# Separation and recovery of bitumen from oil sand using CO<sub>2</sub>-absorbed amine solution and ultrasound

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## 1. Introduction

The world energy demand is increasing by 1.0 % per year due to the development of industries and the expansion of popularity.<sup>1)</sup> However, recoverable reserves of conventional energy such as natural gas and petroleum have decreased annually. Thus, the diversification of energy sources is necessary to prepare for the unstable supply and the soaring price of conventional energy sources.

Bitumen, a kind of extra heavy oil, was extracted from oil sand mainly in Canada and Venezuela. The reserves of bitumen over the world are approximately 300 billion barrels, which is comparable to conventional oil resources, making bitumen attract attention as an alternative energy resource.<sup>2)</sup> Open-pit mining is used for oil sand near the surface (<75 m), and the daily production in Canada was 193,185 m<sup>3</sup> in 2018. <sup>3)</sup> However, since oil sand is a mixture of bitumen (10-15 %), water, and sand, it is necessary to separate and recover bitumen from oil sand efficiently for further utilization. The main industrial process uses high pH (>8.5) and temperature (<100 °C) conditions to promote bitumen liberation from sand.<sup>4)</sup> Hot water could decrease the viscosity of bitumen and make it easy to flow, whereas alkaline conditions could decrease the interfacial tension between bitumen and water, resulting in an easier separation of bitumen and sand. After bitumen liberation, aeration is required to collect bitumen droplets in the suspended slurry since bitumen has a similar density to that of water under 100 °C, which is used as the separation medium. The use of air bubbles to bring bitumen droplets onto the solution surface was considered an effective flotation method. However, there are two critical problems remaining to be solved which decrease the bitumen recovery in the conventional bitumen flotation method. Firstly, since bitumen droplets get ionization and become more hydrophilic in alkaline conditions, it is difficult for hydrophobic air bubbles to attach to bitumen droplets. Thus, a high pH condition that is favorable for bitumen liberation is not suitable for bitumen droplet flotation. the conventional aeration method Secondly, introduces bubbles into the slurry, since bitumen has a density similar to that of water under 100 °C, the inertia or kinetic energy of bitumen needed to induce effective collision with bubbles is anticipated to be

too low for the attachment.<sup>4)</sup>

To solve these two problems, this study focuses on the utilization of the CO<sub>2</sub>-absorbed amine solution combined with ultrasound. Amine solutions, which are widely used as a CO<sub>2</sub> absorbent in CO<sub>2</sub> absorption process in the carbon dioxide capture and storage (CCS) technology, can absorb CO<sub>2</sub> at low temperatures and desorb CO<sub>2</sub> at high temperatures recyclable. When CO<sub>2</sub> is desorbed from CO<sub>2</sub>-loaded amine solution, gas nucleation occurs evenly in the solution. This condition is considered suitable for the collision between CO<sub>2</sub> bubbles and bitumen droplets when CO<sub>2</sub>-absorbed amine solution is used for bitumen flotation. Meanwhile, since CO<sub>2</sub> can form HCO3<sup>-</sup> with OH<sup>-</sup> on the bubble surface under alkaline conditions, the ionization degree of bitumen surface would be mitigated by  $H^+$  from  $HCO_3^-$  and become less hydrophilic, which promotes the attachment of bitumen droplets and bubbles even under alkaline conditions.<sup>5)</sup> Moreover, the usage of ultrasound irradiation for oil sand could help bitumen separation from sand in a hot alkaline solution due to physical effects. Thus, a high bitumen purity and recovery ratio was considered to be achieved with all these beneficial conditions provided by the proposed method in this study for bitumen recovery.

## 2. Experimental

For CO<sub>2</sub> absorption, monoethanolamine (MEA, Wako, 99 wt. %), which is widely used in the CCS process, was selected in this study. The pure CO<sub>2</sub> gas (99.99 vol. %, Japan liquid carbon) was injected into 100 mL of 5 M MEA aqueous solution at the flow rate of 100 mL/min at 40 °C until the CO<sub>2</sub> was statured in the solution. During the absorption, a cooling tube with 4 °C circulation water was set at the outlet to prevent solution evaporation. Since MEA is a first-class amine, the considerable reaction of CO<sub>2</sub> absorption in MEA solution is shown below.  $2RNH_2 + CO_2 \rightarrow RNH_3^+ + RNHCOO^-$  (1) (R: C<sub>2</sub>H<sub>5</sub>O)

The weight change of the solution calculated the CO2 absorption amount before and after CO<sub>2</sub> absorption. The theoretic CO<sub>2</sub> absorption amount for 5 M MEA solution is 110 g/L calculated from formula (1). The CO<sub>2</sub>-absorbed MEA solution was denoted as MEA-CO<sub>2</sub> solution afterward.

