GAS FLOWMETERS REPEATABILITY AND ACCURACY MIGHT BE IMPEDED BY ELEMENTAL SULPHUR DEPOSITION

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SUMMARY

K-Lab uses sonic nozzles as reference flowmeters for gas flow metering. Gravimetric primary calibration of these nozzles in natural gas containing approximately 3 mg/m^3 of hydrogen sulphide has demonstrated a lack of repeatability and accuracy which was totally unexpected. These abnormal results have been identified to originate from the deposition of elemental sulphur in the nozzle throats.

The deposit of sulphur has been observed in the pressure range 20-150 bar. The report describes probable mechanisms of deposition. Hydrogen sulphide (H_2S) and the thermodynamical conditions in the nozzle throat region have been identified as the major contributors to the deposition phenomena. The method employed to reduce the hydrogen sulphide concentration to parts per billion, ppb, level is described. By using a zinc oxide catalyst bed on the gas supply line to K-Lab the sulphur deposition rate is significantly slowed down. Finally a sample of primary calibration results of sonic nozzles in natural gas with and without the catalyst bed installed, are compared with calibration results obtained with nitrogen at overlapping operating conditions.

1 INTRODUCTION

K-Lab (1) uses sonic nozzles in parallel as a reference flowmeter (figure 1). The first primary calibrations of these nozzles with natural gas during 1988, using a gravimetric method (figure 2), show results with a lack of repeatability and accuracy which were outside the design uncertainty of 0.25% on mass flow measurement using the sonic nozzles.

2 BACKGROUND

The lack of repeatability and accuracy of the initial primary calibrations of the sonic nozzles in natural gas using the gravimetric calibration system is presented in figure 3. The gas which is currently used at K-Lab has a typical composition shown in table 1. The nozzles which are built according to ISO-DIS9300 have toroidal throats with diameters varying from approximately 8 mm to 23 mm.

The reason for the lack of repeatability in the calibration results was not immediately identified. However, after having investigated all possible errors which might have been generated by the secondary instrumentation such as pressure and differential pressure transducers, resistance temperature devices, valves, timer etc., the problem was narrowed down to the nozzles themselves. One theory to explain this lack of repeatability was an unstable boundary layer transition within the nozzles. In order to check this theory it was decided to install a boundary layer trip ring inside the smallest nozzle. On opening up the nozzle to install the trip ring a solid deposit was discovered in a location which extended from upstream of the nozzle throat to downstream of the throat as shown in figure 4. The same deposit was observed in all the nozzles. The deposit was collected and analysed and found to be elemental sulphur.

3 OPERATING CONDITIONS AND SULPHUR DEPOSITION

The sulphur deposition occurred at the same time as the discovery of the collapse of 2 cartridges of the 3 compressor inlet filters, releasing dirt, dust and rust. It was proved that there was no relation between the two occurences as the sulphur deposit still appeared in the nozzle throat after having replaced the collapsed filters. A series of tests, varying the operating conditions, was then undertaken. The findings from the investigations are summarized in the following.

3.1 Pressure

Tests to investigate the influence of pressure on the deposit phenomenon, at a fixed gas temperature of 37°C, produced the following findings:

- Deposit of a sulphur layer occurs throughout the pressure range 20 bar to 110 bar.
- The rate of deposition increases with pressure.
- For a given pressure, varying the nozzle throat diameter (from 8 mm to 23 mm) has no influence on deposition.

3.2 Gas temperature

The normal operating temperature of the gas upstream of the sonic nozzles is 37°C, and this was the temperature for all the tests detailed in section 3.1. Tests to investigate the effect of gas temperature on the sulphur deposition produced the following findings:

- At a gas temperature of 56°C (and 75 bara) sulphur deposit was observed.
- At a gas temperature of 6°C (and 78 bara) a very thin coat of sulphur deposit was observed and the deposit

did not stick to the polished stainless steel surface as hard as with the higher gas temperatures used.

3.3 External heating of the nozzles

The nozzle spool piece is normally not insulated and so the air temperature around the nozzle is ambient. A test was carried out with the nozzle spool piece heated to 50°C and the gas temperature was 50°C. The result was that the position of the sulphur deposit was moved downstream approximately 8-20 mm, with the actual nozzle throat being clear of sulphur.

