

## Article

# Research on Optimization of Sulfur Solubility Testing Method for High-Sulfur Natural Gas

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**Abstract:** At present, the methods for sulfur solubility testing of high-sulfur natural gas generally use laboratory proportioning gas samples and then connect equipment to test the sulfur solubility of the gas samples based on the adsorption deposition mechanism. However, these testing methods generally have the following problems: (1) The equipment used in these test methods has safety hazards such as leakage at pipe and valve connections. (2) The sulfur solubility of real gas samples cannot be measured directly. (3) The equipment is difficult to clean, and it is especially difficult to clean the sulfur deposited at pipe elbows and valve connections. This will lead to low sulfur solubility test results. (4) The thermal insulation performance during the test process is not good, and temperature changes have a great impact on gas volume measurement. In order to solve the above problems, a testing method and comprehensive experimental device for the solubility of elemental sulfur in high-sulfur natural gas were established. This test method wraps the entire experimental device with a metal shell, which has good safety and thermal insulation performance, and it uses customized pipeline connections, which have high flushing efficiency, less sulfur deposition, and more accurate experimental results. The upgraded filtration system can directly measure the sulfur dissolution of real gas samples, and a CS<sub>2</sub> solution recovery process is added to reduce the risk of leakage and environmental pollution. This method and equipment were used to test the elemental sulfur solubility determination of real gas samples from a high-sulfur gas well. The research results show that the solubility of elemental sulfur is related to temperature, pressure, and H<sub>2</sub>S concentration and increases with the increase in temperature, pressure, and H<sub>2</sub>S concentration. Compared with the previous method, this method has less residual sulfur during the test process, the measured sulfur solubility is 2.13% greater, and the test results are more accurate and reliable. This research result provides important basic data support for accurately measuring the elemental sulfur solubility of real gas samples in high-sulfur gas reservoirs and dealing with sulfur deposition problems.



**Citation:** Wan, Y.; Wang, L.; Yang, Y.; Ding, Z.; Tang, D.; Zhang, D.; Zhang, L. Research on Optimization of Sulfur Solubility Testing Method for High-Sulfur Natural Gas. *Processes* **2024**, *12*, 1210. <https://doi.org/10.3390/pr12061210>

Academic Editor: Qingbang Meng

Received: 13 May 2024

Revised: 9 June 2024

Accepted: 11 June 2024

Published: 13 June 2024



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## 1. Introduction

High-sulfur gas reservoirs in China contain abundant resources, with cumulative proven high-sulfur gas reserves exceeding 1 trillion cubic meters [1]. Among them, high-sulfur gas reservoirs in the Sichuan Basin have large reserves, high output, and high development value [2,3]. However, during the development process, elemental sulfur will undergo phase transitions. Hydrogen polysulfide is formed by the reaction of elemental sulfur with H<sub>2</sub>S. The reaction is a reversible chemical reaction. As temperature and pressure decrease, hydrogen polysulfide decomposes to form sulfur and hydrogen sulfide. When sulfur reaches the critical saturation state in the gas, the decrease in temperature and pressure will lead to the precipitation of sulfur from the gas phase. When the precipitated

sulfur cannot be carried by fluid hydrodynamics, sulfur accumulates and deposits in formation pores, wells, and surface pipelines. Sulfur deposition will lead to pipeline corrosion and formation and wellbore blockage, affecting the smooth production of gas wells [4–7]. It will also affect the fracture conductivity in the production process of a gas well, and the decrease in the conductivity in production will significantly reduce the recovery rate of the gas well [8].

Elemental sulfur generally exists in the form of hydrogen polysulfide and other compounds under initial reservoir conditions. However, during the production of high-sulfur gas reservoirs, the temperature and pressure are continuously reduced. When sulfur in gases reaches critical saturation levels, elemental sulfur accumulates and deposits in pore space, wellbores, and shaft linings. It affects two-phase seepage, reduces conductivity, blocks fracture channels, and causes gas well production reduction or shutdown [9–11]. At the same time, for high-production gas wells, due to high production and high flow rate, sulfur elements are easily carried out, and it is difficult for deposition to occur. However, the higher the production allocation, the faster the formation pressure drops, and the solubility of sulfur decreases rapidly, causing more sulfur elements to precipitate, affecting production capacity [12,13]. Therefore, it is necessary to accurately measure the elemental sulfur solubility in high-sulfur gas wells to optimize the gas well working system and solve the problem of sulfur deposition. For accurate experimental testing of sulfur solubility, scholars have proposed different methods.

