

# The role of minerals in hydrogen sulfide generation during steam-assisted recovery of heavy oil

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**ABSTRACT:** Heavy oil is recovered from reservoirs using steam-assisted technology, which can lead to H<sub>2</sub>S generation if the oil is relatively sulfur rich. We have used laboratory aquathermolysis to simulate the steam-assisted gravity drainage process and have compared free heavy oil with that contained within the mineral matrix. The presence of a mineral matrix was found to affect the amount of H<sub>2</sub>S produced and the chemical properties of the oil generated. Our findings show that H<sub>2</sub>S production is initiated by the presence of naturally occurring minerals at specific temperatures and pressures, and production techniques which avoid these conditions will minimize H<sub>2</sub>S production.

Keywords: aquathermolysis, hydrogen sulfide, mineral effects, SAGD

## 1. Introduction

Heavy oil is generated by the degradation of conventional oil. The in-situ recovery of heavy oil from reservoirs utilizes the ability of steam to transfer heat to the oil thereby reducing its viscosity. Steam-assisted recovery, however, does not only involve the transfer of heat. Chemical reactions are promoted by the steam and hot water and the umbrella term aquathermolysis is used to describe the myriad reactions that may take place.<sup>1,2</sup> Fortunately, aquathermolysis can be reproduced in the laboratory and the reaction products quantitatively determined. Laboratory aquathermolysis has already provided an insight into the chemical effects of steam-assisted recovery including gas generation and in situ refining.<sup>3,4</sup>

One important area, which is of great interest, particularly for sulfur-rich heavy oils, is the effect of the reservoir mineral matrix on any reactions which occur.<sup>5</sup> Published work has demonstrated the importance of the mineral-organic interface in hydrocarbon partition during steam-assisted recovery.<sup>6</sup> Mineral matrices have been associated with a reduction of viscosity during aquathermolysis.<sup>7,8</sup> Previous work has associated mineral matrices with the production of CO<sub>2</sub> but not H<sub>2</sub>S at 240 °C.<sup>9</sup> A lone report has been made on an increase in H<sub>2</sub>S production due to the mineral matrix at 280 °C.<sup>10</sup>

In this study, we have used laboratory aquathermolysis to simulate the gases, liquids and solids that are produced during steam-assisted recovery of a sulfur-rich heavy oil. We have focused on differences produced by the presence and absence of a mineral matrix. A crude oil and a corresponding oil-containing core were subjected to the same aquathermolysis procedure and the products quantitatively compared. Our data reveal the effects of mineral matrix on steam-assisted chemical reactions and highlight the importance of geological and geochemical context for the recovery of heavy oil.

## **2. Materials and Methods**

**2.1 Samples:** For the investigation of mineral matrix effects, a typical core (hereafter “core”) and crude oil isolated from that core (hereafter “crude”) from Alaska was used. The core-crude pair is from a reservoir with a temperature range of 18-23°C<sup>11</sup>. The core is 8.5 cm in diameter and encased in plastic. Samples for aquathermolysis were removed from the frozen core using a spatula. The crude oil contained ca. 1.5% S, had a viscosity of 39.43 Pa \* s at 25°C, API gravity of 12.90 and when fractionated had the following characteristics: saturates = 35%; aromatics = 53%; resins = 4%; asphaltenes = 8%. The solvent-extract (93:7 dichloromethane:methanol (DCM:MeOH)) yield of the core was 5.7% weight percent. The solvent extract had the following characteristics: saturates= 43%; aromatics = 7%; resins = 47%; asphaltenes = 3%. The composition of the core mineral matrix was determined by X-ray diffraction using a Panalytical X’Pert Pro Alpha-1 system, with phase quantification performed by Rietveld refinement using the X’Pert software to be 86% quartz, 7% kaolinite, 4% feldspar, 2% illite and 1% ferroan clinocllore. The initial organic sulfur content of the asphaltene fraction of the core and crude samples was characterized using pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) as described below. Previous work on sulfur-rich heavy oil has revealed that the major host of organic sulfur is the asphaltene fraction <sup>4</sup>, so this fraction is

