OILFIELD RESERVOIR SOURING

Prepared by CAPCIS Ltd, UMIST, and BP Exploration for the Health and Safety Executive
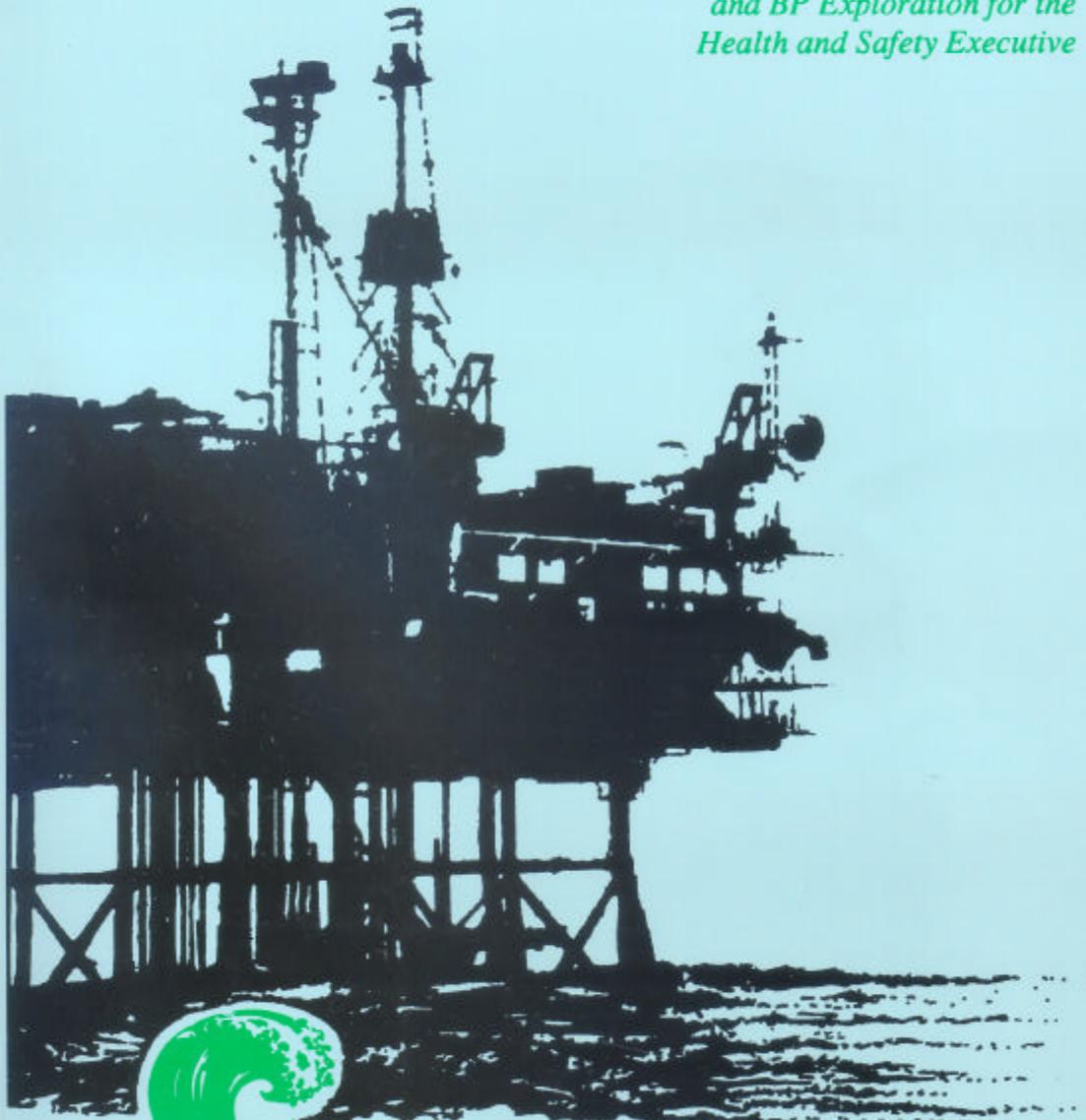
Offshore Technology Report

Health and Safety Executive

OILFIELD RESERVOIR SOURING

Authors

Bob Eden, Consultant
CAPCIS Ltd
Bainbridge House
Granby Row
Manchester M1 2PW

Patrick J Laycock, Senior Lecturer
Department of Mathematics
UMIST
Sackville Street
Manchester M60 1QD

Mike Fielder, Team Leader, Production Chemistry
BP Exploration
BP Exploration Operating Company Ltd
Farburn Industrial Estate
Dyce
Aberdeen AB2 0PB

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SUMMARY

Oilfield reservoir souring has occurred when increasing concentrations of hydrogen sulphide H_2S are observed in production fluids. This foul smelling and corrosive 'sour gas' is toxic to life and liable to cause cracking and pitting of susceptible steels.

The origin of H_2S has generally been linked with secondary recovery. Without secondary recovery over the production life of a reservoir, the reservoir pressure would continuously fall, with consequential decline in production rate which may eventually cease. To maintain production, water, often seawater, is usually injected to maintain pressure and to sweep oil through the reservoir. Many oil operators have associated seawater breakthrough with subsequent souring: attention was focused on the rôle of seawater in the souring process.

In the summer of 1987, the multisponsored £$^1/_3$M UK Oilfield Reservoir Souring Programme was launched. The programme investigated both microbiological (biogenic) and non-microbiological souring mechanisms and was completed three years later, culminating in public presentation (1).

A survey of the initial condition of forty production wells from ten North Sea fields was conducted at the beginning of the programme. From the gas phase H_2S criteria, 10% were deemed sour, the balance ranging down to below the gas phase detection level for H_2S of less than 0.5 ppmv. Statistically, a weak but positive correlation was found between the oil formation's iron sulphide (primarily pyrite) content and gas phase H_2S concentration and a negative correlation with the formation's iron carbonate (siderite) content. It appeared that a protective 'Siderite Shield' would actually mitigate H_2S production. The pyrite/siderite balance therefore dictated the initial H_2S concentration, presumably reflecting some ancient equilibrium. In turn, the presence or otherwise of H_2S in the gas phase generally dictated the starting choice of engineering materials for either sweet or sour service.

At typical temperatures (to 120ºC) and pressures (to 500 atm) found in a North Sea reservoir, the geochemical effect of seawater on reservoir components was not demonstrated in the laboratory to produce H_2S. However, statistical analysis demonstrated strong correlations between seawater injection parameters and subsequent souring; more specifically those conditions which created a downhole environment in which anaerobic sulphate-reducing bacteria could live. This was reinforced by field evidence.

The thesis of this report supports a biogenic souring model to explain an unexpected increasing mass of H_2S in produced fluids. Applied research into the practical control of souring continued with the 1991 launch of the £½M international 'Sweetwater Programme'. The results of this latter programme are outwith with scope of this document.

GLOSSARY OF TERMS

Anaerobic	In the absence of oxygen, cf aerobic.
Autoclave Test	High pressure (to 5000 psig) and temperature (to 350ºC) apparatus for evaluation of H_2S evolution under a variety of mineralogical and physical parameters.
Barrel, bbl	Petroleum barrel; a unit of measure of crude oil and oil products equal to 42 US gallons (158.99 litres).
Biocide	Usually refers to a chemical agent that is intended to kill microbiological life, as opposed to sterilisation by heat or ultraviolet radiation.
Biogenic	Arising from living processes.
Biogenic Souring	The appearance of sour gas in production fluids as a consequence of the introduction and activity of sulphate-reducing bacteria generating H_2S within a waterflooded zone of (particularly) a petroleum reservoir.
Catalyst	A material that increases the rate of a reaction without undergoing change itself.
Dynamic TVS	A predictive tool emulating reservoir behaviour in terms of changing H_2S production over the lifetime of that reservoir.
Endothermic	Heat absorbing, cf exothermic, (heat evolving).
Geochemical Souring	A proposed mechanism to account for the appearance of sour gas in production fluids as a consequence of organic or inorganic chemical reactions generating H_2S within a waterflooded zone of (particularly) a petroleum reservoir.
Geological Souring	The presence or appearance of ancient sour gas within or from a formation and unrelated to modern microbiological or geochemical processes.
Gothic Arch	The visual appearance of the pressure/ temperature curve within the boundary of which bacterial growth occurs.

Growth Domain	The extent of conditions within which bacterial growth can be supported, eg pH, pressure/ temperature, substrate availability.
h-SRB	*Archaebacteria* which grow optimally at 'hyperthermophilic' temperatures >80ºC.
Hydrogen Sulphide, H_2S	Also referred to as 'sour gas', hence reservoir souring. A heavier than air toxic gas with an eight hour time weighted average occupational exposure limit of 10 parts per million by volume (ppmv) and a ten minute exposure limit of 15 ppmv by inhalation (HSE 1990). Dissolved in aqueous environments this gas can cause corrosion and structural failure of certain steels by their cracking and pitting.
Inoculum	A (relatively) small aliquot of substance containing micro-organisms.
Isotope Fractionation	The sifting of S^{32} from a mixture of sulphur isotopes during the production of H_2S from sulphate. This process enriches for S^{32} and is an indicator of whether the H_2S production process was geochemical (no fractionation) or biological. It cannot differentiate between modern or ancient biogenic activity.
Milligrams per litre, mg/l	A concentration term to define amount of substance which is used as a practical numerical equivalent to the derived SI unit of milligrams per cubic decimeter ($mgdm^{-3}$). Erroneously and often considered to be equal to dimensionless parts per million (ppm).
Minimum Infective Dose	The minimum number of organisms required for sustained growth when introduced into a new environment.
m-SRB	Mesophilic sulphate-reducing bacteria which grow optimally within the temperature range 20-40ºC.
Negative Shift	The shift of ratio of S^{34} to S^{32} to an increase in S^{32} concentration by biogenic fractionation.
Non-microbiological	In the context of Reservoir Souring, the meaning can be considered synonymous with 'geochemical' or 'geological'.
Parts per million by volume, ppmv	Commonly used as a term for gas concentrations to define amount of substance which is the molar volume ratio of a specified gas within a gas phase and is a numerical equivalent to the derived SI unit of cubic centimetres per cubic metre (cm^3m^{-3}).

Parts per million by weight, ppmw	Commonly used as a term for concentration to define amount of substance which is actually a mass ratio and is a practical numerical equivalent to the derived SI unit of milligrams per kilogram ($mgkg^{-1}$).
Pressure/Temperature or P/T Profile	The combination of pressure and temperature which define the growth limits of micro-organisms.
Redox	Reduction/oxidation. High redox potentials (E_h *positive*) reflect oxidising conditions and low redox potentials (E_h *negative*), reducing conditions.
Redox Poising	Capable of sustaining a set redox potential.
SeRec	The name given to the database of injection and production parameters used to calibrate Dynamic TVS, the Reservoir Souring predictive tool.
Shelf Breakdown	When H_2S appears at the wellhead later than expected and ascribed to the exhaustion of siderite scavenging property, (see below).
Siderite Shield	The so-called protective nature and diagrammatic appearance on 3-axis plots, of siderite scavenging H_2S from slow pyritic breakdown.
Souring Model	A quantitative model devised to assist in the understanding of a reservoir's propensity or otherwise to sour.
Standard cubic foot of gas, scf	The volume of gas contained in one cubic foot of space at a temperature of 60ºF (288.7K) and a pressure of 14.65 pounds per square inch absolute (1 bar = 0.987atm). Millions of standard cubic feet of gas are denoted by mmscf.
Substate	Any material required for the growth or metabolism of an organism.
Thermal Viability Shell or TVS	That portion or the water flooded reservoir which by virtue of its temperature limits alone could support either m-SRB or t-SRB activity.
t-SRB	Thermophilic sulphate-reducing bacteria which grow optimally at temperatures >55ºC.

1. INTRODUCTION

1.1 WHAT IS OILFIELD RESERVOIR SOURING?

Increasing mass of hydrogen sulphide (H_2S) per unit mass of total produced fluids is the phenomenon of souring, and a well which produces H_2S is said to be sour, in contrast to a sweet well, which does not produce H_2S. However, because low gas phase concentrations of H_2S, up to around 3 parts per million by volume (ppmv), are typically benign or even beneficial in their effects on oil well and processing equipment, the transition from being sweet to being sour is usually referred to a baseline of around 3ppmv rather than zero. And this concentration is typically measured in the gas phase relative to a partition from an aqueous phase at/or less than pH5 at Standard Temperature and Pressure (STP, OºC and 1 absolute atmosphere).

To increase the yield from hydrocarbon reservoirs, water is pumped under pressure into the reservoir to shepherd the crude oil towards the production wells and to maintain reservoir pressure. In the North Sea, this waterflood is seawater. At the outset of the Reservoir Souring Programme, the North Sea was largely defined as 'sweet'. In such reservoirs carbon dioxide is generally present in variable, usually percentage, concentrations in the gas phase, whereas H_2S is measured in terms of up to a few parts per million by volume.

The corrosivity of co-produced water from an oil reservoir can change over its lifetime. This is particularly marked in fields that are initially considered sweet, but produce more H_2S in later life, in some cases at concentrations of up to many thousands of parts per million by volume in the gas phase. Whilst carbon dioxide can cause very severe corrosion (ie general and pitting) of steels, H_2S corrosion is more localised, and can cause Sulphide Stress Corrosion Cracking (SSCC), Hydrogen Embrittlement (HE), Hydrogen Induced Cracking (HIC) or Stress Orientated Hydrogen Induced Cracking (SOHIC). Hence, increasing H_2S will not necessarily cause a pro-rata increase in general corrosion rate, but rather lay susceptible materials prone to catastrophic failure.

The phenomenon of unexpected increase in hydrogen sulphide concentrations in produced fluids from petroleum reservoirs has been observed over a period of many years in different areas of the world (2-6). In recent years at least two major North Sea oil fields are reported to have recorded higher concentrations of hydrogen sulphide in produced fluids after seawater breakthrough occurred (7). Most workers in this subject had directed attention to the activities of sulphate-reducing bacteria (SRB) and considerable money had been invested in biocide treatment programmes for seawater injection, with the principal aim of killing or controlling this group of microorganisms (8-10).

The evidence for involvement of SRB in the souring mechanisms was, however, largely circumstantial, though these organisms had been frequently isolated from injection waters and produced waters where problems had occurred. Indeed they appeared to be part of a natural habitat in deep wells (11); the numbers detected had often been low compared with the very large numbers of SRB frequently isolated from surface environments where sulphide corrosion or fouling problems had manifested themselves. SRB are, however, almost universal in distribution and indeed can be isolated in low numbers from many natural soils, sediments and waters, including seawater. However there were instances of souring problems where no SRB had been isolated from produced waters. The latter were variously ascribed to bad isolation techniques or activity of SRB in remote parts of a reservoir producing sulphide which was then transported through the reservoir with the waterflood, to be produced with the reservoir fluids.

Oil-bearing reservoirs provide environments which combine high pressures with high temperatures. Stott and Herbert (12,13) carried out detailed studies into the effects of such conditions on growth, sulphate reduction and other physiological processes of a large number of mesophilic sulphate-reducing bacteria (m-SRB) isolated in the 'traditional' manner from the North Sea. Their overall conclusion was that though many strains of mSRB from the North Sea are remarkably barotolerant (up to 640 atmospheres) the high temperatures and paucity of conventional m-SRB nutrients in reservoirs made it difficult to understand how such microorganisms could possibly constitute a problem in these environments.

In the mid 1980's developments in the understanding of the microbiology of SRB called into doubt the classical isolation techniques used at that time and had again 'thrown open' the question of sulphate-reducing bacterial activity under the conditions which occur in petroleum reservoirs. At the same time, the belief was gaining credence in the oil industry that some mechanism of geochemical souring may be occurring in these high-pressure, high temperature environments, though there was no consensus of opinion as to the type of mechanism nor was there any published evidence to support the belief.

The engineering, environmental and safety costs associated with reservoir souring have brought about the need for an ever better understanding of this phenomenon.

The aim of the Reservoir Souring Programme was to review the ideas and developments in the field of reservoir souring at that time and to outline the basis of a thorough study with the North Sea environment in mind. It was planned to resolve the microbiological/geochemical souring debate and to offer tentative means of prediction and, if possible, any guidance towards the control of souring.

2. BACKGROUND

Along with many different parameters measured whilst drilling exploration and appraisal wells on a discovery structure, Drill Stem Tests (DST's) provide both reservoir and fluid characteristics which determine the types of hydrocarbon processing facilities required for subsequent field development. The fluids produced during a DST, often of the order of several thousands of barrels, are representative of those fluids present in the reservoir which have been in equilibrium with their surroundings over geological timescales. Apart from the drilling and testing activities, they have undergone little if any change, have not been subjected to contamination by any external agents and are therefore often relied upon to reflect accurately the long term hydrocarbon fluid characteristics and likely production profiles. This early information is used to evaluate the economics for subsequent field development.

Many of the discoveries made in the North Sea contain little or no hydrogen sulphide and consequently, with little evidence to suggest otherwise, some of the early platform facilities have been designed and manufactured to process only these 'sweet' fluids. If the fluids remain sweet, as is the case in many developments, then this philosophy would ultimately prove the most cost effective option. The extra cost of installing equipment capable of processing 'sour' fluids, ie containing H_2S as defined by the NACE MR0175 Standard for Oilfield Equipment (14), would increase substantially the capital development costs of each project.

However in some cases, the onset of souring has occurred during the subsequent commercial production (development) of the field. In these cases two major problems are then faced if facilities have not been designed and manufactured for sour service:

- The operation of wells and associated processing equipment must be maintained within the NACE standard to ensure that the partial pressure[*] of H_2S does not exceed the maximum limit of 0.05psia, and

- The export of fluids from the facility must be controlled to maintain the concentration of H_2S in the fluids within any agreed limits.

These problems have, in some cases, severely restricted production potential with corresponding loss of revenue to the operator. If the concentration of H_2S continues to increase such that the partial pressure of H_2S cannot be contained within the NACE limit or export of fluids within the agreed pipeline specifications becomes impossible, then in some cases wells or even process systems have to be closed in. Expensive options to combat these problems then become the only solution. These include:

- Well workovers to replace tubing and wellheads with upgraded materials

- Suitable coating of unlined vessels or, if impractical, replacement with vessels, manufactured from materials capable of sour service duty

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H_2S partial pressure = system pressure x H_2S mole fraction and H_2S
concentration ppmv = <u>H_2S partial pressure psia x 106</u>
<div align="center">*System pressure psia*</div>

- Changeout of other associated equipment including pipework, instrument control lines and valves which come into contact with the sour fluids

- Addition of H_2S removal equipment to enable gas export to meet any pipeline specifications.

Clearly all of the above options potentially interfere with normal production operations, are expensive and labour intensive. In some cases retrofitting, for example of H_2S removal equipment, may not be possible given the limited space and weight loadings associated with offshore installations.

One alternative to the use of engineering solutions is the addition of H_2S scavenger chemicals at suitable points in the system. Whilst their effects and performance have now been well established, they are not presently considered to be cost-effective long term solutions to the problem.

In terms of safety, once souring has occurred, the monitoring of H_2S in specific areas becomes mandatory. In addition the implementation of appropriate safety procedures has to be rigidly enforced. Whilst this is necessary for all installations producing sour fluids, the costs of retrofitting monitoring equipment are substantially higher than if installed during the construction phase.

Given the above issues, which are by no means exhaustive, the aim of the industry is to develop new fields using the most cost-effective facilities which will be suitable throughout the life of the field. The onus is therefore to predict more accurately from early exploration and appraisal data whether a reservoir will sour and, if so, when and by how much. Clearly any predictive model must afford a high degree of confidence if expensive consequences of over or under design of new oilfield facilities is to be avoided.

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3. AN INVESTIGATION OF GEOLOGICAL AND GEOCHEMICAL SOURING MECHANISMS IN THE NORTH SEA

3.1   BACKGROUND

Petroleum reservoirs present such adverse physical environments for the existence of any form of life that several workers have expressed the view that some geochemical process is at work in the phenomenon of reservoir souring (1,15); however most reports on the occurrence of souring have assumed that the causative agent of hydrogen sulphide production is microbiological.

The non-microbiological souring mechanisms that have been suggested may be categorised as follows:

- Thermochemical sulphate reduction (15)

- Thermal decomposition of organic sulphur compounds (denaturation) (15)

- Dissolution of pyritic material (16)

- Redox reactions involving bisulphite oxygen scavengers (17).

All of these mechanisms have been relatively neglected and very little is understood about them.

3.1.1 Thermochemical sulphate reduction

This appears to be the most plausible geochemical mechanism for souring and the only one for which there is any real evidence in the literature.

That thermochemical sulphate reduction is a feasible mechanism is evidenced by the Le Blanc process for soda manufacture, in which a mixture of sodium sulphate and coke is heated for a considerable period at high temperature:

$$Na_2SO_4 \quad \xrightarrow{\text{coke}} \quad Na_2S + 2CO_2$$
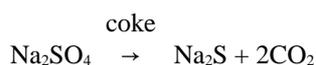
However the strongly endothermic process is normally operated at 1000ºC and is not significant below 700ºC. Sulphur, as the sulphate ion, is however present in sufficient quantity in injected seawater to account for the quantities of observed H_2S in produced fluids. There are also substances present, particularly in the oil which could be reducing agents for this process and it has been shown that clay and other minerals are a rich source of catalysts for a wide variety of reactions. Perhaps under milder conditions than usually employed in the Le Blanc process it is possible with this combination for such a reaction to proceed.

Attempts to show thermochemical sulphate reduction by coal, crude oil, oil shales, starch and glucose at either room temperature for very long periods (18) or at 300ºC (19) have failed.

However, Orr (15) has concluded that thermochemical sulphate reduction can occur at temperatures between 77-121°C in the presence of pre-existing H_2S as a catalyst, eg:

$$SO_4^{2-} + CH_4 \rightarrow H_2S + CO_2 + 2OH^-$$

It is unclear how elevated pressures would affect the above reaction but the implication would seem to be that at temperatures around 100°C slightly sour reservoirs may become sourer in the presence of sulphates.

3.1.2 Thermal decomposition

The implication of Orr's work is that only a reservoir which already contains some H_2S can become more sour by thermochemical sulphate reduction. For a completely sweet reservoir one source of trace H_2S is from the activity of SRB in topsides facilities containing deaerated injection water. Another mechanism which may lead to generation of relatively low concentration of H_2S is thermal decomposition of organic sulphur compounds which are present in some crude oils (15). The drawback of such mechanisms is that they require high temperatures and are not associated with sulphate reduction, nor are they related to seawater injection.

Organic sulphur compounds range from the very stable aromatic sulphides to very unstable thiocarbamates and it is likely that in the vast array of compounds found in crude oil that analogous compounds are present. Most sulphur compounds under appropriate reducing conditions will provide H_2S, eg thiocarbamate hydrolysis:

$$RCS_2R + 3H_2O \rightarrow RCO_2H + 2H_2S + ROH$$

and thioether reduction:

$$\overset{[H]}{RSR \rightarrow 2RH + H_2S}$$
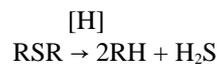
Inorganic sulphur compounds are most likely to be in the form of insoluble metal sulphides or soluble sulphates. No doubt there are other inorganic forms of sulphur which might be present, including the elemental form, but they are considered unlikely.

