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ESTIMATION OF H_2S GENERATION BY MINERAL DISSOLUTION

APPLICATION TO SWEET OIL RESERVOIR SOURING

S David Marsland* and Richard A Dawe*

ABSTRACT

There are increasing incidences of oil reservoirs containing inherently sweet oil (free of H_2S) producing, after a period of time, sour oil (appearance of H_2S at the separator at concentrations as high as 30 ppm). The sources are currently uncertain but if they are related to a reservoir rock volume containing iron sulphide a simple model can be developed to relate levels of H_2S in the gas phase measured at surface conditions with the total mass flow rate of H_2S in the reservoir fluids (oil, gas and water). This can in turn be related to rates of dissolution within the reservoir. In this paper the model is presented with examples using typical quantities followed by a discussion of the effects of iron sulphide concentrations in the reservoir bulk volume, porosity, H_2S concentrations in the oil and water phases, gas-oil-ratio and water-cut. The partition of H_2S between the water, oil and gas can be important within the reservoir, and even small concentrations in the water can flash significant H_2S concentrations into the gas at surface, especially at high water-cut.

1.0 INTRODUCTION

Unexpected souring (appearance of H_2S at the well-head) of originally sweet oil (free of H_2S) reservoirs causes concern [1] because of the danger to the health and safety of personnel in the work environment, the lack of H_2S handling facilities on existing sites, the increased corrosion of existing production facilities and reduction in revenues because of sour oil and gas. Despite this concern about oil reservoir souring, the cause of H_2S generation within an originally sweet reservoir is uncertain. Within the petroleum literature a wide range of possible mechanisms have been proposed [1]. These include;

(i) thermochemical reduction of sulphate from sea water [13,14],

(ii) reduction of sulphite oxygen scavengers [1],

(iii) decomposition of sulphur-containing organic compounds [15,16],

(iv) the action of sulphate reducing bacteria [2-12] and

(v) possible reduction of pyrite minerals contained within the reservoir formation [17-21].

For oil reservoirs which have turned sour during water flooding, possibility (i) has been discounted from thermodynamic considerations and because the reservoir temperatures are not high enough, i.e. >300°C. The levels of chemical additives introduced into injection water as bacteriocides, corrosion or scale inhibitors are too low for route (ii) to account for the observed levels of souring, whilst route (iii) has been considered unlikely because the reservoir temperatures are not high enough unless the decomposition is catalysed by strains of bacteria introduced into the reservoir with the injection fluids. The introduction of sulphate reducing bacteria into the reservoir around the well-bore has been considered a possible explanation for souring, route (iv). However, the change in physical and environmental conditions to which the bacteria must adapt are dramatic; nevertheless this mechanism for reservoir souring has been much discussed in some detail within the petroleum literature and is accepted by many as the only route [2-12]. Despite the large quantities of iron sulphide minerals within the reservoir very little work has been undertaken to establish the conditions required for route (v) to become active; acid conditions and a reducing potential will be needed and these may be possible within reservoirs [18-21].

Currently, the only parameter which has been correlated in some cases with the increasing level of souring has been an increasing water-cut [1]. This occurs in reservoirs where secondary recovery schemes using water injection have been implemented. This injection water often contains different ions to those of the formation water which could be altering the physical conditions within the reservoir, e.g. lowering the reservoir temperature, causing chemical scale or changing the pH of the water. The observation that souring has also been observed in dry wells suggests that H_2S generation takes place within the reservoir rather than at or around the producing well-bore, and that the mass transfer of H_2S within the gas, oil and water is fast in comparison to the movement of the flood front within the reservoir.

In this work we have taken an inorganic generation route i.e. mechanism (v), whereby H_2S is generated

* *Mineral Resources Engineering Department, Imperial College, London*

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from iron sulphides within the reservoir. A simple model has been developed to relate observed levels of H_2S in the gas at surface conditions, to the total mass flow rate of H_2S in the reservoir produced fluids. These levels of souring can be related to a reservoir rock volume containing iron sulphide, which in turn can be related to the rates of dissolution determined from experimental investigations. This can give an estimate of the pH and redox potential required in the reservoir if iron sulphides are to be considered as a source for generating H_2S [18].

