

## Introduction

As operators drill deeper into higher pressures and temperatures as well as begin exploiting resource plays such as gas shale and liquid rich shale, the concentrations of gas contaminants such as H<sub>2</sub>S and CO<sub>2</sub> become more and more important, especially in prescribed low cost developments. The NACE MR0175 is a standard that provides guidance for the selection of proper materials resistant to sulphide stress cracking with the current partial pressure limit of 0.05 psi for H<sub>2</sub>S (Bush, 1998). Given the HPHT environments currently being explored (e.g., >15000 psi), only small quantities of H<sub>2</sub>S (>3-4 ppm) are needed to cross the threshold for deployment of significantly more costly metal chrome alloys essential to avoid corrosion and failure. Thus, getting an accurate measure of the concentration, understanding the source, mechanism of formation and distribution of H<sub>2</sub>S becomes critical, especially in low concentration regimes. Low-level H<sub>2</sub>S detection and sampling methods have been discussed and documented previously (Elshahawi and Hashem, 2005, Hashem et al., 2007), but measurement of the concentration is not enough to assess the source.

To understand the source of H<sub>2</sub>S, sulphur isotope mapping of pyrite, organic sulphur, anhydrite and H<sub>2</sub>S is crucial. If the source is understood, the distribution and risk within a field or within a given exploration play can be assessed. Several mechanisms of H<sub>2</sub>S formation have been identified in natural gas accumulations: bacterial sulphate reduction (BSR), thermochemical sulphate reduction (TSR), thermal chemical alteration (TCA) of sulphur rich organic material (i.e. either high sulphur kerogen and/or oil) (Orr, 1977), and mineral-fluid equilibration of sulphide; the latter mechanism usually resulting in low level 'background' H<sub>2</sub>S (Smith, 1980). All of these mechanisms yield unique  $\delta^{34}\text{S}$  values for H<sub>2</sub>S as well as mineral formations such as pyrite, calcium carbonate, and organic solids such as pyrobitumen.

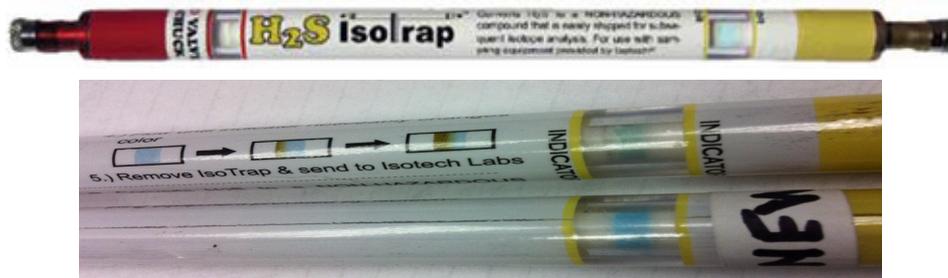
This paper discusses a case study of a discovered field where low level H<sub>2</sub>S (25-40 ppm) is present in the hydrocarbon accumulation along with pyrite, anhydrite and pyrobitumen in the reservoir rock. Reservoir temperature is well above the TSR threshold of 140°C, so it was initial speculation that the pyrobitumen and H<sub>2</sub>S were most likely due to TSR. However, petrographic inspection of the anhydrite showed little corrosion or replacement with carbonate, and the pyrobitumen showed no telltale signs of TSR, based on reflectance analysis carried out in a similar manner as done by Stasiuk (1997) on pyrobitumen samples from the Western Canada Sedimentary Basin; of which, it was obvious TSR was the main reaction form. Additionally, a number of other near field exploration opportunities existed, so a clear understanding of the source of the H<sub>2</sub>S was needed to properly risk the remaining portfolio. Proper planning and novel techniques for the sampling of the reservoir fluid, preservation of the H<sub>2</sub>S and analysis of the  $\delta^{34}\text{S}$  values for H<sub>2</sub>S are described along with the business impact of the results.

## Methods

For the open hole sampling, the methods described in detail by Hashem et al. (2007) were utilized so as to preserve as much of the H<sub>2</sub>S in the samples as possible without loss to the tools' pumps, flow lines and seals. Additionally, the tool was fitted with the largest sample volume tanks feasible, specially coated, so as to preserve and maximize the gas volume that would be needed for the H<sub>2</sub>S sulphur isotope measurements. A total of 6 sample tanks were deployed in this mode.