3.1.3 Dissolution of pyritic material

Pyrite contained in reservoir rock can be leached out as particles of small dimension which may react with the environment according to the following reactions:

$$FeS_2 + 8H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- \tag{a}$$

$$\text{or } FeS_2 + 4H^+ + 2e^- \rightarrow Fe^{2+} + 2H_2S \tag{b}$$
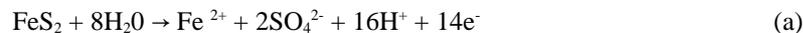
Pyrite oxidation (a) is known to be a slow process which requires the presence of a powerful oxidant at a high potential (20). This process is, therefore, effectively ruled out in the reducing conditions found in petroleum reservoirs. Pyrite reduction (b) is possible at lower pH values.

To calculate the progress of reaction (b) on a theoretical basis is very complex. Literature values for the pK of the solubility product for iron sulphide vary from 16.9 to 18.8, which would reflect a 100 fold variation in calculated H_2S concentration. It seems clear that the

extent of such a reaction may only be found for a particular system by experimentation rather than theoretical calculation.

Such a hypothesis presupposes a ready supply of pyritic material and some degree of acidity in the reservoir (less than pH7 at least, seawater is generally at pH6.5-7.5 when injected).

Pyrite, FeS_2, is widely distributed in formation rocks and therefore has to be considered as a source of the observed geological H_2S, although it is not obvious why the process should not have been proceeding during the prehistory of the field. However, a statistical study of oilfield pyrite versus H_2S at the wellhead run in parallel to this study, see Section 3.1.5, demonstrated a correlation between wellhead H_2S and formation pyrite. Clearly its normal inactivity would have to be affected by the changed conditions of oil recovery during recent times. These changes might lead to:

- Reduction in particle size and therefore generation of new and possibly chemically reactive surfaces

- Activation of the surface by chemical reaction with an additive followed by hydrolysis, as exemplified in the bisulphite mechanism below

- Activation of the surface as above but followed by a reduction process involving perhaps indigenous reducing agents, most probably a component of the Oil. generating H_2S.

3.1.4 Redox reactions involving bisulphite oxygen scavengers

This mechanism has been suggested by a number of oil companies (17). Oxygen scavengers used in injection waters invariably comprise sulphite, and in many cases are ammonium bisulphite.

These compounds are redox poising agents and are known to stimulate the growth of sulphate-reducing bacteria. It is unclear if they could give rise to H_2S by purely chemical reactions occurring downhole. However since relatively low concentrations of these compounds are injected into the reservoir it would appear that they would be required to perform some catalytic function in order to give rise to high levels of H_2S.

Normally these compounds react completely with oxygen to yield sulphate, the added concentration of which is negligible compared with the concentration of sulphate (2650mg/1) already present in seawater:

$$2NH_4HSO_3 + 0, \rightarrow (NH_4)_2\ SO_4 + H_2SO_4$$
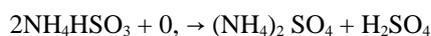
In a system where dosages are well controlled, the excess ammonium bisulphite injected downhole will be low, generally less than lmg/l. Since ammonium bisulphite is present only as an oxygen scavenger it is not likely to be the principal sulphur source for hydrogen sulphide, although it is considerably easier to reduce to sulphide than the sulphate ion.

It is more likely that the bisulphite could be involved either as a catalyst in the conversion of some other sulphur-containing substance, or that it is modifying the surface of an inert sulphur-containing solid in the reservoir so making it more reactive, thus generating H_2S. Since metal sulphides can vary enormously in reactivity depending on their crystalline form and especially the nature of the surface, this becomes an interesting possibility. It can be noted here that freshly precipitated ferrous sulphide dissolves in acids within seconds although geological samples of pyrite can he treated with hydrochloric acid without significant decomposition.

3.1.5 Mineral scavenging

In addition to the above, an H_2S scavenging mechanism was briefly investigated. From the 1988 statistical study mentioned in Section 3.1.3 numerical evidence further supported the existence of a protective facility in the formation accorded by siderite (ferrous carbonate), ie the 'Siderite Shield', capable of removing newly formed H_2S from the flooded formation. The combined effect of pyrite and siderite is illustrated in Figure 1, the ratio of mineral volumes dictating the reservoir fluids' starting H_2S concentration prior to secondary recovery.
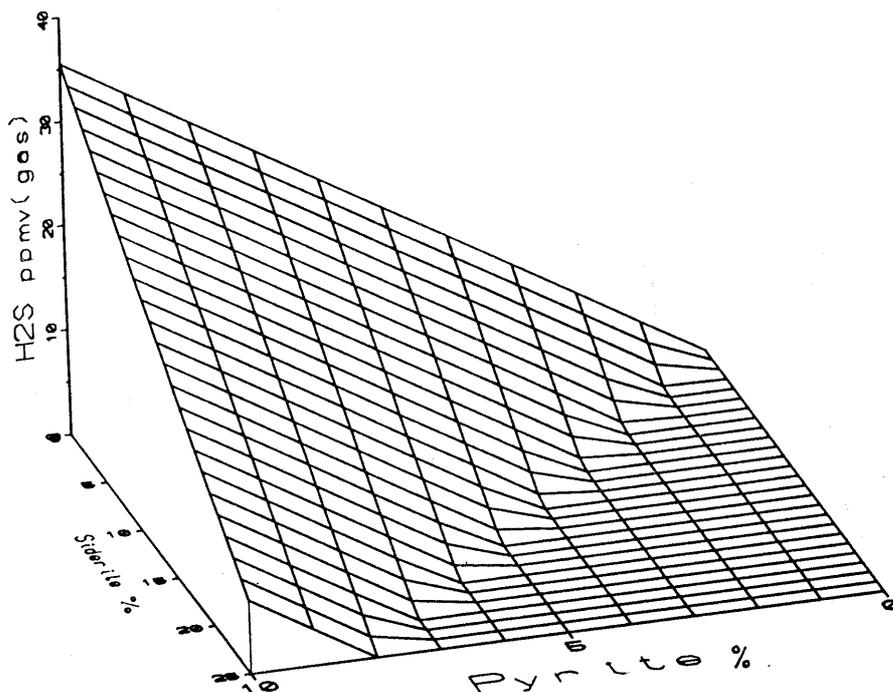
Figure 1

**The 'Siderite Shield', a three dimensional representation of gas phase
H2S vs pyrite/siderite volume in the reservoir water-flooded zone**

3.2   RESEARCH PROGRAMME

3.2.1 Introduction

This section concerns the practical examination of geochemical souring mechanisms which have been suggested on the basis of materials naturally present, entering incidentally, or deliberately added to the injection water, thus generating hydrogen sulphide detectable in the produced fluids.

It is important in evaluating the mechanisms discussed in Sections 3.1.1 to 3.1.4 to consider the concentrations of H_2S formation which are considered relevant. On the one hand, if chemical formation of H_2S has occurred only since the well has been completed, perhaps a relatively fast reaction occurs. However, if a catalytic material has been introduced   which   is

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dispersed widely in the reservoir, even a low rate of reaction coupled with partitioning of H_2S into the gas phase might give the observed result. Clearly it was necessary within this examination to differentiate ultimately between mechanisms initiated by the exploitation of the reservoir and those which have been proceeding at a slow rate during the life of that reservoir.

3.2.2 Equipment for downhole static tests

The equipment used to study the production of H_2S by a chemical, rather than a biological means must be capable of operating at 'downhole' conditions, ie up to say 120°C and 5000psig. It is normal research and development practice to exaggerate conditions so as to maximise chemical effects. This may mean operating at up to 350°C at 5000psig. The equipment must also be designed so as to alter the chemical reaction as little as possible, ie by wall effect (metal ions present), temperature effects (local hot spots) or general effects such as agitation and H_2S adsorption. Since H_2S is adsorbed on to metal surfaces it is important to minimise the contact of metal with the test fluids when looking for low H_2S concentrations (0-2ppmv range) in the gas phase. This can be done using polymeric coatings or linings of glass or ceramic. An autoclave system was used to test a specific case from Statoil's Veslefrikk field in previous trials (21).

However, in order to optimise the many conditions required for this programme, it was proposed to use Carius tubes.

3.2.3 Carius tubes

Carius tubes are long glass tubes (approx 50cm) sealed at each end with a pressure handling capability of approximately 140-200psig at 200°C. They have a holding volume of approximately 100ml. In use the tube is sealed at one end, charged with the reactants/test fluids and then sealed at the other end. The tube is then protected in a steel guard vessel and placed in a thermostatically controlled oven.

At the end of the test period the tube is opened into a vacuum system and the evolved gases are then available for analysis.

3.2.4 Determination of hydrogen sulphide concentration in gas samples

Several analytical procedures for H_2S were considered at the outset of the programme, eg Gas Liquid Chromatography (GLC) and wet chemical methods ($CdCl_2$). The initial requirements were to detect the presence of H_2S in a given experimental regime and then, when such a regime was identified, to quantify the H_2S. The major problem with H_2S measurement at a low concentration is the chemisorption effect (chemical bonding of H_2S to material surfaces). The loss of just a few ppmv H_2S at a concentration of 10-20ppmv can give a significant error. For GLC, for example, the sample pathway must be as free of metal surfaces as possible. It was therefore decided to use a simple detection system which eliminated sample handling problems, ie Dräger tubes. These are available in ranges from 0-15ppmv ± 0.5ppmv to 100-2000ppmv ± 100ppmv for H_2S detection (for conversion to ppmw see Section 7.6.1). The tubes are designed not to register other sulphur-containing contaminants, eg mercaptans, and are very simple and reliable to use. When using Dräger tubes, sample transfer is unnecessary, the tube being connected directly to the gas source. This system gave accurate and repeatable results over a whole range of tests allowing processing of large numbers of experiments in a reasonable time.

3.3 EXPERIMENTAL TRIALS

Ten trials were run in total. The rationale of the trials and results are briefly described below. For comparison, in the Veslefrikk field study, a system containing seawater and downhole material was run at 160°C and 5000psig. Geochemical H_2S generated at around 180ppmv in the gas head space by an unknown mechanism, but not at the lower temperatures found in the reservoir, served as an indicator as to the concentration of H_2S that could be expected in the Carius tube trials.

3.3.1 Trial 1, proving trial

The initial experiment evaluated combinations of formation material, seawater and distilled water at 150°C over one month. There was no significant H_2S yield.

3.3.2 Trial 2, proving trial

A repeat of the above but at 190°C H_2S was generated in cases where oxygen scavenger and crude oil were present together. Formation solids at this time contained crude oil.

3.3.3 Trial 3, proving trial

A trial to 'home in' on H_2S production. H_2S was associated with crude oil and water added as either formation water, seawater or distilled water showed a significant increase in H_2S at the higher temperature of 195°C (cf 150°C Trial 1). Where formation water was used, the H_2S production was reduced.

3.3.4 Trial 4, effects of pyrite and effects of oxygen scavenger

This trial was to investigate the separate effects of pyrite FeS_2, and ammonium bisulphite oxygen scavenger. All formation solids were subjected to Soxhlet extraction using 1:1:1 trichloroethane to remove all oil residues. (This procedure was continued for all trials).

No additional production of H_2S was associated with the presence of pyrite. Ammonium bisulphite gave a dramatic increase in H_2S yield and this was shown to be from the chemical reaction of the scavenger on the oil rather than its physical deoxygenating effect. The scavenger was however tested at around 1000mg/l, ie approximately three orders of magnitude above the typical injection water residual concentration.

The pH of the formation, sea and distilled waters was 8.2, 7.9 and 5.6 respectively; there was no direct simple correlation between these pH's and the H_2S levels generated.

3.3.5 Trial 5, effects of siderite

This trial briefly investigated the effect of siderite on H_2S production.

Two Carius tubes were loaded, one with distilled water and crude oil and the other with distilled water, crude oil and siderite, natural iron carbonate $FeCO_3$. The tube containing siderite gave H_2S at 60ppmv in the gas head space after 12 days at 190°C, and that without siderite gave 250ppmv after the same period.

Ibis result appeared to show a suppression effect by siderite.

3.3.6 Trial 6, effect of ammonium bisulphite

The effect of differing concentrations of ammonium bisulphite oxygen scavenger was assessed.

Three concentrations viz, 10mg/l, 100mg/l and 1000mg/l were tested. There was an increase in H_2S evolution in all cases. However, the results were similar giving around twice the control concentration, ie not of the same magnitude as in Trial 4 for the high scavenger concentration. The micro-technique used to transfer concentrated oxygen scavenger in Trial 4 may have been the reason for higher H_2S yield, since the concentrate received less handling than in the earlier trial and was thus less prone to oxygen pick-up.

3.3.7 Trial 7, rate measurements

The aim of this experiment was to investigate the rate of production of H_2S by reaction between crude oil, seawater and formation solids at various temperatures so that H_2S evolution at reservoir temperatures (80-120ºC) could be predicted. The three temperatures proposed were 120ºC, 150ºC and 175ºC.

At 175ºC the H_2S concentration showed a slow increase over the period starting from lppmv after 3 days increasing to 12ppmv after one month. The rate of production was very low and this work was not repeated at lower temperatures.

3.3.8 Trial 8, water effects

This was a repeat of Trial 4. Both seawater and formation water gave depressed H_2S yields compared with distilled water.

3.3.9 Trial 9, scavenger temperature profile

This trial was designed to estimate the quantities of H_2S that could be generated downhole from typical residual scavenger concentrations in injected seawater. The experimental temperatures chosen were 175ºC, 185ºC and 195ºC.

Extrapolation to reservoir temperatures indicated that the normal residual scavenger concentrations in injected seawater would not directly generate H_2S and thus this contribution to souring appeared negligible.

3.3.10 Trial 10, further investigation into oxygen scavenging

Variations between the findings in Trial 4 and Trial 6 concerning the yield of sulphide from the addition of oxygen scavenger had been attributed to the residual concentration of the scavenger. Ibis control experiment compared diluted and undiluted scavenger addition giving the same final oxygen scavenger concentration. The Carius tubes were held at 195ºC for 12 days prior to testing.

These results were in line with the original findings from Carius tube Trial 4. At a low scavenger level of 5mg/1 there did not appear to be any significant enhancement of H_2S evolution. This low concentration of scavenger is in keeping with normal residual concentrations and thus its interaction with reservoir liquids would not appear to constitute a major source of souring in the field.

3.4   CONCLUSIONS

Four geochemical mechanisms implicated as possible causes of elevating concentrations of H_2S in reservoir produced fluids were experimentally investigated.   The mechanisms associated with seawater injection included thermochemical sulphate reduction, thermal decomposition of crude oil, pyritic dissolution and reactions involving bisulphite oxygen scavenger.

All experimental work was conducted using reservoir fluids supplied by one operator. As such, the conclusions necessarily relate to those fluids, but it is suspected that a wider view could be taken. This view was supported by the findings from the Veslefrikk field study. The source of the H_2S from the Veslefrikk study was not fully established at the time but can in the light of the Carius tube trials be more clearly understood.   The H_2S concentrations from the Veslefrikk work compared favourably with the results from the Carius tube trials.

- For H_2S production, the system must contain both water and crude oil.

- Thermochemical sulphate reduction did not occur under the test conditions.

- Thermal decomposition of crude oil can occur at temperatures above normal reservoir conditions.   It is deduced that thermal decomposition is oil-specific. Furthermore, it has been shown by extrapolation to typical North Sea reservoir temperatures (ie up to 120°C) that this is not a significant souring mechanism.

- Pyritic dissolution has not been demonstrated experimentally. (There is, however, a statistical correlation between pre-existing H_2S and the pyrite/pyrrhotite content of a formation, see Sections 3.1.3 and 3.1.5.)

- Reactions involving bisulphite oxygen scavenger at higher temperatures and concentrations than found in practice produce large amounts of H_2S. A control experiment indicated that the generation of H_2S by the addition of bisulphite is due to chemical effects of bisulphite and not the physical effect of deoxygenation. Extrapolation to reservoir temperatures and concentrations suggests that the probability of this mechanism being responsible is insignificant. The stimulatory effect of scavengers on microbial activity either by FeS production or redox poising was not studied in this programme.

- The effect of mineral scavenging of H_2S has been studied briefly.   Inhibitive geochemical mechanisms that suppress the evolution of H_2S were found. Firstly the reaction of H_2S with siderite appeared to reduce the production of H_2S from the crude oil/water system.   Ibis mechanism may have wider implications in the appearance of biogenic H_2S. Secondly, the experimentally observed effect of formation water on the evolution of H_2S from crude oil showed that water added to the system as formation water must contain a component (or components) capable of either scavenging or inhibiting the production of .H_2S.   An inhibitive geochemical mechanism may go some way towards mitigating an early appearance of sour gas after seawater breakthrough.

- The Carius tube method was a cost effective means of screening for souring and mitigation mechanisms without incurring the high cost of autoclave tests.

4. WATER INJECTION AND BIOGENIC SOURING

4.1   SULPHATE-REDUCING BACTERIA

All photosynthetic organisms and many non-photosynthetic ones assimilate sulphur in the oxidised, inorganic form of sulphate. The main occurrence of sulphur in the cell is in the reduced organic state as a constituent of amino acids and sulphydryl groups.

Assimilatory sulphate reduction resembles nitrate assimilation in that both processes only produce enough reduced species for the needs of an organism. Sulphide is also formed more directly by the activities of the sulphate-reducing bacteria (SRB). These consist of at least two genera (*Desulfovibrio and Desulfotomaculum*) of obligate anaerobes which oxidise hydrogen and organic compounds using sulphate. This *dissimilatory* sulphate reduction is apparent in mud at pond bottoms, in bogs and on the sea-bed. Sulphate concentration is high in seawater and consequently its reduction is an important factor in the mineralisation of organic matter on the ocean floor; signs are the odour of hydrogen sulphide and the pitch black colour of mud in which it occurs. These sulphides are a serious nuisance in some coastal areas. H_2S only accumulates in nature under anaerobic conditions; it is rapidly and spontaneously oxidised in the presence of air to elemental sulphur.

The H_2S formed in the biosphere is largely converted to sulphur: only a small part of it subsequently becomes sequestered in the form of insoluble sulphides of heavy metals. The economic consequences of sulphate-reducing bacteria are diverse and usually disadvantageous. They have been implicated in spoilage of stored petroleum and certain canned foods in addition to the well known anaerobic corrosion of iron and steel; their activities in oilfield equipment and oil bearing reservoirs have for many years been regarded as a source of considerable economic loss (22,23,24).

The two well established genera of sulphate-reducing bacteria, *Desulfovibrio* and *Desulfotomaculum*, seem to be quite unrelated to each other and their relation to other bacterial groups is obscure. The better known genus, *Desulfovibrio*, is usually mesophilic (preferring a moderate temperature range) and sometimes halophilic (preferring saline conditions); it is thought to contain seven species at the present time. *Desulfotomaculum* species are somewhat more difficult to isolate and purify. They are characterised by spore formation and are sometimes thermophiles (preferring relatively high temperatures); only one halophilic strain has been reported.   Five species are recognised at the present time (25).

The SRB that have been extensively studied in the laboratory can be broadly divided into two groups with respect to the maximum temperature that they will tolerate. Mesophilic isolates will not grow above 45ºC and generally belong to the genus *Desulfovibrio*. Thermophilic isolates grow at temperatures as high as 70ºC - the most common species being invariably *Desulfotomaculum nigrificans*. However, Rozanova and Khudyakova (26) have isolated an apparent *Desulfovibrio* having a maximum growth temperature of 85ºC.

Zobell (27) claimed that he had isolated SRB from an oil-bearing reservoir that would grow at 104ºC under a pressure of 1000atm. There are several more reports claiming sulphate-reduction at the high temperatures and pressures found in relatively deep oil-bearing reservoirs.

Unfortunately these claims were not followed up by well designed laboratory studies which did identify conclusively bacterial involvement in sulphate reduction and characterise the species.

In extensive studies on these 'conventional' SRB isolated from the North Sea environment, including offshore installations, Herbert and Stott (11,12,13) concluded that such organisms would not be able to grow unless the temperature fell below 45°C. Should this occur the chances of SRB growing would still remain slight providing the system remained clean, especially at the high pressures found in injection wells.

This statement did not (as the authors pointed out) exclude the existence of more thermophilic strains of 'conventional' SRB in other parts of the world or of more thermophilic SRB with non-conventional metabolism which would not have been isolated by 'classical' techniques.

Pure cultures of 'conventional' sulphate-reducing bacteria generally dissimilate a very restricted range of carbon substrates (eg lactate and malate) only to the acetate level of oxidation. However, a true acetate-oxidising, sulphate-reducing bacterium of the spore-forming group, has been isolated. It is distinctive in not utilising the common substrates of other sulphate-reducing bacteria (28). Successful isolation of *Desulfotomaculum acetoxidans* has prompted a search for related types able to metabolise lower fatty acids (eg propionate and butyrate). Widdel and Pfennig (29) have now described oval to rod shaped, Gram-negative, nonsporulating sulphate-reducing bacteria, isolated from brackish water and marine mud samples, which use acetate as the sole electron donor. The organisms oxidise acetate to CO_2 stoichiometrically.

Sulphate-reducing bacteria have also been described which oxidise other short-chain fatty acids in freshwater and marine sediments (30). The new genera *Desulfobulbus* and *Desulfobacter* have been tentatively proposed.

The existence of sulphate-reducing bacteria which utilise acetate and other fatty acids raises the question of their possible activity in subsurface injection waters and petroleum reservoirs. It is likely that produced waters which are often rich in total organic carbon may contain high concentrations of acetate and other fatty acids. If the latter is the case then the problem of carbon source for SRB in reservoirs would be solved.

Wake et al (31) have shown that anaerobic reduction of sulphate by hydrocarbons is an energy consuming reaction, ie the opposite of what is required by bacteria to sustain their growth. Early attempts by workers (32,33) to show anaerobic oxidation of hydrocarbons by bacteria had failed despite reports to the contrary in the older Soviet literature. However, a recent worker, Stetter, has identified *Archaebacteria* growing at temperatures in excess of 80°C (34) dubbed 'hyperthermophilic' bacteria which are reported to be capable of metabolising hydrocarbons as a carbon source (35).

4.2   SRB AND INJECTED SEAWATER

In the case of the North Sea offshore oilfields, injection seawater contains SRB that have been acclimatized to a relatively shallow environment which is cold, (as low as 5°C) and at only moderate pressure (20atm at a depth of 180m). When introduced into the reservoir these bacteria will be subjected to the much higher pressures that prevail and also to higher temperatures. However there will be a reduction of the reservoir temperature in the region of the injection well.

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The injection of deaerated cold seawater into a formation can provide a number of key elements for microbiological H_2S generation. The combination of all these elements would lead to souring as follows. The cooling effect of the seawater reduces the temperature of the rock around the injector to within the thermal viability limits of life, leaving in its wake rock cooled down to typically no less than 15°C. The deaerated seawater is poised at suitable reducing conditions for anaerobic sulphate-reducing bacteria (E_h below -100mV) and the high sulphate availability (2650mg/1) supplies the reducible sulphur source. The pH of the seawater or seawater/formation water mix is within the required range for microbial activity (pH6-9) and the flooding ensures an ever increasing mixing zone with the formation water in which growth conditions can be met. Finally the seawater is the vector for continued SRB inoculation.

In the absence of SRB there would be no biogenic souring. However, in the unsterile conditions associated with oil recovery, 100% kill rates will never be achieved by either biocide or ultraviolet treatments and viable bacteria will reach the formation. The rate and extent of bacterial growth would be dependent upon the other key elements *in toto*. For example, a suboptimal redox potential would result in suboptimal growth and as the redox potential moves progressively more positive than E_h = -100mV, SRB growth could stop altogether. Biogenic souring would not be expected in reservoirs where any one of the key elements is entirely compromised.