Kennedy et al. [14] measured the sulfur solubility in methane, carbon dioxide, hydrogen sulfide, and mixtures of these gases and proved that sulfur solubility is related not only to temperature and pressure, but also to gas components. The method involves using a hard glass tube filled with glass wool to adsorb the elemental sulfur precipitated from the gas to be tested, then passing oxygen through it and igniting it, followed by absorbing the combustion products with a weak solution of sodium carbonate, and finally calculating the sulfur content through back titration. The sulfur dissolution measured by this method is low and poses safety risks. Roof [15] modified Kennedy's test method and measured sulfur solubility in pure hydrogen sulfide using carbon disulfide to absorb the gas during the test. Compared with Kennedy's experimental method, the safety is greatly improved, but a hand pump is used to control the back pressure. The back pressure control accuracy is low, which affects the full adsorption of elemental sulfur, and the conclusions drawn are limited to low-temperature and low-pressure conditions. Based on the Roof test method, Swift et al. [16] extended the tested temperature and pressure conditions to formation conditions and concluded that under a certain pressure, as the temperature increases, the solubility of elemental sulfur increases. The disadvantage is that the gas used in the test is pure gas, and the results are quite different from the solubility of elemental sulfur in the actual natural gas in the formation. Brunner and Woll [17] improved the test methods of Roof and Swift. Their test principle is also to absorb the precipitated sulfur with a  $\text{CS}_2$  solution and then evaporate and measure the sulfur mass. The difference is that they indirectly obtained the volume of the gas by condensing the pure hydrogen sulfide gas and then weighing it, which made up for the accuracy problem of the gas metering device at that time. However, weighing solid hydrogen sulfide gas had greater safety risks. Brunner et al. [18] extended the study of Kennedy et al. and measured the solubility of sulfur in a number of different acid gas mixtures. The results show that in multi-component mixed gases, the  $\text{H}_2\text{S}$  content has the greatest impact on elemental sulfur, and the solubility of elemental sulfur increases with the increase in  $\text{H}_2\text{S}$  content. Gu et al. [19,20] discovered that the solubility of elemental sulfur in  $\text{CH}_4$  and  $\text{CO}_2$  was poorly studied experimentally. They used a static method device to measure the solubility of sulfur in pure gases of  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{S}$  and their mixtures. It was concluded that the content of  $\text{H}_2\text{S}$  in the gas component is the main factor affecting the solubility of elemental sulfur. Fu et al. [21] established a method for calculating the sulfur saturation of formations and found that physical deposition is the main method of elemental sulfur deposition. In order to accurately obtain the saturated elemental sulfur content in high-sulfur gas reservoirs, Yang et al. [22] measured the solubility of elemental

sulfur in high-sulfur gas at certain temperatures and different pressures. Experiments have shown that the solubility of elemental sulfur in high-sulfur gases increases as the pressure increases. The experimental process was optimized based on the static method experimental device, which was equipped with an upgraded filter so that the experimental device could directly measure the sulfur solubility of real gas samples. However, it did not guarantee a constant temperature throughout the experimental process. Temperature changes have an impact on gas measurement. Serin et al. [23] used chromatographic analysis to study the solubility of sulfur in supercritical CO<sub>2</sub>, supplementing the research on the solubility of sulfur in CO<sub>2</sub> at lower temperatures. The advantage of this method is that the volume of the sulfur-containing gas sample is known and the amount is small. However, the disadvantage is that the mass spectrometer is sensitive to detection. The residual sulfur in the device will significantly reduce the measured sulfur solubility. And real gas samples cannot be measured. Cloarec et al. [24], based on the test method of Serin et al., improved the gas expansion equipment of the equipment and added a set of sulfur capture devices. This resulted in less residual sulfur in the device and more accurate experimental results. Zhang [25] tried to measure the sulfur solubility of real gas samples and added a condensing device based on the Brunner test method. It connects high-sulfur gas saturated with elemental sulfur to a condensing device and calculates the solubility of elemental sulfur in high-sulfur gas reservoirs by precipitating elemental sulfur in the condensing device. However, he did not consider that elemental sulfur easily deposits at pipeline elbows and valves, and the device was not equipped with corresponding reinjection purge equipment, resulting in a low measured sulfur solubility. Zeng et al. [26] designed a downhole sampler suitable for ultra-deep high-sulfur gas fields to provide more accurate data samples for the dynamic detection of gas fields, considering the characteristics of the large buried depth, highly heterogeneous reservoir, and complex gas–water relationship of the Puguang gas field. Based on the test method of Cloarec et al., Wu et al. [27] added a gas metering device to measure the sulfur solubility of real gas samples by controlling the gas volume entering the mass spectrometer. However, sulfur deposition in pipelines still has a great impact on test results.

