Possible Sources of Hydrogen Sulphide in Petroleum Reservoir – Challenges and Implications

*Ameloko Anthony, Fadairo Adesina, Rotimi O John and Isiramen Oseme,
Department of Petroleum Engineering, Covenant University Ota, Nigeria
*Corresponding e-mail/Tel: aduojo2001@yahoo.com /2348036878319

Abstract

Hydrocarbon reservoir souring occurs when concentration of H_2S increases over time in production fluids. The existence of sulphur compounds in hydrocarbon stream creates many problems of sulphur deposition in the vicinity of the wellbore hole, in well completion and/or production equipment. The scaling and corrosive sour fluid is toxic to life and liable to cause cracking and pitting of susceptible steels in oil and gas operations.

Studies have shown clearly that the outset of petroleum reservoirs that are initially considered 'sweet' produce more H_2S in their later life. The phenomenon of unexpected increase in H_2S concentration in produced fluid from petroleum reservoir has been observed over a period of years in different areas of the world. The source of H_2S has been generally associated with the water injection scheme over the production life of petroleum reservoir.

This paper presents an overview of all possible causes of unexpected increase in gas phase H_2S concentration in petroleum reservoir. The challenges and implications in later future are been considered with the Gulf of Guinea environment in mind.

It is concluded that review of possible sources of H_2S and biocidal control technology should be highly promoted and exploited prior to water flooding scheme on any gulf of guinea petroleum reservoirs.

Keywords: Reservoir, hydrocarbon, souring, formation, flooding, corrosion

INTRODUCTION

Reservoir Souring is the gradual increase of H_2S content within the produced fluid from the hydrocarbon formation. Increasing mass of hydrogen sulphide (H_2S) per unit mass of total produced fluid is the phenomenon of souring, and a well which produces H_2S is said to be souring, in contrast to a sweet well, which does not produce H_2S. Hydrogen sulphide is likely to become more common in produced hydrocarbon fluids, as the exploitation of deep reservoirs increases and unconventional resources get recovered significantly, such as heavy oils or bitumen. Hydrogen sulphide presence in produced oil and gas results in operational, environmental and treatment problems. Hydrogen sulphide is corrosive in nature and has deleterious effects on human life and petroleum equipments (down-hole and surface equipments). The symptoms of reservoir souring have usually been treated by shutting in wells and sweetening the sour fluid. The overall economic impact of microbial reservoir souring has been very significant occurrence during production of such formation. The few available technologies for preventing the occurrence have shown limited success. Therefore, it is imperative to understanding the origin, implications and challenges as possible means for petroleum production engineer for checking or controlling the production of H_2S in petroleum reservoirs.

Possible Sources of Hydrogen Sulphide (H_2S)

A. *Non microbiological mechanisms*: The non microbiological mechanisms responsible for reservoir souring have been reported by *Bob Eden et al[1]* (CAPCIS Ltd and BP Exploration) as follows:

Thermo-chemical Sulphate Reduction (TSR)
TSR is the phenomenon producing the largest amount of hydrogen sulphide and is usually observed in carbonate reservoirs containing anhydrite. Natural TSR occurs at depths greater than about 4000 m corresponding to temperatures greater than about 120 °C. Induced TSR can happen in shallower reservoirs, where steam is injected for enhanced oil recovery. Thermo-chemical sulphate reduction implies hydrocarbon oxidation, sulphate reduction and production of secondary carbonate minerals, besides CO_2, H_2S and organosulphur compounds. This phenomenon involves hydrocarbon oxidation and sulphate reduction and produces as by-products, hydrogen sulphide, carbon dioxide, carbonate minerals and heavy organosulphur compounds.