3.4 Mechanical design

The following tests were done:

- Changing nozzle inlet wall shape and truncating a nozzle at the throat plane, the sulphur deposit still occurred.
- Changing nozzle material to teflon, the sulphur deposit still occurred.
- Installation of boundary layer trip ring, the sulphur deposit still occurred.

3.5 Nozzle location

It was assumed early in the test programme that the sulphur deposit was due to the closed loop mode of operation of K-Lab, as this is one of the major differences between K-Lab and the other gas laboratories. However, the sulphur deposit still occurred when sonic nozzles were located on the feed line to K-Lab and when K-Lab was operated in a blow down mode through a sonic nozzle.

3.6 Hydrogen sulphide concentration

As can be seen in table 1, the gas that K-Lab uses contains very small amounts of sulphur based components. The major contribution is the hydrogen sulphide, H_2S, whose concentration in the test period of reference was around 3 ppm (3 mg/m^3), well within the contractual specifications for the H_2S concentration for the gas.

Table 2 shows possible different chemical reactions leading to sulphur formation.

An extensive monitoring of the H_2S content in the loop was performed whilst it was pressurized and during circulation of the gas. The loop and storage tank was filled with a gas whose H_2S concentration was 3 mg/m^3. After circulation through the loop for 3 days the concentration was reduced to 1.4 mg/m^3 in the storage tank, while it became 0.05 mg/m^3 in the loop. The results are shown in table 3. A deposit of sulphur was found in the nozzle.

3.7 Addition of hydrogen

Next a test was run to see whether addition of a limited amount of hydrogen to the gas would have the same effect on the disappearance of the hydrogen sulphide in the tank and the loop. Hydrogen was therefore injected into the natural gas to give 10 ppm by volume. This injection showed no retarding effect on the disappearance of hydrogen sulphide which became undetectable after 2-3 hours, as can be seen in table 4. Continuous injection of hydrogen upstream of the nozzle to maintain the concentration at 10 ppm had no effect. After 3 hours the sulphur deposit was again observed in the nozzle.

3.8 Removal of hydrogen sulphide

The studies performed from November 88 to February 89 indicated clearly that H_2S was the major contributor to the sulphur deposit. It was therefore decided in February 1989 to install at the gas inlet supply to K-Lab a zinc oxide catalyst bed able to reduce the H_2S concentration to 10 ppb. The filtration bed was commissioned during spring 1990 and a picture of it is shown on figure 5. Tests have confirmed that the zinc oxide bed reduces the H_2S concentration to 10 ppb.

4 PRELIMINARY TEST RESULTS WITH THE ZINC OXIDE BED

Primary calibrations of the sonic nozzles in natural gas at 100 bar were restarted in July 90. No sulphur depositions were observed during this calibration sequence.

However, at 150 bar sulphur reappeared in the nozzles. When the pressure was reduced again to 100 bar there was still indication of sulphur deposition in the nozzle throats, whereas no sulphur deposit had been obtained prior to the 150 bar tests.

K-Lab's current knowledge proves that a zinc oxide filter on the gas supply line, reducing the H_2S concentration to 10 ppb, delays significantly the sulphur deposition rate in the sonic nozzle throats. Whilst sulphur deposition occurred even at 20 bar with H_2S at 3 ppm, the appearance of the deposit now only appears at and above 100 bar with the present design.

5 SULHPUR DEPOSITION IN SONIC NOZZLE THROATS AND DISCHARGE COEFFICIENTS

During the period 1988-1990 K-Lab has run a primary calibration programme on natural gas without catalytic

reduction of hydrogen sulphide (NAT GAS OLD), with hitrogen (N_2) and natural gas with catalytic reduction of hydrogen sulphide (NAT GAS NEW). Table 5 shows the range of operating conditions within which these primary calibrations have been performed.

To show the influence of the sulphur deposit in the nozzle throat, primary calibration results obtained on the standard nozzle having a 8.20 mm diameter throat on NAT GAS OLD, N_2 and NAT GAS NEW are shown in figure 6.

While N_2 and NAT GAS NEW data show an uncertainty better than 0.2%, the spread in the NAT GAS DATA especially at 75 bar ($Re_{throat} \# 10 * 10^6$) and 100 bar ($Re_{throat} \# 13.5 * 10^6$) is above 2%.

The ISO-DIS 9300 tabrelated data are indicated for comparison purposes.