Based on the research of the above scholars, it is found that when the solubility of elemental sulfur in high-sulfur natural gas is measured by mass spectrometer, although smaller sulfur-containing gas samples are required and the test is less dangerous, the mass spectrometer analysis is sensitive, and the standard sample configuration and the deposition of sulfur content in the pipeline will significantly affect the test results, so the traditional adsorption deposition method is selected as the theoretical basis for the optimization method. However, the previous adsorption deposition method has the following shortcomings: 1. The sulfur solubility of real gas samples is rarely measured directly. 2. The deposited sulfur at pipeline elbows and valve connections cannot be cleaned well, making the measured sulfur solubility low. 3. There is a lack of transition area between the reaction, condensation, and metering systems for reducing the impact of temperature changes on the metering results. 4. The back pressure control system has low accuracy, and there are fluctuations in the airflow when measuring real gas samples, which affects the full adsorption of elemental sulfur. 5. A CS<sub>2</sub> solution needs to be added multiple times during the test, which poses risks of leakage and environmental pollution. In order to develop high-sulfur gas reservoirs more safely and rationally, it is necessary to design a safer and more accurate sulfur solubility testing method based on the shortcomings of the previous condensation adsorption method.

## 2. Integrated Equipment for Sulfur Solubility Testing

The test method is based on the condensation adsorption mechanism and uses a solvent (CS<sub>2</sub>) that can quickly dissolve elemental sulfur in the gas and does not react with other components as the absorption liquid. It involves calculating the solubility of elemental sulfur in high-sulfur natural gas by measuring the elemental sulfur content in the absorption liquid and the gas volume passing through the meter. By first measuring the sulfur

solubility of several pressure- and temperature-sensitive points of the experimental gas sample and then using the interpolation method to calculate the elemental sulfur content of the experimental gas sample at different temperatures and pressures, the supporting design experimental device has the following advantages: 1. The entire set of equipment is wrapped in a metal shell, which improves the safety of the test and ensures constant temperature throughout the process, reducing the interference of temperature changes on the test results. 2. It uses two sets of customized filters to filter formation water, drilling fluid, and other impurities in real gas samples and directly tests the elemental sulfur solubility of real gas samples. 3. The use of customized pipelines can effectively flush the deposited sulfur at pipeline elbows and valves, and the sulfur solubility measurement results are more accurate. 4. The back pressure control system is more accurate and can adjust the back pressure according to the flow rate at the outlet of the metering system to ensure full adsorption of elemental sulfur. 5. A  $\text{CS}_2$  recovery system is added, which can condense and recover  $\text{CS}_2$  steam during the test, reducing the risk of leakage and environmental pollution.

### 2.1. Test Device

The sulfur dissolution test uses an independently developed and designed elemental sulfur solubility meter (Figure 1). The device has a maximum working pressure of 100 MPa and a maximum working temperature of 150 °C. The entire set of equipment is made of Hastelloy alloy, which can meet the test requirements of temperature resistance, pressure resistance, and corrosion resistance. Compared with the previous test device for measuring elemental sulfur solubility, this device has improved and optimized the test process and upgraded many key components. The optimized test device mainly consists of six parts: sample transfer and sample preparation system, back pressure control system, condensation adsorption system, flow metering control system, off-gas treatment system, and carbon disulfide reinjection system.

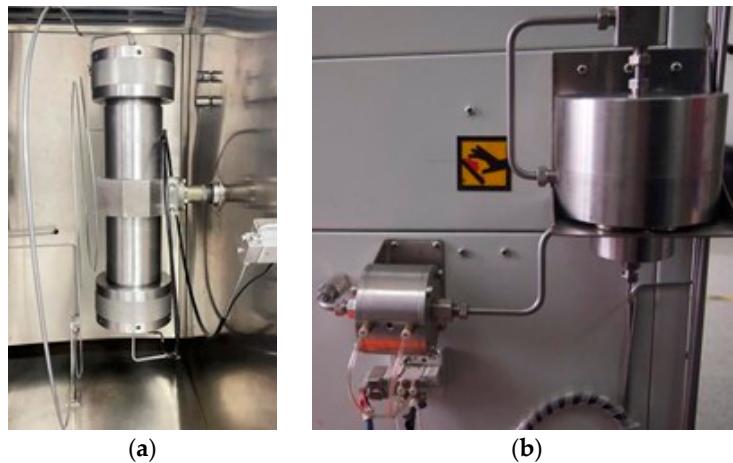


**Figure 1.** Integrated equipment for sulfur solubility testing.

#### 2.1.1. Sample Preparation System

The sample preparation system is shown in Figure 2a. The system mainly consists of a constant pressure and speed Duplex pump, a sample preparation device, an air bath thermostat, a filter, and a swing device. Its main function is to simulate the depletion exploitation method by controlling temperature and pressure, gradually reducing the test pressure and temperature and thereby directly measuring the content of elemental sulfur in the sample. At the same time, excess sulfur powder can also be added before introducing the gas sample to make the elemental sulfur in the gas sample reach a saturated state, thereby measuring the solubility of elemental sulfur under different temperature and pressure conditions. In order to test sulfur solubility more accurately and safely, the testing process and equipment have been optimized as follows: (1) In order to improve the thermal insulation performance, air bath heating is used instead of electric heating,