Thermal decomposition of organic sulphur compounds (denaturation)
thermal decomposition of organic sulphur compounds generate relatively low concentration of H_2S. The drawback of the 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, e.g. thiocarbamate hydrolysis:

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

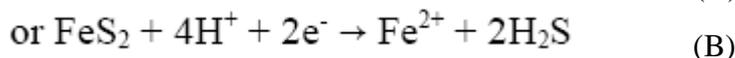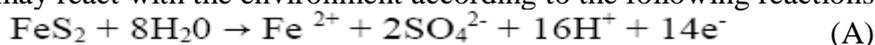and thioether reduction:

$$RSR \xrightarrow{[H]} 2RH + H_2S$$

Inorganic sulphur compounds are most likely to be in the form of insoluble metal sulphides or soluble sulphates.

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:

$$FeS_2 + 8H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- \qquad (A)$$

$$\text{or } FeS_2 + 4H^+ + 2e^- \rightarrow Fe^{2+} + 2H_2S \qquad (B)$$

Pyrite oxidation (A) is known to be a slow process which requires the presence of a powerful oxidant at a high potential. This process is, therefore, effectively ruled out in the reducing conditions found in petroleum reservoirs. Pyrite reduction (B) is possible at lower pH values and the progress of reaction 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.

Redox reactions involving bisulphite oxygen scavengers
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 down-hole. 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/l) already present in seawater:

$$2NH_4HSO_3 + 0, \rightarrow (NH_4)_2\,SO_4 + H_2SO_4$$
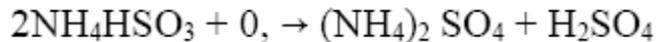
In a system where dosages are well controlled, the excess ammonium bisulphite injected down-hole will be low, generally less than lmg/l. Since ammonium bisulphite is present only as an oxygen scavenger it is not likely to be the principal sulphur source for hydrogen sulphide, although it is considerably 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 it is modifying the surface of an inert sulphur-containing solid in the reservoir so making it more reactive, thus generating H_2S.

B. Microbial or Biological mechanisms**:** Recent studies have shown that reservoir souring (in offshore fields) occurs mostly during secondary recovery and this is as a result of using seawater in water flooding. The microbial mechanism for the generation of H_2S is the Bacterial Sulphate Reduction by Sulphate Reducing Bacteria (SRB). It is now widely accepted that the reduction of sulphate by sulphate reducing bacteria (SRB) is the most significant mechanism of H_2S production in reservoir souring as a result of water flooding (Ligthelm et al., 1991; Sunde et al., 1993). The introduction of seawater which is saline in nature is responsible for the introduction of bacteria into the reservoir with SRBs being the most dominant and hence most troublesome bacteria present in the oil reservoir. Generally, bacteria may be naturally present in the reservoir in dormant form and receive a nutrient supply due to the introduction of the flood water. This increased supply will promote bacteria growth within the reservoir. Generally, anaerobic conditions exist in the reservoir, and bacteria able to cope with low amounts of oxygen or the absence of oxygen will preferentially proliferate. Generally, the most dominant form of bacteria is the so called Sulphate Reducing Bacteria, SRB. SRBs metabolize sulphates from the injected seawater and produce hydrogen sulphide gas as a waste gas. The injection of seawater or other water containing sulphate and which is usually saline in nature is a common practice used to increase oil recovery beyond primary production by maintaining reservoir pressure and sweeping oil towards production wells. Flooding of a reservoir with natural brines (seawater) usually has undesirable consequences since the brine may be responsible for the introduction and/or accelerated growth of bacteria within a reservoir.

For reasons of corrosion control, steps are taken to remove oxygen from injected water and this provides an environment conducive to the growth of the obligately anaerobic bacteria, SRB. In addition production chemicals, such as antifoams, scale inhibitors, and chemical oxygen scavengers are dosed into the injection water; these may add to the nutrient pool of nitrogen, carbon, and phosphorus available for SRB growth (Sunde et al, 1990). Although steps are taken to minimize the activity of bacteria in water injection systems, typically by continuous chlorination and batch dosing with organic biocides, the efficacy is variable.

