Hydrogen Sulphide Measurements in SAGD Operations

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Abstract

A new method of measuring hydrogen sulphide concentrations in gas streams, suitable for SAGD operations, is reported. The method is independent of the steam content up to 70 mole %, the composition, temperature and pressure of the gas, and has been tested and validated in the field. The method has a standard error of about 5%. By contrast, the stain tube (Draeger) measurements performed routinely on various gas streams at SAGD pilots are shown to be correct only within an order of magnitude of the reading by the new method. Factors between two to ten were common between stain tube readings and the corresponding true readings taken immediately after or before the stain tube readings.

The results have implications for plant safety procedures. It is suggested that certain plant streams be sampled only by operators wearing self-contained breathing apparatus; stain tube readings of the past have suggested this to be not necessary.

There are further implications for understanding of partitioning of produced hydrogen sulphide in process streams.

Introduction

The production of hydrogen sulphide and carbon dioxide together with other minor gases in thermal recovery projects such as Steam Assisted Gravity Drainage is a common observation. The process giving rise to these gases is a high temperature hydrolysis of aliphatic sulphur linkages in the bitumen, dubbed "aquathermolysis" by Hyne et. al[1-3]. For Athabasca, the amount of hydrogen sulphide typically produced per tonne of bitumen varies between 6 and 75 litres. Considerably more carbon dioxide is produced, usually in the range from 900 – 10,000 litres per tonne. It is shown elsewhere[4] that such production rates of hydrogen sulphide can easily give rise to H_2S concentrations of about 20,000 ppm in the produced gases of a SAGD production project.

Hydrogen sulphide measurement has usually been performed by means of stain tubes. The reason is that laboratory analysis of gas from a normal stainless steel gas cylinder will not give meaningful results. It has therefore been customary to measure the main gases from a cylinder in the laboratory, but to measure H_2S concentrations in the field by means of stain tubes.

This technique, while probably suitable for the natural gas industry, is problematic in SAGD work. It has been shown that hydrogen sulphide is highly soluble in steam condensate at temperatures of interest in SAGD[4]. Moreover, the solubility goes through a minimum at approximately 180˚ C. As a produced gas line or facility with a significant steam pressure is being sampled, the quality of the steam must necessarily change in the sampling line and in the stain tube itself. Hydrogen sulphide will re-partition accordingly. It is improbable that hydrogen sulphide is quantitatively determined by the stain tube from both phases. Therefore it is doubtful whether stain tube measurements are reliable in this situation.

Design of Sampling Train

A sampling train suitable for the purpose at hand would ideally be easy to assemble from conventional sampling equipment, but would still be able to determine the composition of gas in terms of water vapour, hydrogen sulphide, and non-condensible gas content. The simplest method would force all steam to condense early in the train, regardless of quality, and chemically and quantitatively trap hydrogen sulphide in the same location in the train.

The train designed for this purpose is shown schematically in Figure 1. Steam is forced to condense in a Greenburg-Smith impinger commonly used for stack surveys. The impinger volume chosen must be at least 1 litre to accommodate high steam percentages. Hydrogen sulphide is trapped by copper sulphate solution to make copper sulphide,

$$Cu^{2+} + H_2S \rightarrow CuS + 2H^+ \qquad \dots\dots(1)$$

The content of condensed water after the test is easily measured by weighing both the first impinger and the drying tube before and after the test. The solution containing the precipitated copper sulphide is then quantitatively recovered from the impinger in the field, and the copper sulphide separated in the laboratory. Chemical dissolution of the separated precipitate then permits analysis of the total amount of copper recovered, and calculation back to the amount of hydrogen sulphide trapped. Correction for the precipitate mass is then made to the water weight.

The dried non-condensible gas is measured by means of a dry test meter at the end of the train. Recombination calculations then permit the calculation of steam content, hydrogen sulphide concentration, and non-condensible gas content in the stream under test.