which makes heating safer and more uniform. (2) In order to ensure the sealing safety of the mixing chamber, the use of valves and the occurrence of leak points are minimized. Therefore, there is only one temperature probe in the mixing chamber, and the pressure is automatically controlled by a constant pressure and speed Duplex pump. (3) In order to directly measure real gas samples, two sets of filters are equipped to filter out formation water, drilling fluid, and other impurities that may be present in real gas samples. When one group becomes clogged, another group can be switched.



**Figure 2.** (a) Sample preparation system; (b) back pressure control system.

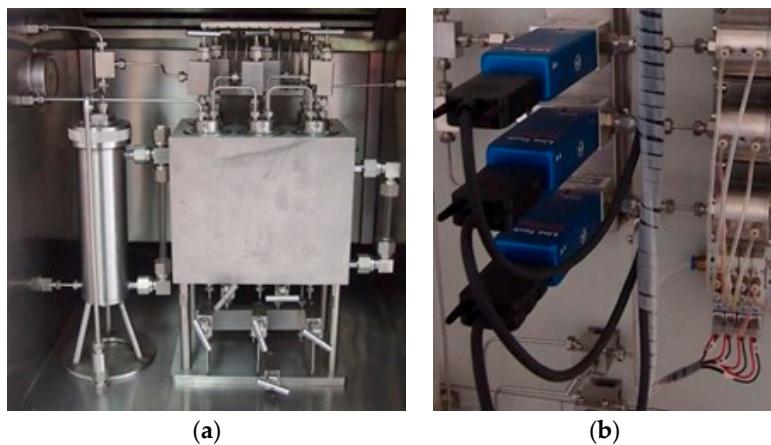
#### 2.1.2. Back Pressure Control System

The back pressure control system is shown in Figure 2b. The system mainly consists of an emergency brake valve, a back pressure tracking pump, and a back pressure valve. Its main function is to slowly balance and reduce the pressure of the high-pressure, high-sulfur gas sample in the mixing chamber to normal pressure (0.1 MPa). The critical point of elemental sulfur solubility is reached through the reduction in pressure, causing elemental sulfur in the gas to precipitate. In order to test sulfur solubility more accurately and safely, the testing process and equipment have been optimized as follows: In order to directly measure real gas samples, a high-precision back pressure tracking pump and a piston needle back pressure valve were selected to improve the stability of the back pressure system, stabilize the gas flow rate, and allow the elemental sulfur in the gas to be fully absorbed by the condensation adsorption system.

#### 2.1.3. Condensation Adsorption System

The condensation adsorption system is shown in Figure 3a. The system mainly consists of an air bath thermostat, a coil, and an adsorption tank. Its main function is to lower the temperature of the gas sample and use  $\text{CS}_2$  solution to adsorb elemental sulfur in the gas. In the previous test process, the condensation adsorption system mostly used several glass bottles in series, and the bottle mouths were sealed with rubber stoppers. However, during the actual test process, due to the instability of the airflow, it is easy for the rubber stopper of the last glass bottle to collapse when the gas flow suddenly increases, posing a safety hazard. Moreover, when the high-temperature airflow in the mixing chamber directly enters the  $\text{CS}_2$  solution, it will cause part of the  $\text{CS}_2$  solution to volatilize, making the gas measurement result larger. To test sulfur solubility more accurately and safely, the testing process and equipment have been optimized as follows: (1) To improve the accuracy of measurement, a section of coil pipe is added before and after the adsorption tank and an umbrella-shaped gas–liquid separation device is installed in front of the flow meter to reduce the impact of temperature changes and  $\text{CS}_2$  vapor on the measurement results. (2) To enhance the safety of the sulfur solubility testing, the adsorption tank is constructed with a whole digging approach, carving out six interconnected tanks on a single piece of

Hastelloy alloy material. The top of the tanks is also sealed with Hastelloy alloy material, ensuring both the safety of the equipment and the thorough adsorption of elemental sulfur.



**Figure 3.** (a) Condensation adsorption system; (b) metering system.

#### 2.1.4. Metering System

The metering system is shown in Figure 3b. The system mainly consists of pneumatic valves, flow meters, and pressure sensors. Its main function is to measure the gas volume after reducing the pressure to normal pressure. To test sulfur solubility more accurately and safely, the testing process and equipment have been optimized as follows: (1) Because the minimum flow rate measured by the flow meter is 5% of the maximum range, to improve the accuracy of measurement, three anti-sulfur flow meters with different ranges were selected and automatically switched according to the flow rate during the test. (2) For real gas samples, even if the gas pressure is reduced to normal pressure, the gas flow will still be unstable. To directly measure the real gas sample, a flow control system is designed to control the back pressure according to the flow rate at the outlet end of the flowmeter, to avoid the flow rate at the outlet end suddenly reaching 0 or increasing suddenly.