6 FUTURE WORK

The current work at K-Lab aims at improving the operating process to achieve conditions where the sulphur deposit problem can be considered as negligible. Actions are presently being undertaken to circumvent or eliminate the sulphur problem. Figure 7 shows possible routes which will be followed.

In addition extended primary calibrations at high pressure will be run in order to obtain a reliable data base for assessment of the repeatability which can be achieved at the present time.

All tests so far have demonstrated that sulphur deposits in the nozzle throat do not perturbate the measurement of stagnation pressure and temperature at the nozzle inlet.

References

(1) High pressure calibration of sonic nozzles in natural gas. P.L. Wilcox - Int. Gas Research Conference, Tokyo Nov. 1989.

(2) Deposition of elemental sulphur (S_8) in nozzles at K-Lab. K. Brekkhus. Int. report Statoil GASS-T No. 1098.

Component	Mol. %
N_2	0.72
CO_2	0.81
C_1	85.30
C_2	12.24
C_3	0.35
iC_4	0.03
nC_4	0.05
iC_5	0.00
nC_5	0.00
nC_{5+}	0.00
Molecular Weight	18.49
Gross Calorific value MJ/sm³	39.7-43.7
Wobbe Index MJ/sm³	48.4-52.8
HC dewpoint at 51 bar	−11°C max
Water dewpoint at 69 bar	−18°C max
O_2, Mol %	0.1 max
CO_2, Mol %	2.5 max
H_2S, mg/sm³	4.7 max
Mercaptans, mg/sm³	14.2 max
Total sulphur, mg/sm³	142.0 max

Table 1. Mean gas composition.

$$CO_2 + H_2S \text{ ----- } CO + H_2O + S \quad (1)$$

$$2H_2S + SO_2 \text{ ----- } 3S + 2H_2O \quad (2)$$

$$2H_2S + O_2 \text{ ------ } 2S + 2H_2O \quad (3)$$

$$CO_2 + 2H_2S \text{ ---- } 2S + 2H_2O + C \quad (4)$$

$$SO_4^{--} + 3H_2S \text{ ---- } 4S + 2H_2O + 2OH^- \quad (5)$$

$$H_2S \text{ ------ } S + H_2 \quad (6)$$

$$Fe(OH)_2 + H_2S \text{ ------ } FeS + 2H_2O \quad (7)$$

$$FeS + H_2S \text{ ------ } FeS_2 + H_2 \quad (8)$$

$$Fe_2O_3 + 3H_2S \text{ ---- } Fe_2S_3 + 3H_2O \quad (9)$$

$$2Fe_2S_3 \text{ ------ } 3FeS + FeS_2 + S$$

$$COS + Fe_2O_3 \text{ ----- Fe sulphide} + S + CO_2 \quad (10)$$

$$3COS + Fe_2O_3 \text{ ----- } 2FeS + S + 3CO_2 \quad (11)$$

Table 2. Chemical reactions which might lead to sulphur formation.

Time	Sales gas (H_2S) mg/m³	Stor. tank (H_2S) mg/m³	Loop (H_2S) mg/m³	Circulation
24/11-1300	2.97	-	-	No
-1400	-	3.00	3.01	No
24/11-1800	-	2.61	ND	Yes
25/11-0400	-	2.07	ND	Yes
-0840	-	1.81	ND	Yes
26/11-1000	-	1.45	ND	Yes
27/11-1000	-	1.42	ND	Yes

Table 3. Monitoring of H_2S concentration in storage tank and loop (ND = non detectable)

Time	Samplepoint	Results (H_2S) mg/m³	Comments
1015	Sales gas	1.29	H_2 injected
1015	Storage	1.18	Closed
1015	Loop	1.14	No circulation
1115	Loop	0.19	Circulation
1315	Storage	1.18	Closed
1315	Loop	ND	Circulation

Table 4. H_2S concentration in the storage tank and loop after hydrogen injection (10 ppm)

	NAT GAS OLD	N_2	NAT GAS NEW
Throat diam. (mm)	8.20_11.76_16.50 23.22	-"-	-"-
Pressure	20-155 bar	20-100 bar	75-150 bar
Gas temper	37 °C	-"-	-"-
Throat Re	$2.8x10^6$-$2.9x10^7$	$2.2x10^6$-$3.8x10^7$	$9.7x10^6$-$5.6x10^7$
Calibration period	04.88 - 10.88	04.89 - 11.89	07.90

Table 5 Range of operating conditions for primary calibration data of sonic nozzles at K-Lab reported in figure 6.

