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**Laboratory simulation of H<sub>2</sub>S and CO<sub>2</sub> generation in steamed oil sands, Orinoco Belt, Venezuela**

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### **Introduction**

The studied field is located in the Orinoco Belt, East of Venezuela. The Oil in Place (STOIP) volumes on this field exceed 30 Gbbl. However, the nature of the crude (Extra Heavy Oil, 8°API) results in a limited recovery factor. An Enhanced Oil Recovery (EOR) Pilot Project is currently being implemented in order to quantify the additional recovery that can be expected with steam injection techniques.

One of the main expected issues associated to steam injection is the *in situ* production of H<sub>2</sub>S and CO<sub>2</sub>. Due to the detrimental effects of these gases and to the constraints they impose on facilities design, it is of paramount importance for this EOR project to understand the origin of these acid gases, in order to be able to predict their concentration in production fluids.

This paper presents the results of laboratory experiments that were carried out to address this issue.

First, a geochemical characterization study was done on 4 oil sand cores. Oil composition variability and sulphur content distribution in the oil sand cores were assessed, along with the total and labile sulphur content of the crude oil. The geochemical heterogeneity at the scale of the core was evaluated. The matrix mineralogical composition was also determined in order to investigate possible chemical interactions between oil and minerals.

The following step consisted in simulating in laboratory the physico-chemical reactions occurring in the reservoir during steam injection, through aquathermolysis experiments (Hyne *et al*, 1984). The resulting gas, oil and mineral were recovered, quantified and characterized, in order to quantify H<sub>2</sub>S and CO<sub>2</sub> generation and to obtain leads on their origin.

### **Geochemical characterization of the oil sands**

First, the geochemical heterogeneity at the scale of the cores was evaluated. In heavy oils, the sulphur is concentrated in the C14+ fraction; more specifically the sulphur belongs to the NSO fraction and to the so-called aromatic fraction. Consequently C14+ fraction sulphur content and NSO content can be considered as relevant properties with regard to the issue of H<sub>2</sub>S generation. In this respect they were measured in different samples collected from each core, in order to determine their spatial variability. The results showed that 3 cores display homogeneous properties at decimetric length scale. On the contrary, one core showed a gradient of C14+ fraction content, associated with a gradient of porosity and a gradient of sulphur content. Consequently, it was decided to evaluate the effect of this gradient on gas production. Hence the

upper part and the lower part of this core were selected to undergo separately the aquathermolysis experiments.

Secondly, a detailed geochemical characterization of the samples dedicated to aquathermolysis experiments was carried out.

Five oil sand samples, issued from the 4 cores, were chosen for the aquathermolysis experiments. Each sample was mixed for homogenization, aiming at ensuring favorable conditions of reproducibility. As the oil sands were soft enough, they could be mixed manually with a spatula instead of mechanically. With this procedure, it was possible to avoid crushing the solid grains and hence preserving the original specific contact areas between the bitumen and the mineral matrix.

The geochemical characterization showed that the 5 oil sand samples had close geochemical properties:

- The 5 oil sands contained 14 to 16 wt% of C14+. The C6-C13 content was not quantified but was estimated to be lower than 2 wt% of the oil sand.

- The 5 heavy oils (C14+) had almost identical SARA compositions: 52 to 55wt% resins, 24 to 25wt% aromatics, 13 to 14wt% saturates and 8 to 11wt% asphaltenes/nC7. The resins were the dominant fraction, which is a typical property of heavy oils. It was noticed that the resins were the main carrier of sulphur in the oil: they were carrying 65 to 69wt% of sulphur in the oil, whereas the aromatics were carrying 20 to 24wt% and the asphaltenes/nC7 only 10 to 13wt% of sulphur in the oil.

Moreover, it appeared with the Rock-Eval investigation that only 11% of the total sulphur in the oil was exhibiting a refractory behavior to thermal treatment. This suggested that the other 89% of the total sulphur in the oil could be a source of H<sub>2</sub>S upon steam treatment. This assumption was not confirmed in the present study, because the duration and the temperature of the aquathermolysis experiments were not high enough.

- The 5 sand matrices were containing approximately 90wt% of quartz and less than 10wt% of potassium feldspar. They were also containing few percents of kaolinite and carbonates: calcite and possibly siderite and dolomite. The metal elements in presence were aluminium (0.85 to 1.52 wt%), potassium (0.02 to 1.14 wt%), calcium (0.08 to 0.17wt%) and iron (0.06 to 0.18 wt%). The matrices were containing a very small amount of sulphured coke, with an organic sulphur content of 1wt% of the matrix. Mineral sulphur was below the quantification limit (<0.1%). Hence, it was deduced that the matrices were not containing any sulphate, pyrite or sulphide. This is an important point, which indicates that during steam treatment H<sub>2</sub>S originated only from sulphur occurring in bitumen and not from the minerals. It excludes the possibility of any thermochemical sulphate reduction (TSR), which is a major process for H<sub>2</sub>S production and induces high contents in H<sub>2</sub>S. It also indicates that pyrite cannot be involved in the reaction and in the H<sub>2</sub>S fate.