There are several reasons for the choice of copper sulphate to trap the hydrogen sulphide. First, it is required that the separated precipitate be highly insoluble in water, easy to separate and analyse, and that it be insoluble in the acid that is generated during the trapping reaction. The metals meeting this requirement include mercury, lead, cadmium, arsenic, silver and bismuth, as well as copper. Copper is chosen over mercury, lead, cadmium, and arsenic by virtue of its lesser toxicity. The trapping solution needs to be concentrated to the extent of approximately 2 mole/L, and unnecessary exposure of the sampling personnel to the solutions of high-
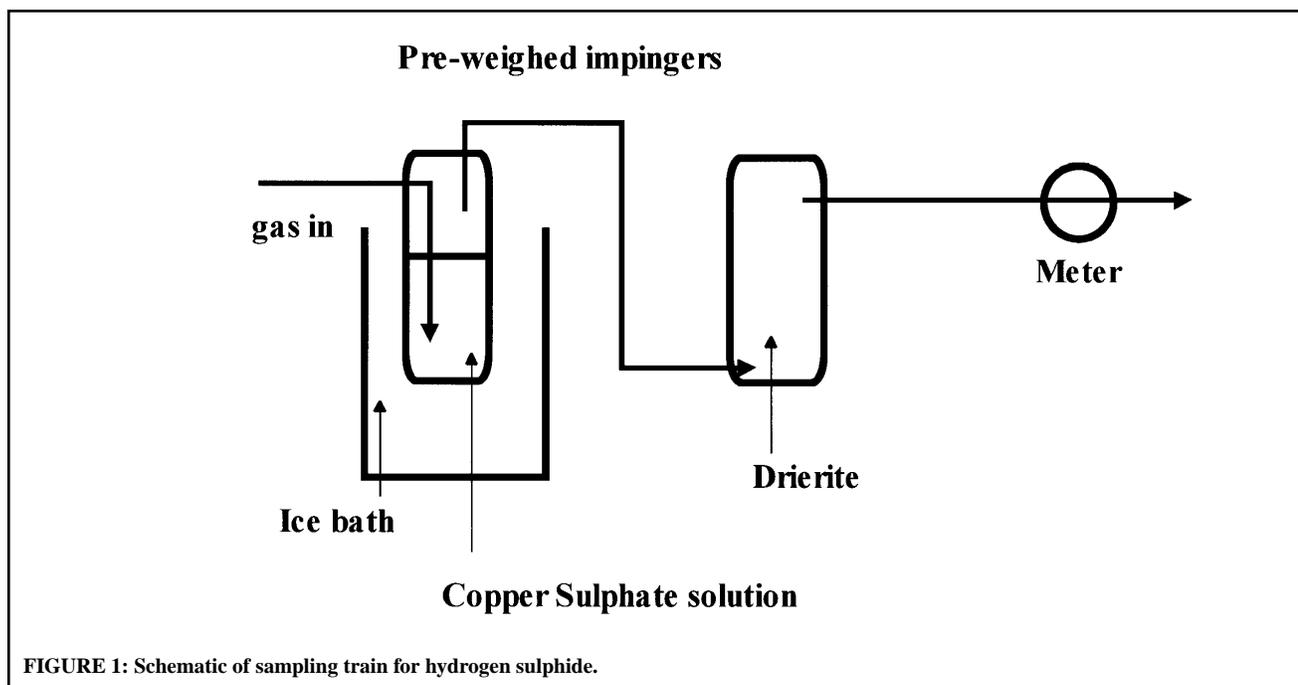
FIGURE 1: Schematic of sampling train for hydrogen sulphide.

ly toxic substances needs to be avoided. Copper sulphate is cheaper than the bismuth and silver salts, and the copper sulphide product is also extremely insoluble in water.

A theoretical disadvantage of the use of copper sulphate arises from the potential to make copper sulphide of two valencies of copper; cupric sulphide, CuS, and cuprous sulphide Cu_2S, especially under reducing conditions. A test of the system in the laboratory, with test gases of known composition, showed that only the cupric sulphide is formed under the conditions of such tests. The details of the calibration are shown in Table 1.

An error analysis of the method gives a standard error of 5.2%. The capture efficiencies of the Greenburg-Smith impingers are known to be of the order of 99.8%. No hydrogen sulphide odour was detectable at the dry test meter outlet when streams of up to 8,000 ppm hydrogen sulphide were tested in the field. With the odour threshold of hydrogen sulphide at approximately 10 ppb, the capture efficiencies of the impingers are, in fact, essentially quantitative for hydrogen sulphide in this application.

The technique is, by design, independent of the changes of steam quality that may occur at sampling points and the distribution of hydrogen sulphide between the gas and liquid phase.

Field Trials

With the sampling train tested and calibrated in the laboratory, a number of field tests were conducted at the Gulf Surmont pilot near Fort McMurray, Alberta. The error analysis had shown that in order to minimize error propagation due to the dry test meter, it was necessary to collect at least 600 litres (20 cubic feet) of non-condensible gas. This necessitated sampling times of the order of at least one hour. The tests were run with flow rates of the order of 10 litres per minute through the dry test meter. Pressure control was achieved by the use of needle valves at sampling points.

Gas streams with more than 70% steam would exceed the capacity of the Greenburg-Smith impingers to collect water, and

thus, shorter sampling times would be required. This would lead to a higher standard error. However, this problem was not encountered during the collection of the data reported here.