4.2.1 Colony establishment of SRB

It is suggested that the first sulphate-reducing organisms to colonise the formation are the mesophilic SRB (m-SRB). These organisms are detectable in seawater but numbers are low, typically below 10 organisms per ml. Subsequent to biocidal water treatment, numbers often drop to below detection levels. However, the large volumes of water associated with typical injection procedures ensure that organisms can make their way into the formation and in sufficiently large numbers to enable colonies of bacteria to become established downhole. These 'mid temperature seeking' bacteria grow between 8°C and 45°C. From the thermal geometry downhole, m-SRB are restricted to a region close to the injector, a Thermal Viability Shell (TVS) measured in many tens of feet rather than hundreds of feet radius, (see Chapter 6).

Between 45°C and 80°C, thermophilic SRB (t-SRB) will grow. Postgate (25) noted that the growth of sulphate-reducing bacteria appeared to be encouraged by the presence of finely divided iron sulphide. Since the growth of m-SRB would yield H_2S, iron sulphide and metabolites leaking from the cells, then the pre-existence of an m-SRB population may be required before t-SRB can establish. The t-SRB organisms will colonise a TVS up to as little as a few hundred feet to, in some mature cases, several thousand feet radius from the injector (depending on the results of heat balance calculations) and may even 'ride' the moving 45-80°C thermal zone which is created across the thermal front.

Finally, hyperthermophilic SRB (h-SRB) grow at temperatures previously deemed beyond a thermophilic maximum. These strictly anaerobic organisms are in a different taxonomic group from the others and called ancient or *Archaebacteria*. These organisms live in and around sub-sea volcanic vents and during the course of the Reservoir Souring Programme were isolated by Professor K O Stetter (Regensberg University) from production wells in the North Sea. Genetically identical to organisms from different parts of the world, it is suggested that very large crude carrier (VLCC) ballast dumping in the locality of water injection systems could be the responsible vector.

These *Archaebacteria* have been recovered from the open sea near to volcanic activity and more recently from an injection water source (35). This recovery demonstrates that they can survive (probably in low numbers) both the thermal and positive redox stresses of transfer

between suitable growth sites. These organisms are not considered as important a souring organism as the t-SRB for two reasons. The first is that t-SRB activity establishes over many years, a comparable timeframe with the production life of a reservoir. The major biogenic souring of the reservoir over this period will have already been caused by the t-SRB activity. Second is that sulphate-reducing activity of h-SRB appears to be less than that of t-SRB. Although h-SRB could occupy a larger TVS than the t-SRB, their late establishment and reduced efficiency of the associated downhole 'bioreactor' mitigates the h-SRB rôle.

4.2.2 Thermophilic SRB and the growing TVS

The t-SRB are considered the main causative agents of biogenic reservoir souring. Although at the limit of detection in injection water, backflushed injection and produced breakthrough water from soured injector/producer pairs have t-SRB counts up to 10^6/ml. A micrograph of a pair of t-SRB recovered from produced water from the Thistle field is given in Figure 2. A growing t-SRB TVS is illustrated diagrammatically in Figure 3 (but not the moving 45-80ºC thermal zone). In Figures 3(a)-(c) the t-SRB TVS can be seen to grow to a stable maximum. The appearance of biogenic souring is dependent on both the initiation of a TVS and injection seawater breakthrough carrying the metabolically produced H_2S to the producer. The passage of seawater through the TVS boundary to the producer can be several tens of times faster than the speed of the boundary of the growing TVS itself. Since the movement of seawater is faster across the boundary than the growth of the boundary, H_2S generated within a TVS can be transported outwards. Note that the initial breakthrough seawater will not have passed through a TVS. Any biogenic H_2S appearing at the producer at this time will have been generated in the moving thermal zone and its concentration and would be expected to decrease until H_2S from a TVS is produced.

4.2.3 Biogenic sour gas production or not?

Assuming all growth requirements can in part be met, then the combination of a yes/no answer to the question of TVS initiation and seawater breakthrough can be used to explain the appearance of H_2S post seawater breakthrough. In wells where there is no seawater breakthrough, whether or not there is a TVS, no increase in H_2S production can be expected. In wells where there is seawater breakthrough, H_2S will only appear once injected seawater has transported H_2S from an initiated TVS to the producer. This is summarised in the truth table, Table 1.

Table 1
Truth table of TVS initiation versus Seawater
breakthrough showing nature of produced fluids

	TVS Initiation	
Seawater Breakthrough	Yes	No
Yes	Sour	Sweet
No	Sweet	Sweet

The *variable* time to appearance of H_2S post seawater breakthrough is addressed in Chapter 6.

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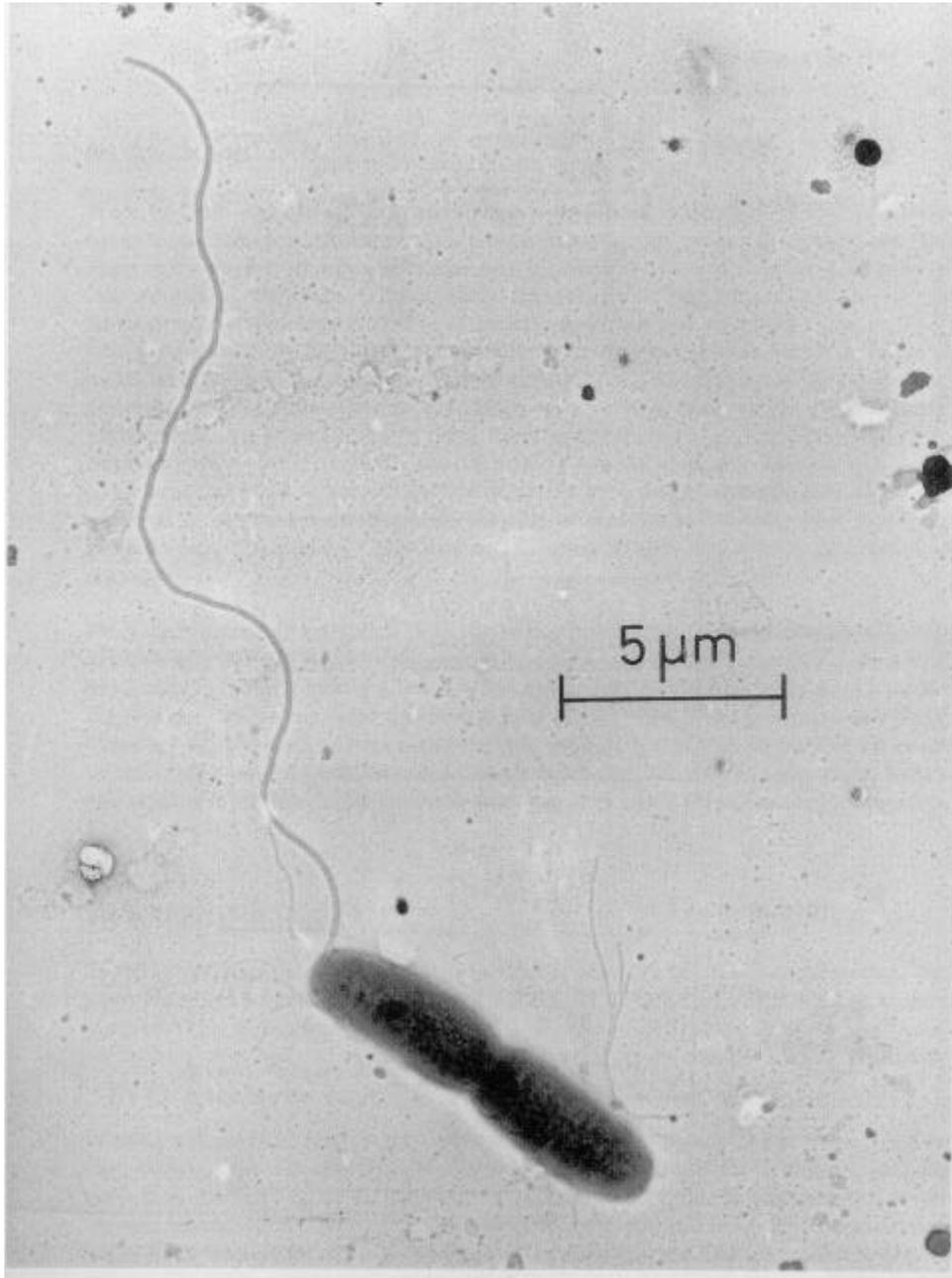
Figure 2
Photograph of a flagellated t-SRB recovered from the BP Thistle field
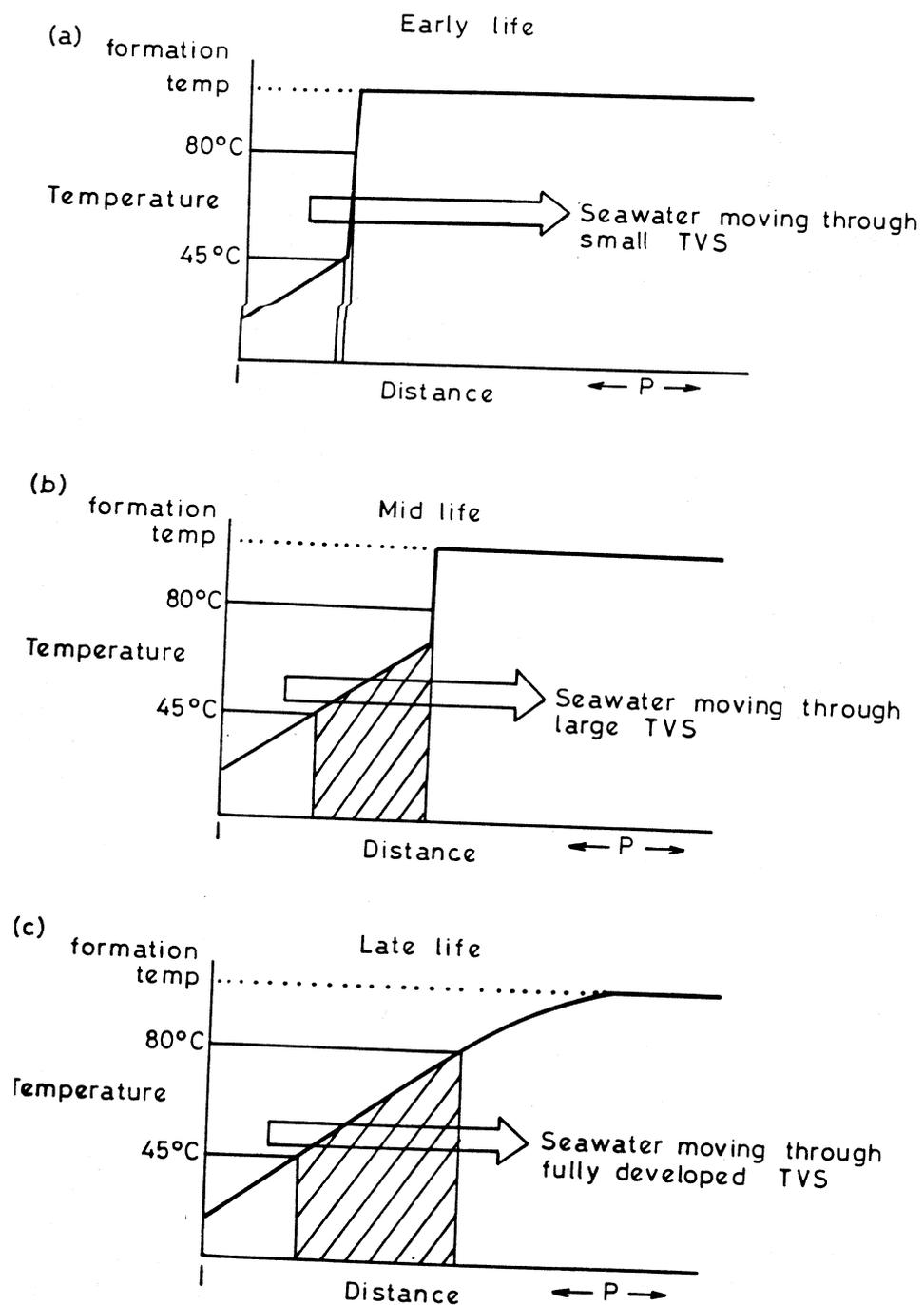
Figure 3
The development of the thermophilic sulphate-reducing bacteria's Thermal Viability
Shell between the injector (I) and the producer (P), showing seawater passing through
the thermal gradient with the producer at a variable distance from the injector

5. EFFECT OF PRESSURE AND TEMPERATURE ON THE SURVIVAL OF THERMOPHILIC SRB AND THE IMPLICATIONS ON BIOGENIC SOURING

5.1 BACKGROUND

Work by Stott and Herbert (13) established a number of mesophilic sulphate-reducing bacteria (m-SRB) pressure/temperature growth envelopes for isolates from the North Sea. Their study was carried out to determine whether those m-SRB which could be introduced into petroleum reservoirs with injected seawater, were capable of growth at the temperatures and pressures prevailing in the formation close to the injection wellbore. Their findings demonstrated sulphate reduction, and hence sulphide production, could occur at a maximum pressure and temperature of 640 atmospheres (9400psig) and 45°C respectively. However, growth above 300atm (4400psig) was, at best, poor. Although mesophilic bacterial sulphide generation could occur under reservoir conditions, the swept volume of reservoir which could support such mesophilic sulphate-reducing bacteria activity is considered too small to account for the quantities of hydrogen sulphide that have been observed in some produced fluids. In the case of the Thistle field, levels of hydrogen sulphide were significantly higher than neighbouring facilities and activity of t-SRB was suspected.

Production history of the Thistle field shows that hydrogen sulphide production was first detected in 1982 and rapidly increased to plateau levels in 1985. Calculated daily H_2S production in the gas phase was between 150 and 200kg/day, with approximately a further 70-100kg/day remaining in the produced oil and water phases. Wells producing significant quantities of H_2S were, without exception, also producing seawater. In view of the range of H_2S production from well to well, ie from zero to over 30kg/day in some cases, Thistle was selected as the most likely candidate for recovery of t-SRB for laboratory investigation.

5.2 EXPERIMENTAL

In 1987 an offshore microbiological sampling programme (2 visits) was implemented. The objective of the programme was to enumerate and isolate any viable SRB from all sources sampled. Ten production wells of varying flowrates, H_2S concentrations and water chemistries were selected in addition to certain areas in the produced water processing facilities.

In order to ensure the best chance for detection, a range of culture media was utilised on each sample. Care was also taken to minimise the risk of thermal shock to any organisms present by maintaining the second batch of samples at 60°C during transportation to the onshore laboratory. Enrichment cultures of t-SRB were obtained from the produced water taken from three of the wellheads and a further one from the produced water treatment system. The saline culture medium developed to maintain the organisms was similar to that used by Pfennig et al in 'The Prokaryotes' (36) but also containing the volatile fatty acid ions (VFA's) of acetate, propionate and butyrate but less complex in terms of trace constituents. The growth medium was broadly similar in chemical composition to a formation water/seawater mix.

Cultures from one production well, A43(12), were studied. Pressure cylinders and hydraulic fluid were pre-heated to avoid thermal shock to the cultures. Four subcultures (10ml) were loaded into each cylinder and pressurised. Pressure was held for at least seven days prior to depressurisation and investigation.

Growth was indicated by blackening of the ferrous ion-containing cultures. Those which had not blackened were reheated to 60ºC, but at atmospheric pressure. Time to blackening was then recorded. The initial pressure/temperature envelope was established for the Thistle field culture from well A43(12). Cultures from well A36(15) and the produced water flotation cell 'B' were investigated at atmospheric pressure and 72ºC and the well A05(25) culture additionally at 60ºC. During this work, a culture from well A43(12) was stored for 100 days at 4ºC. At the end of this period it was returned to the incubator at 60ºC.

5.3 SUMMARY OF RESULTS

- The results of the sampling programme are given in Appendix 1, Tables 1-5.

- Chemical analyses of the medium for sulphate and VFA's showed that the cultures did in fact carry out true dissimilatory sulphate reduction rather than merely putrefactive, fermentative reactions, ie the cultures did contain sulphate-reducing bacteria.

- The investigation of the pressure/temperature envelope of Thistle t-SRB culture from well A43(12) showed the limit of growth at atmospheric pressure to be between 45ºC and 75ºC. Growth has been shown to be possible at up to 500 atmospheres (7250psig) at the optimum temperature range of 60-65ºC. Survival and subsequent growth was observed for cultures held at 625 atmospheres (9060psig) and 70ºC for several weeks.

- Studies of further cultures of t-SRB from wells A50(40), A05(25), A36(15) and the produced water flotation cell 'B' demonstrated matched pressure/temperature profiles with that of well A43(12).

- The pressure/temperature 'Gothic Arch' growth domain is given in Figure 4. This curve is a composite from all Thistle cultures. If these data are plotted with a pressure/temperature profile for a mesophilic culture of T-945, see Figure 5, and on to this annotated the pressure difference between the injectors and producers, then the water flood can be seen to pass through the pressure and temperature conditions which support either m-SRB or t-SRB activity, or both, (see Figure 6).

- The 100 day culture from well A43(12) stored at 4ºC blackened after two weeks when incubated at 60ºC.

5.4 DISCUSSION

The Thistle cultures from each well studied did not display a difference in temperature or pressure tolerance over the range of pressures and temperatures tested. This is presumptive evidence that the t-SRB in the cultures are of the same type. The cut-off for t-SRB growth within a period of 7 to 13 days of incubation appears to be 500 atmospheres (7250psig). The *survival* of cultures at higher pressure of up to 600 atmospheres (8700psig) for 7 days, but not showing active growth, could have implications on interpretation of t-SRB detected at the wellhead, ie detection of t-SRB would not necessarily imply they have been active downhole especially if the pressure/temperature combinations have been unsuitable.
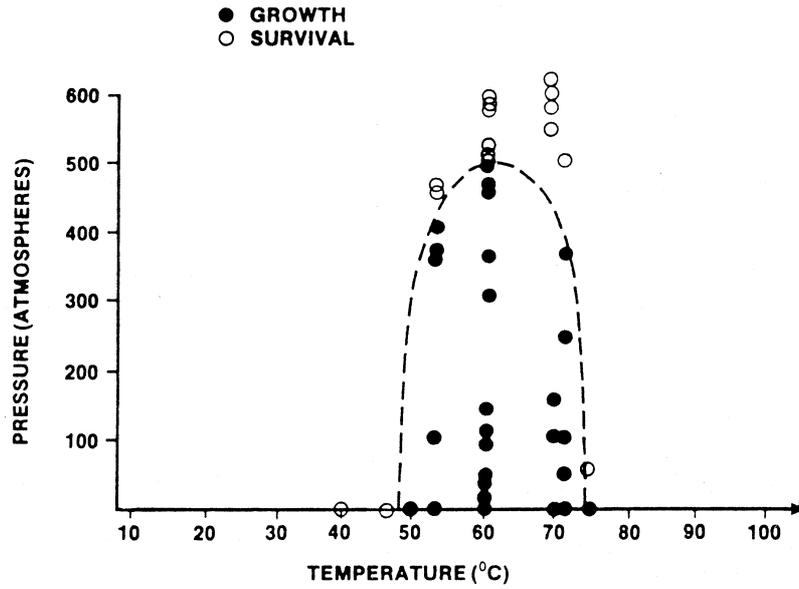
Figure 4
Accrued pressure versus temperature results for t-SRB cultures
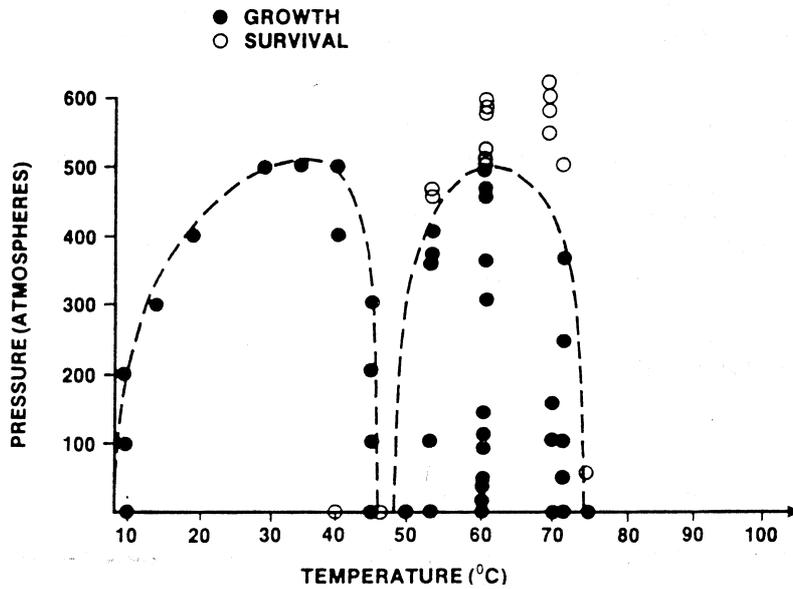
Figure 5
Accrued pressure versus temperature results for both t-SRB cultures and m-SRB culture T945

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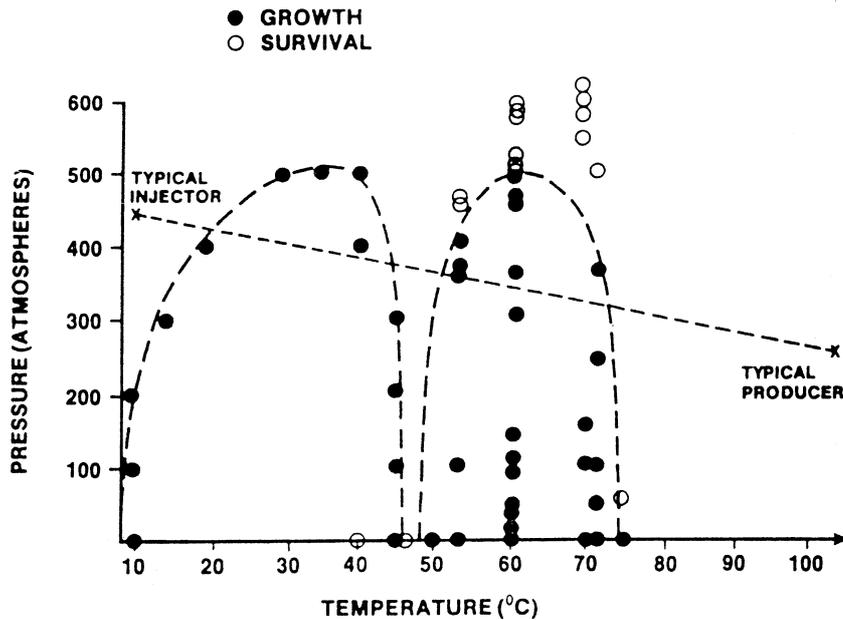
Figure 6
Pressure/temperature profile of typical Thistle producer-injector pair, viz-a-viz SRB Gothic Arches

With a knowledge of the downhole temperatures and pressures, it may be possible to classify t-SRB detected at the wellhead into 'settlers' which grow downhole, and 'transients' which do not grow but survive these conditions and indeed may colonise the inner wall of the production tubulars, ie transients may be detectable at the wellhead before a significant appearance of H_2S in the produced fluids. From Figure 6 it is clear that both m-SRB and t-SRB growth can be sustained downhole providing nutrient, pH and redox conditions are suitable.