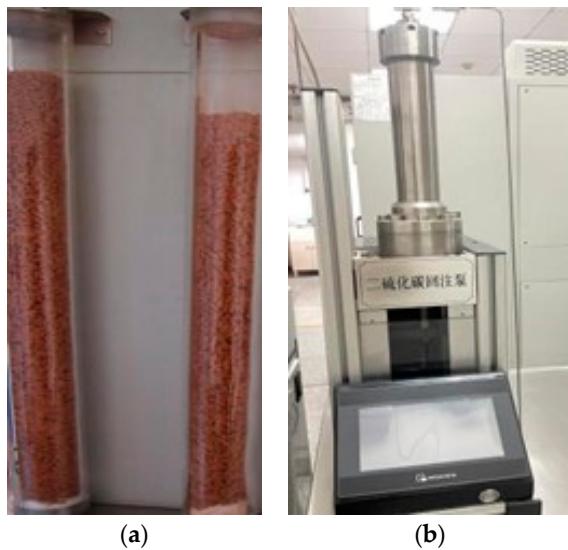
#### 2.1.5. Off-Gas Treatment System

The off-gas treatment system is shown in Figure 4a. The system consists of three glass cylinders with a length of 1 m containing a desulfurizer. Its main function is to absorb waste gas during testing to avoid leakage and environmental pollution. Previous sulfur dissolution test methods mostly used solutions to absorb exhaust gas, but this method requires frequent replacement of the absorption solution and has safety hazards. To test sulfur solubility more safely, the testing process and equipment have been optimized as follows: Three exhaust gas recovery tanks are used. The tanks are independent of each other and can be switched freely. When all the desulfurizer in one tank turns black, it can be quickly switched to another one. The inlet and outlet of the used tail gas recovery tank can be sealed with dead-end plugs to prevent any leakage and environmental contamination.

#### 2.1.6. Carbon Disulfide Re却jection System

The carbon disulfide re却jection system is shown in Figure 4b. The system is mainly composed of a constant speed and constant pressure and speed Duplex pump and a pneumatic valve. Its main function is to clean the pipeline after the test is completed and collect elemental sulfur that may precipitate outside the adsorption system. To test sulfur solubility more safely, the testing process and equipment have been optimized as follows: (1) To enhance the flushing efficiency, the entire set of equipment employs custom pipelines, which can effectively flush elemental sulfur from difficult-to-clean areas such as valve connections, thus improving measurement accuracy. (2) To improve the safety of the test, a CS<sub>2</sub> recovery system was added. After the test, the toxic and harmful CS<sub>2</sub>

liquid is condensed and recovered for reuse, thereby reducing environmental pollution and safety hazards.



**Figure 4.** (a) Off-gas treatment system; (b) carbon disulfide reinjection system.

## 2.2. Test Process

- (1) After checking the air tightness of the equipment, put excess sulfur powder (50 g) into the sample preparation room. Adjust the temperature and pressure of the equipment to the set values, then transport the gas in the sampling chamber to the sample preparation chamber, and rock and mix for more than 24 h, so that the elemental sulfur solubility of the gas in the system reaches saturation.
- (2) As a result of the back pressure being controlled, the gas in the sample preparation is slowly (5 mL/min~10 mL/min) passed through the elemental sulfur adsorption system, and the gas volume passing through is measured with a gas metering device.
- (3) When the gas pressure in the sample preparation room drops to 0.1 MPa, clean all pipelines with CS<sub>2</sub> solution and add the cleaning solution to the adsorption tank. The solid material obtained by heating the CS<sub>2</sub> solution in the adsorption system is weighed with a precision balance to obtain the mass of elemental sulfur. At the same time, CS<sub>2</sub> steam is condensed and recovered.

To simulate the depletion exploitation method, during measurement, a back pressure system is used to gradually reduce the formation pressure to the wellhead pressure at a certain temperature. The elemental sulfur solubility was calculated for each pressure point. Each pressure point is determined using the same method used to determine elemental sulfur content.

## 2.3. Test Data Processing Methods

According to the gas state equation, the sulfur-containing gas volume measured during the test process can be converted into the gas volume  $V_0$  under standard conditions. The calculation formula used is

$$V_0 = \frac{P_1 \times V_1 \times 293.15}{101.325 \times (273.15 + t_1)}$$

where  $V_0$  is the volume of gas under standard conditions (101.325 kPa, 20.0 °C), m<sup>3</sup>;  $P_1$  is the atmospheric pressure during testing, MPa;  $V_1$  is the gas volume under the pressure of  $P_1$ , m<sup>3</sup>;  $t_1$  is the test temperature, °C.