most important for characterizing the initial organic sulfur present. The pyrolyzate of the asphaltene fraction of the unaltered crude oil was found to produce C<sub>1</sub> and C<sub>2</sub> benzothiophenes. The pyrolyzate of the asphaltene fraction of the unaltered core extracted with DCM:MeOH (93:7) contained C<sub>1</sub>- and C<sub>2</sub>-benzothiophenes, dibenzothiophene, and C<sub>1</sub>- and C<sub>2</sub>-dibenzothiophenes.

**2.2 Aquathermolysis:** Approximately 50 g of sample (material removed from the frozen core with a spatula) or 5 ml (crude) were added to a high pressure and temperature reactor made of Hastelloy C267, which has previously been shown to have the least catalytic effect<sup>12</sup>. (Model 4740, Parr Instruments) Enough water was added to ensure the sample was submerged in liquid water throughout the experiment. The remaining headspace within the reactor was purged with nitrogen and the reactor was sealed and placed in an oven. Pressure was monitored throughout the experiment using a dedicated pressure gauge attached to the reactor. Aquathermolysis experiments were performed on samples at 150 °C (<690 kPa; <100 psig), 175 °C (<690 kPa; <100 psig), 200 °C (1030 kPa; 150 psig), 225 °C (2760 kPa; 400 psig), 250 °C (4140 kPa; 600 psig), 275 °C (5520 kPa; 800 psig), 300 °C (8620 kPa; 1250 psig) and 325 °C (12070 kPa; 1750 psig). Each experiment ran for 24 hours. The experimental approach, including duration, has been used previously to successfully simulate steam-assisted gravity drainage, which can involve temperatures of up to 250°C, in heavy oil sand reservoirs<sup>3,13-15</sup>.

**2.3 Post experiment sampling:** Once the experiment was complete and the reactor cooled to 25°C, over approximately 12h, gases were extracted from the reactor headspace by releasing a needle gauge and allowing the gas to flow into a Tedlar sample bag. Gas was collected from the bag for analysis using a gas-tight syringe. The gas quantities in the syringe were scaled to reveal the total quantities in the reactor headspace. Following gas sampling, the reactor was opened and any oil floating on the surface of the water (the flotante) was transferred to a test tube using a polytetrafluoroethylene (PTFE)-coated spatula. Heavy oil which sinks in the water

and rests above the oil-covered mineral layer in the reactor (the sinkate) was recovered using a PTFE-coated spatula once the water had been pipetted into a beaker. The residual oil (the residue) was extracted with DCM/MeOH by sonication for 15 minutes, followed by centrifugation and collection of the supernatant as described above. Any material remaining in the vessel was removed with DCM/MeOH and any material resistant to solvent extraction (cake) was removed using mechanical force to ensure no contamination of subsequent experiments could occur.

**2.4 Fractionation and quantitative analysis:** Samples of the flotates, sinkates and DCM/MeOH-soluble fractions (residues) were further separated into maltene (saturate, aromatic, resin) and asphaltene fractions) by silica gel column chromatography. Asphaltenes were precipitated from the sample using an excess of *n*-heptane with a 12 hour settling time; further separation was achieved by centrifugation. The precipitation process was repeated three times in total, and the products combined.

**2.5 Gas Chromatography-Flame Photometric Detection:** Gases produced were analyzed using a Perkin Elmer AutoSystemXL gas chromatograph-flame photometric detector (GC-FPD). Samples (500  $\mu$ l) were injected at a 10:1 split with the injector at 220 °C. Separation was performed on a J&W GS-Q column (30 m length, 0.32 mm internal diameter). Helium at constant column flow rate of 2 ml min<sup>-1</sup> was used as the carrier gas. The GC oven temperature was held for 4 min at 35 °C and then programmed at 10 °C min<sup>-1</sup> to 220 °C, and held for 6 min. The FPD was held at 300 °C with a hydrogen flow of 75 ml min<sup>-1</sup> and air flow at 90 ml min<sup>-1</sup>.