Reservoir souring as a result of water injection into the reservoir and the presence of SRBs has been reported in the Gulf of Guinea on the Bonga field. Conditions on the Bonga field have been noted to be conducive to Sulphate Reducing Bacteria (SRB) to develop and hence reservoir souring follows. The conditions as stated are as follows:
- ✓ Reservoir temperature in the main reservoir (-702) is $63^{o}C$, which is well within the suitable range of $15\text{-}95^{o}C$.
- ✓ Formation water is moderately saline, Total Dissolved Solids (TDS) of some 1 to 5% wt, which is well below the maximum limit of 15 to 20%.
- ✓ Also, in case any H_2S is formed it will not react with the mineralogy, as the scavenging mineral content (e.g. siderite) is zero in the main reservoir.

✓ Formation water in a number of Bonga reservoirs features variable Volatile Fatty Acids (VFA), but unfortunately no data is available for the main reservoir. However, water compositions of the nearby reservoirs indicate that the VFA level may be high and bacteria have sufficient metabolizable carbon energy source to grow.

CHALLENGES OF RESERVOIR SOURING

Hydrogen sulphide is highly undesirable in the produced fluids since it is corrosive and toxic in nature. Consequently, the presence of hydrogen sulphide as a contaminant adversely affects the sales quality of the exported oil and gas. It is thus normal practice to attempt to prevent microbial growth within the reservoir by the injection of biocides to the injected water in order to sterilize the system and therefore prevent proliferation of bacteria. Typical biocides include chlorine, aldehydes such as gluteraldehde, thiazolines and quaternary amines. However, the continual addition of biocides is too costly to practice and more usually a sweep dosage at suitable intervals is used to sterilize the system. Despite biocide addition, it is almost impossible to prevent the introduction of all bacteria to a reservoir and a reduced rate of souring still occurs.

If SRBs could be excluded from oilfield operations, then it would be possible to control reservoir souring. There is, however, growing evidence that petroleum reservoirs have microflora that may include mesophilic and thermophilic SRB (McInerney et al., 1993; Magot et al., 2000). Even if the producing zone of a reservoir did not have an indigenous SRB population, it is well known that the drilling muds often contain viable population of SRB (Dow, 1987), and this is a vehicle for contaminating the water flooded zones at an early stage of reservoir development. In addition any activity that requires injection of liquid into an injection well, such as injection test or fracture initiation, has the potential to introduce SRB into a near-wellbore-zone, which will eventually be subject to high flux of nutrients in the injected water steam. As previously noted, injected water itself, also introduces active SRB into the reservoir. Even if the viable SRB population density is low, the high rate of water injection into each well ensures that the near-well-bore region receives a significant inoculation each day.

Additionally, due to the surface active nature of the majority of biocides, the biocides are readily absorbed to the surfaces of minerals such as clays found in reservoir sands. It is therefore not normally possible to achieve penetration of the biocide deep into a reservoir. Hence elimination of bacteria naturally present within a reservoir or introduced by the flood water and moving with oil/water flood front boundary is not normally achievable using conventional biocides. One way to obtain an end product having acceptably low levels of H_2S is the removal of that gas by treating the extracted hydrocarbons. This will normally require the installation of process equipment to remove the hydrogen sulphide gas, for example, flaring, treating with amines scrubbers to absorb the gas or addition of chemicals to scavenge by reaction to produce a neutralized compound.

Corrosion caused by hydrogen sulphide is known as 'Sour Corrosion'. Hydrogen sulphide is about 70 times more soluble in water than oxygen. Hydrogen sulphide represents a particularly serious corrosive problem because it can attack steel by three different mechanisms: acid attack, galvanic attack, or hydrogen attack.