5.5 CONCLUSIONS

The Gothic Arch established for the Thistle field culture from well A43(12) is the same as that for cultures from wells A50(4), A36(15) and flotation cell 'B'. This is presumptive evidence that the cultures isolated were of the same type.

- The t-SRB were capable of growing between 45°C and 75°C at up to 500 atmospheres.

- These bacteria survived at 625 atmospheres and 70°C for several weeks and for up to 100 days at 4°C under anaerobic conditions, demonstrating their wide barotolerance and thermotolerance.

- The Gothic Arch growth boundary could be used to describe other sulphate-reducing organisms with a range of temperature and pressure tolerances. The existence of such organisms should not be ignored when predicting t-SRB (or m-SRB) activities. Reservoirs where areas of the formation meet the conditions within the pressure/temperature boundaries should be considered susceptible to microbiological proliferation.

- The investigation undertaken on Thistle demonstrates the possibility that t-SRB could be responsible for some, if not most of the H_2S production from wells having seawater injection breakthrough. The presence of t-SRB at the numbers measured is indicative that t-SRB are entering the reservoir via seawater injection and migrating into those zones where the conditions are favourable for high growth rates.

Further work in conjunction with Regensberg University was undertaken to determine whether other SRB, viable at even higher temperatures than t-SRB, are present in Thistle produced fluids. Hyperthermophilic SRB (h-SRB) were found to be present and growing at up to 105ºC (34). The reservoir swept volume capable of sustaining microbiological growth has therefore increased even further, reinforcing the case for microbiological activity as the predominant cause of reservoir souring.

6. VIABILITY SHELL THEORY

6.1 BACKGROUND

An adaption was made to the mathematical models proposed by R J Platenkamp (36) for linear and radial flood patterns describing injection performance in terms of temperature distributions around water injectors. This has enabled calculation of the changing volumes of water downhole that, from thermal considerations, could support sulphate-reducing bacterial (SRB) activity in a so-called 'Thermal Viability Shell' (or TVS for short). The resultant model predicts that the propensity of an injected sweet reservoir to show souring is dependent upon the establishment of a stable viability shell in either the mesophilic (20-40ºC) or thermophilic (40-80ºC) SRB temperature ranges. The model suggests that souring from thermophilic sources is potentially more serious than mesophilic sources in North Sea reservoirs. The presence or absence of wellhead hydrogen sulphide at breakthrough can also be described in terms of the model, as can sharp increases in H_2S subsequent to many years sweet service.

6.2 DOWNHOLE BIOREACTOR

Statistical analysis of reservoir souring data collected on wells operated by several operators in the North Sea has shown the strongest single group of predictors for souring to be those associated with water injection; in particular, the rate of water injection, the duration of injection, and the amount of any breakthrough into production.

Independent from this analysis, work within the programme has shown the presence of mesophilic, thermophilic and hyperthermophilic bacteria in produced fluids. Furthermore, experimental work has demonstrated, and measured the capacity of, such bacteria to function and multiply at temperatures and pressures similar, or close to, those found downhole in North Sea reservoirs.

These results have been coupled with results due to Platenkamp which show, and define the size and shape of, a temperature gradient around water injectors. With typical injection and reservoir parameters, this temperature gradient will cross the viability range for the above mentioned bacteria. We should also point out that although seawater is rich in sulphate for bacterial reduction, it lacks the necessary organic carbon for growth, whereas the reverse is often true for the downhole reservoir environment, prior to injection. This suggests the possibility of a stable region becoming established around an injector in which all the conditions necessary for thermophilic bacteria to flourish exist, and to thereby produce H_2S. It is the purpose of this chapter to describe a mathematical model for this situation.

6.3 BACTERIAL GROWTH RATES

Experimental results over a range of pressures and temperatures for mesophilic bacteria in an aqueous environment matched to North Sea conditions are reported in the PhD thesis of Stott (12). The consumption of sulphate (concentration initially set at the North Sea norm of 2650mg/1) followed a classic 'S-curve' over time which we have approximated with a trilinear model, as illustrated in Figure 7 for an experiment run inside the viability region for these particular bacteria - which lay between $T_L = 20$ºC and $T_U = 50$ºC.
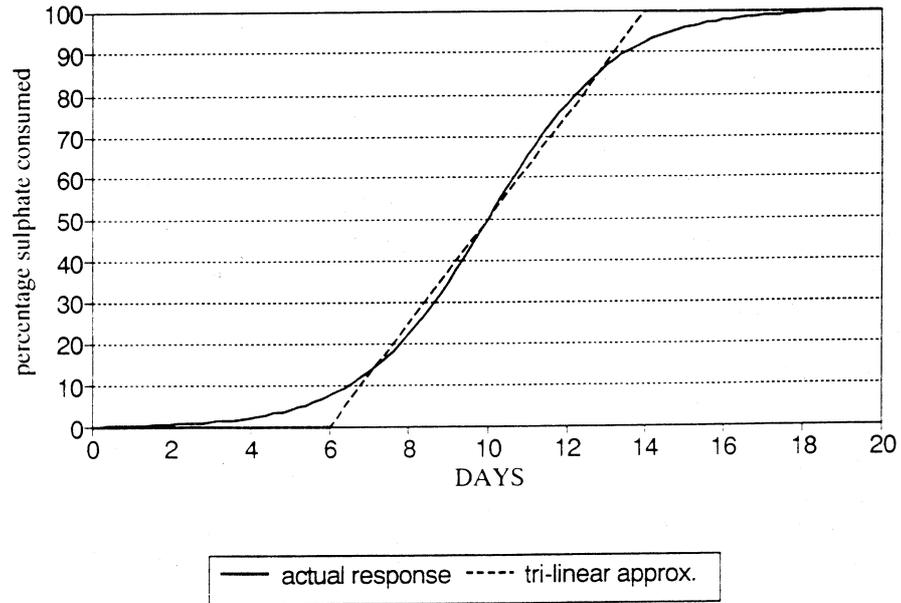
Figure 7
An illustration of the trilinear approximation showing the percentage sulphate consumed against time for m-SRB in a batch culture

Statistical techniques were used to find a best fitting consumption rate, as a function of pressure, P in atmospheres, and temperature, T in ºC for the slope, ß, of the middle line in this trilinear approximation. Independent work by CAPCIS suggests that this behaviour is matched by other thermophilic and barotolerant bacteria. We have therefore adjusted this fitted function to dimensionless temperature, so as to produce an 'S-curve' for bacteria with alternative values for T_L and T_U. This has its middle line slope given by:

$$ß = 0.6134P - 10.67T_o - 0.07048PT_o + 1.476\,T_o^2 + 0.001015P\,T_o^2 - 0.0249\,T_o^3$$

$$\text{Where} \qquad \frac{T_o - 20}{50\text{-}20} \;=\; \frac{T\text{-}T_L}{T_U\text{-}T_L}$$

The 'S-curve' formulation is completed by setting ß to zero whenever the pressure is so large as to give a negative value for ß and whenever T lies outside the viability region (T_L, T_U).

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6.4 MODELLING THE TEMPERATURE PROFILE

Constructing mathematical models which attempt to describe fully the complex flow of the various fluids through the vast volumes of fractured, folded and layered rock in a typical reservoir can be compared with attempting to model the flow of traffic in London on the basis of information from the main junctions of the city's orbital motorway, plus a handful of one-off measurements on a few randomly selected roads inside: the main picture is clear, but any detailed model is likely to assume a totally false uniform road grid, etc. Nevertheless, there are several commercially available reservoir simulators which operate with varying degrees of success. The downhole temperature profiles are not usually obtained, but theoretical analyses have been made, usually concentrating on the induced viscous or fracturing effects. See for example Platenkamp (37) Perkins & Gonzalez (38), and Marx & Langenheim (39).

It is generally agreed, and confirmed by observed data, that if cold water is injected into hot reservoir rock, then a 'cold front' is established around the injector and this cold front moves outwards into the reservoir. To a first approximation, this front is usually modelled as a 'step function', with an instantaneous jump from a cool temperature to the ambient reservoir rock temperature. Assuming an effectively infinite 'heat cap' of the non-porous rock above and below the porous layer, it is clear that this 'step' must decrease as the cold front moves outwards, since the area of flooded rock exposed to the heat flux from this heat cap steadily increases whilst, at a constant injection rate, the cooling capacity of the injected water is fixed. This is depicted in Figure 8 (from Plantenkamp, courtesy of SPE).
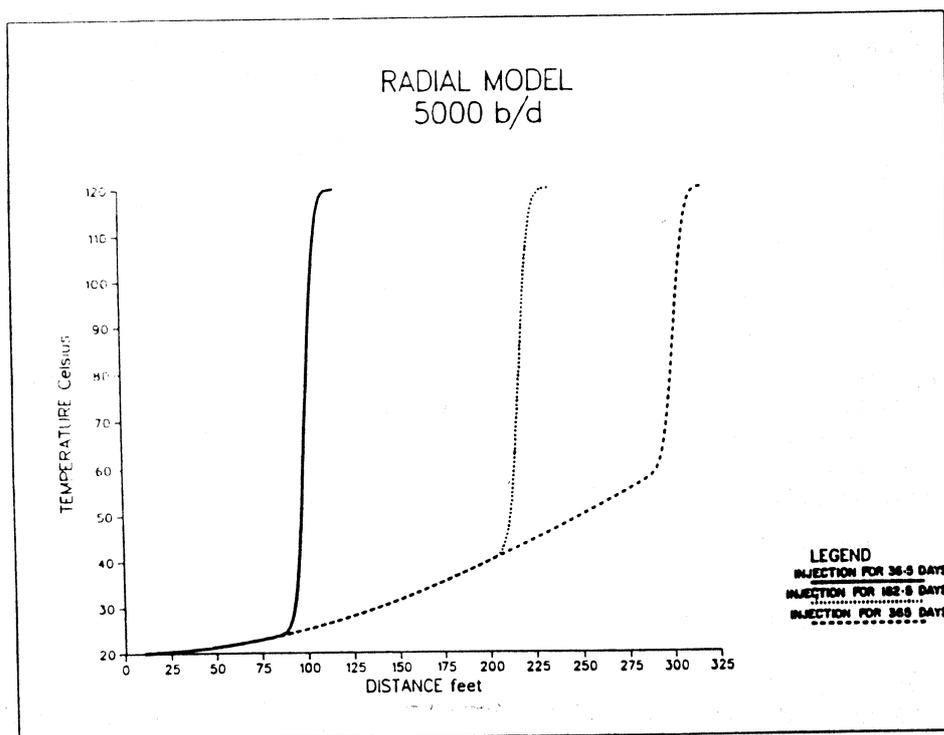
copyright Society of Petroleum Engineers 1985
Figure 8
The Platenkamp cooling curve showing the temperature profile
as a function of time for radial water drive

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Eventually, this 'step' vanishes completely, and there will be an equilibrium temperature profile, with the heat flux from the surrounding rock then being precisely that required to heat all the injected water to ambient temperature as it flows into the reservoir. In the simplest models this may take a nominally infinite time to be established, with the 'step' decaying exponentially (or as r^{-4}, where r is radial distance from injector). But taking 0.1°C, as representing measurement accuracy or the size of intrinsic fluctuations, produces the profile in a finite time.

Assuming radial flow through a uniform porous layer of fixed thickness, the cold front X_{cf} is found at a fixed fraction, K_c say, behind the flood front, R_{inj}. That is $X_{cf} = K_c R_{inj}$. Platenkamp uses a simple heat balance to show that $K_c = \sqrt{[\rho_w c_w \phi)/(\rho_e c_e)]}$, where ρ_w is the specific heat of water, c_w the density of water and the product $\rho_e c_e$ the effective heat capacity of the flooded rock. Values from 0.1 to 0.5 have been quoted as typical for K_c. Note that it immediately follows that the injected water is flowing *through* the cold front and at a relative velocity K_c^{-2} times (hence typically 4 to 100) that of the cold front, at that particular distance from the injector.

Assuming vertical symmetry and allowing for viscous heating, it can be shown (see Appendix 2) that at equilibrium the temperature profiles for the injected water and reservoir rock satisfy a pair of simultaneous second order partial differential equations. This model is physically unrealistic near the injector ($r = 0$), so the possibility of a fully analytic solution based on Bessel functions cannot be realized. However, for large r, the particular solution plus the complementary function must be of the form:

$$T_F + ar^{-4} + br^{-c}e^{-rd}$$

A curve fitting exercise on the Platenkamp results for a selected radial injector therefore seemed a reasonable approach. This was then converted back to dimensionless units so that it could be used on other wells with the same general environment, giving the following formula for the stabilised temperature profile around such an injector:

$$10^5 \left[\frac{T_{cf} - T_{inj}}{T_{res} - T_{inj}} \right] = 16.684Z + 0.40804Z^2, \; T_{cf} < T_{res}$$

where $Z = (40/h \sqrt{715/\rho_e 7 c_e}$, T_{cf} is the temperature (in °C) immediately behind the cold front at X_{cf} and T_{inj} is the injection temperature (in °C).

Platenkamp also describes a linear flow model, in which a 'tube' of water with diameter h emerges from the injector. Although all our development for the radial model can be followed through for this linear model, we have mostly not found the results useful for our particular purposes. Also we think we have accommodated those aspects which are favourable by a 'pie-slice' technique, as described below.

6.5   WATER VOLUME IN THE VIABILITY REGION

Suppose T_L and T_U are respectively the lower and upper temperature bounds for the particular bacterial type we wish to model downhole. The most general situation occurs when:

$$T_{inj} < T_L < T_U < T_{res}$$

So that, at the start of injection, none of the injected water is in the viability region, which is in the form of a shell (or flattened torus) around the injector. Then, at time t_L (in days) the cold water front will cross the T_L boundary and the viability shell will start to grow. It will reach its maximum size at time t_U, when X_{cf} crosses the T_U boundary and remain at that size

indefinitely, with injected water being continuously flushed through this TVS bringing fresh supplies of substrates to the bacteria. This is illustrated in Figure 3.

Correspondingly, at the producer, there will be an earliest moment, t_1 say, when injected water which has passed through the initial viability region can first arrive; and there will be a later time, t_2 say, subsequent to which all injected water will have passed through the fully established TVS. We have found that these (injection) times, t_1 and t_2, can each vary from days to years for producer wells in the North Sea, depending on the particular reservoir parameters. For example, the first quantities of sour water to reach the producer may arrive at, or shortly after, breakthrough, or they may take years to arrive. Similarly, water from a fully established TVS may start arriving more or less immediately after breakthrough - though this is likely to be associated with a relatively small TVS - or it may take years to build up to its full potential - which will then typically imply a large TVS. The need to explain such variability in time to souring does not therefore require an H_2S scavenging model to cause a delay in the appearance of H_2S. The consequences of mineral scavenging by the Siderite Shield and subsequent saturation (the postulated 'Shield breakdown') could, however, further delay biogenic souring.

We have also observed that breakthrough typically occurs long before the time predicted by the full 360 degree radial model, given the rate of injection, (average) formation thickness, and injector-producer distance. We have allowed for this in our model by assuming that injected water fans out into arcs (or 'pie-slices') of the full model and have scaled up or down accordingly so as to give a 'virtual' injection rate, whilst assuming no other effects on the thermodynamics, (see Figures 9 and 10).

Suppose breakthrough occurs at (injection) time t_b at a producer which is at a distance r_p ft horizontally from the relevant injector - which has injected V_b cu ft of water by that time, at an implied average injection rate of q bwpd (barrels of water per day). Then, since the implied 'full model' volume of injected water for that breakthrough date would be:

$$V_{Fb} = \phi \pi r_p^2 h = q_F b t_b$$

where q_F is the equivalent implied bwpd and:

$$b = 5.615 \text{ (cu ft per barrel)}$$

the total 'pie-slice' percentage is $p = 100 V_b / V_{Fb}$

At an arbitrary time t, the actual volume of injected water, measured relative to the implied daily rate at breakthrough, would be:

$$V_t = qbt$$

Note that, given a well profile the 'true time' could then be determined from this water volume assessment, which is the basic clock for this 'water-driven' model. Also, at an arbitrary time t, with $t_L < t < t_U$, the volume of water in the viability shell will be:

$$V_t = qb(t - t_L)$$

rising to its maximum value at time t_U - from its minimum value of zero for all times earlier than t_L. For a fixed temperature range ($T_L - T_U$), this volume increases rapidly with T_L leading to our conclusion that thermophilic bacteria are potentially more serious as a source of reservoir souring.
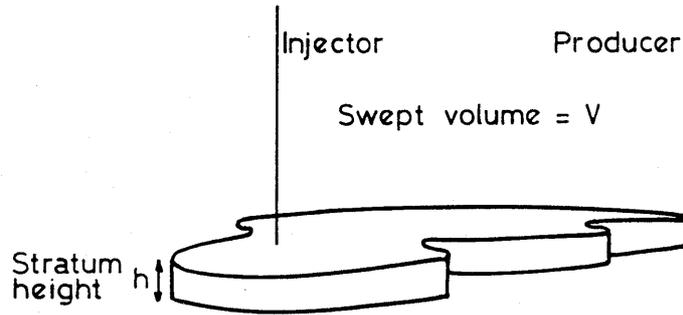
Figure 9
Model illustrating radial fanning of injected water
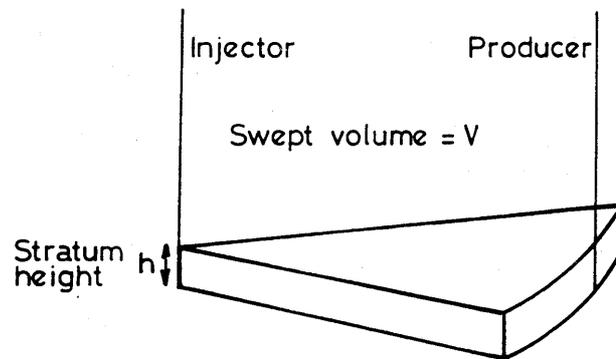
Figure 10
**Illustration of injection water swept into a single 'pie slice'. This pie slice
is used to determine the parameters for a nominal full radial TVS**

By equating the volume of rock occupied by the injected water to V_t, after allowing for the 'pie-slice' effect, we can obtain the following expression for R_{inj}, the radius of the injected water front, at time t:

$$77 R_{inj} = \sqrt{100 bqt/(p\phi\pi h)}$$

Finally, given appropriate information on reservoir pressures, the above formulae can be used to determine the temperature and pressure history for any arbitrarily chosen small volume of water as it passes through the reservoir, from the injector to the producer. Coupled with the previously derived expression for sulphate consumption by mesophilic bacteria in North Sea water we can integrate this consumption rate over this history to give the following basic expression for the hypothesized amount, S, of sulphate consumed (per litre) by bacterial activity in produced water at a given time t:

$$S = \int \beta dt$$

where $\beta = \beta(x(t))$ for travel time t and the integral is truncated at the North Sea norm of 2650mg/1 or at some lower concentration if appropriate. An analytic expression for this integral is described in Chapter 8. We have calibrated this as a predictor for produced H_2S against observed results for a selection of North Sea Wells with some success. These details are also given in Chapter 8.

6.6   NUTRITIONAL FACTORS

Although the extent of the downhole microbiological activity can create a bioreactor of many hundreds of thousands of cubic metres of cooled waterflooded rock, the efficiency of microbiological reduction of sulphate to sulphide is low. Typically, in a reservoir that provides the fundamental growth requirements for the different types of SRB, the sulphate conversion is up to 5% that of pressurised laboratory grown counterparts. The difference is currently ascribed to (primarily) sub-optimal nutrition downhole. Formation water supplies an adequate carbon source in the form of acetate (up to approximately 1000mg/l) but can be lacking in, for example, phosphorus or nitrogen (40). Any reservoir treatments or water injection practice that redresses the short supply could be responsible for a dramatic increase in the appearance of H_2S in breakthrough water, eg phosphorus containing scale treatments or nitrogen containing oxygen scavenger (ammonium bisulphite) could supply the missing element necessary for a significant increase in H_2S production from an establishing SRB population.

An increase in downhole 'nutritional ceiling' from 2% to 5% actually represents a potential increase in H_2S production of 150%. An inventory of formation water components and injection material compared against microbiological requirements would be the first necessary step in identifying the key element required for boosting SRB growth. Perturbations of this downhole bioreactor, in common with any other bioreactor, thus should just as readily mitigate H_2S production as promote it. (See also comments in Chapter 8).

7. AN INVESTIGATION OF H₂S PARTITIONING FOR NORTH SEA PRODUCTION FLUIDS

7.1 INTRODUCTION

Early exploration for oil and its production from the North Sea, indicated that the fields generally produced light sweet crudes with very little or no hydrogen sulphide being present. As a consequence of this the materials of construction selected for some developments for downhole tubulars, well flowlines and manifolds, separators, pipelines and other equipment items were suitable only for sweet rather than sour H_2S-containing crudes. The North Sea continued to produce sweet oil for a number of years, but by the early to mid '80s evidence began to emerge of a small but increasing presence of H_2S in the crude oil from certain fields and wells, where secondary recovery by seawater injection was practiced. With time the sourness of crudes increased and more wells and fields became affected.

These trends naturally concerned field operators whose facilities had been constructed for sweet service. Out of this concern came a requirement to identify the source, monitor the concentration and assess the partitioning of H_2S between oil, gas and produced water. Such information is a clear necessity in order to assess the corrosion impact on production facilities and what remedial and H_2S removal measures might be taken.

The source of H_2S has been attributed to one or more of the following mechanisms:

- The action of thermophilic sulphate-reducing bacteria primarily on sulphates in seawater injected for secondary oil recovery

- Thermochemical sulphate reduction in seawater

- Decomposition of sulphur containing organic compounds present in the crude oil and/or hydrolysis by reaction with formation water at high downhole pressures and temperatures

- Dissolution of mineral sulphides in geological structures around oil deposits

- Redox reactions involving inorganic oxygen scavengers.

This chapter describes a method of determining the partitioning of H_2S, from whatever source, between oil and water phases downhole or gas, oil and water phases topsides from an analysis of the wellhead gas composition and H_2S concentration.

7.2 LITERATURE REVIEW AND PROJECT RATIONALE

The literature contains many references to the solubility and partial pressures of H_2S, CO_2, CH_4, and other low paraffins both individually and in various combinations in a wide variety of liquid organic compounds (41-80), water (43,44,65,81-90) and aqueous solutions of inorganic compounds (51,91-100). There are relatively few publications which deal with the solubility and partial pressures of these gases in produced crude oils (101-103) and formation waters, but what literature there is indicates a distribution ratio in the range of

3-7:1 for H_2S in pure paraffins and $H_2S/CO_2/CH_4$ in various combinations in other paraffins and other organic compounds (100-132).

These data and those for other organic compounds generally give rise to a similar range of distribution ratios with water as the second liquid phase (133). Generally speaking, H_2S is considerably more soluble in organic compounds than in water and aqueous salt solutions, the solubility increasing with increase in aromatic nature and decreasing with increase in paraffin and polar nature. The diversity of organic compounds other than paraffins present in various crude oils may therefore markedly affect the solubility of H_2S in the crude oil and its distribution between crude oil and water. The variability of crude oil probably explains the wide range of distribution ratios cited in the literature. Clearly a heavier, more aromatic, crude has a higher H_2S solvency than a lighter, predominantly paraffinic, crude. There is also a possibility that H_2S may react chemically with certain compounds which could be present in crude oil or even formation water and appear to affect, artificially, the distribution ratio of H_2S between crude oil and water.