2.0 BACKGROUND

Levels of H_2S are usually reported as a concentration of H_2S in the gas at surface conditions. However, to assess the concentration of H_2S being produced in the reservoir, it is necessary to calculate the equilibrium concentration of H_2S in the gas, oil and water. Figure 1 illustrates schematically the volumetric relationship between gas, oil and water at reservoir and surface conditions. The volume of reservoir gas at reservoir conditions expands as it is produced and travels to surface, the exact volume change depending on the pressures and temperatures involved. As the pressure drops, gas also comes out of solution from the gas dissolved in the oil and water. Due to the changes in pressure and temperature and the release of solution gas the oil and water also change volume. The values of these changes are specific to the particular oil and the conditions and can be measured in the laboratory or estimated using empirical relationships [22,23]. Clearly, because of the dissolved gas within the oil, the composition of the hydrocarbon phases change as the fluids are brought from reservoir to surface conditions, and hence the H_2S distribution within these phases changes.

If the distribution of H_2S amongst the three phases at surface conditions is known, then the H_2S concentration entering the well-bore from the reservoir can be estimated (as will be shown in the next section) because there is no offtake between the reservoir and the well-head, assuming that the concentration of any background H_2S is already known. Usually H_2S is detected in the gas but it can be carried in significant amounts in both the oil and water flowing in the reservoir. However, difficulties in estimation and measurement can occur due to the partitioning of H_2S between the oil and water and the gas and the flashing into the gas of much of the dissolved H_2S. Thus the transport of H_2S to the surface from the reservoir is somewhat more complicated than may be first envisaged.

3.0 ESTIMATION OF H_2S CONCENTRATIONS IN GAS, OIL & WATER

It is at the surface, either the well-head or the separator, where samples of fluids from the reservoir are normally taken rather than bottom hole. In this work the term well-head is used to mean surface conditions at either the well-head or separator. At these conditions we assume for convenience that ideal conditions are approximately obeyed, thus the partial pressure of H_2S, p_{H_2S} can be calculated from the measured concentration, i.e. volume (mole) fraction of H_2S in the gas. The fluid analyses can be "converted" to reservoir conditions using appropriate formulae developed below. If the well-head pressure is P_{wh}, then:

$$p_{H_2S} = y_{H_2S} P_{wh} \qquad (1)$$

where y_{H_2S} is the mole fraction of H_2S in the gas. If the conditions are not ideal then appropriate fugacity and activity arguments can be developed.

The relatively low concentration levels of H_2S (< 10 mol m^{-3}) expected as a result of reservoir souring and the high reservoir pressures mean that the partial pressures of H_2S will be low, and hence Henry's Law may be used to express the solubility of H_2S in the liquid phase. Otherwise Gerrard's Reference Line Method or various complex cubic equations of state [24] can be used since these take into account the non-idealities of the system. From the well-head partial pressure of H_2S, the mole fraction of H_2S in the oil can be expressed as:

$$p_{H_2S} = k_o x_o \qquad (2)$$

and in the aqueous phase:

$$p_{H_2S} = k_w x_w \qquad (3)$$

where k_o, x_o and k_w, x_w are Henry's constants and the liquid mole fraction of H_2S in the oil and water (brine) phase, respectively.

4.0 H_2S GENERATION RATES FROM PRODUCTION DATA

The total H_2S mass flow rates at reservoir condition M_{rH_2S} is also the total mass flow rate at the well-head (i.e. surface) conditions, M_{whH_2S}, since there is no offtake up the tubing. Thus

$$M_{wh_{H_2S}} = M_{r_{H_2S}} = m_{g_r} M_{g_r} + m_{o_r} M_{o_r} + m_{w_r} M_{w_r} = m_{g_{wh}} M_{g_{wh}} + m_{o_{wh}} M_{o_{wh}} + m_{w_{wh}} M_{w_{wh}} \qquad (4)$$