Fig.1 SCHEMATIC LAYOUT OF THE K-LAB TEST LOOP

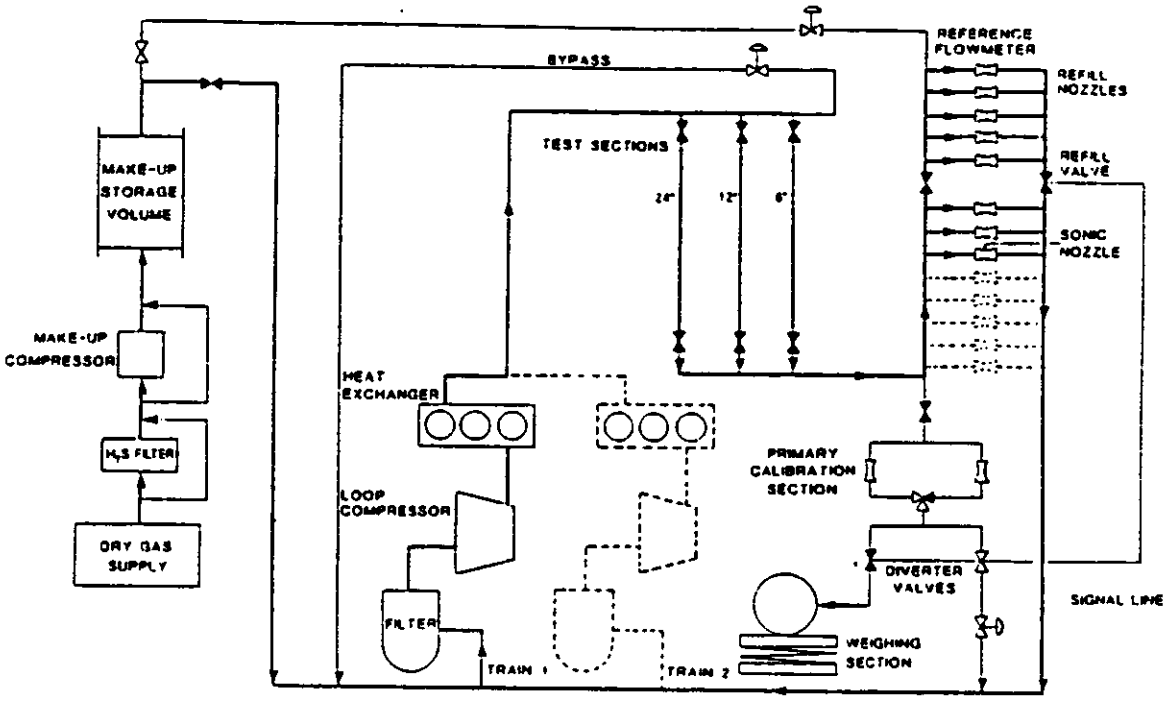


