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The desulphurization process of bitumen using ultrasound

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1. Introduction

The two largest oil sand deposits are located in Canada (Alberta) and Venezuela (Orinoco). Oil sand consists of a mixture of water, fine solid, sand and bitumen (heavy oil). Recently, bitumen becomes an important source to generate energy as fuel. In order to use bitumen as a fuel source, the main industrial processes recover bitumen from oil sand using hot water and steam. Previous study has been reported that bitumen was successfully recovered from oil sand and then collected using ultrasound irradiation and hydrogen peroxide solution[1].

Alberta bitumen includes 4.6±0.5 wt% of sulphur. Based on the analysis of X-ray absorption near-edge structure spectroscopy (XANES), 62% is aromatic and 38% is aliphatic sulphur[3,4]. Due to the high percentage of sulphur content, the upgrading process of crude bitumen into a synthetic crude oil produces sulphur oxide (SO_x) that causes acid rain and environmental pollution. Hence, bitumen requires desulphurization process to meet the sulphur emission regulation. Therefore, the aim of this work is to remove sulphur from bitumen during the recovery process from oil sand. Many studies has been carried out on focusing desulphurization of crude oil. Oxidative desulphurization is the current method for the desulphurization technology because it can be carried out under mild conditions such as low temperature and pressure. Hydrogen peroxide has been used widely as an oxidizing reagent because it has strong oxidant and low cost. Aromatic sulphur is dominant in bitumen, hence it is difficult to remove the sulphur because it just only oxidized the sulphur in bitumen into sulfone (S-O-S). So that, alkali treatment is needed to remove the oxidized sulphur. In this study, we focused on the removing of sulphur from bitumen using oxidation process followed by alkali treatment. Ultrasound irradiation was used in this work to improve the removal ratio of sulphur from bitumen under mild conditions. The analysis of desulphurized amount from bitumen, we used X-ray fluorescence spectrometer (XRF) to determine the intensity of sulphur in bitumen.

2. Experimental method

Solutions (20 ml) containing different concentrations of hydrogen peroxide (H_2O_2; 0.03, 0.3, 3, 30 wt. %) were prepared in a beaker. To increase the surface reaction between bitumen and solution, bitumen (1 g) was heated to reduce the viscosity and poured slowly onto the surface of the solution. Bitumen in the beaker was irradiated by ultrasound for 10 min or allowed to react without ultrasound irradiation for 10 to 180 min at room temperature. A saturated solution (20 ml) of sodium hydroxide (NaOH) was prepared and poured onto the solution. The solution was irradiated by ultrasound for 10 min or allowed to react without ultrasound irradiation for 10 to 180 min at room temperature. All the reagents were analytical grade and purchased from Wako corp. (Japan). Ultrasound irradiation was carried out at a frequency of 28 kHz. After these processes, the treated bitumen was collected, dried and weighed.

The intensity of elements (Sulphur (S), Vanadium (V), Nickel (Ni)) in the bitumen was analyzed using an energy dispersive X-ray fluorescence spectrometer (XRF; Shimadzu EDX-7000) with vacuum measurement unit and a 5mm of collimator. Experiments at individual conditions were conducted twice.

3. Result and discussion

The intensity of S, V and Ni in raw bitumen is shown in **Table 1**. The result of these experiments will focus on the change of the intensity of S, V and Ni without considering the change of any other elements in the raw bitumen.

Fig. 1 show the effect of oxidation (H_2O_2) reaction time and **Fig. 2** show the effect of desulphurization (NaOH) reaction time process on sulphur intensity without using ultrasound irradiation. In each process, the sulphur intensity in the bitumen is almost same after the irradiation of 10 min. These results indicate that it is sufficiently for the sulphur in bitumen to oxidize into sulfone and remove it into the solution as the form of Na_2SO_3 within 20 min. (H_2O_2 reaction: 10 min; NaOH reaction: 10 min)

Fig. 3 shows the change of the intensity of sulphur in bitumen treated by the different concentrations of H_2O_2 for 10 min followed by 10 min of desulphurization process without using ultrasound irradiation. The higher the concentration of H_2O_2, the sulphur intensity in bitumen became

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Table 1. The intensities of elements in bitumen.

Element	Intensity [cps/μA]
S	70.41
V	1.42
Ni	1.18

lower. From this result, H_2O_2 (30 wt. %) is needed to oxidize sulphur to sulfone sufficiently before it is being removed by the desulphurization process.

