

Hydrogen Sulphide Measurements in SAGD Operations. – Part II

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ABSTRACT

In a previous paper, a method suitable for the measurement of hydrogen sulphide concentrations in SAGD process streams was described. The method is applicable to measuring hydrogen sulphide, non-condensable gases, and steam in lines or units containing up to 70% steam, and avoids the errors inherent in stain tube and Tutweiler measurements.

This paper describes the extension of the method. It is

now possible to modify the method to accommodate steam concentrations as high as 98.5% at one extreme, and very dry gases at the other. In each case modifications of the original train, that are required to obtain accurate data, are described.

Procedures for meeting regulatory requirements, such as hydrogen sulphide and sulphur dioxide emission measurements, are also described.

INTRODUCTION

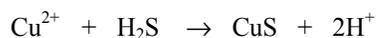
In a previous paper, a new method for sampling of produced gases from SAGD facilities was described¹. The method is capable of accurately measuring hydrogen sulphide concentrations, and was shown to be superior to the commonly used stain tube methods. The latter methods were shown to deviate from true concentrations by as much as an order of magnitude. This deviation is thought to be due to the presence of a high mole fraction of steam in the facilities under test.

The method also gives the mole fraction of steam, and that of the total non-condensable gases. The standard error was calculated to be of the order of 5.3%, provided it was possible to collect a sufficiently large volume of non-condensable gas. The upper limit of the method is reached when the steam mole fraction exceeds 70%. A schematic of the sampling train is shown in Figure 1.

Over the last three years, it became necessary to measure hydrogen sulphide concentrations in SAGD facilities under more extreme conditions. In the first case, a hydrogen sulphide concentration was required for a facility gas containing a mole fraction of steam in excess of 98%. In the second case, the gas in the facility was almost dry. Both cases presented significant challenges to measurement, as is shown below.

DESIGN OF ORIGINAL SAMPLING TRAIN

In the sampling train shown in Figure 1, all of the steam is forced to condense early in the train, regardless of the quality of the steam. The hydrogen sulphide is chemically trapped in the same location in the train, by use of a copper sulphate solution. Use is made of the reaction



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. Corrected water mass yields the mole fraction of steam, and the dry test meter volume yields the mole fraction of non-condensable gases.

An error analysis of the method gives a standard error of about 5%. The sampling train has been successfully tested in the field and calibrated in the laboratory. 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 liters (20 cubic feet) of non-condensable gas. This normally necessitates sampling times of the order of at least one hour. However, this first error analysis was conducted by keeping the mass of condensed water at a constant average value, a fact that will become significant in the discussion to follow.

HIGH STEAM FACILITIES

Gas streams with more than 70% steam cannot be sampled with the sampling train shown in Figure 1. Such tests would exceed the capacity of the Greenburg-Smith impingers to collect water, and thus shorter sampling times would be required. Also, the volume of non-condensable gas measured at the dry test meter would be unacceptably low.

A further factor that prevents the collection of a large amount of gas is the attainable rate of heat transfer between the impinger and the surrounding ice bath. At a high rate of steam condensation, a considerable amount of water vapour will not condense in the first impinger. This residual water vapour may rapidly exceed the capacity of the drying tube, and as this tube is heated, water vapour will escape to the dry test meter, thus compromising the test.

The challenge to be met is therefore the optimization of water collection in the sampling system, with much smaller volumes measured in the dry test meter, while still retaining a standard error of approximately 5% for the method. The volume of gas collected must be maximized before the rate of heat transfer becomes limiting.

The error analysis for the sampling system is shown in Appendix 1. The approach taken in defining the variance is to consider replicability of measurement between different persons, rather than considering the standard error of particular instruments per se. This approach is required because of the need to transfer and separate chemical solutions in the field, the replicability of which is a function of individual technique.

In the error calculation of Appendix 1, the amount of water collected is treated as a variable. It is clear

that the analysis does not mathematically separate the terms related to collection of water and of non-condensable gas. The total of the terms, denoted as α in Appendix 1, therefore needs to be sufficiently large to minimize error, as opposed to merely the gas volume being large. This fact suggests a solution to the high steam problem, in that a large volume of water in the impingers can compensate for the low volume of gas measured in the dry test meter.