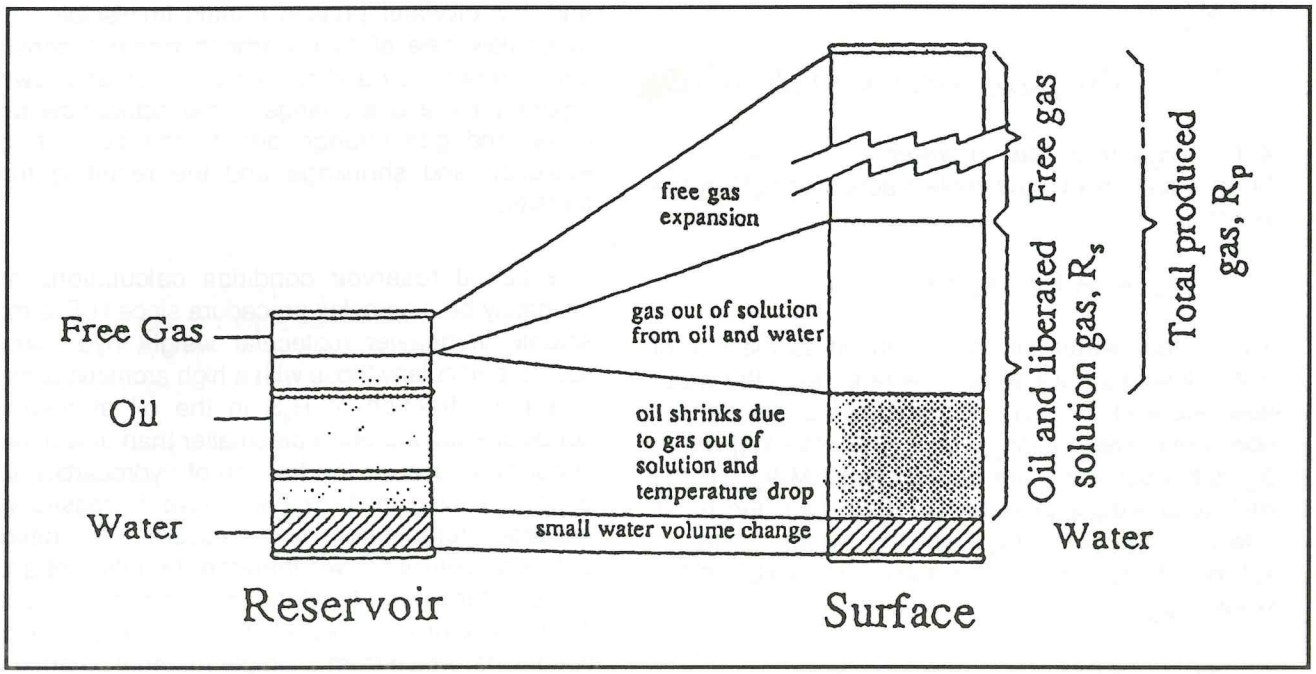

Figure 1 Schematic of the volume relationships of gas, oil and water between reservoir and well-head conditions.

where $m_{g,o,w}$ are the H_2S mass fractions and $M_{g,o,w}$ the total fluid mass flow rates of the gas, oil and water either at reservoir (r) or well-head (wh) conditions. The values of m and *M* at reservoir and well-head conditions will be different because of the mass transfer between the oil and water and gas, especially gas out of solution, as the fluids move from the reservoir to the well-head (Figure 1). The values are interrelated and can be calculated or measured in the laboratory as discussed later [22,23].

For a concentration of A ppm (v/v) of H_2S in the well-head (surface) gas, the H_2S concentration in the oil and water phases can be calculated using the well-head production parameters normally monitored.

Let Q_o be the surface volumetric flow rate of the oil which has a surface density of ρ_o. Then the surface mass flow rate of oil is $Q_o\rho_o$ (= $M_{o_{wh}}$).

Let R_p be the surface gas to oil ratio in volumes per volume, so that the surface gas flow rate will be R_pQ_o and if the surface gas density is ρ_g, the surface mass flow rate of gas is $R_pQ_o\rho_g$ (= $M_{g_{wh}}$).

4.1 H_2S flow rate in gas

At surface conditions, the gas can be assumed to be ideal (i.e. PV = nRT, where n is the number of moles and R the gas constant) thus for a concentration of A ppm (v/v) of H_2S in the surface gas (i.e. A volumes of H_2S are in 10^6 volumes of gas) the mass flow of H_2S per 10^6 volumes of gas is $P_{wh}AMW_{H_2S}/RT$ and the total mass flow is $P_{wh}10^6\ MW_g/RT$, where MW_{H_2S} and MW_g are the molecular weights of H_2S (= 34.02) and the gas respectively.

