Abstract

Oxidation of lignite with H₂O₂ solution to produce dissolved organic carbon (DOC) for generating biomethane by methanogen cultivation is an important stage of subsurface cultivation and gasification methods. To obtain more insights into this process, changes of lignite mechanical properties were investigated after its oxidation to produce DOC. Core specimens 30 mm in diameter and 60 mm in height were immersed into 1 wt.% H₂O₂ to achieve a liquid-to-solid ratio of 5:1. Values of pH and $E_h$ were measured at arbitrary time intervals together with concentrations of H₂O₂ and DOC. P-wave velocity and density were measured before and after immersion. A series of uniaxial compression tests was carried out for both chemically reacted (H₂O₂-immersed) and non-reacted (H₂O-immersed) specimens. The concentration of DOC, which is the substrate of methanogen cultivation, increased due to the oxidation of lignite at decreased pH by H₂O₂. P-wave velocity showed positive correlations with strength, static tangent modulus, and dynamic Young’s modulus. The average P-wave velocity ($V_p$) decreased by about 1.5% from its initial value due to the average density decrease of 0.6% resulting from the above chemical reaction. This decrease was associated with microcracking caused by swelling and grain boundary change due to leaching. The influence of the above chemical reaction on the mechanical properties of lignite is small, despite the formation of DOC to produce biogenic methane.

Keywords: Induced oxidation, Lignite, P-wave velocity, Uniaxial compression test, Mechanical properties

1. Introduction

Lignite seams of the Tenpoku coal field in Hokkaido, Japan, are considered to be used for biomethane production by subsurface cultivation and gasification (SCG, Aramaki et al., 2015; Tamamura et al., 2016), with the formation of dissolved organic carbon (DOC) from lignite by induced oxidation using hydrogen peroxide (H₂O₂) being the first stage of this method. Subsequent stages feature methanogen cultivation to produce biomethane, using the DOC as a substrate, and the last stage corresponds to gas recovery. The formation of DOC for methanogen cultivation via chemical reactions can change the mechanical properties of lignite, which is the subject of this research.

2. Experiments

A lignite block was collected from a streamside outcrop at Horonobe, Hokkaido, Japan (Fig. 1a). 30-mm-diameter core specimens were prepared perpendicularly to the face cleat of the block. Next, the core ends were cut and polished to achieve a parallelism of 0.01° at a height of almost 60 mm. The obtained specimens were immersed into a 1 wt.% solution of H₂O₂ having a liquid-to-solid ratio of 5:1 (Fig. 1b). Values of pH and $E_b$ were measured together with H₂O₂ and DOC concentrations at arbitrary time intervals. P-wave velocity and density of core specimens were measured before and after immersion.

P-wave velocity was measured by a Sonic Viewer-SX instrument (Oyo Corporation, Model 5251C) having a frequency band with a lower limit of 10 ± 2 kHz, an upper limit of 1000 ± 200 kHz, and a cut-off frequency of 200 ± 40 kHz. A series of uniaxial compression tests was carried out on
both chemically reacted (H₂O₂-immersed) and non-reacted (H₂O-immersed) specimens by MTS 815 at a strain rate of 10⁻⁵ s⁻¹ (0.036 mm/min).

Fig. 1. Location of lignite deposit and immersion of core specimen. (a) Streamside outcrop at Horonobe, Hokkaido, Japan; (b) Immersion of lignite specimen

3. Results

3.1 Chemical indices and concentrations of dissolved oxygen, organic carbon and H₂O₂

The 1 wt.% H₂O₂ concentration at the liquid and solid ratio of 5:1 gradually decreased with time and reached to zero on 21st day (Fig. 2a). The initial dissolved oxygen (DO) concentration (8.36 mg/L) in solution increased to 47.8 mg/L and then decreased with time, subsequently reaching a minimum of 6.37 mg/L on the 21st day (Fig. 2b) during the reaction. The DOC concentration gradually increased with time as the concentration of H₂O₂ decreased, reaching a value of 740 mg/L when all H₂O₂ was consumed. The initial pH of 6.06 decreased with time and reached a value of 2.83, whereas the initial $E_h$ of 515 mV increased and subsequently decreased to 440 mV on the 21st day (Fig. 2c).

Fig. 2. Temporal changes in the concentration of H₂O₂, dissolved organic carbon (DOC), and chemical indices. (a) H₂O₂ concentration and DOC; (b) Dissolved oxygen (DO) and DOC; (c) pH and $E_h$

3.2 Changes in P-wave velocity and density

Changes in P-wave velocity and density were examined for eight specimens. The P-wave velocity range before oxidation equaled 2.26–2.38 km/s with an average of 2.31 km/s. After oxidation, this range equaled 2.20–2.31 km/s with an average of 2.26 km/s (Fig. 3a). Before oxidation, the sample density ranged from 1.304 to 1.354 g/cm³ with an average of 1.335 g/cm³, equaling 1.304–1.346 g/cm³ with an average of 1.328 g/cm³ after oxidation (Fig. 3b). After oxidation of lignite induced by 1 wt.% H₂O₂, the average P-wave velocity decrease equaled 1.96 ± 1.07% and the average density decrease equaled 0.53 ± 0.33% (Fig. 3c). Thus, the slight decrease of P-wave velocity was caused by
the decrease of density as a result of chemical oxidation. This density decrease was associated with microcracking caused by swelling and grain boundary change due to leaching (Alam et al., 2016).

### 3.3 Uniaxial compressive strength (UCS)

A series of uniaxial compression tests was performed for seven non-reacted (H₂O-immersed) specimens and eight reacted (H₂O₂-immersed) ones. Non-reacted (H₂O-immersed) lignite showed an average UCS of 16.6 MPa with an average P-wave velocity of 2.26 km/s. Reacted (H₂O₂-immersed) lignite showed an average UCS of 20.4 MPa with an average P-wave velocity of 2.29 km/s (Figs. 4a and 4b).

UCS showed a positive correlation with P-wave velocity, which could be expressed as follows (Fig. 4c).

\[
\text{UCS} = 139(V_p - 2.159)
\]  

(1)

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

### 3.4 Static and dynamic moduli of elasticity

For non-reacted (H₂O-immersed) lignite, the average static tangent modulus (STM) equaled 2.50 ± 0.50 GPa, and the average dynamic Young’s modulus (DYM) equaled 3.24 ± 0.39 GPa (Figs. 5a and 6a). Reacted (H₂O₂-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. 5b and 6b), which could be expressed as follows.

\[
\text{STM} = 9.9(V_p - 1.976)
\]  

(2)

\[
\text{DYM} = 8.7(V_p - 1.862)
\]  

(3)
where STM and DYM are in GPa and \( V_p \) is in km/s.

Fig. 5. Static tangent modulus and P-wave velocity of lignite immersed in water and hydrogen peroxide. (a) Average static tangent modulus; (b) P-wave velocity and static tangent modulus

Fig. 6. Dynamic Young's modulus and P-wave velocity of lignite immersed in water and hydrogen peroxide. (a) Average dynamic Young's modulus; (b) P-wave velocity and dynamic Young's modulus

3. Conclusions

\( \text{H}_2\text{O}_2 \) solution induces oxidation of lignite to produce DOC, resulting in an average P-wave velocity decrease of 1.96% and an average density decrease of 0.53%. P-wave velocity showed positive correlations with the strength, static tangent modulus, and dynamic Young's modulus of samples. The influence of \( \text{H}_2\text{O}_2 \)-induced oxidation (at a liquid-to-solid ratio of 5:1) on mechanical properties is small, despite the formation of DOC for methanogen cultivation to produce biomethane from lignite.

References