It may, in the future, be possible from detailed compositional data of a particular crude oil and formation water combination to use an 'aromaticity factor', a 'polar factor' and 'chemical combination factors' to predict the solubility of H_2S in each phase and its distribution between them. For the present, however, it remains necessary to determine these data experimentally and analytically for a particular crude oil/formation water system. Such experimental data, if properly analyzed, should provide the basis for a suitable prediction science. The work reported in this chapter was carried out on a 'typically light North Sea crude' (Total Alwyn North Field) and a 'typical formation water' from the same well and should have reasonable applicability to most North Sea Oil production systems. Typical compositions of crude oil, gas and formation water are shown in Tables 2-5 respectively.

Table 2
A North Sea whole crude oil composition at reservoir conditions

Compound	Formula	Mole %	Weight %
Carbon dioxide	CO_2	0.29	0.09
Nitrogen	N_2	0.59	0.12
Methane	CH_4	14.08	1.66
Ethane	C_2H_6	5.60	1.24
Propane	C_3H_8	9.91	3.22
Isobutane	C_4H_{10}	1.76	0.75
n-Butane	C_4H_{10}	6.42	2.75
Isopentane	C_5H_{12}	1.71	0.91
n-Pentane	C_5H_{12}	3.52	1.87
Hexane	C_6H_{14}	4.41	2.79
Heptane	C_7H_{16}	5.64	3.94
Octane	C_8H_{18}	5.54	4.41
Nonane	C_9H_{20}	4.45	4.05
Decane	$C_{10}H_{22}$	3.67	3.74
Undecane and higher hydrocarbons	$C_{11}H_{24}+$	32.41	68.46
TOTAL		100.0	100.0

Table 3
A North Sea produced gas composition (at STP)

Compound	Formula	Mole %
Carbon dioxide	CO_2	2.44
Nitrogen	N_2	2.00
Methane	CH_4	49.71
Ethane	C_2H_6	16.01
Propane	C_3H_8	19.37
Isobutane	C_4H_{10}	2.13
n-Butane	C_4H_{10}	5.29
Isopentane	C_5H_{12}	1.01
n-Pentane	C_5H_{12}	1.23
Hexane	C_6H_{14}	0.53
Heptane and higher hydrocarbons	$C_7H_{16}+$	0.28
TOTAL		100.0
Hydrogen	H_2O	<20ppmv
Ammonia	NH_3	non detected
Helium	He	trace

Table 4
A North Sea formation water

Component	Concentration mg/l
Magnesium	15
Calcium	130
Strontium	15
Barium	27
Sodium	6730
Potassium	170
Chloride	10060
Sulphate	4
Carbonate	-
Bicarbonate	1320
Phosphate	4
Nitrate	5
Acetate	630
Propionate	90
Butyrate	42

The methodology and computation of H_2S solubilities in crude oil and formation waters and the derivation of distribution ratios based on the respective partition coefficients could use Henry's Law, Gerrard's Reference Line method (54,57,134) and could use various complex cubic equations of state (101-103,133-150). Gerrard's elegant and realistic method and the cubic equations of state have been used to model the real world and make corrections for the inherent non-ideality of H_2S as the use of Henry's Law has been criticised for this reason. Both of these methods are therefore applicable to relatively high H_2S partial pressures

obtained where high H_2S mole fractions and total system pressures cause significant deviation from ideal gas behaviour assumed by Henry's Law. The methods require comprehensive compositional data for gas, oil and water phases and, in order to use other cubic equations of state, moderately high computational power.

Table 5
Physical properties of the formation water described in 4 above, as supplied

Property	Value
pH (surface condition)	8.1 (at 20ºC)
Density, kg/l	1.012 (at 15ºC)
Total Dissolved Solids (TDS), mg/l	18,040
Resistivity, ohm.m	0.43 (at 20ºC)

In the North Sea, where the level of souring is low and not expected to rise above about 300mg/kg (ppmw) in the oil phase even in the anticipated worse case, the use of Henry's Law is fully justified. This is because at these concentrations the partial pressure of H_2S, which is of paramount importance, is low at wellhead and even at reservoir pressures; and total system pressures are well below the point where non-ideal gas behaviour starts to become measurably significant. Furthermore, under downhole conditions, at pressures above the bubble point, there is no separate gas phase, and hence the question of applicability of Henry's Law or not is irrelevant. It is on this basis, therefore, that the present determination and calculation methodology were developed.

7.3 EXPERIMENTAL WORK

It was recognised at the outset of this work that the preferred experimental method would be to charge an autoclave with crude oil, formation water either alone or separately, and gas in the appropriate ratios, agitate to promote intimate mixing, bring to temperatures and pressures appropriate to simulate wellhead or downhole conditions, and after reaching equilibrium sample each phase for H_2S analysis. It was also recognised, after due consideration and some initial trials, that such an experimental approach was fraught with difficulties. These difficulties included adsorption of HS on the vessel walls, which at the low concentrations (10s to 100s ppmw) would markedly affect the results and, moreover the experimental practicality of on-line sampling, sample storage, preservation and pressure let down was a problem. Because of these problems an alternative, but nevertheless perfectly valid, experimental approach was adopted.

Discussion earlier in this chapter stated that it is the partial pressure, not the total system pressure, which is important. This led to a method whereby the vapour pressure above crude oil and formation water and solutions of known H_2S concentration in these media were separately determined at ambient pressure and temperatures of up to 100ºC. This enabled the H_2S partial pressure to be obtained over a range of H_2S concentrations and temperatures for both H_2S-crude oil and H_2S-formation water solutions by simple subtraction of the solvent vapour pressure from the solution vapour pressures at the same temperature. The H_2S partial pressures obtained at ambient pressure were of the same order

as one might anticipate the H_2S partial pressure to be in a production system and well below the point where non-ideal behaviour becomes a significant factor. The rationale behind the method is that H_2S in the gas phase is in dynamic equilibrium with H_2S in the liquid phase, the concentration of which is determined by analysis to allow the calculation of the partition coefficients of H_2S between crude oil and formation water and the distribution ratio.

7.3.1 Determination of H_2S partial pressures

A bulk sample of crude oil was stripped of gas and the lighter liquid fractions, both of which were considered likely to affect the accuracy of the determinations and experimental reproducibility by producing a considerable 'low fractions' and 'other gases' partial pressure.

About 1000g of crude oil was distilled under reflux for 20 minutes at about 70°C and the lighter fractions and dissolved gases removed. The loss amounted to around 0.4%.

Vapour pressure determinations on crude oil and on formation water were carried out using an isoteniscope. Samples of oil or water were introduced into the isoteniscope and the samples and apparatus deaerated by evacuation to <1mmHg, the oil sample being frozen to avoid boiling under vacuum.

The isoteniscope bulb was virtually filled with test liquid, fitted to a mercury manometer, immersed in a water bath and the vapour pressure of the sample measured at a large number of discrete temperatures in the range 20°C to 100°C. The heating/cooling rate of the water bath was 1°C/minute and vapour pressure determinations were made on the heating and cooling cycles. Typically 40-70 temperature points were measured for each determination.

Saturated solutions of H_2S in deaerated crude oil and in deaerated water were prepared and the concentration of H_2S in each was determined by the methods described below. The vapour pressure/temperature curves of each of the solutions were determined by the method described above for crude oil and produced water, with the exception that they were not vacuum degassed in the isoteniscope. The saturated solutions were successively diluted with degassed crude oil or produced water in a standard volumetric flask to give crude oil/H_2S and formation water/H_2S solutions with a range of H_2S concentrations. These solutions were stored in totally filled (no air space) polypropylene stoppered glass bottles until required for vapour pressure/temperature curve determinations as above, the concentration of H_2S being measured immediately prior to testing, (see Section 7.3.2).

The work on produced water and produced water/H_2S solutions was carried out first because earlier trial runs had indicated that traces of heavier hydrocarbons left on the inside glass walls of isoteniscope appeared to affect significantly the reproducibility of runs, presumably by selective absorption of H_2S.

Vapour pressure determinations on crude oil/H_2S solutions were carried out after the work on produced water, the isoteniscope being rinsed with petroleum ether and thoroughly dried between runs.

7.3.2 Determination of hydrogen sulphide concentration in crude oil and formation water samples

Because of the dark colour of the crude oil samples an indirect method of analysis to quantify the concentration of the H_2S was developed.

Oxygen-free nitrogen was blown through the sample of crude oil/H_2S solution into a second Dreschel bottle containing approximately 10g of KOH in about 200ml of distilled water. The KOH solution had previously been deoxygenated by blowing oxygen-free nitrogen through it for 5 minutes. The H_2S-containing crude oil was degassed for 4 hours, the time necessary to achieve total removal of H_2S from the sample. No H_2S was detected in the gas after passing through the KOH solution. All apparatus joints were sealed with Nescofilm. For H_2S saturated solutions the KOH/sulphide solution was made up to 250ml. A 10ml aliquot was added to 25ml of glacial acid and 50ml 0.05M iodine solution. This was then titrated against 0.0653M thiosulphate. Near to the end point 3 drops of starch solution were added to clarify the end point. The end point was indicated by a solution colour change to bright yellow. The end point was sharp and reproducible. For more dilute solutions the size of the aliquot taken was increased to 50ml. The titration results were used to calculate the H_2S concentration in solution. For saturated solutions the results obtained confirmed the approximate concentrations derived on the basis of increase in weight after saturation with H_2S.

The determination of H_2S concentration in formation water was more straightforward because of the absence of an interfering dark coloration. Suitably sized aliquots were simply added to 50m.1 of 0.05M iodine solution, acidified with glacial acetic acid and titrated against 0.0653M thiosulphate to a bright yellow end point. Saturated solutions of H_2S in either crude oil or formation water are somewhat unstable and lose H_2S on standing.

7.4   RESULTS

The results of the vapour pressure measurements are produced graphically. Figure 11 shows the vapour pressure versus temperature profiles for crude oil with the various amounts of H_2S. Figure 12 shows similar profiles for formation water.

The results for medium to high H_2S concentrations indicate large differences between the vapour pressure of the crude oil and vapour pressure of crude oil plus H_2S. A similar trend was observed for formation water. Note that the lowest dissolved H_2S concentrations and the 0ppmw control curves on both figures appear out of sequence. This is regarded to be an experimental anomaly.

Vapour pressures at temperatures above 100ºC were obtained by extrapolation of refined data. Vapour pressure measurements for formation water with and without H_2S and crude oil with and without H_2S were used to calculate partition coefficients of H_2S between oil and water at various temperatures and pressures.
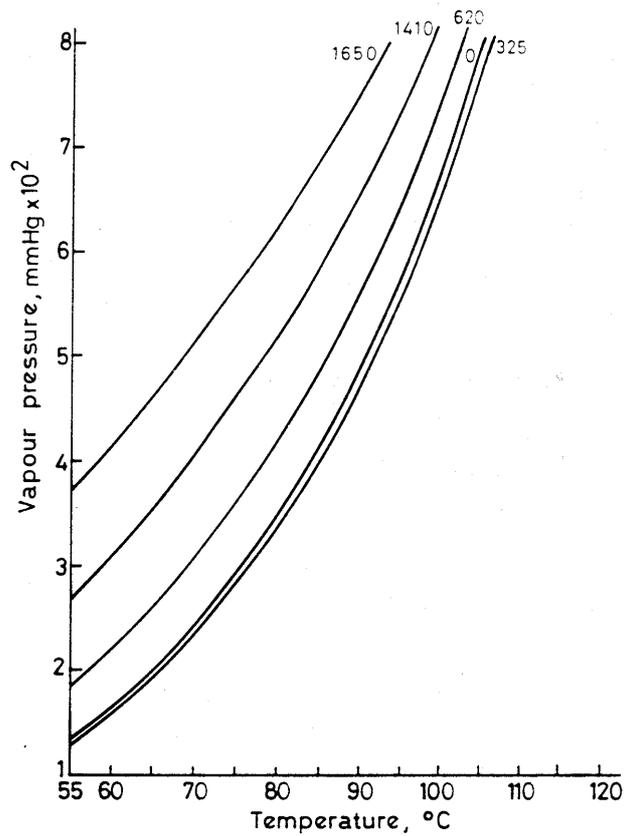
Figure 11
**Vapour pressure vs temperature for samples of crude oil
with and without dissolved H₂S in ppmw**

The smooth curves presented in Figures 11 and 12 are least square curves fitted using a Gauss iterative procedure of the form:

$$p = k^1 \exp \frac{k^{11}}{T}$$

where p is the vapour pressure of H₂S in mmHg
k^1 and k^{11} are the fitted constants
and T the absolute temperature

The data presented in Figures 11 and 12 are used below to derive partition coefficients between oil and water, which in turn are related to the H₂S concentration in the gas phase.
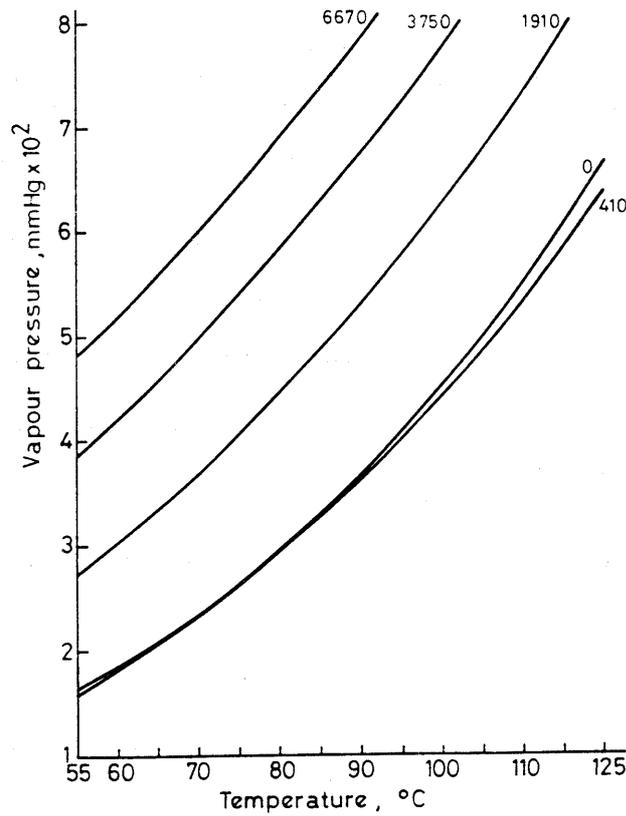
Figure 12
**Vapour pressure vs temperature curves for samples of formation water
with and without dissolved H₂S in ppmw**

7.5 DETERMINATION OF H₂S PARTITION COEFFICIENTS IN CRUDE OIL AND PRODUCED WATER

The H_2S partial pressures [$p(H_2S)$] as a function of temperature were determined from the difference between the smoothed vapour pressures of the H_2S solutions and the vapour pressure of the 'pure' oil and water, respectively. At constant temperature the partial pressures are linear functions of liquid phase composition, within the experimental error, and therefore Henry's Law can be applied. Only the results for the highest H_2S concentrations were used in deriving Henry's Law constants since, for these, the vapour pressure difference is the highest and, therefore, the error smallest. Henry's Law constants derived from the partial pressures are recorded in Table 6 and Figure 13. These were defined as follows:

$$K_o = \frac{p(H_2S)/mmHg}{X_o(H_2S).ppmw}$$

$$K_w = \frac{p(H_2S)/mmHg}{X_w(H_2S).ppmw}$$

Here X_o and X_w are H_2S concentrations in oil and water, respectively.

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Table 6
Henry's Law constants for H₂S in crude oil and formation water. Note that all H₂S is in the undissociated form, ie partitioning from the aqueous phase at/or less than pH5

$t^o/^oC$	50	60	70	80
K_o x 10^2 K_w x 10	4.53 1.38	5.03 1.57	5.49 1.70	5.92 1.77
Units of K = mmHg/ppmw (H₂S)				

Within experimental error, the values of K are linear functions of temperature. Thermodynamically, one would expect log $_eK$ to be a linear function of $1/T$, but for small ranges of temperature a linear dependence of K on T is acceptable.

The partition coefficient for the distribution of H₂S between oil and water (K_{ow}) can be derived as follows:

$$p(H_2S) = K_oX_o = K_wX_w$$

$$K_{ow} = X_o/X_w = K_w/K_o$$

Values of K_{ow} are recorded in Table 7 together with the result of a direct measurement at 20°C. The values of K_{ow} are essentially independent of temperature (average value 3.1) but somewhat lower than the separate measurement at 20°C.

Table 7
Partition coefficient (K_{ow}) for the distribution of H₂S between crude oil and formation water

$t^o/^oC$	20	50	60	70	80	100	120
K_{ow}	4.1	3.0	3.1	3.1	3.0	(3.2)	(3.2)
values in parenthesis are extrapolated.							
K_{ow} = ppmw H₂S in oil/ppmw H₂S in water.							

The derived values of K_{ow} refer to partial pressures of less than one atmosphere, p_o. At higher pressures K_{ow} is given by the following equation:

$$1n\frac{[K_{ow}(p)]}{[K_{ow}(p_o)]} = \int_{p_o}^{p} \frac{(\bar{V}_w - \bar{V}_o)dp}{RT}$$

$\bar{V}_w$ and $\bar{V}_o$ are the respective partial molar volumes of H₂S in water and oil at infinite dilution. Values for these quantities are not available. If they were approximated by the pure component molar volumes (hypothetical quantities in this case) then the right hand side of the equation would vanish and K_{ow} would be independent of pressure, which is the assumption made in this analysis. This assumption is justified because even at the high downhole pressures the H₂S partial pressures are relatively low and also the experimental error in K_{ow} is almost certainly higher than any expected pressure induced variation.

7.6   ESTIMATION OF H₂S DISTRIBUTION AT DOWNHOLE PRESSURE

At the wellhead three phases may exist - gas, oil and water. A total mass balance gives:

$$M_g + M_o + M_w = M \text{ (The total mass flow rate)}$$

The overall H₂S concentration Z/ppmw is given by:

$$Z = \frac{X_g M_g + X_o M_o + X_w M_w}{M}$$

where $X_g = 10^6 m(H_2S)/M_g = 10^6$ x mass fraction of H₂S in the gas phase

$$X_o = p(H_2S)/K_o, \quad X_w = p(H_2S)/K_w$$

The H₂S partial pressure is determined from the product of the H₂S mole fraction in the gas phase and the total pressure.

At downhole pressures (P) above the bubble point pressure, a mass balance gives:

$$M_w^1 = M_w, \quad M_o^1 = M_g + M_o$$

A mass balance on the H₂S gives:

$$ZM = X_o^1 M_o^1 + X_w^1 M_w^1$$

$$= K_{ow}^1 X_w^1 M_o^1 + X_w^1 M_w^1$$

$$X_w^1 = \frac{ZM}{K_{ow}^1 M_o^1 + M_w^1} = \frac{Z(M_o^1 + M_w^1)}{K_{ow}^1 M_o^1 + M_w^1}$$

If the oil/water ratio $M_o^1/M_w^1 = R$, then:

$$X_w^1 = \frac{Z(R+1)}{(K_{ow}^1 R)+1} = X_o^1 = \frac{Z(R+1)}{R+1/K_{ow}^1}$$

The H₂S concentration may also be determined graphically using a so-called solute-free composition diagram (see Figures 14 and 15) showing H₂S aqueous phase concentrations in ppmw(mg/kg) to 10ppmw and 100ppmw respectively. On these diagrams the abscissa represents a mass fraction of water:

$$\frac{M_w^1}{M_w^1 + M_o^1} = \frac{1}{R+1}$$

and the ordinate the H₂S concentration, $\frac{10^6 m(H_2S)}{M_o^1 + M_w^1}$

Correction for the consequence of high pH converting H₂S to dissociated species (HS⁻ and S²⁻) in the water phase can be achieved by using:

$$Z \rightarrow \frac{Z}{1 + 10^{(pH-6.7)}}$$

40
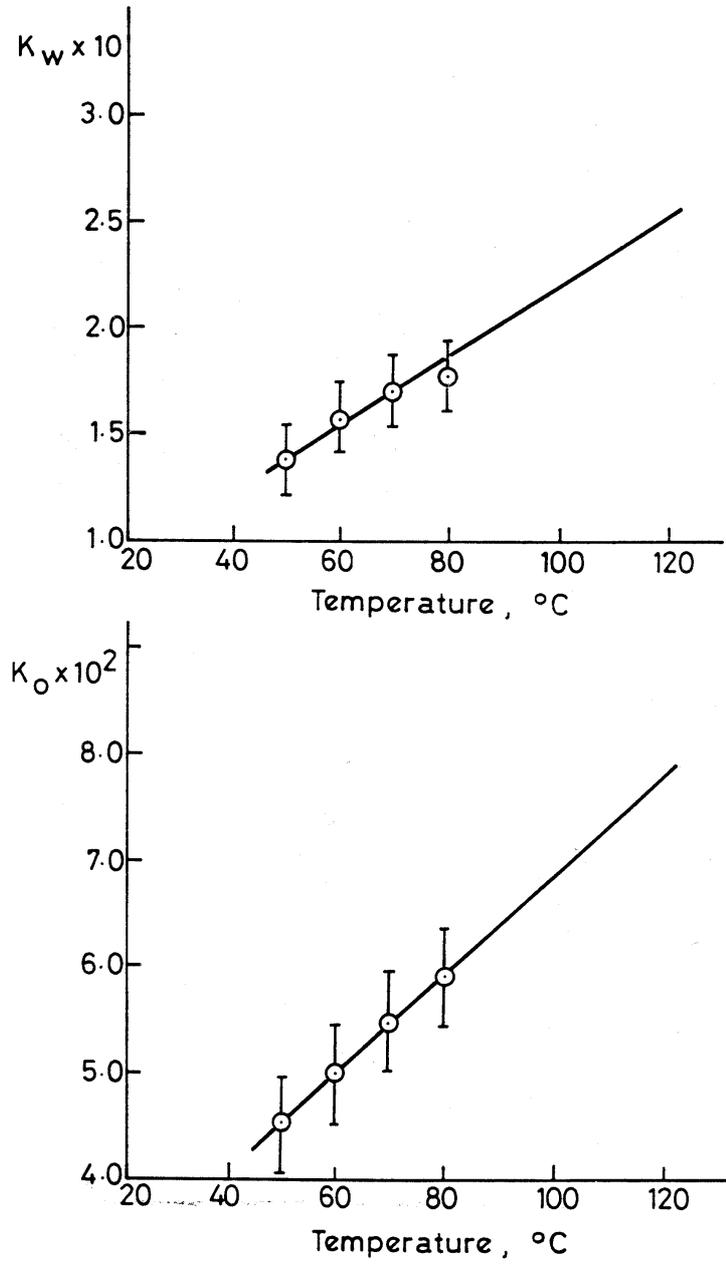
Figure 13
Henry's Law constants for H₂S in crude oil (K_o) and formation water (K_w)