If the concentration of H_2S is low, i.e. $A << 10^6$, then the mole fraction of H_2S in the gas $\simeq 10^{-6}A$.

Hence from equation (1), the partial pressure of H_2S in the gas is

$$p_{H_2S} = A\ P_{wh} / 10^6 \qquad (5)$$

Also the mass fraction of H_2S in the gas,

$$m_{g_{wh}} = A\ MW_{H_2S} / 10^6\ MW_g \qquad (6)$$

and thus the mass flow of H_2S in gas,

$$m_{g_{wh}}M_{g_{wh}} = A\ MW_{H_2S}\ R_pQ_o\rho_g / 10^6 MW_g \qquad (7)$$

4.2 H_2S flow rate in oil

From equation (2), the mole fraction of H_2S in the oil is

$$x_o = A\ P_{wh} / k_o\ 10^6 \qquad (8)$$

If MW_{oil} is the molecular weight of oil and remembering that mole = mass/molecular weight and the mass of H_2S << mass of oil so that $x_o \approx$ moles H_2S/moles oil, then the mass flow fraction of H_2S in the oil is $m_o = x_oMW_{H_2S}/MW_o$, thus the mass flow of H_2S in the oil,

$m_{o_{wh}} M_{o_{wh}}$, is

$$m_{o_{wh}} M_{o_{wh}} = (MW_{H_2S}\, Q_o \rho_o / MW_{oil})\ x\ (AP_{wh}/k_o\, 10^6) \quad (9)$$

4.3 H_2S flow rate in water

From equation (3), the mole fraction of H_2S in the water is

$$x_w = A\, P_{wh} / k_w\, 10^6 \quad (10)$$

The surface water-cut, W, is defined as the rate of water flow rate/(oil + water flow rate), then the water flow rate = Q_o [W / (1 - W)] volumes and the mass flow rate of water is $M_{w_{wh}} = Q_o\, \rho_w$ [W / (1 - W)] where ρ_w is the surface water density and if MW_{water} is the molecular weight of water (= 18.0), then the mass flow fraction of H_2S, $m_{w_{wh}}$, in the water is $m_{w_{wh}} = x_w MW_{H_2S}/MW_w$. Hence the mass flow of H_2S in the water $m_{w_{wh}} M_{w_{wh}}$ is

$$m_{w_{wh}} M_{w_{wh}} = (MW_{H_2S}\, Q_o \rho_w\, [W/(1-W)] / MW_{water})\ x\ (A\, P_{wh} / k_w\, 10^6) \quad (11)$$

4.4 Total H_2S mass flow rate at well-head

The total mass flow rate of H_2S at the well-head is from equations (5) to (11)

$$M_{wh_{H_2S}} = A\, 10^{-6} Q_o MW_{H_2S} \left[\frac{R_p \rho_g}{MW_g} + \frac{\rho_o P_{wh}}{k_o MW_o} + \frac{W \rho_w P_{wh}}{(1-W)\, k_w MW_w} \right] \quad (12)$$

This mass of H_2S will then flash from the water and oil into the gas if the pressure is reduced to stock tank conditions. It is also the total mass flow rate of H_2S from the reservoir into the well-bore, M_{rH_2S}, but H_2S will be distributed in different proportions according to the reservoir and well-head Henry constants, k_o and k_w.

4.5 The mass flow rate at reservoir conditions

From equation (4), M_{whH_2S} at the well-head is also the total mass flow rate of H_2S in the reservoir, M_{rH_2S}. As mentioned earlier M_{rH_2S} can also be calculated using reservoir data and estimating the H_2S concentration in the oil, water and gas phases at reservoir conditions. This can be done using surface to reservoir parameters [18,24,25] and, in the first instance, assuming that the mass flow rate of water between the reservoir and surface remains constant and that oil/water phases remain immiscible. The mass flow rate of hydrocarbons remains constant between reservoir and surface although as shown in Figure 1 there is a change in the actual flow rates of oil and gas change due to the solution gas evolution and shrinkage and the resulting mass transfer.