The quantitative collection of the precipitate is achieved in a manner similar to that used in stack tests. The solid phase may, to a minor extent, be splashed from the impinger into tubing and joints. Recovery of these amounts, as well as residues adhering to the impinger glass, is achieved by means of distilled water rinsing and brushing of the joints and interior glass surfaces, and thus brush rinses need to be collected also. This caused minor problems due to wettability of the copper sulphide in some cases. Depending on the source under test, wettability of the precipitate varied. This problem was overcome by following a distilled water rinse with a small toluene rinse. In this manner, no difficulties were encountered with the quantitative recovery of the used impinger contents.

The separation of the copper sulphide from the resulting water/toluene mixture in the laboratory is a straightforward procedure. The separated solid is taken up in hot nitric acid, the solution is made up to volume with distilled water, and measured for copper content by inductively coupled argon plasma spectrophotometry.

A comparison between stain tube measurements and the tests with the designed train from the same source was run and is summarized in Table 2. For this purpose, the streams were tested with Draeger tubes before and after each test, and the average was taken. It is clear that the Draeger tube readings, although they are

TABLE 1: Laboratory calibration of method and stoichiometry tests.

Run No.	Theoretical Cu Recovery	Cu Recovery Found
1a, 1b	1.4608 gram	1.392 ± 0.068 gram
2	1.5594 gram	1.569 gram

TABLE 2: Field results.

Location	H_2S Concentration by Sampling Train, ppm	H_2S Concentration by Stain Tube, ppm
Produced Gas Cooler, prelim.	777	500
Produced Gas Cooler	555	400
Produced Gas Separator	569	400
Produced Gas Separator	480	225
Produced Gas Cooler	370	1,000
Gas Boot Overhead, prelim.	223	1,200
Gas Boot Overhead	246	1,200
Gas Boot Overhead	264	800
Gas Boot Overhead *	18 *	200

instantaneous rather than integrated readings, differ significantly from the results obtained with the sampling train.

For the purpose of personnel safety, a recommendation was made to plant operators to double any stain tube reading made for safety purposes when a decision about the need to use self-contained breathing apparatus is made.

One sample in Table 2 is marked with an asterisk. Although the deviation of the stain tube result from the sampling train measurement is high, this result has a further significance. During the 1-hour period of this test, the well tied into this gas boot was noted to produce bitumen with an essentially zero water cut. The effects on the train were immediately noticeable. First, the steam pressure declined and considerably less steam condensate was collected in the first impinger. Second, instead of the usual 1,500 – 2,000 mg copper sulphide collected from the first impinger, only 9 mg were collected. Third, the throughput of gas in the dry test meter declined rapidly, but did not go to zero.

In another paper[4], it has been shown theoretically that hydrogen sulphide from aquathermolysis in SAGD is almost entirely produced, and is produced solely via the produced water, owing to its solubility at the SAGD steam zone temperature. Likewise, carbon dioxide and methane are predicted to be produced via dissolution in water, although for methane a minor contribution via bitumen (i.e., Athabasca bitumen) is likely. This field result confirms the theoretical prediction for hydrogen sulphide. It also predicts that a small amount of gas, likely methane, is produced by means other than dissolution in water. The findings are thus consistent with the theoretical predictions.

Conclusions

A method for measurement of hydrogen sulphide in SAGD operations, which does not suffer from the errors inherent in stain tube measurements, has been developed and verified in both the field and the laboratory.

A theoretical prediction that hydrogen sulphide in a SAGD production project is produced entirely via dissolution in produced water has been confirmed in the field.

Acknowledgements

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Author's Biography

Harald Thimm is a principal of Thimm Engineering Inc., a consulting firm specializing in environmental science, chemistry, and engineering. Before 1990, he spent 12 years at the Energy Resources Conservation Board (ERCB, now EUB) as a senior environmental advisor and senior petroleum engineer, and at AOSTRA. Before the period at the ERCB he was an environmental consultant at Chemex Labs in Calgary and an agricultural scientist at the State Laboratories in Melbourne, Australia. Dr. Thimm holds a B.Sc. (Hons) degree in chemistry from Monash University, Australia, a Ph.D. in chemistry from the University of Manitoba, and an M.Eng. in petroleum reservoir engineering from the University of Calgary. He is a member of the Petroleum Society, APEGGA, SCI, CHOA, and the Royal Society of Chemistry (UK). He was named a Fellow of the Chemical Institute of Canada in 1992 and Fellow of the American Institute of Chemists (AIC) in 1993. He is currently a member of the board of directors of the AIC.