Fig.2 PRIMARY CALIBRATION SECTION

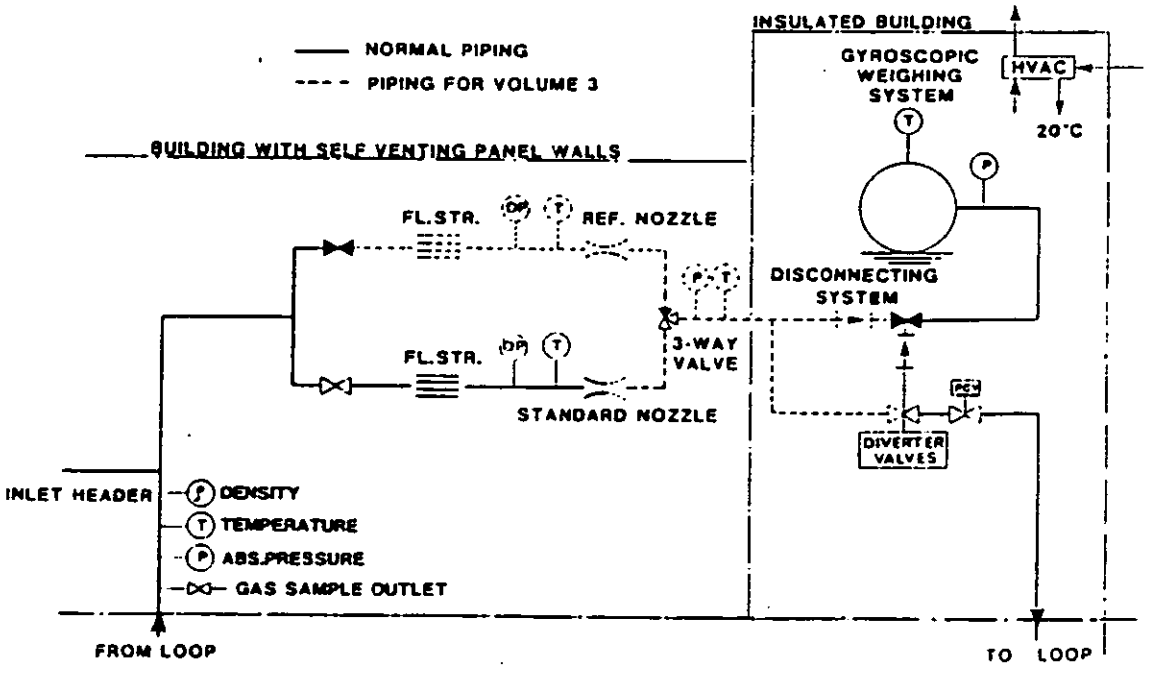
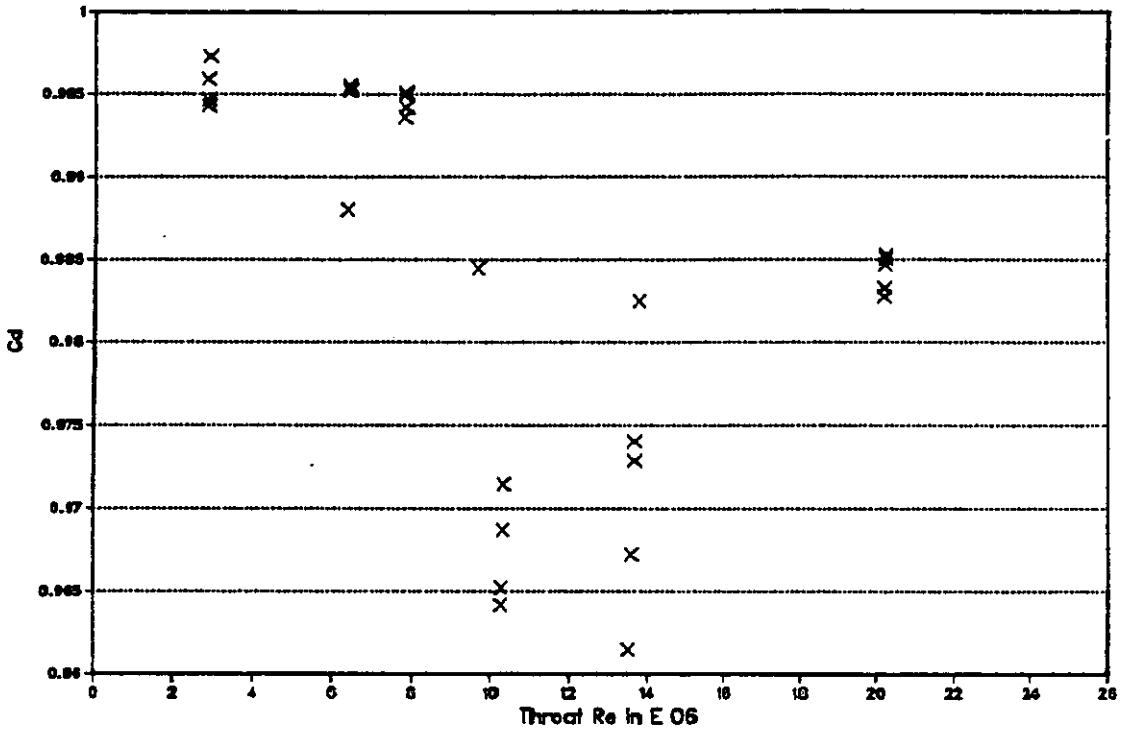