### **Aquathermolysis experimental study**

The aquathermolysis study was conducted aiming at assessing the capacity of the oil sands to generate gas and especially H<sub>2</sub>S and CO<sub>2</sub> upon steam treatment. The experiments involved heating few grams of oil sand with water such as V<sub>oil</sub>=V<sub>water</sub>, at 250°C under 45 bar. Three durations of aquathermolysis were investigated: 14 days, 28 days and 56 days. These experimental conditions were chosen to be as representative as possible of the conditions prevailing in the actual reservoir area affected by chemical reactions during steam injection. At

the end of each aquathermolysis experiment, the produced H<sub>2</sub>S, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> were quantified in absolute amounts.

The results showed that as far as aquathermolysis proceeds, the production of gas increases. Whatever the oil sand, the produced gas was composed mainly by CO<sub>2</sub>, amounting 70 to 90mol%. The produced H<sub>2</sub>S was in significant concentration, from 3 to 11mol%. H<sub>2</sub> production reached 2 to 7mol%, and CH<sub>4</sub> production reached 4 to 7 mol%. Hydrocarbon gases, C<sub>2</sub> to C<sub>4</sub>, reached around 1mol% each, indicating a slight hydrocracking of the oil.

Although exhibiting similar compositions, the 5 oil sand samples produced a significant difference in the quantities of gas upon aquathermolysis: gas production varied from 1.1 to 1.8 [g gas]/[kg oil sand] after 56 days of aquathermolysis, according to the considered sample. This variability is mainly the result of the CO<sub>2</sub> production, varying from 0.9 to 1.6 [g CO<sub>2</sub>]/[kg oil sand] according to the considered sample.

This variability of CO<sub>2</sub> production could clearly be related to the carbonates content and calcium content in the sand matrix, though these contents were very small: around 0.1wt% of calcium in the matrices. Such a correlation suggests that calcite in the sand matrix, even in very small quantities, induces significant CO<sub>2</sub> generation under steam treatment at 250°C. Besides this mineral origin, an organic origin of CO<sub>2</sub> exists, as it was observed on similar aquathermolysis experiments carried out on the oil extract only. This is consistent with CO<sub>2</sub> data obtained by Clark and coworkers from aquathermolysis experiments performed on thiolane and thiophene, at 300°C (Clark *et al.*, 1983)

In considered experimental conditions, after 56 days of aquathermolysis, H<sub>2</sub>S production was varying from 0.02 to 0.12 [g H<sub>2</sub>S]/[kg oil sand] according to the considered sample. H<sub>2</sub>S production could be correlated with the sulphur content of heavy oils, and with the "Rock-Eval pyrolyzable sulphur" content.

It is important to note that a difference of sulphur content in heavy oil of only 0.1wt% induces an increase of H<sub>2</sub>S production of 0.04 [g H<sub>2</sub>S]/[kg oil sand] after 56 days of aquathermolysis, which represents approximately 30% to 200% of the total H<sub>2</sub>S production. This shows that if, for operational purpose, we intend to predict properly H<sub>2</sub>S production and its concentration, then a precise quantification of sulphur in oil is required (absolute uncertainty for S content <0.1wt%).

The elements Al, Fe and K, which were found in the matrices, are known to promote catalysis oxidation, decarboxylation and hydrogenation of organic compounds. In this respect, it is possible that they played a catalytic role on gas production such as H<sub>2</sub>S and CO<sub>2</sub>.

Another important point to note is that the maximum and the minimum of gas production generated by the 5 different oil sand samples are associated with two samples collected from the same core and separated by only 20cm. The top of the core produced approximately 50% more gas than the bottom. The other samples from other wells produced intermediate quantities of gas. This leads to underline that laboratory results should be interpreted keeping in mind that the heterogeneity in the reservoir can be at a very small scale (20cm here) and may have significant effects. Hence this confirms that a small scale screening study is appropriate to estimate the spatial variability of the steam treatment impact. For example, a simple screening study could be directed only on sulphur and carbonates quantification, since these characteristics seem to be key points for gas production in these EOR and geological contexts. Accordingly the Rock-Eval appears as a good tool for this purpose, with a rapid time of analysis and with a level of precision for sulphur and mineral carbon quantification which is probably sufficient to screen the spatial relative risk of CO<sub>2</sub> and H<sub>2</sub>S production.

## References

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