The actual reservoir condition calculations may ultimately be a complex procedure since H_2S is more soluble in heavier molecular weight hydrocarbon liquids, particularly those with a high aromatic content. The mole fraction of H_2S in the oil at reservoir conditions will therefore be smaller than at well-head conditions because the fraction of hydrocarbon light ends dissolved in the oil will have increased with increased temperature and pressure. The needed partition coefficients will therefore be different and if those determined at well-head conditions are used, it is likely to give an over-estimation of x_o at reservoir conditions, which from a simple material balance will in turn lead to an under-estimation of x_w. Therefore, in calculating the concentrations of H_2S in the gas, oil and water for a particular system composition, it is necessary to consider the partition coefficients determined at both well-head and reservoir temperatures and pressures.

If H_2S generation within the reservoir is associated with the waterflooded region, either at the mixed oil-water interface, or in the flooded zone, the use of equations (2) and (3) are still valid, because equilibrium between the phases would be maintained due to the slow advancement of the water front and the relatively rapid mass transfer of H_2S between the phases.

5.0 CONTACTED IRON SULPHIDE RESERVOIR VOLUME

An estimate of the volume of reservoir formation which must be contacted to generate the H_2S by the dissolution of iron sulphide can be made using the rates of generation of H_2S obtained from laboratory experiments e.g. [18] to [21] but modified by suitable factors governed by the reservoir conditions.

The reactions controlling the dissolution of pyrite and pyrrhotite are strongly dependent on the solution pH and redox potential [18-21]. The dissolution of pyrite can be represented as:

$$FeS_2 + 4H^+ + 2e = Fe^{2+} + 2H_2S \quad (13)$$

and for pyrrhotite, as:

$$Fe_{1-x}S + 2xH^+ + 2xe = (1-x)FeS + xH_2S \quad (14)$$

$$(1-x)\,FeS + 2(1-x)H^+ = (1-x)Fe^{2+} + (1-x)H_2S \quad (15)$$

Reaction (14) is the reduction of the pyrrhotite surface to a 1:1 Fe:S stochiometry, a prerequisite to the non-oxidative dissolution of FeS, which is shown in reaction (15). More complicated reaction schemes such as leaching routes have been presented in the literature [26,27] but, at present, no route has been definitely proved.

If R' is an experimentally measured reaction rate (e.g. kg/m² per time period), then on a time basis, e.g. daily, yearly etc, the area of iron sulphide which must be contacted to generate an observed H_2S level is given by:

$$\text{Area of iron sulphide contacted/m}^2 = \frac{cM_{wh_{H_2S}}}{R'} \quad (16)$$

where c is a constant converting the expression to suitable units.

A method of relating the area of iron sulphide contacted to the reservoir volume is by considering the mineral sulphide presence within the reservoir. Iron sulphides are known to occur both as small nodules (in the range 10 - 1000 μm dimension) and as pore linings. For the initial calculations, the nodules can be represented as small spheres for which the surface area to volume relationship can be expressed as $4\pi r^2:(4/3)\pi r^3$, where r represents the average radius of the nodules. Since the nodules are within a sandstone matrix only a fraction, f, of the surface will be exposed to the pore fluids. Therefore, the volume of iron sulphide which is contacted per day to generate an observed rate of H_2S souring is given by:

$$\text{Volume of iron sulphide contacted/m}^3 = \frac{c'M_{wh_{H_2S}}\ r}{f\ R'} \quad (17)$$

and c' another conversion factor constant.
If ø represents the formation porosity and B, the reservoir bulk volume fraction occupied by iron sulphide, then the reservoir volume contacted to generate an observed level of H_2S souring is given by:

$$\text{Volume of reservoir contacted to generate observed level of } H_2S \text{ souring/m}^3 = \frac{c'\,M_{wh_{H_2S}}\ r}{f\,B\,(1-\phi)\,R'} \quad (18)$$

For pore linings, the degree of cementing of the iron sulphide within the sandstone matrix can vary significantly, therefore the surface area to volume relationship will also vary greatly. For instance, if the iron sulphide completely fills the pore space, the surface area to volume ratio is small, and conversely, if the iron sulphide is present only as a thin lining to the pore wall, the ratio of surface area to volume will be large. Thus an order of magnitude estimation is only possible.

This method of relating experimental measured rates of H_2S generation to a reservoir volume provides a route for estimating the total amount of iron sulphide required to react to generate the observed levels of reservoir souring. A more accurate method would be to model with time the change in exposed surface area of the nodule due to dissolution, including taking into account the geological description of the mineral sulphide distribution within the reservoir.