FIG.3
DISCHARGE COEFFICIENTS IN NATURAL GAS MEASURED AT K–LAB
PRIOR TO INSTALLATION OF HYDROGEN SULPHIDE CATALYST BED



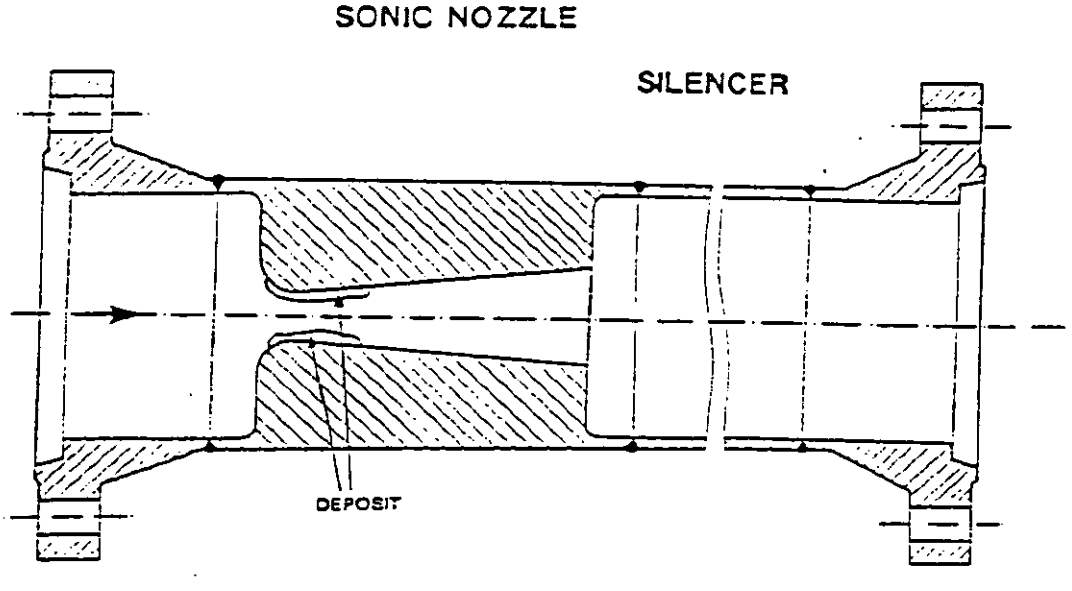


