores perpendicular to the face cleat, unoxidized lignite displayed an average UCS of 10.5 MPa with an average P-wave velocity of 2.24 km/s, and induced-oxidized lignite displayed an average UCS of 13.5 MPa with an average P-wave velocity of 2.27 km/s. Longer axial fractures in parallel to the face cleat, and shorter axial fractures perpendicular to the face cleat, were observed after compression (Fig. 11).

Fig. 10: Strength and P-wave velocity of unoxidized (H2O-immersed) and induced-oxidized (H2O2-immersed) specimens, prepared in parallel or perpendicular to the face cleat.

Fig. 11 Fractures (parallel or perpendicular to the face cleat) after compression tests of unoxidized (H2O-immersed) and induced-oxidized (H2O2-immersed) specimens.

3.6 Tensile strength

A series of Brazilian tests was carried out on disc specimens of both unoxidized (H2O-immersed) and induced-oxidized (H2O2-immersed) specimens. The load was applied perpendicular to the face cleat, where the main fracture formed in the loading direction (Fig. 12b). The tensile strength of unoxidized lignite ranged between 0.35–2.41 MPa with a P-wave velocity of 1.62–2.45 km/s. For induced-oxidized lignite tensile strength ranged between 1.15–1.87 MPa with P-wave velocity of 1.81–2.06 km/s. Tensile strength displayed a positive correlation with P-wave velocity (Fig. 12a), which could be expressed as follows:

\[
\sigma_T = 1.51V_p - 1.143
\]  

where \(\sigma_T\) is in MPa, and \(V_p\) is the P-wave velocity in km/s.

4. Discussion

In SCG method, the reaction of H2O2 solution and lignite produces low molecular weight organic acids as substrates for methanogen cultivation and the production of biomethane. Lignite core specimens were immersed into 1 wt.% H2O2 solution using a liquid:solid ratio of 5:1, at atmospheric pressure, and a temperature of 25 ± 1 °C. The lignite was oxidized by immersion in solution. This produced DOC that increased with time, and with a concurrent decrease in H2O2 concentration and pH (Fig. 2). The reaction mechanism is described by Tamamura et al. (2016).

The density of H2O2-immersed lignite cores decreased with time, due to the chemical reaction, and the P-wave velocity decreased at certain days (Fig. 4)—whereas the properties were constant in water (H2O-immersed). The decreases were because of formation of microcracks due to swelling and grain boundary changes due to leaching (Alam et al. 2016) as lignite-carbon is decomposed by the chemical reaction (Tamamura et al. 2016) and coal is brittle due to glassy, strained and crosslinked molecular system (Larsen et al., 1997). The fracture patterns reflect the brittleness of the lignite (Fig. 11).
Higher uniaxial compressive strength was observed for samples with a higher P-wave velocity, and vice-versa (Fig. 6), since P-wave velocity is inversely proportional to the number of fractures (Chang et al. (2006); Castagna et al., 1993; Leucci and Giorgi, 2005). The P-wave velocity displayed a positive correlation with strength, stiffness, and tensile strength (Figs. 7, 8, 9, and 12 and as described by Eqs. 1, 2, 3, and 4) regardless of the oxidation of the lignite. P-wave velocities slightly decreased (1.79 ± 0.89%) by the chemical reaction (Fig. 5). Intense oxidation (where the color changed from black to yellowish-brown) was observed at most parts of the exposed surface of the core lignite specimen (Fig. 3) because of the direct contact with the solution. It should be noted that these observations are also observed in naturally oxidized lignite. Only slight oxidation might have occurred in the inner parts, with almost no change in visual color at the experimental condition. Therefore, the effect of the chemical reaction on the mechanical properties of lignite can be ignored during reactor design for SCG. The influences of fracture on the mechanical properties of lignite were supposed to be stronger than those induced by experimental oxidation. Why specimens with longer fractures in parallel to the face cleat were stronger than those with shorter fractures perpendicular to the face cleat (after compression, Fig. 10) should be investigated in the future.

5. Conclusions

Induced oxidation of lignite produces dissolved organic carbons (DOC), resulting in an average P-wave velocity decrease of 1.79 ± 0.89% and an average density decrease of 0.54 ± 0.28%. Intense oxidation was observed at most parts of the exposed surface of lignite specimens, whereas only slight oxidation might occur at the inner portions. P-wave velocities showed a positive correlation to the strength, static tangent modulus, dynamic Young's modulus, and tensile strength of lignite samples regardless of oxidation. The influences of fracture on the mechanical properties of the lignite were supposed to be stronger than that by the induced oxidation under the experimental condition. The damage to lignite by H₂O₂ can be ignored when designing SCG reactors (for the experimental conditions), as the P-wave velocity slightly decreased while producing DOC, and the effects on the mechanical properties by induced oxidation is not obvious. The effects on the mechanical properties by a chemical reaction under confining pressure and pore pressure will be investigated in the future.

References

A.A. Griffith: Philos. Trans. R. Soc. Lond. 221A (1921), 163-198.