6.0 H_2S GENERATION ESTIMATION

Order of magnitude estimations of the extent of H_2S generation in the oil reservoir using these equations requires 'typical' values of reservoir properties in order to calculate the mass flow rate of H_2S and its distribution in the gas, oil and water phases. If the amount of iron sulphide in the reservoir is estimated at 0.05% of the reservoir bulk volume, a porosity of 20% and a fraction of the nodule exposed to pore fluids as 25% (in these calculations a value of B typical of North Sea Brent sandstone reservoirs has been used). Other typical data needed include k_o = 468 psi per mole fraction [26] and k_w = 7291 psi per mole fraction [26] and we assume a constant value for r of 100 x 10^{-6} m although it can be readily varied if necessary, and a well-head pressure of 155 psi and temperature 104°C.

Using equations (1) to (12), the level of H_2S in the gas, oil and water at surface conditions at a range of water cuts and gas oil ratios can be estimated. A range of conditions are shown in Table 1 along with the volume of reservoir which must be contacted, and the amount of iron sulphide consumed to generate the specified level of hydrogen sulphide (for conversions the density of 'FeS' is 4650 kg/m³ and the density of FeS_2 is 5018 kg/m³ [25]). The non-explicit data used in run 1 can be scaled to give the data in the other 23 runs, thus the oil rate is presented as 2000 units/time and in our calculations represents 320 m³/day; R' the reaction rate is presented as 1 unit and represents 4.3 x 10^{-7} kg/m² per day. Actual reaction rate data would need to be obtained experimentally. The calculations in this paper are carried out to indicate the sensitivity of the

various parameters. The constants c and c' are 65.535 and 21.845 respectively [18].

7.0 DISCUSSION

Table 1 gives only a few example calculations. Many further calculations were carried out using equation (12). From Table 1 and these further calculations the following conclusions were made:

1. For a constant level of total H_2S at the surface, then as the rate of reaction increases the volume of reservoir contacted decreases (e.g. runs 1 and 2).

2. From equation (18) the relationship between the experimental rate of iron sulphide dissolution and the contacted reservoir volume means any variation of the parameters f, B, r, ϕ and R' will produce a simple response in the contacted reservoir volume (e.g. run 3).

3. For a constant level of H_2S concentration in the well-head gas, the change in the total amount of H_2S produced at the surface (carried in the gas, water and oil) is affected by the change in water cut. With increasing water-cut (more water, less oil for constant total fluid flow rate), the quantity (mass) of H_2S in the gas and oil decreases whilst the quantity (mass) of H_2S carried in the water increases (runs 4 to 7). Thus the total mass of H_2S being produced at the well-head can increase with increasing water-cut.

4. Table 1 shows that at a fixed GOR (gas-oil-ratio, R_s, Figure 1) as the water-cut increases the concentration of H_2S in the gas increases. As the GOR increases for a constant water-cut, the concentration of H_2S in the gas decreases. Figure 2 shows how if the concentration of H_2S in the gas remains constant, then the total H_2S produced is a function of water-cut, increasing significantly and rapidly at water-cuts above 0.7 and at lower gas-oil-ratios. Thus, in a reservoir where the pressure is maintained by water injection, and/or aquifer expansion, if the level of reservoir souring is judged only by the concentration of H_2S in the gas at surface conditions, the reservoir would be observed to be becoming more sour (increasing concentrations of H_2S in the surface gas), although if the GOR remains constant the total mass flow rate of H_2S remains constant. The phase in which the H_2S is being generated (i.e. a water-sulphide reaction or an oil-sulphide reaction) is also important. If H_2S is formed in the water, then due to the gas-water partitioning H_2S will flash into the gas and, at high water cuts, high levels of H_2S may be seen in the surface gas even though the reaction in the reservoir is modest.

5. For a fixed total H_2S surface mass flow rate (which is also a constant total rate of H_2S generation within the oil reservoir) runs 8 to 24 show the effects of different distributions of mass of H_2S in the gas, oil and water at various water-cuts and produced GOR.