According to the volume of sulfur-containing gas in the standard state and the mass of elemental sulfur measured by a precision balance, the solubility of elemental sulfur in sulfur-containing gas is calculated. The calculation formula used is

$$C = \frac{m_1}{V_0}$$

where  $C$  is the elemental sulfur content in sulfur-containing gas,  $\text{g}/\text{m}^3$ ;  $V_0$  is the volume of gas under standard conditions ( $101.325 \text{ kPa}$ ,  $20.0^\circ\text{C}$ ),  $\text{m}^3$ ;  $m_1$  is the mass of elemental sulfur,  $\text{g}$ .

### 3. Test Results

The samples used in the test came from two production wells in a gas field in the Sichuan Basin. Samples 1 and 2 are taken from the same gas sample of production well 1, and samples 3 and 4 are taken from the same gas sample of production well 2. For samples 1 and 3, the new method was used to measure sulfur solubility. For samples 2 and 4, a traditional method was used to measure sulfur solubility. The natural gas components of the gas samples from production well 1 are as follows:  $\text{H}_2\text{S}$  content is 6.75%,  $\text{CH}_4$  content is 84.31%,  $\text{C}_2\text{H}_6$  content is 0.07%,  $\text{CO}_2$  content is 8.5%,  $\text{N}_2$  content is 0.36%,  $\text{H}_2$  content is 0.01%,  $\text{H}_2$  content is 0.003%. For production well 2, the natural gas components of the gas samples are as follows:  $\text{H}_2\text{S}$  content is 16.78%,  $\text{CH}_4$  content is 79.1%,  $\text{C}_2\text{H}_6$  content is 0.06%,  $\text{CO}_2$  content is 5.12%, and  $\text{N}_2$  content is 0.31%. The test results are as follows Tables 1 and 2.

**Table 1.** Solubility of gas samples from Well 1 at different temperatures and pressures.

| Pressure/(MPa) | Solubility at Different Temperatures/(\text{g}\cdot\text{m}^{-3}) |        |        |          |        |        |
|----------------|---|--------|--------|----------|--------|--------|
|                | Sample 1  |        |        | Sample 2 |        |        |
|                | 110 °C  | 90 °C  | 70 °C  | 110 °C   | 90 °C  | 70 °C  |
| 10             | 0.4589  | 0.3369 | 0.1976 | 0.4578   | 0.3338 | 0.1974 |
| 20             | 0.5142  | 0.3927 | 0.2834 | 0.5001   | 0.3855 | 0.2793 |
| 30             | 0.5838  | 0.4259 | 0.3429 | 0.5665   | 0.4215 | 0.3375 |
| 40             | 0.6491  | 0.5384 | 0.4158 | 0.6268   | 0.5198 | 0.4029 |
| 50             | 0.7958  | 0.6479 | 0.4428 | 0.7609   | 0.6206 | 0.4256 |

**Table 2.** Solubility of gas samples from Well 2 at different temperatures and pressures.

| Pressure/(MPa) | Solubility at Different Temperatures/(\text{g}\cdot\text{m}^{-3}) |        |          |        |
|----------------|---|--------|----------|--------|
|                | Sample 3  |        | Sample 4 |        |
|                | 90 °C   | 70 °C  | 90 °C    | 70 °C  |
| 10             | 0.5762  | 0.2301 | 0.5736   | 0.2296 |
| 20             | 0.8437  | 0.3643 | 0.8315   | 0.3593 |
| 30             | 1.1726  | 0.5842 | 1.1541   | 0.5784 |
| 40             | 1.2733  | 0.9017 | 1.2444   | 0.8821 |