Pure H_2S lies at infinity on the ordinate. Tie-lines connecting equilibrium H_2S concentrations in oil and water phases are easily constructed. For a given value of $X_w^1, X_o^1 = K_{ow}^1 X_w^1$. To use the diagram, the point with co-ordinates $\left(Z, \frac{1}{R+1}\right)$ is located and the tie-line passing through this point gives X_o^1 and X_w^1 directly, (see Figures 14 and 15).
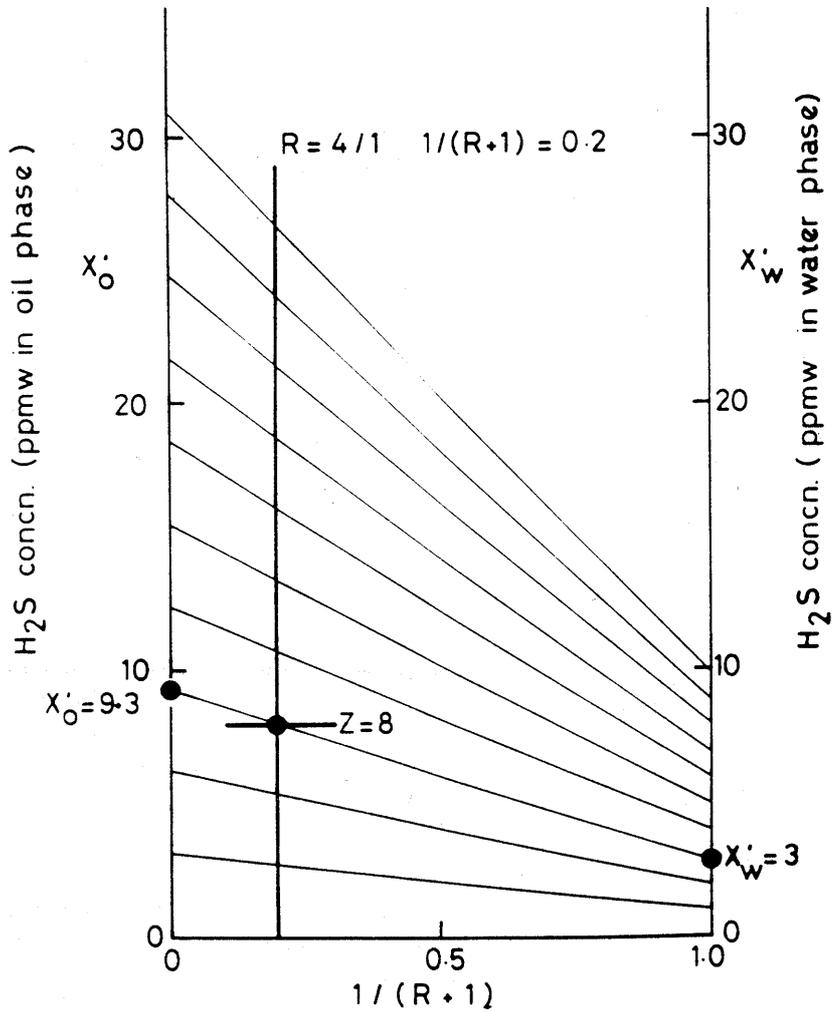
Figure 14

Liquid-liquid equilibrium diagram for H_2S/oil/water for H_2S up to 10ppmw in the water phase $K_{ow} = 3.1$, R = oil/water ratio, X_o and X_w = H_2S concentration in oil and water phases in ppmw respectively, Z = overall H_2S concentration, ppmw
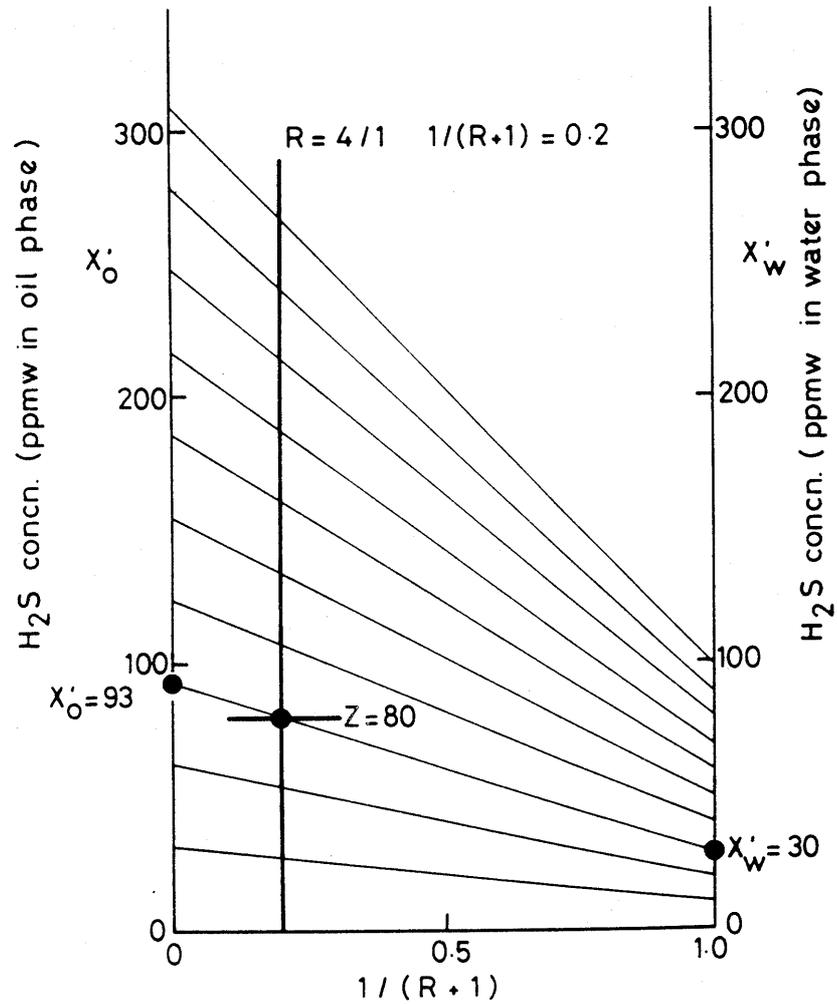
Figure 15
Liquid-liquid equilibrium diagram for H_2S/oil/water for H_2S up to 100ppmw in the water phase $K_{ow} = 3.1$, R = oil/water ratio, X_o and X_w = H_2S concentration in oil and water phases in ppmw respectively, Z = overall H_2S concentration, ppmw

The following assumptions were made in this analysis.

- Oil and water phases are totally immiscible.

- H_2S partial pressures are linear functions of H_2S concentrations in the liquid phase and Henry's Law constants are independent of pressure. At ambient and wellhead conditions this is a good approximation within the accuracy of the measurements for both oil and water phases.

For ease of measurement the Henry's Law constants were determined at liquid phase concentrations - much higher than those expected at wellhead and downhole conditions - up to 6670ppmw for oil and 1650ppmw for water cf maximum values of 300ppmw and 100ppmw respectively at worst case anticipated operating conditions. For the oil phase it is to be expected that Henry's Law will apply at the lowest concentrations. For the water phase it must be noted that H_2S is a weak electrolyte in aqueous solution. Deviations from Henry's Law would be expected at the lowest concentrations, although these would certainly be smaller than the experimental accuracy. For aqueous solutions at higher pressures, the American Petroleum Institute Technical Data Manual shows that Henry's

Law constants are accurately independent of pressure up to approximately 20atm and substantially independent of pressure up to around 200atm. Of course at pressures above the bubble point pressure (downhole reservoir conditions) no gas phase exists and the pressure dependency of the Henry's Law constant is irrelevant.

- The equations of state discussed in the literature survey require a full compositional analysis for both oil and water phases. These data were not available for the crude oil sample and because of this it was not worthwhile analyzing the water sample alone. With such data, these equations may possibly be employed to refine the analysis of the experimental data.

- The H_2S partition coefficient is riot independent of oil composition. This is an important consideration. At wellhead pressures most of the lighter components enter the gas phase, whilst at downhole pressures these are contained in the liquid phase. It is to be expected that H_2S is more soluble in the heavier (and particularly aromatic) components of the oil. Therefore, at downhole pressures the H_2S concentrations in the oil are likely to be an overestimate since the values of K_{ow} were determined at wellhead conditions. The H_2S concentrations in the water would therefore be an underestimate.

7.6.1 Procedure for determining downhole H_2S concentration from topsides gas phase measurement

- The procedure requires a measurement of the H_2S concentration in the wellhead gas (Y/ppmv H_2S). The mole fraction H_2S, $y = 10^{-6}Y$.

- H_2S is assumed to have partitioned from the aqueous phase at/or less than pH5.

- The partial pressure of H_2S (in mmHg) is calculated from $p(H_2S) = yP$ where P is the total pressure at the wellhead.

- Next - an analysis of the wellhead gas is required, (mole fractions) of all components. The H_2S concentration in the gas phase (X_g/ppmw) is then given by:

$$X_g = \frac{34.08Y}{\sum y_i mw_i}$$

Where y_i and mw_i are the mole fractions and molecular weights respectively of all remaining components. If the gas analysis is in terms of mass fractions m_i then:

$$X_g = 34.08Y\Sigma (m_i/mw_i)$$

- The overall H_2S concentration (Z/ppmw) is calculated from:

$$Z = \frac{X_gM_g+X_oM_o+X_wM_w}{M_g+M_o+M_w}$$

where M_g, M_o and M_w are mass flow rates of gas, oil and water, respectively, and

$$X_o = p(H_2S)/K_o, \ X_w = p(H_2S)/K_w$$

K_o and K_w are taken from Figure 13.

- Under downhole conditions the oil/water mass ratio, R is calculated, $R = (M_g + M_o)/M_w$ at wellhead conditions.

- The point with co-ordinates (Z, $1/R$ +1) is located on Figure 14. The (sloping) tie-line passing through this point gives X_o and X_w in ppmw directly.

7.6.2 Numerical example on H₂S partitioning for a typical production well

- *Gas analysis*

  Average molecular mass of produced gas = 25.4
  Assume measurement at 15°C, 1atm. Since volume of one mole of produced gas at STP = 22.4 litres
  Then density of produced gas = $\left(\frac{273}{273+15}\right)$ x $\left(\frac{25.4}{22.4}\right)$ = 1.075g/litre = 0.001075kg/litre

- GOR = 134 m³/m³ at STP
  bopd = 1832
  since 1 barrel = 159 litres
  the mass of gas, M_g = 1832 x 159 x 134 x 0.001075 kg gas per day (kggpd)
  $\qquad\qquad$ = 41,955 kg gas per day (kggpd)

- 7ppmv H₂S in gas extracted at well head pressure of 130psig (144.7psia) = 9.83atm
  (abs) = 747lmmHg (abs) and temperature = 104°C
  [1atm = 14.72psia = 760mmHg]
  The mole fraction of H₂S, y = 7 x 10⁻⁶. Molecular mass of H₂S= 34.08
  Hence X_g(H₂S) = $y\frac{34.08x10^6}{25.4}$ = 9.39ppmw
  And partial pressure of H₂S in mmHg,
  p(H₂S) = 7 x 10⁻⁶ x 7471 = 5.23 x 10⁻² mmHg

- *Oil analysis*

  Density of oil taken as 0.8 kg/litre
  If production of oil is 1832 bopd,
  M_o = 1832 x 159 x 0.8 kg oil per day (kgopd)
  $\qquad$ = 233,030kgopd
  K constant for oil at 104°C (wellhead gas sample extraction temperature), K_o = 6.7 x 10⁻²
  Hence X_o (H₂S) = $\frac{p(H_2S)}{K_o}$ppmw = $\frac{5.23x10^{-2}}{6.7x10^{-2}}$= 0.781ppmw

- *Water analysis*

  Density of formation water taken as 1.012kg/litre
  If production of water is 4911 bwpd,
  M_w = 4911 x 159 x 1.012kg water per day (kgwpd)
  $\qquad$ = 790,291kgwpd
  K constant for water at 104°C (wellhead gas sample extraction temperature), K_w = 2.25 x 10⁻¹
  Hence X_w (H₂S) = $\frac{p(H_2S)}{K_w}$ppmw = $\frac{5.23x10^{-2}}{2.25x10^{-1}}$= 0.232ppmw

- ***Overall concentrations at wellhead***

$$Z = \frac{X_g M_g + X_o M_o + X_w M_w}{M_g + M_o + M_w}$$

$$= \frac{(9.39x41,955)+(0.781x233,030)+(0.232x790,219)}{41,955+233,030+790,219}$$

$$= \frac{394,046+181,892+183,672}{1,065,205}$$

$Z = 0.370 + 0.171 + 0.172$ (relative amounts in gas, oil and water respectively)
$Z = 0.713$ppmw

- ***Downhill partitioning (no gas phase)***

$Z = 0.713$ and $R = \frac{M_g + M_o}{M_w} = \frac{41,955+233,030}{790,219}$
$R = 0.348$, $\frac{1}{R+1} = 0.742$ and $K^1_{ow} = X_o/X_w$
$= K_w/K_o = 3.358$

These values can be used in Figure 14 by dividing the X_o and X_w axes by 10 to derive X^1_o and X^1_w.

Alternatively they can be used in the equations:

$$X^1_o = \frac{Z(R+1)}{R+1/K^1_{ow}} \qquad \text{and} \quad X^1_w = \frac{Z(R+1)}{(K^1_{ow}R)+1}$$

$$X^1_o = \frac{0.713x1.348}{0.348+1/3.358} \quad \text{and} \quad X^1_w = \frac{0.713x1.348}{(3.358x0.348)+1}$$

$X^1_o = 1.489$ppmw $\qquad$ and $X^1_w = 0.443$ppmw

- ***Summary of results of worked example***

Wellhead $X_g = 9.39$ppmw, X_o 0.781ppmw, $X_w = 0.232$ppmw
Downhill $X^1_o = 1.489$ppmw, $X^1_w = 0.443$ppmw

- *Daily yield of H₂S*

    Wellhead

	Total Production kg/d	H₂S Concentration ppmw	H₂S yield kg/d
Gas	41,955	9.392	0.394
Oil	233,030	0.781	0.182
Water	790,219	0.232	0.184
Total	1,065,204		0.760

    Downhill

	Total Production kg/d	H₂S Concentration ppmw	H₂S yield kg/d
Oil	274,985	1.489	0.409
Water	790,219	0.443	0.350
Total	1,065,204		0.759

    The small difference between wellhead and downhole H_2S yields are a consequence of rounding errors.

7.6.3 Comparison with industry standard H₂S partition coefficients

The Gas Processors Association initiated the GPA Project 752 in October 1975 for the purpose of modifying the Soave Redlich Kwang (SRK) equation to include interactions of water, hydrogen and other synthetic gas (SG) components with hydrocarbons (151). The research report RR-42 describes this modification of the SRK equation and compares predicted phase equilibria and enthalpies with experimental data. The range of experimental values reported for H_2S in these comparisons unfortunately has a minimum at around a gas phase concentration of 300ppmv. However there is good agreement between the modified SRK theory and the H_2S data as reported over this range and this fact has been used to justify extrapolation of these equations down to much lower concentrations of H_2S. These equations and results also have the advantage that they can be calculated over a range of temperatures and pressures. However, at the particular temperatures and pressures used in the experiments described in the earlier sections of this chapter, the modified SRK equations produced significantly different values for K_o and K_w, although there was reasonable agreement for the ratio K_w/K_o.

One reason for these discrepancies may be the lack of control for pH in the formation waters. At the time of writing this matter is unresolved, so that for low gas phase concentrations of H_2S (100ppmv or less) the partition coefficients are not yet safely determined.

8. PREDICTION OF SOURING

If the premises of the Thermal Viability Shell model described above are accepted, then a predicted profile for reservoir souring can be constructed given the information contained in a conventional production fluids profile, as obtained from a standard reservoir simulator, provided the less standard but crucial seawater breakthrough profile is available along with some ancillary information on (average) molecular weights and reservoir dimensions. This profile is constructed for a given injector, around which the TVS becomes established, and its associated producer well - at which the sour fluids from this particular TVS appear. For a reservoir with several injectors and producers, either a 'typical' pair should be selected or else all connected pairs could be examined separately. If one producer is supported by more than one injector, the resultant souring profile would have to be deduced by a pro rata mixing of the individual contributions.

It is appropriate to mention the work of Ligthelm et al (152) at this point, since they give an alternative and conceptually different mechanism for biologically-generated H_2S in a seawater flooded reservoir. In their model there is a once-and-for-all, essentially instantaneous, generation of H_2S at the point where the mixing zone (between injected and formation water) propagates through the reservoir. There is no specific bacterial dependence on temperature or pressure, as for Sunde (153) and the observed variation over time of produced H_2S is attributed to adsorption on to the matrix rock minerals plus partitioning of the H_2S into a stagnant oil phase, followed by a consequent partitioning back into the sweet water injected behind this point of generation.

The biological model used by Sunde (153) invokes the Michaelis-Menton equation, which expresses the mathematical relationship between the initial rate of an SRB enzyme-catalysed reaction, the concentration of the substrate and certain characteristics of the selected enzyme. The resultant of all such enzyme processes is however equivalent to the S-shaped sulphate consumption curve shown in Figure 7, which we have approximated to the trilinear form also shown in that Figure. A single number for rate of sulphate reduction can then be used to control the slope of the middle line in this approximation and a number for the substrate availability controls the plateau value for the maximum sulphate concentration that can be consumed. This latter technique subsumes the need for any detailed mathematical breakdown and accommodates either empirically derived data or field data for history matching.

For the TVS model, an analytic solution to the integral:

$$S = \int \beta \mathrm{dt}$$

given in Section 6.5 above requires an expression for the pressure drop-off from the injector towards the producer. This is known to be rapid, and since, for the purpose of modelling the behaviour of the relevant bacteria, its value at any one point only needs to be known approximately, we have felt able to use simple quadratic decay:

$$P = P_I - dr^2, \ r < r_p$$

Where $d = (P_I - P_p)/r_p^2$, P is the pressure at a point r between the injector at pressure P_I and the producer at pressure P_p and overall distance r_p.

Substituting the expressions for P and T_o as functions of travel time, t, into the expression for β in Section 6.3, gives β as a function of time. The full substitution is given in Appendix 3.

The lower limit, t_L for the travel time used in evaluating the integral is determined by the starting boundary of the TVS, whilst the upper bound, t_U, is the larger of t_L and a number which is the smaller of the outermost boundary crossing time for the TVS when fully established and travel time t_c. This travel time is the time at which the currently produced injected water (for which implied moment the prediction is required) crossed the cold water front (recall that this occurs at a speed which is typically a high multiple of the velocity of this front). Note that this simple procedure only works because of the stability of the temperature profile behind the cold front. For wells with a more complex history, this integral would have to be evaluated in a more dynamic fashion as par; of a full reservoir simulator incorporating temperature variation. As it is, the resultant algebraic expression from this analytic technique is very long and beg evaluated in stages. It was evaluated by us using the computer algebra package MAPLE V, exported as a FORTRAN expression and then imported into the spreadsheet QUATTRO PRO for numerical calculations with actual or simulated well profiles.

We have calibrated this expression against data from several North Sea oil wells. Three aspects became clear during this exercise. Firstly, the downhole sulphate conversion efficiency of the bacteria was low compared with their capabilities at the same temperatures and pressures under laboratory conditions. We estimated this to be at or around 1-5% for the examined wells. This range is consistent with other independent estimates; secondly, regardless of this nominal efficiency, which governs the speed at which the bacteria work, there appeared to be an upper limit to the amount of sulphate which could be consumed. This ceiling, C, was typically of the order of 5% or less and is consistent with an 'available nutrient' description of the bacterial environment; thirdly, this upper limit or ceiling was correlated with the number, D, of injection days, the volume of water, V (in millions of cubic feet), in the TVS and the number, N, of 'turnovers' of the TVS (in terms of injected water). A 'best-fit' to the data gave:

$$C = 10/\{1 + \exp[-7.2 - (1.134 + 0.29 \log_e V) \log_e N + 2.1 \log_e D]\}$$

for the ceiling as a percentage of the maximum possible. This statistically observed behaviour implies that C increases with the number of turnovers at a rate which depends on the size of the TVS, but decreases with increasing age, as measured by D. In particular, for a fixed age, the effective ceiling, C, will increase with injection rate.

This integral of β, as modified by the efficiency and limiting factors, produces a figure for kilograms of H_2S per day at the producer as illustrated in Figure 16 for the sample profile and required ancillary information as given in Appendix 4 for a particular injector/producer pair. This must then be partitioned between the fluid phases to produce concentrations in mg/kg for each phase, as illustrated for downhole conditions in Figure 17 and topsides conditions in Figure 18, for this same example. Note that some measures of H_2S can be failing (eg mass in kg/day) whilst others are rising (eg concentration in mg/kg in the gas phase), showing the need for caution when interpreting one-off wellhead measurements. The key dates and TVS size numbers predicted for this particular demonstration well pair are also given in Appendix 4. The calculations assume low pH($\leq$5), so all consumed sulphate appears as H_2S. Corrections for high pH can be made where necessary.

For history matching with historical well profiles which include measurement of H_2S in the gas phase, the bacterial growth efficiency, nutritional ceiling, pie-slice (or equivalently, breakthrough date) and injection bottomhole pressure decay through the reservoir can be manipulated to provide as much agreement as possible between model and data. If these values differ from the above suggested equation values, then they will be the preferred values for predicting souring performance for other well pairs in the same reservoir. These ideas have been embodied in a spreadsheet package called Dynamic TVS as referred to in Section 9.3 and covered in detail in Appendix 4.

TOTAL MASS of H2S
Changing daily yield

Legend: — Total H2S ·-+-· From TVS ---- From geol.
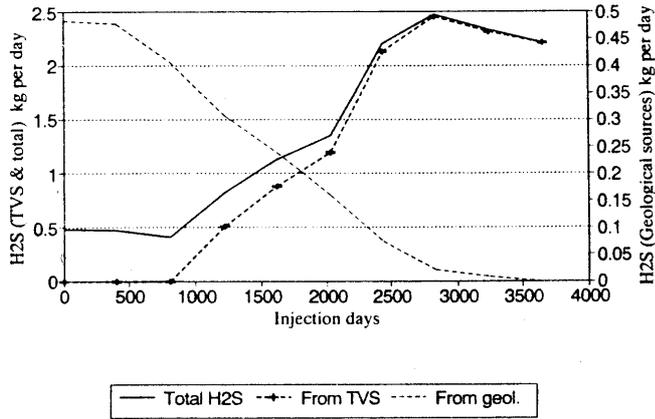
Figure 16

2-PHASE PARTITIONING
Changing H2S downhole

Legend: ---- Oil --*-- Water -■- Mean
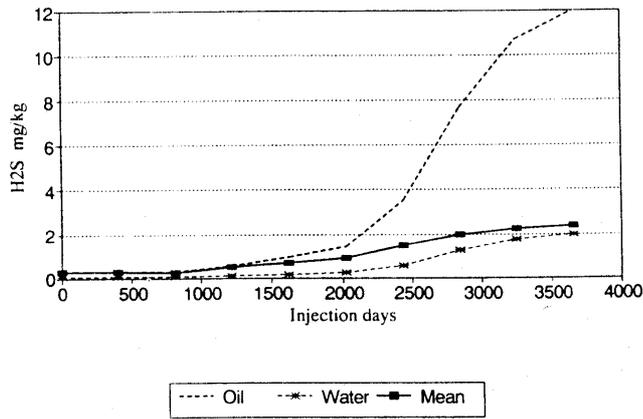
Figure 17

3-PHASE PARTITIONING
Changing H2S in production fluids

Legend: -☐- Gas ---- Oil --*-- Water -■- Mean

Figure 18

50
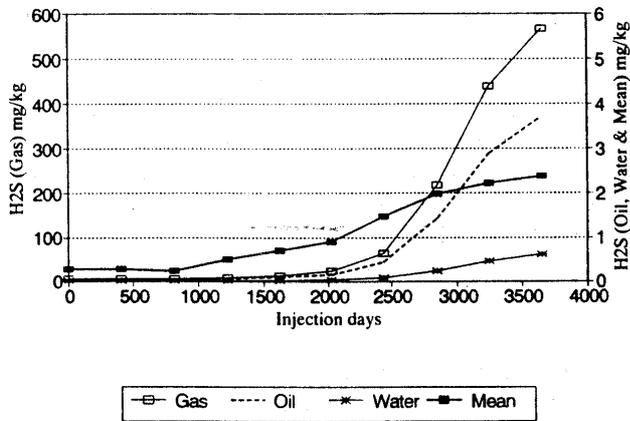
9. CONTROL OF OILFIELD RESERVOIR SOURING

The control of souring has occupied the research of the Sweetwater Programme since October 1991. The topics addressed fall into three categories. Results are outside the scope of this chapter, but the subject areas further investigated following the recommendations of the Reservoir Souring Programme were:

- Microbiological monitoring of injection water quality

- Treatment of injection and production waters

- Prediction of reservoir souring in the field.