For bitumen recovery, oil sand from Canada (bitumen content 13.4 wt. %, diameter < 5 mm) was used in this study. About 3 g of oil sand was weighed and settled in a 100 mL jacket beaker without further

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treatment. 50 mL of MEA-CO<sub>2</sub> solution was then added into the beaker and was heated to 95 °C for 20 min by a hot water circulating machine. Desorbed CO<sub>2</sub> was collected into a gas bag, and the gas volume was measured. A same cooling tube was also used during the treatment. The CO<sub>2</sub> desorption ratio was calculated by the following formula:

 $CO_2$  desorption ratio = Wd (g/L)/ Wa (g/L) (2) Wd:  $CO_2$  desorption weight per liter solution, Wa:  $CO_2$  absorption weight per liter solution

The ultrasound (28 kHz, 200 W) with strong physical effects was chosen to irradiate the oil sand at 95 °C. After the treatment, the upper layer matter and bottom layer matter were collected and dried by vacuum dryer at 55 °C for 24 h. The weights of both matters were measured, and the following formula calculated the yield of each component:

Upper layer yield =  $Wu(g)/Wo(g) \times 100\%$  (3) Bottom layer yield =  $Ws(g)/Wo(g) \times 100\%$  (4) Wu: weight of upper layer matter, Ws: weight of bottom layer matter, Wo: weight of oil sand used

The purity of bitumen contained in the upper layer matter was measured by thermogravimetry analysis (DTG-60H, Shimadzu) with heating the samples to 800 °C under  $O_2$  atmosphere. Finally, the bitumen recovery ratio was calculated by the following formula:

Bitumen recovery ratio = Wb(g)/Wbo(g) (5) Wb: weight of bitumen in the upper layer, Wbo: weight of bitumen in oil sand

#### 3. Results and discussion

For  $CO_2$  absorption results, the  $CO_2$  absorption amount was 134 g/L, which is more than the theoretical value of 110 g/L. This could be explained by part of  $CO_2$  being absorbed by the following formula in this study:

 $RNH_2 + CO_2 + H_2O \rightarrow RNH_3^+ + HCO_3^-$  (6) HCO<sub>3</sub><sup>-</sup> was beneficial for mitigating ionized bitumen surface.<sup>5)</sup> The pH value of MEA-CO<sub>2</sub> solution was around 8, which was an alkaline condition and is suitable for bitumen liberation.

For bitumen recovery results, the yields of the upper layer and bottom layer matter under different treatment conditions are shown in Fig. 1. Total yield of each condition was nearly 100 %, indicating that the proposed treatment did not volatilize or dissolve the sample. It was noticed that with ultrasound treatment, the upper layer yield has increased by 3.7 %. Fig. 2 shows the bitumen recovery ratio, purity, and CO<sub>2</sub> desorption ratio under each condition. Only by heating, the bitumen recovery ratio reached 0.31, and the bitumen purity reached 0.59. When using 28 kHz ultrasound to assist the bitumen recovery, the bitumen recovery ratio and purity both increased to 0.55 and 0.67, indicating that 28 kHz ultrasound promoted the separation of bitumen and sand, so that more bitumen droplets could attach to the desorbed  $CO_2$  to float. As for the  $CO_2$  desorption ratio, ultrasound treatment showed a higher value compared to heating, indicating that the  $CO_2$  desorption ratio was also increased by ultrasound.

### 4. Conclusions

This study proposed a novel method for bitumen recovery by combining  $CO_2$  desorption from amine solution and ultrasound irradiation. The results gained from this study showed a possibility of utilizing the  $CO_2$  desorption process in CCS with ultrasound for a more efficient bitumen recovery technology from oil sand.

#### References

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Fig. 1 Upper layer and bottom layer yield at different conditions.



Fig. 2 Bitumen recovery ratio, purity and CO<sub>2</sub> desorption ratio under different conditions.