### 4. Results

#### 4.1. Effect of Temperature and Pressure on Sulfur Solubility

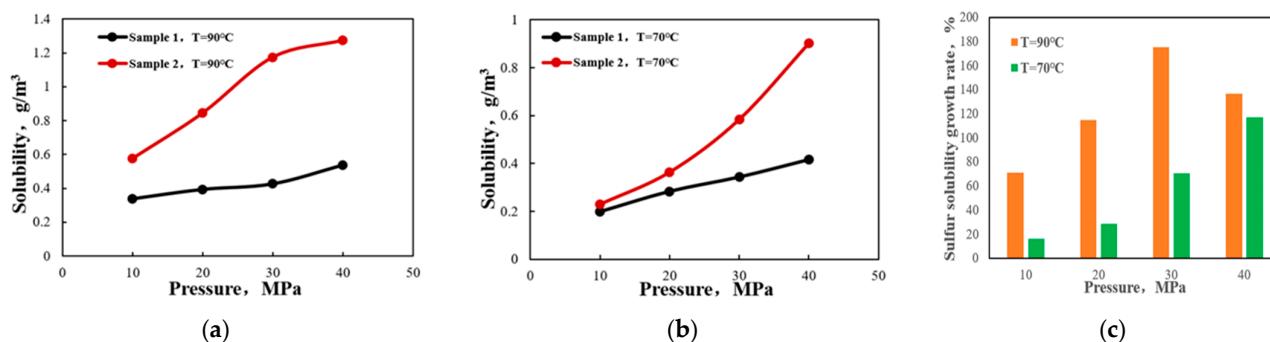
According to the test results, it is found that when the formation pressure is 50 MPa and the formation temperature is 110 °C, the elemental sulfur solubility of sample 1 is 0.7958 g/m<sup>3</sup>. When the formation pressure remains constant and the formation temperature decreases to 70 °C, the elemental sulfur solubility decreases to 0.4428 g/m<sup>3</sup>. Similarly, when the formation temperature remains constant and the formation pressure decreases to 10 MPa, the elemental sulfur solubility decreases to 0.4589 g/m<sup>3</sup>. Similarly, the solubility of elemental sulfur in other samples follows a similar trend. That is, at the same temperature, the solubility of elemental sulfur increases with increasing air pressure. At the same

pressure, the solubility of elemental sulfur increases with the increase in gas temperature. This may be because as temperature and pressure increase, chemical dissolution processes strengthen gradually, accelerating the formation of polysulfide compounds from elemental sulfur in the gas, thereby increasing sulfur solubility in natural gas.

#### 4.2. Effect of Hydrogen Sulfide Content on Sulfur Solubility

The elemental sulfur solubility of sample 1 ( $\text{H}_2\text{S}$  content 6.75%) and sample 2 ( $\text{H}_2\text{S}$  content 16.78%) was compared at the same temperature and pressure. The results are shown in the figure below.

It can be seen from Figure 5 that at the same formation temperature and pressure, the elemental sulfur solubility of sample 2 with high  $\text{H}_2\text{S}$  content is greater than that of sample 1 with low  $\text{H}_2\text{S}$  content, and the difference in elemental sulfur solubility between the two increases with the increase in formation temperature and pressure. It can be concluded that under the same temperature and pressure, as the hydrogen sulfide content increases, the solubility of elemental sulfur shows an upward trend.



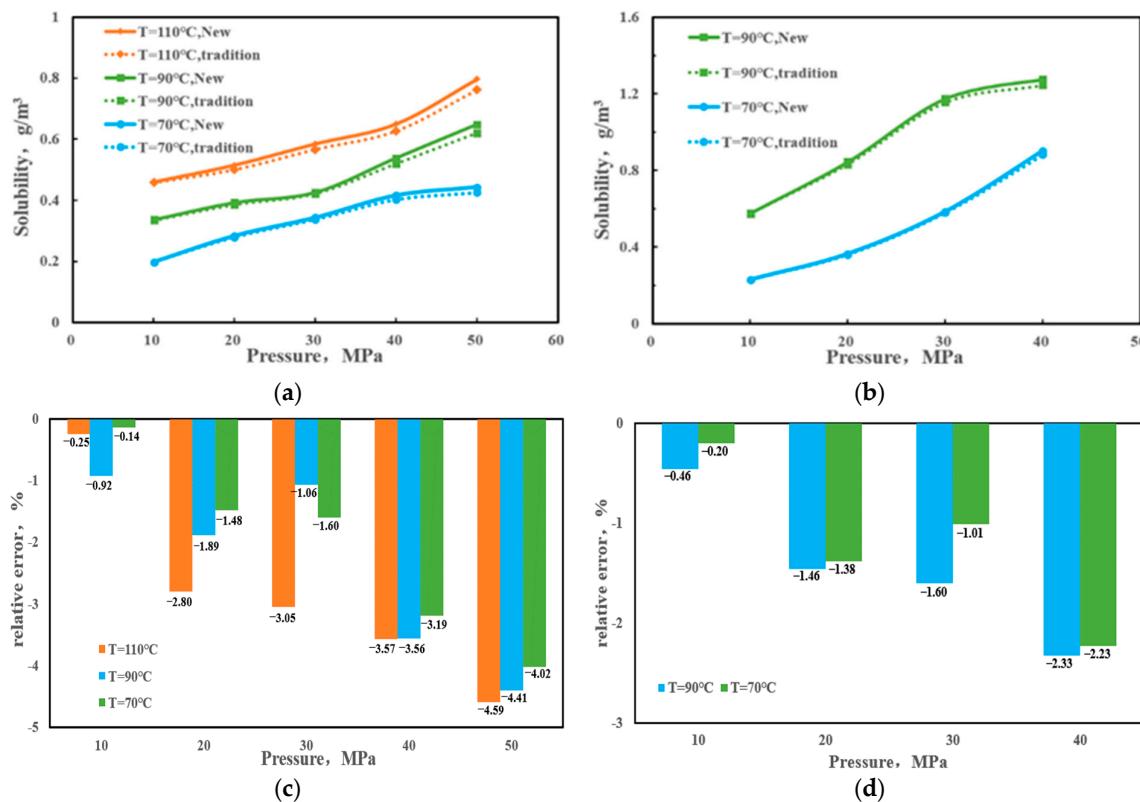
**Figure 5.** This figure shows experimental results of the influence of  $\text{H}_2\text{S}$  content on sulfur solubility. (a)  $T = 90^\circ\text{C}$ , comparison of elemental sulfur solubility; (b)  $T = 70^\circ\text{C}$ , comparison of elemental sulfur solubility; (c)  $T = 90^\circ\text{C}$ , increase in elemental sulfur solubility.