Fig.4 NOZZLE DESIGN SHOWING DEPOSITION REGION

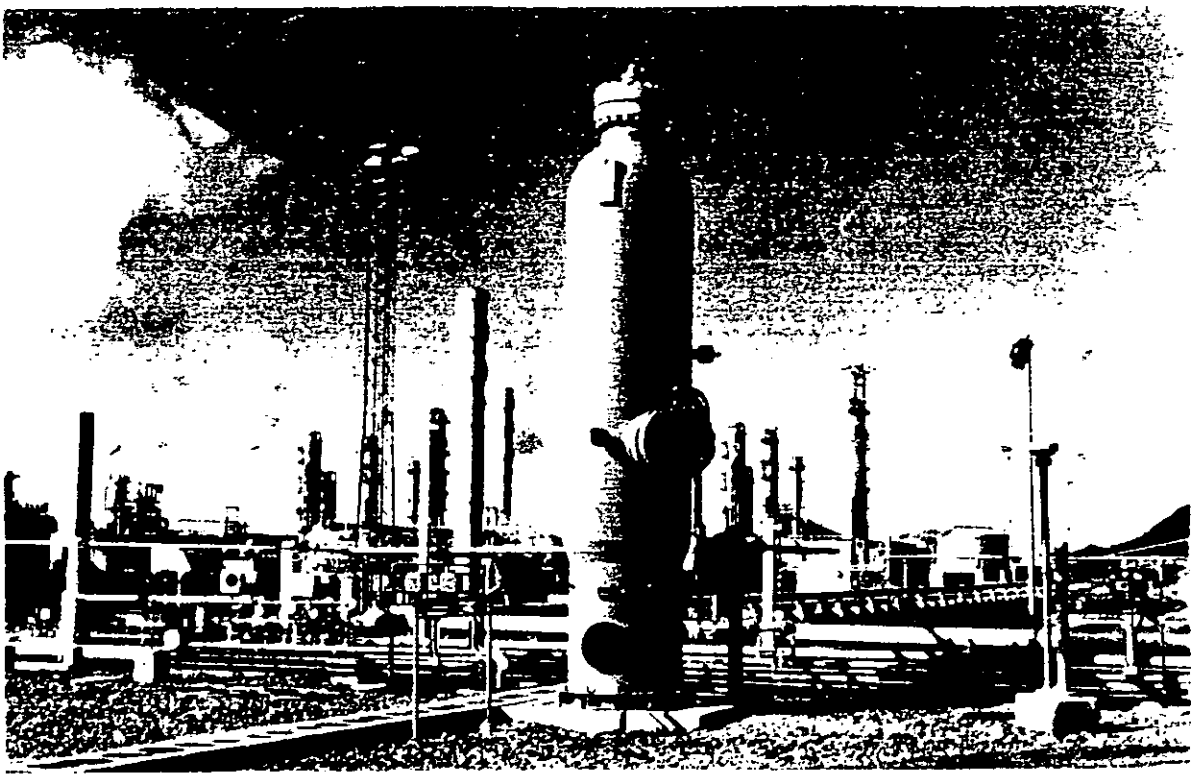
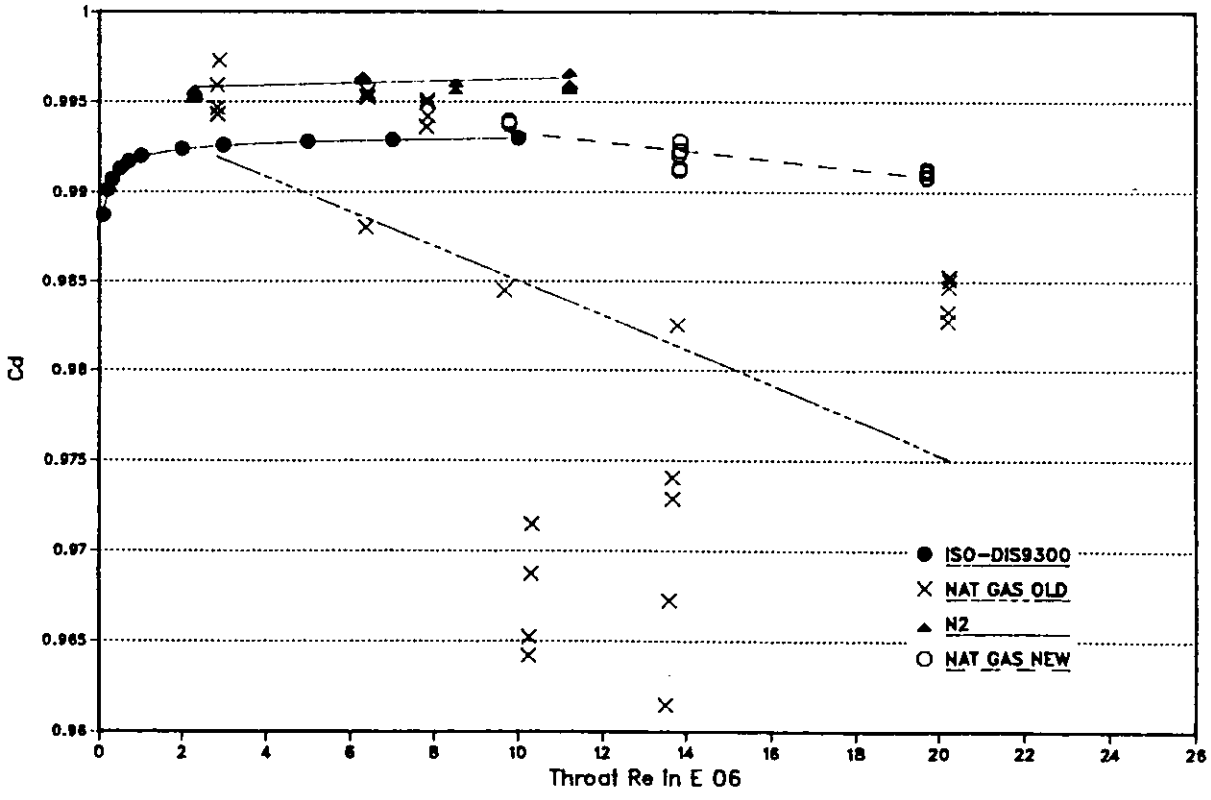