6. The concentration of H_2S in the gas can vary even if the total mass flow rate of H_2S produced at surface remains constant depending on the partition coefficients k_o and k_w. Equations 1 to 4 imply that if the total mass H_2S produced at surface (M_{whH_2S}) is fixed, even with changing GOR and water-cut the volume of the reservoir which must be contacted and the amount of iron sulphide which will be consumed will remain fixed.

8.0 CONCLUSIONS

1. These calculations have been made using rates of H_2S generation observed during iron sulphide dissolution experiments [18]. These rates are for laboratory based "clean" reactions and are used for the demonstration of equation (12) and cannot be used directly for reservoir calculations (discussed below). Whilst the dissolution of pyrite and pyrrhotite have been treated as simple reactions, reactions (13) to (15), this is an over simplification [18]. For instance, the observed

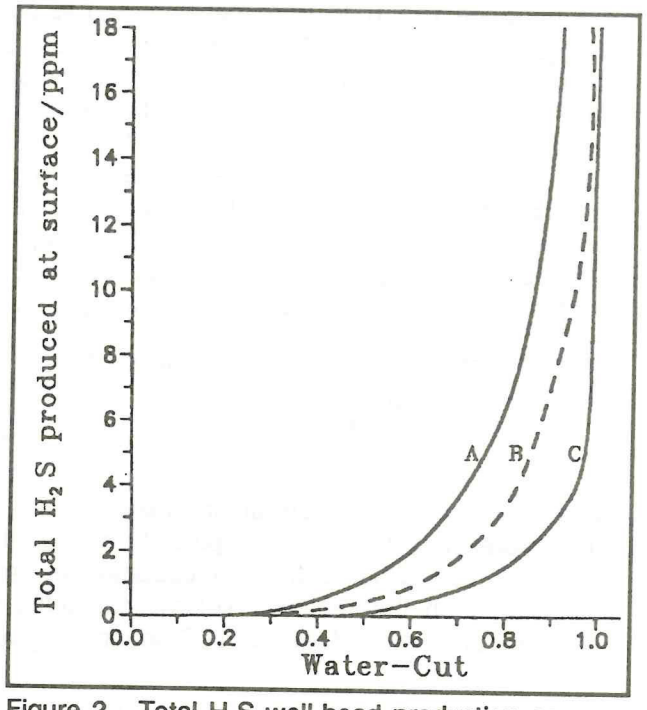

Figure 2 Total H_2S well-head production as function of water-cut and gas-oil ratio. GOR; A = 10 units, B = 20 units, C = 100 units vol/vol.

TABLE 1

Distribution of H_2S in gas, oil and water phases

RUN	Oil rate, Q_o units/time	Water cut, W	H_2S concentration in gas phase, Appm	Gas oil ratio, R_p vol/vol	Total mass flow rate of H_2S, $M_{wh_{H_2S}}$, kg/day	Mass flow rate of H_2S in gas, kg/day	Mass flow rate of H_2S in oil, kg/day	Mass flow rate of H_2S in water, kg/day	Reaction rate R' units/time	Reservoir volume contacted m^3	FeS consumed 10^{-6} m^3day^{-1}	FeS_2 consumed 10^{-6} m^3day^{-1}
1	2000	0	10	178	1.100	0.816	0.284	0	1	878.15	614	387
2	2000	0	10	178	1.100	0.816	0.284	0	100	8.782	614	387
3	2000	0	100	178	11.004	8.164	2.840	0	100	87.82	614	387
4	1800	0.1	10	178	1.002	0.735	0.256	0.012	10	79.998	505	318
5	1200	0.4	10	178	0.709	0.490	0.170	0.048	10	56.549	395	249
6	800	0.6	10	178	0.513	0.327	0.114	0.073	10	40.916	286	180
7	400	0.8	10	178	0.317	0.163	0.057	0.097	10	25.282	176	111
8	1800	0.1	10.98	178	1.100	0.807	0.281	0.0132	10	87.82	614	387
9	1200	0.4	15.53	178	1.100	0.761	0.265	0.075	10	87.82	614	387
10	800	0.6	21.47	178	1.100	0.701	0.244	0.156	10	87.82	614	387
11	400	0.8	34.74	178	1.100	0.567	0.197	0.336	10	87.82	614	387
12	200	0.9	50.28	178	1.100	0.411	0.143	0.547	10	87.82	614	387
13	2000	0	15.90	89	1.100	0.649	0.452	0	10	87.82	614	387
14	1800	0.1	17.33	89	1.100	0.637	0.443	0.021	10	87.82	614	387
15	1200	0.4	23.73	89	1.100	0.581	0.404	0.115	10	87.82	614	387
16	800	0.6	31.49	89	1.100	0.514	0.358	0.229	10	87.82	614	387
17	400	0.8	46.79	89	1.100	0.266	0.266	0.453	10	87.82	614	387
18	200	0.9	61.81	89	1.100	0.252	0.176	0.673	10	87.82	614	387
19	2000	0	24.50	36	1.100	0.405	0.696	0	10	87.82	614	387
20	1800	0.1	26.43	36	1.100	0.393	0.676	0.032	10	87.82	614	387
21	1200	0.4	34.62	36	1.100	0.343	0.590	0.167	10	87.82	614	387
22	800	0.6	43.63	36	1.100	0.288	0.496	0.317	10	87.82	614	387
23	400	0.8	58.99	36	1.100	0.195	0.335	0.571	10	87.82	614	387
24	200	0.9	71.58	36	1.100	0.118	0.203	0.779	10	87.82	614	387

