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Optimization of effective sulfur solvents for sour gas reservoir

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A B S T R A C T

Sulfur deposition attracts great attention for the exploration of oil and gas and is considered one of the most important hazardous processes in China, and all over the world. Thus, investigating a sulfur solvent is absolutely necessary and highly desirable in the sour gas reservoir development. In recent years, various sulfur solvents were developed and applied in different oilfields. However, they have disadvantages in their practical applications. In this paper, a solution is proposed to solve the problem and improve the sulfur dissolving ability. Three types of sulfur solvents were prepared, all of which have their own characteristics and advantages in different cases and compared with the existing sulfur solvents under the same conditions. The solubility of Dimethyl disulfide(DMDS)-based sulfur solvent system was up to 202.8 wt% at room temperature and 1020.0 wt% at 90 °C. Amine solvent systems also achieved high sulfur solubility. The solubility of diethylene triamine-ethanolamine solvent system could reach 79.6 wt% at room temperature and 210.0 wt% in 90 °C. It was shown that a more efficient sulfur solvent system can be achieved by remixing with suitable additives. This paper focuses on a preliminary study of optimizing effective sulfur solvents in order to solve the problems caused by sulfur deposition. In the long run, this may revolutionise the process of exploration, transportation and refining of crude oil or natural gas. Microscopic analysis by Scanning Electron Microscope (SEM) was used to facilitate understanding the mechanism of sulfur dissolution in each system and their differences.

1. Introduction

Sour gas reservoirs are the most important composition of unconventional oil and gas reservoirs, and are widely distributed in China, even all over the world. According to statistical information mentioned in “Sour gas field development technology information publication (edited by China Petroleum and Chemical Corporation)”, more than 300 sour gas fields with industrial value have been discovered all over the world, especially in Russia and Canada, as well as in America, Germany and France. Sour gas is a type of acidic gas which contains 5 ppm H_2S, but in China, 60% gas fields contain 20,000–40,000 ppm H_2S, some are more than 100,000 ppm. For instance, the proved reserve of Puguang Gas Field is 114.363 billion m^3 and the recoverable reserve is 87.832 billion m^3, but it contains 1,195,000 ppm. In such gas reservoir development processes, accompanied with the gas flow, the elemental sulfur would be easily deposited as the condensate in the form of sulfur, especially when the pressure and temperature were reduced (Zeng et al., 2012; Lyle et al., 1978; Clark et al., 1989; Guo et al., 2015; Hu et al., 2011, 2014a). The reservoir and gathering pipeline can become plugged by such deposition of the sulfur, which seriously affects the production of gas well (Li et al., 2011a). In addition, steel can be seriously corroded by mixtures of sulfur and water. Gathering pipeline and casing would perforate and damage, wells may be shut down or even scraped when corrosion becomes too serious. Worst of all, natural gas leakage caused by it would lead to serious environmental pollution and harmful to human health. It is understood that sulfur usually exists in the form of hydrogen sulfide as a natural gas and hydrogen sulfide is highly toxic. Thus, losses brought by it could not be estimated. For example, a sour gas well blowout occurred in Kaixian county of Chongqing in China on December 23, 2003, injuring more than 93,000 people and killing 243 people. Direct economic losses reached nearly 82 million RMB, while indirect economic losses are

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uncountable. Further to that, hydrogen sulfide leakages occur on a yearly basis in sour gas fields all over the world and kill people through leaks caused by pipeline damage. In order for sour gas reservoirs to be economical, a practical and economical method needs to be developed for exploiting these reservoirs. The problem needs to be solved urgently and it is absolutely necessary to carry out the research to develop sulfur dissolving technology and develop novel, efficient and low-cost sulfur solvent systems to prevent sulfur deposits in pipeline and ensure gathering pipeline work properly (Demirbas et al., 2015; Hilzman and Dennis, 1998; Nasr-El-Din and Al-Humaidan, 2001; Wilken, 1991; Hu et al., 2014b; Mahmoud, 2014; Hassan and Behnam, 2015). Herein, three kinds of sulfur solvents will described for different conditions.

2. Experimental and calculation method

2.1. Experimental method

A round bottom flask was charged with a given amount of elemental sulfur and solvent. The mixture was stirred with constant speed for 2 h. The undissolved sulfur could be recovered by filtration and dried in an oven at constant temperature (40 °C) for 24 h. Then it was weighed for calculating the sulfur solubility.

Sulfur dissolving experimental conditions: 25 °C, 0.1 MPa.