The following steps were found to be successful in a field test:

1. Ahead of the first impinger, a 5 liter heavy gauge Nalgene carboy was installed, with a custom made cap fitting. This served as a pre-weighed primary impinger for steam condensation. This pre-impinger was partially filled with ice before weighing, in order to encourage as much heat loss as possible before the gas entered the glass Greenberg-Smith impinger system, where resistance to heat loss is greater. After the test, the dry test meter was disconnected, and the carboy flushed with nitrogen, in order to capture any residual hydrogen sulphide from the pre-impinger water in the copper sulphate impinger.
2. Two dry Greenberg-Smith impingers were added between the copper sulphate impinger and the drying tube, in order to allow for overflow of the first impingers and to encourage the condensation of residual water vapour. This extends the life of the drying tube.

This arrangement was successful in yielding reproducible results of an acceptable error (about 5%). The system allowed for only small volumes of non-condensable gas, as illustrated by the following example. In a typical test, only about 100 liters (4 cubic feet) of gas might be sampled. During this test, over 3000 net grams of water would be collected, and 12 kilograms (26.5 lbs) of ice consumed for cooling. At the end of this test, the drying tube usually becomes too hot to permit further sampling, because water vapour will then enter the dry test meter. It is probably best to use the pre-impinger only once, to ensure its integrity. Re-use after it has undergone a cycle at high temperature may cause failure during a subsequent test.

The modified train is shown in Figure 2.

LOW STEAM FACILITIES

In facilities whose streams are low in water vapour,

obviously no limitations related to heat transfer or water holding capacity will be encountered. The difficulty here arises from a further significant difference from the original procedure.

In the normal course of events in the Figure 1 train, hydrogen sulphide is captured quantitatively in the copper sulphate impinger. As the hydrogen sulphide is captured, a significant quantity of water also condenses. The high solubility of hydrogen sulphide in the cold steam condensate thus probably assists in the capture of hydrogen sulphide.

In a dry stream, the hydrogen sulphide is instead required to quantitatively undergo mass transfer from the gas to the aqueous phase of the impinger, and therefore some kinetic limitation to capture might be anticipated.

In a field test with a dry gas of several thousand ppm hydrogen sulphide content, this was found to be so. In contrast to a normal test with steam condensation, where no odour of hydrogen sulphide was noticeable at the exit line of the train, in the case of a dry gas hydrogen sulphide was noticeable. As anticipated, in the train of Figure 1, the concurrent condensation of steam greatly improves the efficiency of hydrogen sulphide capture.

The problem was overcome by adding a second copper sulphide impinger before the drying tube. The amount of copper sulphide recovered from this second impinger was always small compared to that of the first, so that the accuracy of the results would not be affected. However, the small amount of hydrogen sulphide escaping the first impinger (estimated at less than 0.1% from visual copper sulphide recovery) might be sufficient to damage the dry test meter. Therefore the second copper sulphate impinger is recommended wherever the moisture content of the stream to be tested is expected to be low. The schematic is shown in Figure 3

SULPHUR DIOXIDE EMISSIONS MEASUREMENT

The method of measurement of sulphur dioxide emissions from industrial sources is regulated by well-known stack survey codes, such as the Canadian and Alberta codes, which are essentially similar to internationally accepted standards. One feature of these codes is that a standard error of approximately 10% is attainable, and accepted by regulators.

In SAGD facilities, the steam generators are

typically of a design that precludes use of the accepted stack survey methods. It is also common in SAGD schemes to utilize produced gases, which contain hydrogen sulphide, as fuel gas supplements after removal of steam condensate. As a result, any SAGD scheme will emit sulphur dioxide as the produced hydrogen sulphide burns, but measurement of this emission by conventional stack survey codes is impractical.