The well was drilled with synthetic oil based mud, so criteria needed to be established and agreed with all stakeholders (e.g., drilling superintendent, operational staff, and engineers) for acquisition of high quality fluid samples with oil base mud contamination <5%. A "Sample the Well on Paper (SWoP)" exercise was carried out 6 weeks prior to the wireline operations to bring all stakeholders on board with the objectives of the program, and have agreement with all parties on the critical success factors of the operation. Thus, adequate time on the sample location, roughly 6 hours of pumping, was allowed to provide proper clean up procedures to be employed. In the end, the reservoir fluid samples had <3% OBM contamination; excellent quality samples for PVT, flow assurance, and the H<sub>2</sub>S analyses that we required.

When samples were retrieved to surface, 4 of the sample bottles were transferred, carefully, into a 2L H<sub>2</sub>S inert overpack cylinder and the other two sample bottles were subjected to onsite analyses. Again valve fittings and transfer lines were all made inert to H<sub>2</sub>S scavenging. Onsite H<sub>2</sub>S analysis was done using stain tubes and yielded 10-15 ppm H<sub>2</sub>S. The 2L overpack was utilized to provide as much continuous flow through volume as possible for Isotech's IsoTrap™. The IsoTrap (Figure 1) was designed as a solution to get sulphur isotope data from H<sub>2</sub>S in natural gas, and eliminate the regulatory issues around shipping and handling of high H<sub>2</sub>S samples. For instance, when H<sub>2</sub>S concentration levels are above 5 mol%, you can no longer ship them via air cargo; they must go by ground freight. The IsoTrap converts the sulphur in the H<sub>2</sub>S to an inert solid making for easy shipment of samples from the field to the laboratory. However, the device was designed for sampling of well test or production streams where large flow through volume would not be an issue and enough H<sub>2</sub>S could be trapped to make the necessary measurement. However, for green field exploration or early appraisal, well testing is not often carried out, especially in deepwater or remote locations. We estimated we would need 100L of gas at 20-30 ppm H<sub>2</sub>S concentration to yield the chemical change in the IsoTrap.



**Figure 1** The top picture is of the IsoTrap™ sampling device from Isotech. The bottom picture shows the change in colour of the litmus paper from light blue (New) to light green indicating exposure and trapping of H<sub>2</sub>S. Higher concentrations of H<sub>2</sub>S would yield a more significant colour change.

The pressurized samples were sent to the laboratory for PVT, flow assurance, and preparation of the IsoTrap. Initial thoughts were to try and prepare the IsoTrap in the field from the coated sample cylinders. Past experience has indicated that additional loss of H<sub>2</sub>S in the sample bottles occurs over time between shipment from the operation site to the laboratory, and that the loss can be significant. Again, because we were dealing with low level H<sub>2</sub>S concentrations, any additional loss would make the sampling even more difficult. However, because this was the first attempt at getting an IsoTrap from such samples, we opted to perform this task in a more controlled environment. Thankfully, little loss of H<sub>2</sub>S was noted between the field and the lab. Laboratory procedures were set up and reviewed to provide the following:

- Continuous flow through volume of gas to the IsoTrap
- Measure the volume of gas passed through the IsoTrap
- Provide an inert system that would minimize any scavenging of H<sub>2</sub>S
- Trap any liquid carry over that might occur during flashing of the oil sample and flow of the gas.

The 2L overpack was heat restored for 4 hours and using the approved method, the flashed gas was passed through the IsoTrap. Gas bag samples from the flow line were taken before and after the IsoTrap and subjected to sulphur speciation by ASTM D5504. Results are shown in Table 1. The initial concentration level was slightly higher than measured in the field, 20 ppm versus 15 ppm, and the first gas bag taken after the IsoTrap was predictable in that it measured 0 ppm indicating the IsoTrap was converting all of the H<sub>2</sub>S into solid form. After roughly 100L of gas, the H<sub>2</sub>S value after the IsoTrap had risen to 14 ppm and the litmus paper had noticeably changed colour as shown in the bottom picture of Figure 1 indicating the IsoTrap was saturated relative to the H<sub>2</sub>S.

**Table 1.** Trace sulphur speciation analysis by ASTM D 5504 on gas sample bags taken before and after the IsoTrap.

	GB #1 Before IsoTrap	GB #2 Before IsoTrap	GB #3 After IsoTrap	GB #4 After IsoTrap
Volume of Gas (L)	3	10	13	100
[H <sub>2</sub> S] (ppm)	19.7	19.4	0.0	14.2

## Results

Because reservoir temperatures are well above the temperature limits for BSR (60-80°C), this mechanism was removed as a possible source for the H<sub>2</sub>S in our case study. The two main mechanisms that were thought to be responsible were TSR or TCA, both of which generally occur at temperatures greater than 120-140°C. For TSR, because the main source of sulphur is from anhydrite, the sulphur present in the H<sub>2</sub>S will have sulphur isotopes similar to the anhydrite:

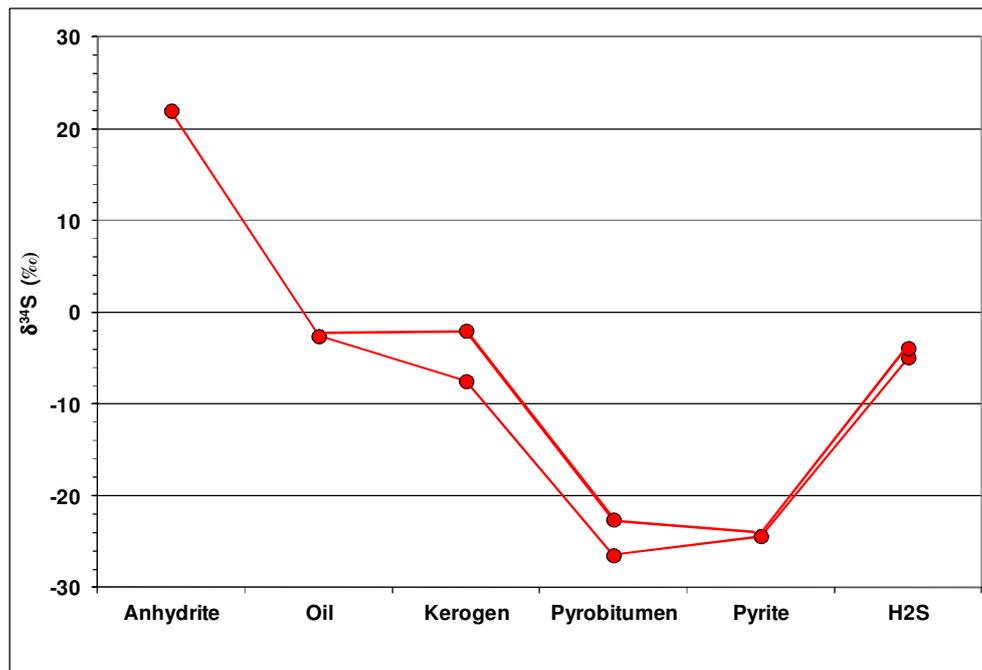


Hydrocarbon accumulations that are impacted by TSR can be very sour with H<sub>2</sub>S concentrations easily exceeding 5mol%. Bulk δ<sup>34</sup>S isotopic analysis on a sample of anhydrite from whole core taken in the discovery well yielded a value of +22.0‰. For TCA, the H<sub>2</sub>S is generated by thermal alteration of organic sulphur, typically in the form of sulphides, in kerogen or oil. Thus, its δ<sup>34</sup>S isotopic value will be significantly lower since organic processes prefer <sup>32</sup>S versus <sup>34</sup>S. Typical values of bulk δ<sup>34</sup>S of kerogen range from -10 to 0‰. Concentrations of H<sub>2</sub>S generated by this process, unlike TSR, are much more modest and do not usually exceed 5mol%. For our project, both source rock material and stock tank oil were submitted for bulk δ<sup>34</sup>S and yielded values of -7.5 to -2.0‰ for the kerogen isolates and -1.8‰ for the stock tank oil. Additionally, sulphur isotopes were measured on pyrite isolated from rotary side wall cores taken in the cap rock just a few meters above the reservoir interval. The values were very negative, -24.4‰, indicating a probable biogenic source. Lastly, bulk δ<sup>34</sup>S isotopic analysis was also done on several pyrobitumen isolates, but it was obvious that it had been impacted by finely dispersed pyrite in the samples because it gave values roughly in the same range as the pyrite: -26.5 to -22.6‰.

The IsoTrap was submitted for sulphur isotope analysis and yielded a value of -3.9‰. A second IsoTrap sample from the follow-up appraisal well gave similar results: -4.9‰ for the sulphur isotopes of H<sub>2</sub>S. The graph in Figure 2 provides a mapping of the isotopic values recorded for anhydrite, kerogen, oil, pyrobitumen, pyrite, and, finally, H<sub>2</sub>S. The results clearly indicate that the source of the H<sub>2</sub>S is most likely TCA of organic sulphur (i.e., cracking of oil to gas in the reservoir).

## Conclusions

A number of novel sampling techniques as well as proper planning and good execution were carried out to determine the sulphur isotopes from low level H<sub>2</sub>S found in a new exploration play. Results indicate that the mechanism of formation of the H<sub>2</sub>S is most likely thermal chemical alteration (TCA) of organic sulphur within the oil. Thus, the concentration levels will be directly proportional to reservoir temperature as it relates to cracking of oil to gas. This result can be applied to the many other prospects within the exploration acreage to risk and assess the presence, concentration levels, and distribution of H<sub>2</sub>S.



*Figure 2. Sulphur isotope map.*

## References

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