In order to study the effect of ultrasound irradiation on the removal amount of sulphur in bitumen, we investigated the intensity of sulphur treated with the presence of ultrasound of each H_2O_2 and NaOH process (**Fig. 4**). The usage of ultrasound irradiation to the oxidation process (experimental conditions 1 and 2) showed that the intensity of sulphur for these experiments are almost the same with the experiment that treated without using ultrasound irradiation (experiment condition 4). This is because the usage of H_2O_2 under ultrasound irradiation can cause the floatation of bitumen and formation of oil-in-water emulsion. Zhang et al. reported that H_2O_2 is a kind of water soluble oxidant, it will form to oil-in-water emulsion if being irradiated with ultrasound. So that, H_2O_2 requires a long time to mix with the oil sufficiently as to increase the oxidation rate of sulphur[5]. Besides, the usage of ultrasound irradiation to the desulphurization process only (experiment condition 3) showed that the reduction of the intensity of sulphur increased a little. Stirring force from the ultrasound irradiation promotes the surface reaction between oxidized bitumen and NaOH solution becomes greater. Thus, the removal rate of sulphur from bitumen into the solution increased. In the future work, we are looking forward optimal conditions for removing sulphur in bitumen.

4. Conclusion

The two steps of oxidizing and desulphurization process are needed for the removal of sulphur in bitumen. After treated with H_2O_2 (10min) and NaOH (10 min) solution, the intensity of sulphur in bitumen decreased. Additionally, the usage of ultrasound irradiation under desulphurization step improved the removal rate of sulphur from bitumen.

References

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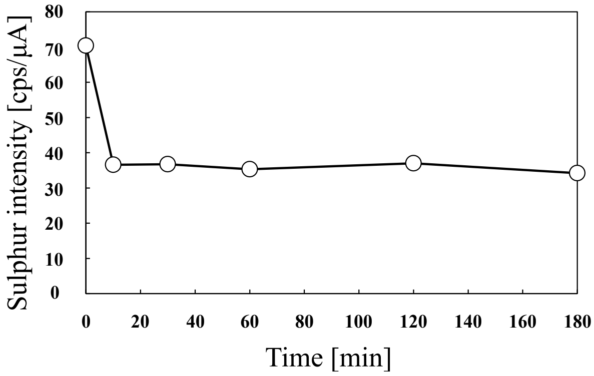

Fig. 1. Change of sulphur intensity by H_2O_2 (30 wt. % reaction time. (NaOH reaction time: 10 min)

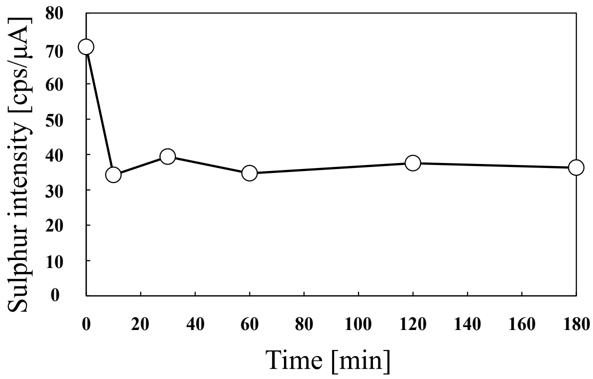

Fig. 2. Change of sulphur intensity by NaOH reaction time. (H_2O_2 reaction time: 10 min)

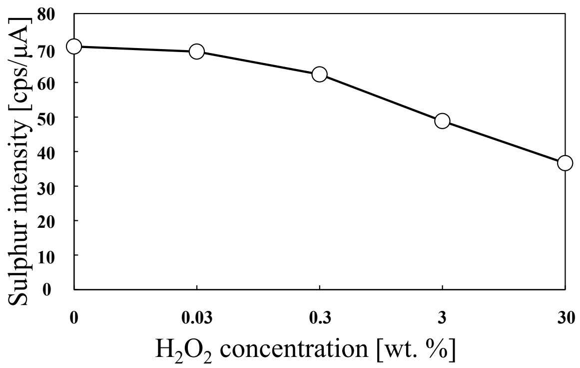

Fig. 3. The effect of H_2O_2 concentration on the desulphurization of bitumen

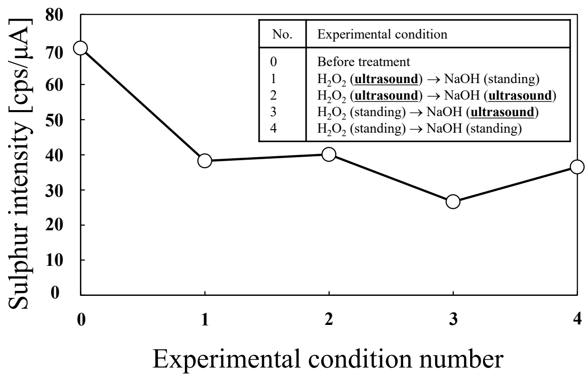

Fig. 4. Sulphur intensity of bitumen after treated with H_2O_2 (30 wt. %) and NaOH with/without ultrasound irradiation