The observation above, with respect to low steam sources, represents a way of overcoming this problem. It is possible to measure the hydrogen sulphide in the dry fuel gas. If an adequate amount of gas is sampled through the dry test meter, a standard error of 5% is readily achievable. By combination of the result with an orifice meter reading of the fuel gas, an overall error of 10% for sulphur dioxide emissions is readily attained. Thus we have an alternative to the stack survey codes for SAGD, but with a similar error margin. There should be no need to re-design SAGD steam generators to enable conventional stack surveys for sulphur dioxide.

CONCLUSIONS

1. A previously reported method for measurement of hydrogen sulphide in SAGD operations, previously applicable to wet gas streams with no more than 70% steam, is capable, with minor modification, of application to dry gas streams, and gas streams with over 98% steam.
2. Application of the modified method to sour fuel gas lines yields an alternative method for estimating sulphur dioxide emissions from SAGD steam generators. The alternative has the same level of accuracy as the stack survey codes in use in Alberta, Canada, and the USA.

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NOMENCLATURE

Φ_1 = standard error of variable I
 C = concentration ratio
 K_0 = orifice meter constant
 T = temperature

P = pressure
 M = molecular weight of gas
 V = volume of gas

REFERENCES

1. H.F.Thimm, "Hydrogen Sulphide Measurement in SAGD Operations", J. Can. Petroleum Technol. 40(1), 51-53 (2001)

APPENDIX 1. ERROR ANALYSIS

For a function R (A,B,C...) which depends on measurement of A,B,C,..., the general equation for error propagation is

$$\sigma_R^2 = \left(\frac{\partial R}{\partial A}\right)^2 \sigma_A^2 + \left(\frac{\partial R}{\partial B}\right)^2 \sigma_B^2 + \left(\frac{\partial R}{\partial C}\right)^2 \sigma_C^2 + \dots$$

If the mass of copper recovered is G, the corresponding amount of hydrogen sulphide formed is G/63.55 moles, because of stoichiometric equivalence. The ratio of hydrogen sulphide to the steam and non-condensable gases is then given by the following equation:

$$C_{H_2S} = \frac{AG}{BM_w + DV_{REF}}$$

Here V_{REF} is the volume of non-condensable gas corrected to the reference temperature and pressure and M_w is the mass of water (steam condensate) collected. The terms A, B and D respectively are the reciprocal molar masses of copper and water ($A=1/63.55$, $B=1/18$) and the reciprocal molar volume of an ideal gas at 25°C ($D=1/24.467$). For convenience we set the denominator = ∇ .

Then it is easily shown by means of the above equations that

$$\left(\frac{\sigma_C}{C}\right)^2 = \left(\frac{\sigma_G}{G}\right)^2 + 0.003087\left(\frac{\sigma_{M_w}}{\alpha}\right)^2 + 0.00167\left(\frac{\sigma_{V_{ref}}}{\alpha}\right)^2$$

The above procedure is repeated for the term V_{REF} , which is expanded to the form

$$V_{REF} = K_0 \sqrt{\frac{T\Delta H}{PM}} \left(\frac{T_{REF}}{T}\right) \left(\frac{P_{REF}}{P}\right) \tau$$

In this equation, K_0 is the orifice meter constant, T the temperature, P the pressure, M the molecular

weight of the gas and ΔH the orifice pressure drop. This procedure gives the error term for the reference volume

$$\left(\frac{\sigma_V}{V}\right)^2$$

as a function of the other measured or calibrated variables in the equation defining the volume. The error in the water volume is easily estimated, and that of the volume obtained as above. It remains only to change the variables to include the term ∇ to complete the error analysis.

The critical aspect of this analysis is that the denominator of the concentration ratio, ∇ , remains intact after mathematical manipulation. Thus, if this term is large, it will suppress the standard error regardless of the relative magnitude of the water or gas terms.

Given the coefficients for the water and gas terms in the error equation, the standard error will normally be governed by the error in measuring G . If ∇ is small by virtue of both water collection and gas collection being small, it is possible to obtain a high standard error. This situation may arise when dry sources are sampled, and only a small volume of gas is collected. That problem is easily avoided.