Fig.5 HYDROGEN SULPHIDE REMOVAL VESSEL

FIG.6
DISCHARGE COEFFICIENTS MEASURED AT K-LAB



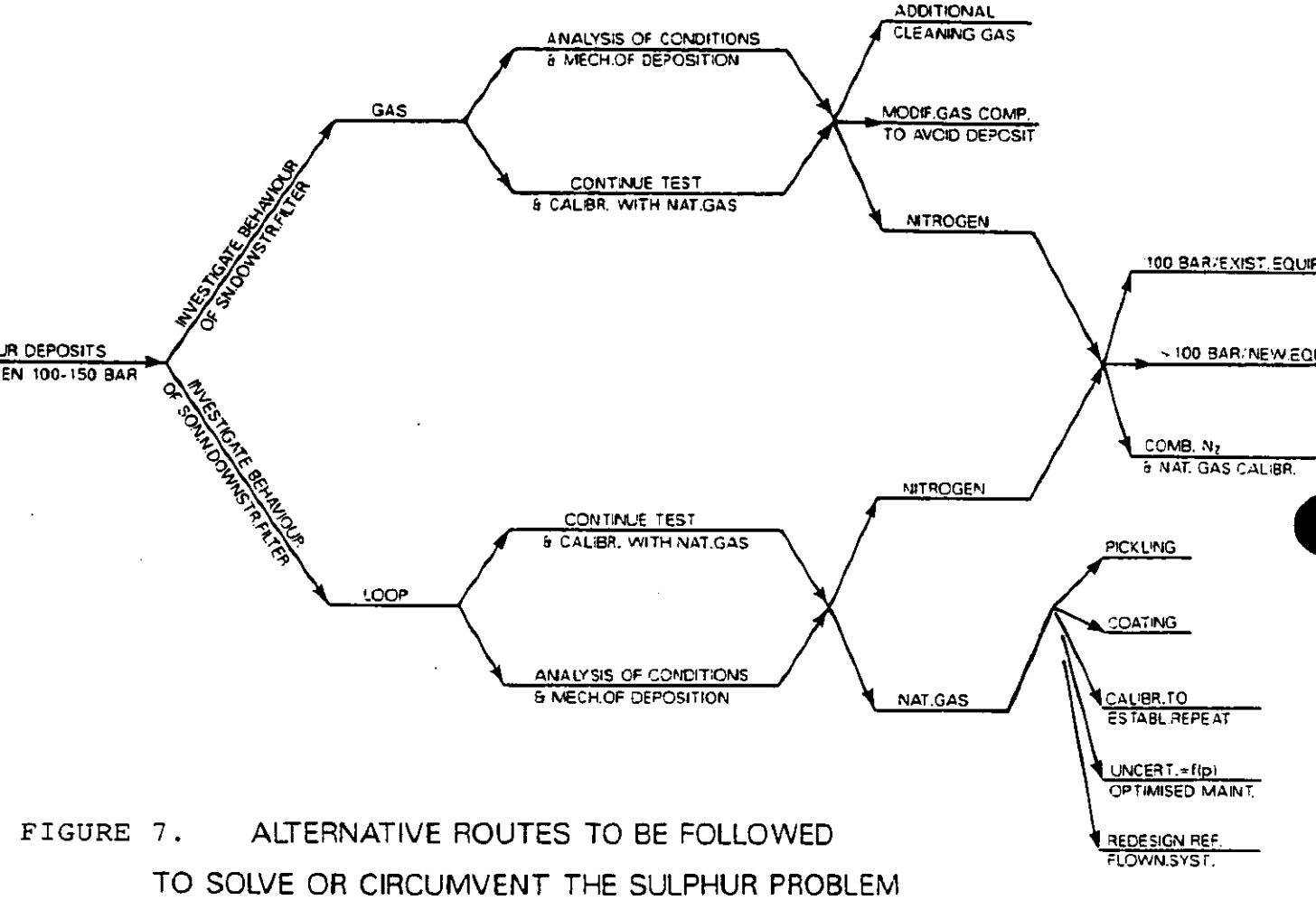


FIGURE 7. ALTERNATIVE ROUTES TO BE FOLLOWED TO SOLVE OR CIRCUMVENT THE SULPHUR PROBLEM

References

[1] Paper presented at the North Sea Flow Measurement Workshop, a workshop arranged by NFOGM & TUV-NEL

Note that this reference was not part of the original paper, but has been added subsequently to make the paper searchable in Google Scholar.