9.1 MICROBIOLOGICAL MONITORING

Microbiological monitoring is undertaken to evaluate the performance of biocidal control. To evaluate the microbiological status of any process system requires a working site knowledge of three parameters, viz the type of organism considered relevant, the appropriate enumeration technique and the appropriate monitoring site, ie

- Heterotrophic aerobes and/or SRB

- M-SRB and/or t-SRB (from production water and backflowed injection water)

- Planktonic and/or sessile populations

giving a choice of six different microbiological assessments.

Regular topsides monitoring most usually involves assessment of planktonic populations of heterotrophs and m-SRB in injection water. However, in the absence of sessile monitoring, this protocol cannot achieve any more than an incomplete view of the microbiological status of a system.

If good topsides facilities housekeeping is adopted with a regular, and suitable, biocide dosing regime, then planktonic bacterial numbers would be expected to be low. However, planktonic m-SRB counts are often so low in North Sea water that consolidation techniques are required for their enumeration. The different qualities of culture medium commercially available for routine culturing can give several orders of magnitude variation when applied to consolidated cultures. Such imprecision can lead the investigator to believe their housekeeping practice is quite adequate for m-SRB control, when in fact bacteria are entering the reservoir in greater numbers than are found in raw seawater. The peculiar situation arises from the 'seeding' effects from sessile populations. A biofouled system is not only tolerant of biocide treatments which would otherwise control a planktonic population, but will readily slough and shed microorganisms from pipewalls into the bulk injection water system boosting the planktonic numbers that can enter the reservoir.

Two areas to consider when monitoring biocide performance in the topside injection streams are thus:

- Accuracy of the planktonic monitoring system Accuracy of the sessile monitoring system.

- Accuracy of the sessile monitoring system.

The determination of these areas is part of continuing research and is pivotal in assessing water quality between and within systems in terms of true microbiological cleanliness. Automatic sessile monitoring linked to biocide dosing is a current research objective.

9.2   TREATMENT OF INJECTION WATER

Even within a hospital operating theatre, a microbe free environment is neither achieved nor expected. Specific precautions are necessarily undertaken and microbes are controlled to acceptable levels. Similarly offshore, a continuous and complete microbiological kill in injection water could not be expected. To date, the authors have found no statistical evidence to date to support biocide treatment ensures continued sweet production. Nevertheless, it is suggested that good housekeeping is the best first step to make better the chances of failure of SRB to achieve the necessary minimum infective dose for colonisation of the reservoir. As an alternative to killing SRB, control by deprivation has been suggested.

During the Reservoir Souring Programme, the metabolism of the t-SRB were found to be (apparently) compromised and unable to reduce sulphate to sulphide when the environmental sulphate concentration was reduced to around 20mg/l. This is quite unlike the m-SRB, which are able to scavenge sulphate at the single-figure mg/l level. Since t-SRB are considered the main causative agents for souring and reverse osmosis (R0) technology for sulphate removal for scale control either can achieve, or is not far from achieving a sub-20mg/l sulphate concentration at high sustainable flow-rates, then the use of RO as a means of souring control - or even desouring - may be feasible. If the low sulphate quantities injected cannot be converted to sulphide, no souring would be expected. Reliance on fault-free biocide dosing is then replaced by reliance on deprivation. Downtime with biocide dosing may enable SRB to enter deep into a reservoir where colonisation and growth would take place away from the effects of renewed biocide treatment. Downtime with desulphation would result in a shorter period of sulphide generation in the TVS until the sulphate ion concentration became limiting.

Substrate deprivation of SRB has lead to two areas of interest:

- The development of a substrate inventory, a so called 'wet desert inventory', of injection water chemicals

- Introduction of competitive flora into the reservoir to scavenge nutrients.

Both areas are under investigation, but initial work has focused upon the stimulatory role that nitrogen, in ammonium bisulphite oxygen scavenger, or phosphorus, in certain types of scale inhibitor may have on SRB activity in a downhole environment which is otherwise limited in these essential elements.

As a final note to this section, the biocidal treatment of production water may be beneficial as a general anti-souring strategy. From surveys for t-SRB conducted in the North Sea it is clear that water from a biologically sour reservoir contains high numbers of these organisms (10^5/ml and above). Considering the high volumes of produced water discharged into the marine environment, such a t-SRB inoculum. could serve to maintain infection via the platform's injection system or initiate an infection on adjacent facilities. The high cost of such treatment would need to be considered against the good neighbour policy and overall desire to control the spread of microorganisms by this route, as indeed would the impact of biocide-treated water into the marine environment.

9.3   PREDICTION OF SOURING IN THE FIELD

The Reservoir Souring Steering Group considered that the ultimate aim of souring research was to be able to estimate future H_2S trends. Chapter 8 covered the mathematical evolution of a souring predictor which has since been developed to the research tool stage. It became clear that the complexity of such a problem would require computer modelling of the interactions downhill. As a predictive tool, such a facility should serve to estimate:

- The expected date of the commencement of souring

- The rate of increase in H_2S generation

- The maximum daily yield of H_2S in kg/day

- The maximum fluid phase concentrations of H_2S in mg/kg (ppmw) and gas phase also in terms of ppmv.

- Whether biocide or other mitigating factors are actually effective against souring.

This tool, Dynamic TVS, was subsequently created to run on reservoir simulator production outputs and so is responsive to changing parameters over the development life of the reservoir.

Dynamic TVS is an emulator of reservoir behaviour and does not attempt to model flood flow and bacterial activity in discrete blocks. The emulator considers the area of interest as a pie-slice from a radial flood model. This pie-slice thus defines the downhole bioreactor in terms of size, and injection rates determine the rate of nutrient and sulphate transport through the relevant Thermal Viability Shell (TVS). The growth of the different TVS's can be calculated as can the activity of the bacteria at the temperatures and pressures and changing nutrient status while the TVS volume is 'turned over' by continual flooding. The predictive output is given as H_2S yield in kg/day and also partitioned concentrations in the different fluid phases throughout the lifetime of the development. It can be noted that the emulator predicts downhole cooling of some (albeit a few) producers and this is also supported by field observation.

Appendix 4, Annexure 1 gives an example of a print-out from the emulator for the fictitious 'Ulay' reservoir and Annexure 2 provides the key. From the responses to the associated questionnaire the first pages of the print-out are the input data concerning reservoir and production parameters and a presentation of the production profile containing data derived from that generated by the operator's simulator. The remaining pages of the print-out are the predictions. In essence, the times to TVS establishment and souring, size of TVS, biogenic and geological H_2S are presented in tabular form. The changing yield of H_2S in kg/day and the concentration of H_2S in mg/kg in the different phases versus time are presented in graphical form.

In the 'Ulay' prediction, biogenic souring appears an inevitable consequence of the seawater injection and subsequent breakthrough. From the bacterial constraints, the nutrition factor (reflecting the 'nutritional ceiling') sets the availability of nutrients to allow for growth and the partial consumption of injected sulphate to 1% of the available sulphate. The growth efficiency factor at 1% of that estimated for active laboratory based cultures at atmospheric pressure (set to 100% as a reference) is modest. Neither pressure, redox nor the pH within the TVS have entirely compromised SRB activity and so H_2S can be biologically generated.

From the upper graph in Annexure 1, p77, it can be seen that the geological souring contribution to the total H_2S yield in kg/day decreases over the 10 year lifetime of the well whilst the biogenic contribution for the most part rises. Biogenic souring commences within 3 years after injection start-up and peaks at 2.85 kg/day following TVS maturity

within 8 years. The microbiological yield of H_2S then drops off. This decrease in yield is explained in terms of decreasing production rates against, to a much lesser degree of influence, a continual lowering of the nutritional ceiling. As the TVS becomes washed through with injection seawater, the seawater/formation water mix in the TVS becomes progressively poorer in formation borne nutrients, supporting less SRB activity and hence less H_2S production. The two and three phase partitioning curves for the same period show an increasing concentration of H_2S in each phase, peaking by the end of the life of the well, in the case of the gas phase at 566mg/kg (382ppmv).

Since results from the Reservoir Souring Programme have shown that certain criteria need to be in place for SRB to become active, control of these criteria could delay or prevent the 'Ulay' biogenic souring. The prediction provides the numerical basis for an antimicrobial souring strategy by enabling the 'Ulay' operator to consider a number of 'what if?' Scenarios. An example would be the use of low sulphate aquifer support rather than seawater support. Alternatively, control may be achieved by injection of water at a temperature above that of the TVS and so limiting the available thermal range in which bacteria can grow. A vigorous approach to biocide treatment may help delay the onset of souring. However, a complete kill, which is unrealistic, would be required to stop 'Ulay' from souring since from the modelling it appears that the nutritional ceiling and not the bacterial efficiency is the prime controlling factor in biogenic souring. This is borne out from North Sea field observation (40).

The most readily implemented strategy for 'Ulay' is perhaps a control option based around the type and concentration of chemicals added to the injection seawater. Deprivation from essential nutrients is perhaps an inexpensive means to attempt suppression of SRB activity, (see Section 6.6) but it is unlikely that souring would be stopped. The authors consider that control of souring by changing the raw injection water specification should only be considered in conjunction with other production requirements. For example, the use of reverse osmosis technology may certainly be of benefit against sour production but its installation may not he justifiable on that criterion alone. As with any production decision, the cost/benefit must be considered and that may even include living with the problem.

The above subject areas are currently under investigation for specific operator applications. For example, validation of the output of the model by monitoring the changing ratio of H_2S from a geological to a microbiological source. This may be confirmed by isotope fractionation of the sulphur in the H_2S (negative shift) in addition to the circumstantial but substantial evidence of t-SRB in production fluids. Nutrient and efficiency effects on pressurised clean sand packs and microbiologically active sand packs in the Sweetwater Programme's 'Genesis' bioreactor are also ongoing. This data is sought for the empirical determination of Dynamic TVS's bacterial constraint factors as well as the evaluation of the effects of different water injection chemicals on the growth or otherwise of SRB.

It is anticipated that generic results and conclusions from field based predictions and investigations conducted within the Sweetwater Programme will be published by the Sweetwater Steering Group in due course.

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APPENDIX 1

Results of Thistle 'A' Sampling Programme

1st and 2nd Survey

Table 1
Physical and Chemical Production Well Data Obtained from Thistle 'A' 1st Survey

Physical and Chemical Parameters	Well Number									
	A02(31)	A04(32)	A05(24)	A09(37)	A11(29)	A21(10)	A36(15)	A41(11)	A43(12)	A45(52)
Date of Sampling	18/6	18/6	17/6	18/6	17/6	18/6	18/6	18/6	18/6	18/6
Wellhead Temp (ºC)	86	67	74	86	87	81	68	92	88	93
FTHP (psig)	210	170	402	167	607	423	95	337	200	227
Gross Rate (bbls/day)	6,898	3,946	7,762	9,010	15,756	4,746	1,195	12,133	9,438	11,940
BS&W (%)	73	58	88	67	96	96	66	93	54	81
Cl^- (mg/l)	13,250	18,650	20,050	19,800	13,000	18,650	17,250	19,800	19,200	19,200
SO_4^{2-} (mg/l)	0	2,250	2,850	2,700	0	2,350	1,800	2,650	2,400	2,500
H_2S (ppm v/v gas)	15	10	3,000	50	8	70	170	1,100	10	100
S^{2-} in solution (ppmw/v)	0.11	0.10	34.72	0.18	0.14	0.21	0.15	10.86	0.16	0.32
pH	7.32	7.18	6.89	7.36	7.11	6.93	7.21	7.28	7.34	7.28
Eh (mV)	-162	-267	-365	-255	-288	-251	-267	-387	-254	-283
Acetate (mg/l)	1,415	372	15	103	1,111	370	695	115	329	115
Propionate (mg/l)	212	55	0	19	141	55	94	15	52	21
Butyrate (mg/l)	57	12	3	1	35	7	0	2	6	0

Table 2
Thermophilic SRB Isolations from Production Well Water Samples Obtained from Thistle 'A' 1st Survey

Media and Incubation Temperature	Well Number									
	A02(31)	A04(32)	A05(24)	A09(37)	A11(29)	A21(10)	A36(15)	A41(11)	A43(12)	A45(52)
Medium 2, 60ºC	-	-	0	-	-	-	-	+	-	-
4, 60ºC	-	-	0	-	-	-	-	0	-	-
7, 60ºC	-	-	+	-	-	-	-	0	-	-
8, 60ºC	-	-	0	-	-	-	-	0	-	-
9a, 60ºC	+	+	+	+	0	+	+	+	+	0
9b, 60ºC	-	-	0	-	-	-	-	0	-	-
10, 60ºC	-	-	+	-	-	-	-	Burst	-	-
9a, 90ºC	0	0	0	0	0	0	0	0	0	0

Thermophiles expressed as positive (+) or negative (0) per 250 ml of liquid sample.

- Not determined

Table 3
Physical and Chemical Production Well Data Obtained from Thistle 'A' 2nd Survey

Physical and Chemical Parameters	A02(31)	A04(32)	A05(24)	A09(37)	A11(29)	A21(10)	A36(15)	A41(11)	A43(12)	A45(52)
Date of Sampling	27/8	27/8	26/8	27/8	26/8	26/8	26/8	26/8	26/8	27/8
Wellhead Temp (ºC)	86	87	74	86	87	81	68	92	88	93
FTHP (psig)	224	137	375	160	672	344	104	332	178	237
Gross Rate (bbls/day)	8,355	4,345	6,092	8,683	13,411	3,376	1,194	9,691	8,238	11,429
BS&W (%)	75	64	90	69	96	95	64	92	53	80
Cl^- (mg/l)	13,450	18,550	19,800	19,650	13,100	18,500	18,100	19,900	19,200	19,500
SO_4^{2-} (mg/l)	0	2,250	2,850	2,700	0	2,300	2,100	2,600	2,500	2,500
H_2S (ppm v/v gas)	15	30	3,200	80	10	75	60	1,000	3	100
S^{2-} in solution (ppmw/v)	0.17	0.21	15.27	0.64	0.03	0.32	0.20	0.28	0.11	0.44
pH	7.08	7.07	7.08	7.83	6.88	6.85	6.92	6.67	7.03	6.98
Eh (mV)	-235	-25	-400	-253	-236	-249	-242	-366	-238	-253
Acetate (mg/l)	735	256	47	60	638	198	246	38	177	90
Propionate (mg/l)	110	30	1	7	87	27	34	4	29	14
Butyrate (mg/l)	25	7	0	2	19	6	12	0	7	5

Table 4
Thermophilic SRB Isolations from Production Well Water Samples Obtained from Thistle 'A' 2nd Survey

		A02(31)	A04(32)	A05(24)	A09(37)	A11(29)	A21(10)	A36(15)	A41(11)	A43(12)	A45(52)
Medium 7,	60ºC										
	250 ml		+	+			+	+		+	+
	100 ml		+				+	+			
	10 ml		+	+				+			
	1 ml			+							
Dilutions -	/ml		10^1	10^1							
Medium 9a,	60ºC										
	250 ml	+	+	+	+			+			+
	100 ml	+	+	+			+	+			
	10 ml		+				+	+			
	1 ml										
Dilutions -	/ml		10^1								
Medium 10,	60ºC										
	250 ml	+	+	+			+	+			
	100 ml	+	+	+				+			
	10 ml						+	+			
	1 ml										
Dilutions -	/ml										
Medium C1,	60ºC										
	250 ml	+	+				+	+			+
	100 ml		+	+				+			
	10 ml										
	1 ml										
Dilutions -	/ml										

Table 4 continued
Thermophilic SRB Isolations from Production Well Water Samples Obtained from Thistle 'A' 2nd Survey

		Well Number									
		A02(31)	A04(32)	A05(24)	A09(37)	A11(29)	A21(10)	A36(15)	A41(11)	A43(12)	A45(52)
Medium C2,	60ºC										
	250 ml		+	+				+		+	
	100 ml		+	+				+			
	10 ml		+					+			
	1 ml		+					+			
Dilutions -	/ml		10^1								
Medium C3,	60ºC										
	250 ml	+	+	+	+			+			+
	100 ml		+	+	+		+	+		+	
	10 ml							+			
	1 ml							+			
Dilutions -	/ml							10^1			
Medium 7,	60ºC										
9a,	90ºC										
10	90ºC										
C1	90ºC										
C2	90ºC										
C3	90ºC										

Thermophiles expressed as positive (+) or negative (0) per 250, 100, 10 or 1 ml of sample for liquids or dilutions per ml.

- Not Determined.

Table 5
Comparison of t-SRB Isolations from Production Wells Between 1st and 2nd Surveys
(60ºC Incubation)

	Well Number									
	A02(31)	A04(32)	A05(24)	A09(37)	A11(29)	A21(10)	A36(15)	A41(11)	A43(12)	A45(52)
First Visit	+	+	+	+	0	+	+	+	+	0
Second Visit	+	++	++	+	0	+	++	0	+	+

* Indicates t-SRB at 4-10 per litre

** Indicates t-SRB greater than 1 per 10 ml

0 Indicates no growth

APPENDIX 2

Derivation of heat flow equations
and Asymptotic Forms

We assume that water at a constant injection temperature T_o is injected at a constant rate q into a homogenous reservoir layer of thickness h and effective (swept volume) porosity ϕ, surrounded by impervious cap and base formation rock layers, which are also considered to be infinite heat sources at constant temperature T_F. We suppose that all relevant variables are only functions of the reservoir layer distance, r, from this injector and time, t; there is good mixing along the vertical.

Let the injected water temperature be $T_l(r,t) = T_W(r,t) + T_F$, and let the corresponding reservoir layer rock temperature be $T_L(r,t) = T_R(r,t) + T_F$ gained from the base and cap rock. Note that T_W and T_R will be negative numbers.

The following heat transports across an elemental strip at distance r will be considered:

      (i)   heat transported across the element by water
      (ii)   heat conducted across the element by water
      (iii)   heat conducted across the element by rock
      (iv)   heat conduction to injected water from impervious layers
      (v)   heat conduction to reservoir rock from impervious layers
      (vi)   heat transfer from reservoir rock to injected water
      (vii)   heat generated by viscous heating

For (i), the rate of heat carried out by water across the surface at r is

$$T_W V_{act} \rho_w s_w \phi 2\pi r h \tag{A2.1}$$

where V_{act} is the actual velocity of the water through the rock pores at this distance, ρ_w is the density of the injected water and s_w is its specific heat.

The mean velocity of the water across the layer at this distance is $s_w V = V_{act} \phi + 0.(1-\phi) = V_{act}\phi$, so we can write (A2.1) as

$$T_W V \rho_w s_w 2\pi r h \tag{A2.2}$$

Also, since

$$q = 2\pi r h V \tag{A2.3}$$

we can write (A2.2) as

$$T_W q \rho_w s_w \tag{A2.4}$$

For (ii), the rate of heat conducted across r is

$$-K_w \frac{\partial T_W}{\partial r} 2\pi r h \phi \tag{A2.5}$$

and then for (iii), the rate of heat conducted by the reservoir layer of rock across r is

$$-K_R \frac{\partial T_R}{\partial r} 2\pi r h (1 - \phi) \tag{A2.6}$$

where K_W and K_R are respectively the thermal conductivities of injected water and reservoir rock.

For (iv), the heat transported from the impervious layers into the water

$$-2k_wT_w2\pi rdr\phi \tag{A2.7}$$

and then for (v), the heat transported from the impervious layers into the reservoir rock is

$$-2k_rT_r2\pi rdr(1-\phi) \tag{A2.8}$$

where k_W and k_R are Newton's law of cooling constants.

For (vi), the heat conducted from the reservoir rock into the injected water is

$$k(T_r-T_w)A2\pi rdrh \tag{A2.9}$$

where A is a permeability constant, assessed as the area of contact per unit volume between the injected water and the reservoir rock. It is a measure of pore size.

And finally, for (vii), the heat generated by viscous heating is

$$\frac{4_q2_u}{(2\pi h)^2} \cdot \frac{1}{r^4} 2\pi rdrh \tag{A2.8}$$

where μ is the apparent viscosity of the water. This is related to the real viscosity by a constant factor which depends on the topology of the pore structure.

Heat conservation for the reservoir rock and the injected water then produces two partial differential equations. For the water:

$$\phi\frac{\partial T_w}{\partial t}\rho_w s_w(2\pi rdr)h = dr\frac{\partial}{\partial r}(T_wV\rho_w s_w2\pi rh)$$

$$+dr\frac{\partial}{\partial r}\left(Kw\frac{\partial T_w}{\partial r}2\pi rh\phi\right) - dr(4\pi rk_wT_w\phi) \tag{A2.11}$$

$$+[k(T_R-T_w)A2\pi rh]dr + \left(\frac{4q^2\mu}{(2\pi h)^2}\cdot\frac{1}{r^4}\cdot 2\pi rh\right)dr$$

Hence

$$\phi\frac{\partial T_w}{\partial t} = -\frac{1}{r}\cdot\frac{\partial}{\partial r}[rT_wV] + \frac{K_w\phi}{\rho_w s_w}\cdot\frac{1}{r}\cdot\frac{\partial}{\partial r}[r\frac{\partial T_w}{\partial r}] - \frac{2k_w}{h\rho_w s_w}\phi T_w$$

$$+ \frac{kA}{\rho_w s_w}(T_R-T_w) + \frac{4q^2\mu}{(2\pi h)^2\rho_w s_w}\cdot\frac{1}{r^4} \tag{A2.12}$$

For the rock, we have

$$(1-\phi)\frac{\partial T_R}{\partial t} = \frac{KR(1-\phi)}{\rho_R s_R}\cdot\frac{1}{r}\cdot\frac{\partial}{\partial r}[r\frac{\partial T_R}{\partial r}] - \frac{2k_R}{\rho_R s_R h}(1-\phi)T_R$$

$$+ \frac{kA}{\rho_R S_R}(T_w-T_R) \tag{A2.13}$$

At thermal equilibrium, $\frac{\partial}{\partial t} = 0$, but observe that $T_R \neq T_W$ and the reservoir rock takes up a temperature between that of the flowing water and the impervious layers. The solution near $r = 0$ is unbounded and hence invalid, but for large r asymptotic arguments show that the particular integral must dominate the complementary function in each case, and we can expect the behaviour to be like $1/r^4$ for large r. In particular, for the injection water, the full solution must look like

$$ar^{-4} + be^{-cr}r^{-d}$$

where a, b, c and d are constants to be determined from the initial conditions and the associated physical constants.