reactions leading to the generation of H_2S at the surface of these minerals are very dependent on the pH of the solution in which the dissolution is carried out, and, on the applied potential at the mineral surface. This potential may be induced by an externally applied potential source, or may be due to the presence of reducing agents within solution. Also the reactions and the processes occurring within the reservoir can be much more complex [26,27].

If iron sulphide dissolution is a cause of reservoir souring, then it is apparent that a detailed knowledge of both the pH and redox potential within the oil reservoir must be available, plus the obvious requirement for sufficient iron sulphide source to be present. For pyrite dissolution to be a source of H_2S generation, it is necessary for a strong reducing agent to be present in solution. The H_2S generating reactions of pyrrhotite in acidic solutions are far more facile than for pyrite, although, except in very low pH environments, there is still the need for a reducing agent to be present. Thus, if a strong reducing agent is introduced into the reservoir possibly in bacteriocides, corrosion and scale inhibitors (the latter two as a result of well treatment), their possible reactions with reservoir mineral sulphides must be further considered.

2. The calculations presented in this paper use a simplistic approach to relating the observed rates of mineral dissolution to areas of iron sulphides contacted in the reservoir environment. Increased accuracy in these calculations require the use of a more sophisticated mineral dissolution model, this being enhanced by a detailed knowledge of the form and distribution of types of iron sulphides in particular reservoir environments [26,27].

9.0 FUTURE

The identification of reservoirs or wells with sweet oil which may become sour with time is not yet possible. It must be remembered that the source(s) of H_2S are not yet unambiguously proven. Before any proof can occur more analysis of wells which have turned sour is needed. This analysis must include a production history, the water cut changes and workover history including any chemicals used, and chemicals injected for corrosion prevention [1]. Then it may be possible to predict potential souring problems and their magnitude. This paper may guide calculations if the iron sulphide route is proven.

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NOMENCLATURE

A	concentration of H_2S in ppm in gas phase [eqn. (5)]
B	bulk volume [eqn. (18)]
f	fraction of surface exposed to pore fluids [eqn. (17)]
k_i	Henry's constant [eqns. (2) and (3)]
m_i	mass fraction of H_2S in phase i [eqn. (4)]
M	total mass flow rate of H_2S [eqn. (4)]
M_i	mass flow rate of a particular phase i [eqn. (4)]
MW_j	molecular mass of species j
p_{H_2S}	well-head partial pressure of H_2S in gas (eqn. 1)
P_{wh}	total well-head pressure (eqn. 1)
Q_o	surface oil volumetric flow (eqn. 5)
R	gas constant
R'	reaction rate [eqn. (16)]
R_p	produced gas-oil ratio (eqn. 5)
r	average radius of nodules
W	volume fraction water cut
x	mole fraction, liquid phase
y	mole fraction, gas phase
ρ_i	density of phase i
ϕ	porosity [eqn. (18)]

subscripts

g	gas
H_2S	H_2S
i	ith species
o	oil
r	reservoir
w	water
wh	surface conditions (well-head or separator)

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