Acid attack — In the presence of water, hydrogen sulphide dissolves to form a weak acid, which then dissolves iron to form complex sulphides. In general terms the corrosive reaction can be described as:

$$H_2S + Fe \longrightarrow Fe_xS_y + 2H$$

Galvanic attack — Iron sulphide is one of the most insoluble compounds known and tends to deposit on, and adhere to, the metal surfaces. Iron sulphide is cathodic to steel and so stimulates the generation of an electric circuit, which results in further attack on the iron. If the entire iron surface is covered with iron sulphide deposits then this will disrupt the adsorption of electrodes at the cathodic sites and stop the reaction. However, iron sulphide films are not normally continuous or adherent.

Hydrogen attack — Hydrogen attack takes two forms, namely "hydrogen blistering" and "hydrogen embrittlement." In both cases hydrogen atoms are generated by the standard corrosive reactions. Under normal circumstances these hydrogen atoms combine in pairs to form hydrogen gas molecules, which escape from the surface into the environment. However, hydrogen atoms are sufficiently small to diffuse into the steel where they cause damage. Some substances such as sulphide ions reduce the rate of formation of hydrogen molecules from atoms. Therefore, in the presence of sulphide ions, there is a greater concentration of hydrogen atoms on the surface and hydrogen damage is more severe.

IMPLICATIONS OF RESERVOIR SOURING

Sour surface metallurgy should be used to protect against sulphide stress-cracking corrosion in facilities where the partial pressures of H_2S exceed certain threshold levels, as defined by the guidelines of NACE International standards under MR0175/ISO-15156. From a survey of 12 reservoirs (Khatib and Salanitro, 1997), it was concluded that in all cases where the injected water contained sulphate, souring to some degree occurred; therefore all new seawater flood projects should be designed for sour service. There is a cost premium, estimated to be 2% of the total project cost, for sour service metallurgy (Al Rasheedi et al., 1999) that could become up to an order of magnitude more significant and more expensive, should retrofitting become necessary. On a $1 billion dollar project, metallurgy upgrades would cost in the region of $20 million at the outset of the project but up to $200 million if retrofitting after initial design and construction had commenced. Khatib and Salanitro (1997) estimate that using sour service materials could add hundreds of thousands of dollars to the cost of each well, resulting in millions of dollars of added costs to an entire project.
Similarly it is common for oil and gas export lines to have a maximum allowable concentration of H_2S that is calculated to maintain structural integrity. If the H_2S concentration cannot be controlled below this critical concentration, the export of fluids would be curtailed with subsequent loss of revenue.

A characteristic of reservoir souring is that not all production wells show the same increases in H_2S concentration at the same time. If the aim is to lower the concentration of field gas H_2S to below a critical value, it may be possible to accomplish this by selectively shutting in the wells producing the greatest mass of H_2S (Al-Rasheedi et al., 1999). This obviously incurs a cost in terms of lost or deferred production, although in practice these wells tend to have high water cuts, which limit the financial penalty.

Sour facilities entail additional cost in preventing operator exposure to toxic H_2S; control of oil-wet, iron sulphide pads that reduce separator performance; management of iron sulphide solids that interfere with produced water cleanup; and accumulation of iron sulphide-based solids that may promote under deposit corrosion and foul equipment such as pump strainers. Chemical scavenger treatment that removes H_2S from the production gas may also impose significant financial costs; owing to the volume that must be transported and stored offshore, these treatments may have significant logistics implications. Similarly, batch biocide water

injection system designed to control reservoir souring require frequent, high dosage applications with cost implications (Larsen et al., 2000).

Continuous treatment of injected seawater with a nitrate salt, a relatively recent technique in the oil industry, and costs around $0.76 to $1.19 per kg of sulphide removed (Jennemann et al., 1997). Additional facilities such as nanofiltration units, proposed to control souring by removal of sulphate from injected seawater have a significant capital cost.

CONCLUSION

Reservoir souring is essentially microbial and as stated occurs as a result of water injection in the process of secondary flooding particularly in offshore fields.

ACKNOWLEDGMENT

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