**2.6 Gas Chromatography-Mass Spectroscopy and Pyrolysis Gas Chromatography-Mass Spectroscopy:**

Aromatic fractions were re-dissolved in DCM at a concentration of ca. 1 mg ml<sup>-1</sup> and analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS) using an Agilent Technologies 7890 N gas chromatograph coupled to an Agilent Technologies 5975C mass selective detector (MSD).

Injection of one  $\mu\text{l}$  of sample was splitless at 270 °C, separation was performed by a DB-5MSUI column (J&W; 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ), with helium carrier gas at a constant column flow of 1.1 ml min<sup>-1</sup>. The GC oven temperature was initially at 50 °C for 1 min, then ramped at 5 °C min<sup>-1</sup> to 310 °C where it was held for 20 min.

For the on-line analysis of asphaltene fractions by Pyrolysis Gas Chromatography-Mass Spectroscopy (Py-GC-MS) samples were placed in quartz sample tubes, loaded into a CDS Analytical Model 2500 Plus autosampler pyrolysis unit and subjected to pyrolysis (610 °C at a heating rate of 20 °C ms<sup>-1</sup> for 15 s). The products were introduced to the GC at a 25:1 split ratio with the injector at 270 °C. All other GC-MS conditions were the same as for the above liquid samples except that the GC oven temperature was held for 2 min at 40 °C and then programmed at 5 °C min<sup>-1</sup> to 310 °C, the final temperature was held for 8 min.

### **3. Results and Discussion**

The flotates from the crude experiments are maltene-rich, with maltenes representing over 90% by mass in all cases. In the temperature range at and above 250 °C, a residue appears and the percentage of maltenes in these is higher in the crude oil residue than in the corresponding core-derived residues. These core-derived residues are asphaltene rich. The difference in asphaltene content for residues from the crude and core samples (Figure 1) must result from the presence of matrix minerals; the most likely candidate would be the clays kaolinite and illite, as has been previously suggested<sup>7</sup>. A similar redistribution of asphaltenes has been observed in our previous work on other oil sands, both sulfur-rich and sulfur-poor.<sup>3,4</sup>

The aromatic fractions of the flotates and residues of the core and crude experiments contain no sulfur-bearing free compounds detectable by GC-MS at temperatures lower than 250 °C. Above 250 °C, the aromatic fractions of these samples contain a variety of methylated dibenzothiophenes, consistent with the degradation of the sulfur-bearing asphaltene fraction of

the sample with increasing temperature. The appearance of sulfur-bearing asphaltene degradation products has been previously observed and is independent of either the mineral matrix or the sulfur content of the oil.<sup>3,4,16</sup> Complete SARA fractionation data is supplied in Supplementary Table 1.

Measurable amounts of H<sub>2</sub>S were observed from the core experiments at temperatures at and above 250 °C. This is consistent with previous work, in which a sulfur-rich oil sand sample produced H<sub>2</sub>S at temperatures of 250 °C and above.<sup>4,10</sup> No H<sub>2</sub>S was observed in any of the crude experiments, independent of experimental temperature (Figure 2). The presence of free aromatic compounds in both core and crude samples indicate degradation of S-rich asphaltenes with aquathermolysis but the lack of H<sub>2</sub>S resulting from the crude experiments indicates minerals, possibly clays, are required to produce H<sub>2</sub>S.