APPENDIX 3

Sulphate Consumption Rate Parameter as a Function of Travel Time Through the TVS

The sulphate consumption rate parameter, β as a fraction of travel time through the TVS is given by:

$$\beta = 0.6134F - (10.67 + 0.07048F)G + (1.476 - 0.001015F)G^2 - 0.0249G^3$$

Where $F = P_{inj} - \frac{dt}{A}$

and $G = \{a + b[T_{inj} + c(16.684\frac{gt^{\frac{1}{2}}}{A^{\frac{1}{2}}} + 0.40804\frac{g^2t}{A})]\}$

with $a = 20 - 30\ T_L/(T_L - T_U)$

         $b = 30/TU$

         $c = 10 - 5[T_{res} - T_{inj}]$

         $g = \frac{40}{h}\sqrt{\frac{715}{\rho_e c_c}}$

         $A = \frac{\rho\%\phi\pi h}{100q}$

         q = oil production rate

         p% = effective % size of the pie slice into reservoir

APPENDIX 4

Example of Dynamic TVS©

Reservoir Souring Predictor Output

EXECUTIVE SUMMARY

Data for the injector/producer pair I11/P21 on the ESSENTIAL/ULAY reservoir was input to the Dynamic TVS souring emulator. A prècis of the results is as follows:

- Assume injection start-up by early 1991 (client data)

- Commencement of biogenic souring by late 1993

- Maximum H_2S yield in all production fluids estimated at around 2.47kg/day by late 1998

- Maximum gas phase H_2S estimated at around 566mg/kg(382ppmv) by early 2001

We suggest the following sensitivities be run:

- Bacterial constraints (nutrition factor)

- Bacterial constants (efficiency factor)

- Injection rate

- Breakthrough date

All the predictor outputs are given in Annexure 1, and explanations of these terms in Annexure 2.

Annexure 1

LAYCOCK & EDEN
DYNAMIC TVS PREDICTION MODEL

SOURING Profiles from BACTERIAL & GEOLOGICAL Sources
THERMAL VIABILITY SHELL : RADIAL MODEL

FIELD	ESSENTIAL			Today's date
RESERVOIR	ULAY			10-May-93
AGE	UPPER JURASSIC			
LITHOLOGY	SANDSTONE			

FIXED POINTS : CLIENT DATA

Injection Well	Date inj started	Porosity ratio	Av stratum height ft	Rock heat cap kcal/(deg C kg)
I11	Mar-91	0.22	73	644

Sulphate mg/l	Av inject bwpd	Inj Temp deg C	Form Temp deg C	Inject press psig
2650	10269	19	84	5500

Production Well	Date prod started	Br'kthru date	Dist from inj feet	Product press psig 4780
P21	Nov-90	Oct-93	3700	

Geological Pyrite%	Parameters Siderite%	<OR >	Form water orig ppmw	Oil density kg/l	Produced gas molecular wt
1.2	1.6		0	0.8	23

CALCULATED AND STANDARD CONSTANTS

Gas density gm/cm^3	Gas pressure mm Hg (abs)	BUBBLE POINT Pressure mm Hg	
1.027E-03	760	38000	
Injector Pressure ATM	Producer Pressure ATM	Std Temp deg C	Std Press. ATM (abs)
374	325	0	1
KO	Partition coefficients	KO at STP	KW at STP
0.0781		0.0541	0.4446
	KW		
	0.4818		

LAYCOCK & EDEN
DYNAMIC TVS PREDICTION MODEL

SOURING Profiles from BACTERIAL & GEOLOGICAL Sources
THERMAL VIABILITY SHELL : RADIAL MODEL

FIELD	ESSENTIAL		Today's date
RESERVOIR	ULAY		10-May-93

INJECTION & PRODUCTION PROFILE

Injection Well:
I11

Production Well:
P21

Date	Day	Inject bwpd	Oil Bopd	Water bwpd	Breakthrough prop	STP GOR m^3/m^3	Historial H$_2$S/Gas ppmv
01-Mar-91	1	10471	12969	0	0.00	58.10	NA
09-Apr-92	407	12118	12730	0	0.00	58.30	NA
20-May-93	813	12588	11271	929	0.00	55.90	NA
30-Jun-94	1219	11530	10210	1774	0.20	58.30	NA
10-Aug-95	1625	10177	8155	3092	0.25	60.70	NA
19-Sep-96	2030	9588	6126	4200	0.30	57.10	NA
30-Oct-97	2436	9294	3342	6560	0.40	55.80	NA
10-Dec-98	2842	9083	1034	6900	0.50	55.10	NA
20-Jan-2000	3248	8977	430	6100	0.60	55.50	NA
01-Mar-2001	3654	8871	302	5500	0.70	54.90	NA

PRODUCTION PROFILE
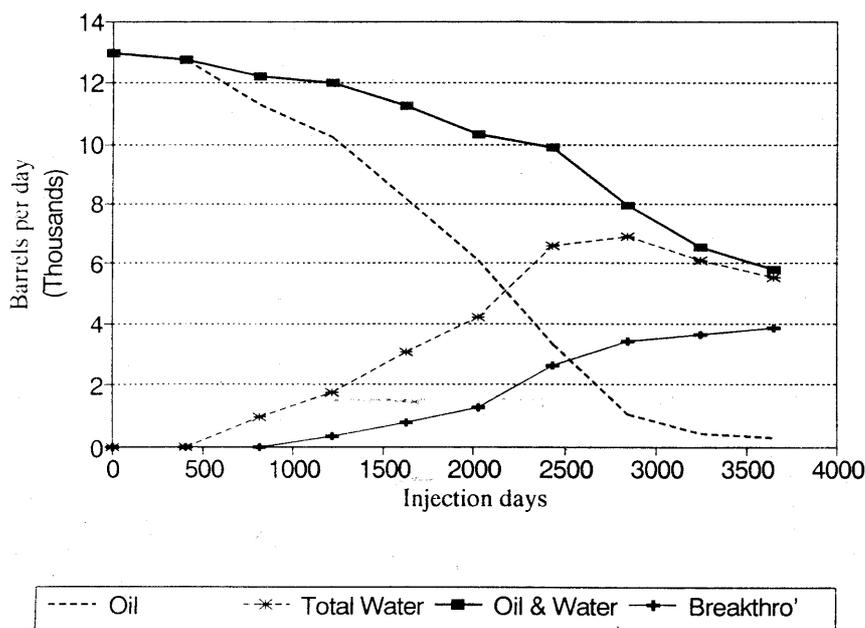
LAYCOCK & EDEN
DYNAMIC TVS PREDICTION MODEL

SOURING Profiles from BACTERIAL & GEOLOGICAL Sources
THERMAL VIABILITY SHELL : RADIAL MODEL

FIELD   ESSENTIAL   Today's date
RESERVOIR   ULAY   10-May-93

PREDICTED SEQUENCE OF EVENTS

	Model	Start
Date for prediction Mar-2001	br'kthru	souring
	Oct-93	Dec-93
Observed	B'thru yrs	Sour yrs
pie-slice%	from inj	from inj
8.13	2.67	2.76

TVS INFORMATION

Start of	Finish of	Finish of
this Shell	this Shell	all Shells
Apr-91	Jul-91	Aug-91
yrs (tL)	yrs (tU)	yrs (tF)
from inj	from inj	from inj
0.13	0.41	0.43
Start of	Finish of	Finish of
Shell (ft)	Shell (ft)	all Shells
453	796	823
(from injector)		
Effective	Refill time	Number of
final TVS size	for TVS	turnovers
(mm cu ft)	(days)	to pred. date
1.76	30	115.06

HISTORY MATCHING DYNAMIC TVS TO EXISTING H$_2$S PROFILE

	Bacterial Constraints:		B'thru par:	Geological		PARTITIONING	
	Nutrition	Efficiency	% size	sources	Pressure	Temp	Pressure
	factor	factor	pie-slice	H$_2$S scale	fall-off factor	deg C	ATM(abs)
	1.00	1	8.13	1	1	15	1
	PREDICTIONS @ 100% support from nominated injector						Historical
	H$_2$S/Gas	H$_2$S Total	TVS	GEO+FOR	TOTAL	TOTAL	H$_2$S Gas
Date	ppmv	ppmw	H$_2$S kg/day	H$_2$S kg/day	H$_2$S kg/day	H$_2$S 1/day	ppmv
01-Mar-91	2.4	0.3	0.00	0.48	0.48	318	NA
09-Apr-92	2.4	0.3	0.00	0.48	0.48	313	NA
20-May-93	2.4	0.2	0.00	0.41	0.41	267	NA
30-Jun-94	5.2	0.5	0.51	0.31	0.82	539	NA
10-Aug-95	8.6	0.7	0.89	0.24	1.12	739	NA
19-Sep-96	14.5	0.9	1.19	0.16	1.35	890	NA
30-Oct-97	43.2	1.5	2.13	0.07	2.20	1447	NA
10-Dec-98	146.8	2.0	2.45	0.02	2.47	1623	NA
20-Jan-2000	296.3	2.2	2.32	0.01	2.33	1528	NA
01-Mar-2001	382.0	2.4	2.21	0.00	2.21	1453	NA

LAYCOCK & EDEN
DYNAMIC TVS PREDICTION MODEL

SOURING Profiles from BACTERIAL & GEOLOGICAL Sources
THERMAL VIABILITY SHELL : RADIAL MODEL

FIELD   ESSENTIAL   Today's date
RESERVOIR   ULAY   10-May-93

PRODUCTION FLUIDS : PREDICTIONS
H_2S DOWNHOLE AND TOPSIDE, PARTITIONING

Well No: P21

	All sources DOWNHOLE Two-phase partition, mg/kg		All sources, at STP TOPSIDE Three-phase partition, mg/kg		
Date	XO'	XW'	XG	XO	XW
01-Mar-91	0.27	0.0442	3.61	0.0237	0.0038
09-Apr-92	0.2737	0.0444	3.61	0.0237	0.0038
20-May-93	0.2604	0.0422	3.61	0.0237	0.0038
30-Jun-94	0.5691	0.0922	7.74	0.0509	0.0082
10-Aug-95	0.9384	0.1521	12.76	0.838	0.0136
19-Sep-96	1.4309	0.2319	21.50	0.1412	0.0229
30-Oct-97	3.5129	0.5693	64.06	0.4208	0.0682
10-Dec-98	7.6969	1.2473	217.53	1.4290	0.2316
20-Jan-2000	10.6871	1.7318	439.05	2.8842	0.4674
01-Mar-2001	11.9752	1.9406	566.11	3.7189	0.6026

PRODUCTION FLUIDS : PREDICTIONS
H_2S TOPSIDE: MASSES AND SOURCES

Well No: P21

	All sources TOPSIDE Two-phase partition, mg/kg			All sources, at STP TOPSIDE: H_2S IN gas (ppmv) Three-phase partition		
	kg/day	kg/day	kg/day	TVS	Pyr/Sid	Formation
Date	Gas H_2S	Oil H_2S	Water H_2S			
01-Mar-91	0.4446	0.0392	0.0000	0.00	2.44	0.0000
09-Apr-92	0.4379	0.0384	0.0000	0.00	2.44	0.0000
20-May-93	0.3718	0.0340	0.0006	0.00	2.44	0.0000
30-Jun-94	0.7523	0.0660	0.0024	3.27	1.95	0.0000
10-Aug-95	1.0311	0.0869	0.0068	6.78	1.83	0.0000
19-Sep-96	1.2279	0.1101	0.0155	12.80	1.71	0.0000
30-Oct-97	1.9501	0.1789	0.0720	41.77	1.46	0.0000
10-Dec-98	2.0239	0.1880	0.2571	145.59	1.22	0.0000
20-Jan-2000	1.7091	0.1576	0.4588	295.32	0.98	0.0000
01-Mar-2001	1.5340	0.1430	0.5333	381.31	0.73	0.0000

TOTAL MASS of H2S
Changing daily yield
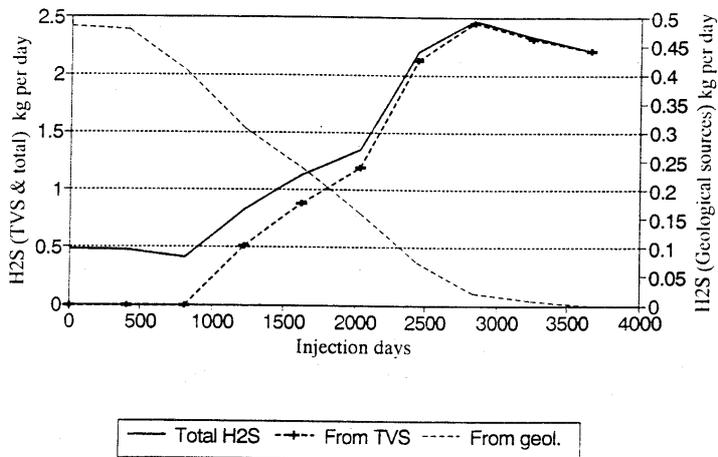
Legend: Total H2S — From TVS — From geol.

2-PHASE PARTITIONING
Changing H2S downhole

Legend: Oil — Water — Mean

3-PHASE PARTITIONING
Changing H2S in production fluids

Legend: Gas — Oil — Water — Mean
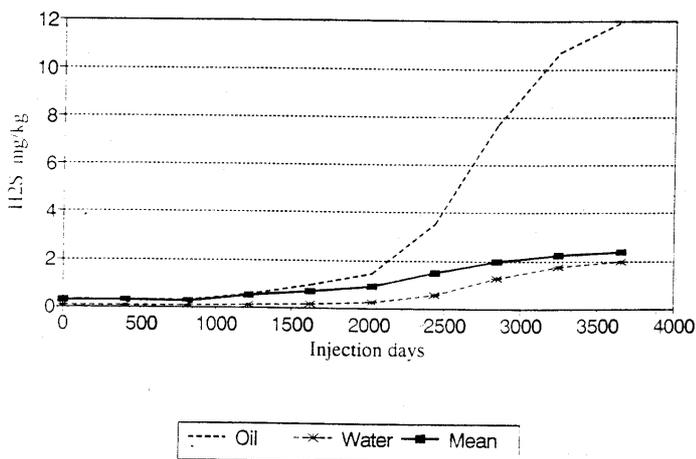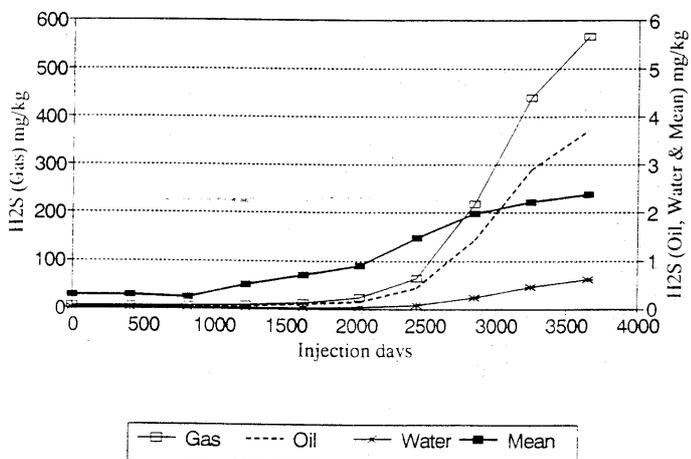
Annexure 2

Explanatory notes for the predictor output of DYNAMIC TVS©

FIXED POINTS : CLIENT INPUT DATA / Predictor Output Part 1

Date injection started: This can be a predicted date.

Porosity ratio: The number is always less than 1. A value of 0.25 is typical.

Av stratum height ft: This is the average stratum of height of the zone being flooded throughout the swept area of that zone. For multiple zones additional questionnaires must be completed.

Rock heat cap kcal/(deg C kg):   This is the average rock heat capacity from the flooded zone, *free of water*. An internal formula calculates the rock and water heat capacity. A typical number for the rock heat capacity is 644 kcal/(deg C kg) for sandstone.

Sulphate mg/l: This is the sulphate content of the flood water. Any departures from the original floor source should be noted on the questionnaire with the dates when this change took place.

Av inject bwpd: This number can either be entered or will be calculated from the production profile supplied.

Inj Temp deg C: Is the flowing bottomhole temperature.

Form Temp deg C: Is the uncooled flowing reservoir temperature.

Inject press psig: Is the bottomhole flowing pressure in pounds per square inch gauge.

Breakthrough date: Is the date when injection water first appears at the producer.

Dist from inj ft: Is the distance between the injector and the producer in feet and relates to the injector referenced on the first line.

Product press psig: Is the bottomhole shut-in pressure.

Geological parameters <OR> Form water orig ppmw pyrite% siderite%:	Either the mineralogical status of the production zone or the H_2S concentration in the formation water in ppmw can be entered. The program is designed to cope with either/both inputs. Pyrite% is the volume percent of any iron sulphide mineral, including pyrrhotite. Siderite% is the volume percent of iron carbonate. A statistical algorithm has been designed to estimate formation water H_2S in ppmw from the ratio of pyritic species to siderite.
Oil density kg/l	Is typically around 0.08 kg/l.
Produced gas molecular weight:	Is typically around 25.

CALCULATED AND STANDARD CONSTANTS / Predictor Output Part 2

Gas density gm/cm^3:	Is calculated from the molecular weight of the gas.
Injector Pressure:	Is read from the first part of the questionnaire and converted to atmospheres.
Producer Press:	Similarly, this figure is converted to atmospheres.
Std Temp deg C:	Is by convention 273K and given as 0ºC.
Partition Coefficients:	Relative to a low pH, ie partitioning from the aqueous phase at/or less than pH5.
KO:	This is the estimated partition coefficient of the oil. An operator's actual figure could also be used here.
KW:	As above but for the formation water.
KO at STP:	Partition coefficient of oil at 0ºC and 1 atm.
KW at STP:	As above but for the formation water.

INJECTION & PRODUCTION PROFILE / Predictor Output Part 3

This is client input data where data sets associated with ten equal time steps are sought, the first day of injection support being day 1. The production profile is normally required from this date unless an extended period of primary recovery is anticipated. In this case data at ten additional equal time steps relating to the primary production period are required.

GRAPH OF PRODUCTION PROFILE / Predictor Output Part 4

This page is the graphical presentation of the production profile supplied in tabular form.

PREDICTED SEQUENCE OF EVENTS / Predictor Output Part 5

This is the first page of predictions and relates to the size, shape and location of the Thermal Viability Shells downhole.

Date for prediction:	Is a date at or before the end of the production life of the reservoir.
Model Breakthrough:	Is the date calculated to coincide with the actual breakthrough date which is used for internal calculation purposes.
Start Souring:	Is the commencement of the appearance of biogenic souring.
Observed pie-slice:	Is that percentage of a radial flood that matches the injection rate and distance between the injector and producer to the 'Model Breakthrough'.
Breakthrough yrs from inj:	Is the period between injection start-up and appearance of injection water in the production fluids.
Sour yrs from inj:	Is the period between injection start-up and appearance of biogenic H_2S from the TVS in the production fluids.

TVS INFORMATION

Start of this Shell:	Follows seawater injection when the lower thermal boundary of the TVS has established (primarily thermophilic-SRB).
Finish of this Shell:	Is when the upper thermal boundary of the TVS has established (primarily thermophilic).
Finish of all Shells:	Is the date when the thermal profile in the formation is effectively unchanging, ie the cooling effect of water injection balances the heating effect of the formation.
TL yrs from inj:	Time to establish the lower thermal boundary (see Start of Shell).
TU yrs from inj:	Time to establish the upper thermal boundary (see Finish to Shell).
TF yrs from inj:	Time to reach thermal equilibrium (see Finish of all Shells).

Start of Shell (ft):	Distance between injector and lower thermal boundary. This is a useful indicator as to the distance a biocide would have to travel to be effective in damaging thermophilic SRB.
Finish of Shell (ft):	Distance between injector and upper thermal boundary.
Finish of Shells (ft):	Distance between injector and effectively stable near-formation temperature zone. Note that the injector/producer distance can be smaller than this value, ie the producer will experience bottomhole cooling.
Effective final TVS size (mm cu ft):	Is the estimate of the volume of rock and water within the thermal limits of the TVS in millions of cubic feet.
Refill time for TVS (days):	Is the estimated time to fill the TVS at the average flood rate.
Number of Turnovers to pred date:	Is the number of times the TVS will have effectively been 'washed through' by multiples of its flooded volume to the date of the prediction.

HISTORY MATCHING DYNAMIC TVS TO EXISTING H_2S PROFILE / Predictor Output Part 6

This section allows existing H_2S data to be used to modify the bacterial activity parameters from their default values for history matching the prediction. Since bacterial activity is based upon history matched data from the SeRec data base, these inputs can be bettered by using existing client data or by laboratory generated data.

Bacterial constraints:	Are two scaling factors (default value, 1, to match the SeRec database) dictating the bacterial conversion of sulphate to sulphide, viz the 'nutritional ceiling' and the 'efficiency'. The nutritional ceiling is set by the essential nutrient in short supply downhole. The percentage is thus the proportion of sulphate that can be converted to sulphide given this limitation. Note that injection water chemicals could *increase* this number and hence observable H_2S. The efficiency is the rate at which the metabolically stressed SRB can convert sulphate to sulphide. The slow passage of injection water through the formation mitigates the importance of bacterial efficiency and so the nutritional ceiling is the chief constraint on H_2S production
B'thru % size pie-slice:	This is read from part 5 of the predictor 'Observed pie-slice'.
GEOLOGICAL sources H_2S scale:	Is the history matching factor for the appearance of H_2S from a sour aquifer where the H_2S level was statistically derived from the pyrite/siderite content.

Pressure fall-off factor:	Is a scaling factor for history matching operating in the pressure domain.
PARTITIONING:	Temp. deg. C and Pressure ATM (abs) are the selected temperature and absolute pressure for the partitioning.
PREDICTIONS @ 100% support nominated from injector:	Each injector/producer pair is considered separately and is then pro-rata combined to give the final producer H_2S profile.
H_2S/Gas ppmw:	Is the part per million by volume concentration of H_2S in the gas phase.
H_2S/Total ppmw:	Is the concentration of H_2S in mg/kg totalled over all three phases.
TVS H_2S kg/day:	Is the mass of H_2S in kg/day derived from the TVS.
GEO + FORM H_2S kg/day:	Is the mass of H_2S from both biological and geological sources.
TOTAL H_2S kg/day:	Is the mass of H_2S from both biological and geological sources.
TOTAL H_2S l/day:	Is the volume of H_2S in litres produced per day at the partitioning temperature and pressure.
Historical H_2S/Gas ppmv:	Is supplied data for history matching.

PRODUCTION FLUIDS : PREDICTIONS / Predictor Output Part 7

H_2S : DOWNHOLE AND TOPSIDE, PARTITIONING

These are the concentrations of H_2S in mg/kg for the two and three phase partitioning against time, reflecting the sources of H_2S and changing ratios of production fluids from the specified production well.

PRODUCTION FLUIDS : PREDICTIONS / Predictor Output Part 8

H_2S TOPSIDE: MASSES AND SOURCES

These are the production rates of H_2S in the gas, oil and water phases in kg/day and H_2S concentration in the gas phase in terms of ppmv derived from biological and geological sources from the specified production well.

GRAPH OF TOTAL MASS OF H_2S / Predictor Output Part 9

A double axis graph presenting the tabulated data from part 8 showing the long term trends in H_2S production.

GRAPH OF 2-PHASE PARTITIONING / Predictor Output Part 10

A single axis graph presenting tabulated data from part 8 showing the long term downhole partitioning of H$_2$S. Note the mean value is between the oil and water curves, a consequence of averaging the H$_2$S concentration between fluids of different densities.

GRAPH OF 3-PHASE PARTITIONING / Predictor Output Part 11

A double axis graph presenting tabulated data from part 8 showing the long term topside partitioning of H$_2$S.

LIST OF FIGURES

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