2.2. Sulfur solubility calculation method

It is well known that solubility is defined as the percentage of solute dissolved in the unit mass solvent. It is mathematically described by:

$$Y = \frac{M_1 - M_2}{M} \times 100\% \quad (1)$$

where Y = solubility of the solvent, M = amount of the solvent, M_1 = initial amount of the sublimed sulfur, M_2 = final amount of the undissolved sublimed sulfur.

3. Screening experiment

3.1. Screening of main solvents

In the experiments of main solvents screened, the amount of each solvent was set to 25 g. A given amount of sulfur was added to the solvent and ensured that it was saturated by sublimed sulfur, then calculating the solubility using the formula above.

3.1.1. Screening of common solvents

The sulfur solubility in various common solvents was tested and the corresponding results are shown in Fig. 1. The results show that the solubility of DMDS is significantly higher than the other solvents. The difference of sulfur solubility might be relative to the chemical structures of solvents. DMDS is a stable pale yellow liquid which works as an effective product in the sulfide process because of its high sulfur content. It is also the sulfiding industry's reagent of choice because it offers more sulfur per pound of reagent when compared to its nearest competitor dimethyl sulfide. Initially, it is assumed that the sulfur and ether bond of DMDS may be attributed to its high solubility. However, DME which has an ether structure gave poor results. This is indicative that the sulfur bond will play a more important role to promote the sulfur solubility of the solvent and its dissolution mechanism can be explained as "like dissolves like". Sulfur reagents usually have bad smell. With the various demands of oilfields, alternative sulfur solvents should be further explored. A comparison of dichloromethane and xylene indicates that an aromatic ring can improve the sulfur solubility. It is therefore necessary to study the sulfur solubility of benzene derivatives.

3.1.2. Screening of benzyl solvents

The results of the study on sulfur solubility of benzyl solvents are shown in Fig. 2. It can be seen that the sulfur solubility of styrene is higher than the other benzyl solvents. A comparison of the sulfur solubility of toluene and chlorobenzene shows that the C–Cl bond can significantly increase the sulfur solubility. However, a comparison of styrene and chlorobenzene indicates that the double bond is more crucial to the sulfur solubility than C–Cl bond. Unfortunately, styrene is easily volatilised at high temperatures (Zhang and Xia, 2012). The sulfur solubility of xylene is higher than styrene at 80 °C. Considering the volatility and price of benzyl solvents, xylene would be employed in further screening experiments.

3.1.3. Screening of amine solvents

Amine solvents have been studied by many researchers. For example, Liu and co-workers revealed that diethylene triamine may be a possible candidate as a sulfur solvent (Liu et al., 2008a, 2008b). To acquire more efficient soluble systems, it is necessary to perform extensive research on amine solvents. Thus, thirteen amine solvents were chosen to test their sulfur solubilities, as shown in Fig. 3.

In a different approach, the process of reacting anmine solvents with sulfur results in the release much heat and thus, an increase in the temperature of the solution, will lead to higher sulfur solubility. Notably, the sulfur solubility of diethylene triamine or propylamine is significantly higher than DMDS at room temperature. By raising the temperature, the dissolution rate of triethylene tetramine became faster than diethylene triamine. In 2014, Guo and coworkers found that the sulfur dissolution rate of triethylene tetramine was 24.65 g/min/L and diethylene triamine was only 22.25 g/min/L (Guo, 2014). However, the sulfur solubility of diethylene triamine was higher than triethylene tetramine albeit at higher temperatures or room temperature. Therefore, it is incorrect to generally conclude that more amine groups in molecules can afford higher sulfur solubility. A comparison of ethanolamine, diethanolamine and triethanolamine indicates that a hydroxy group is unfavorable for the sulfur solubility. It can be seen that the sulfur solubilities of diethylene triamine and propylamine are both beyond 28 wt%. However, we found that during the course of filtration, the solution of diethylene triamine was too sticky to handle. In addition, the boiling point of propylamine is very low (about 48 °C) and thus it is recommended to be used at room temperature.

In order to reduce the viscosity of diethylene triamine sulfur solution, mixed solvent experiments were designed. Other solvents were set to 50 wt% of diethylene triamine and the relative results are shown in the Table 1. In view of the high price of DMDS and high volatility of propylamine, ethanolamine will be most suitable to reduce the viscosity of diethylene triamine sulfur solution and the optimal proportion was found to be 2:1 (diethylene triamine: ethanolamine).

3.1.4. Comparative analysis

It can be seen from the above screening experiments that DMDS, diethylene triamine and propylamine are the most promising candidates as the efficient sulfur solvents. Besides the difference of solubility, some other phenomena were noticed during the course of experiments. The appearance of most of filtering sulfur is similar to the sublimed sulfur and sometimes the color becomes light. However, for the benzyl solvents, especially for benzene and chlorobenzene, some black particles were found in the filtering