While H<sub>2</sub>S has been reported to form directly from the decomposition of the chemical standard thiophene under aquathermolysis at 300 °C<sup>17</sup>, we observe H<sub>2</sub>S at a lower temperature (250 °C) when both sulfur-rich heavy oil and mineral matrix are present. One explanation is suggested by previous work in which mineral interactions with steam produced acidic conditions<sup>18</sup>, which have previously been shown to promote H<sub>2</sub>S generation from the model compound thiophene.<sup>19</sup> Another suggested mechanism involves the coordination of metal ions, specifically Al<sup>3+</sup>, with the thiophenes, activating the compounds and enabling reactions with the water that lead to thiophene degradation and H<sub>2</sub>S generation.<sup>20,21</sup>

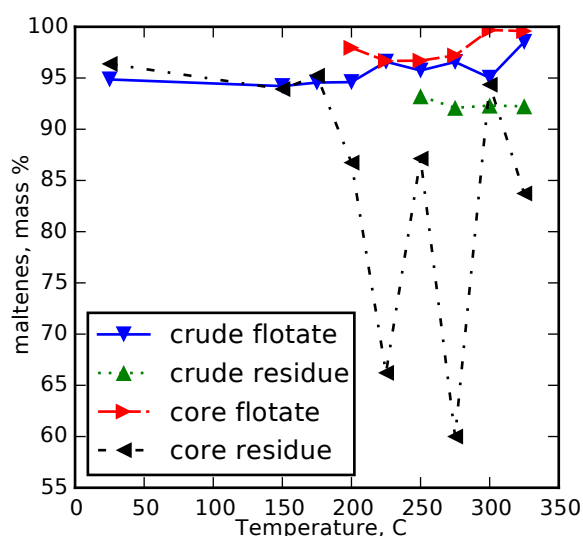
#### **4. Conclusions**

The mineral matrix influences oil chemistry during aquathermolysis by promoting the formation of H<sub>2</sub>S from the smaller sulfur-bearing molecules generated by aquathermolytic breakdown of the high molecular weight asphaltene fraction in the original crude. It follows therefore that minimal H<sub>2</sub>S generation during production would be associated with reservoirs

that are highly saturated with oil and opportunities for oil-mineral surface reactions relatively limited. When this knowledge is combined with an experimentally demonstrated >200 °C temperature threshold for H<sub>2</sub>S generation it is possible to recognize ideal reservoir and production conditions. Our findings highlight the benefits of understanding the geologic context when recognizing the best possible conditions for steam-assisted recovery of heavy oil.

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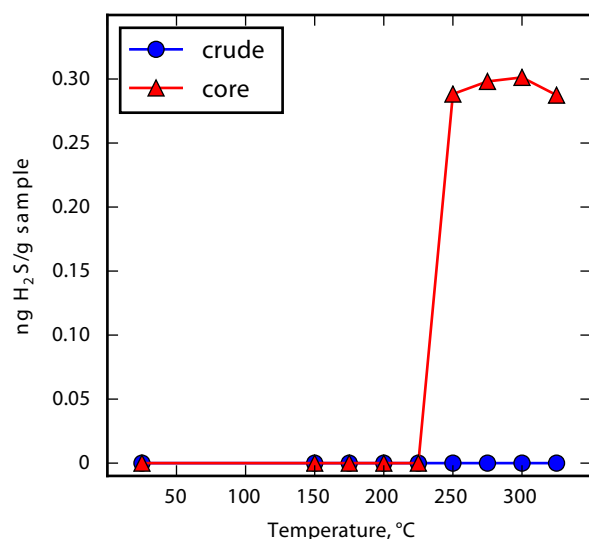
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**Figure 1.** Maltene percentage in oil fractions for crude and core flotates and residues after aquathermolysis at temperatures ranging from 25-325 °C. Data indicate the percentage maltenes by mass determined by isolation from asphaltenes by using precipitation in heptane.

COLOR ONLINE ONLY





**Figure 2.** The production of H<sub>2</sub>S from the core experiments (red triangles) in ng H<sub>2</sub>S/g sample as determined by GC-FPD. No H<sub>2</sub>S was detected in the crude experiments (blue circles).

COLOR ONLINE ONLY

**Supporting Information.** The following files are available free of charge:

Table of detailed SARA analyses of all samples, PDF

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