#### 4.3. Comparison of Results from Different Testing Methods

For Sample 2 and Sample 4, the traditional sulfur concentration testing method was used to test the solubility of elemental sulfur, and it was compared with the results measured by the new method. The results are shown in Figure 6.

According to Figure 6, it can be seen that the solubility of elemental sulfur measured by the new method is generally greater than that measured by the traditional method, and the gap is even greater under high temperature and high pressure. For samples from well 1, when the formation pressure is 50 MPa and the formation temperature is 110 °C, the solubility difference measured by the two experimental devices is 4.59%, while when the formation pressure is 10 MPa and the formation temperature is 70 °C, the solubility difference measured by the two experimental devices is only 0.14%. Excluding the data of the highest and lowest pressure at each temperature-sensitive point, the solubility of elemental sulfur measured by the new method is on average 2.13% greater than that measured by the traditional method.

An analysis shows that, on the one hand, chemical dissolution plays a dominant role under high temperature and pressure. The equipment supporting the new testing method can better maintain the temperature and pressure required by the experiment. However, for the traditional testing method, the temperature and pressure will decrease slightly over time, the dissolved elemental sulfur in the gas sample will be relatively small, and the final elemental sulfur precipitated will decrease. On the other hand, the supporting equipment of the new test method uses customized pipeline connections and adds a  $\text{CS}_2$  reinjection process. After the test, the pipeline was cleaned repeatedly. There was less residual sulfur in the pipeline, more elemental sulfur was collected, and the measured solubility of elemental sulfur was relatively large.



**Figure 6.** This figure shows a comparison of results from different testing methods. **(a)** Comparative results of elemental sulfur solubility of well 1 samples; **(b)** comparative results of elemental sulfur solubility of well 2 samples; **(c)** difference in solubility of elemental sulfur in well 1 samples; **(d)** difference in solubility of elemental sulfur in well 2 samples.

## 5. Conclusions

- (1) Based on the fact that sulfur solubility measurement methods have low accuracy and can rarely directly measure real gas samples, a testing method and integrated testing equipment for elemental sulfur solubility in high-sulfur gas reservoirs were established. This test method wraps the entire test device with a metal shell, which has good safety and insulation. Using customized pipeline connections, the flushing efficiency is high, there is less sulfur deposition, and the test results are more accurate. The upgraded filtration system can directly measure the sulfur dissolution of real gas samples. The CS<sub>2</sub> recycling process is increased to reduce the risk of leakage and environmental pollution.
- (2) A new method was used to test the solubility of elemental sulfur in real sulfur-containing gas samples from a gas well. The results show that the solubility of elemental sulfur is positively correlated with temperature, pressure, and H<sub>2</sub>S content and increases with the increase in temperature, pressure, and H<sub>2</sub>S concentration.
- (3) The same gas samples were tested using new methods and traditional methods. The results show that the new method obtains more elemental sulfur; the measured sulfur solubility is correspondingly greater, with an average difference of 2.13%; and the test results are more accurate and reliable.

**Author Contributions:** Conceptualization, Y.W. and L.W.; methodology, Y.Y.; validation, Z.D., D.T. and D.Z.; investigation, L.Z.; resources, L.W.; data curation, Y.Y.; writing—original draft preparation, Y.W.; writing—review and editing, L.W.; supervision, Y.Y.; project administration, L.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author. The data is unavailable due to privacy.

**Conflicts of Interest:** Authors Ying Wan, Li Wang, Yan Yang, Zhao Ding, Daqing Tang, Dihong Zhang and Linling Zhang were employed by the Exploration and Development Research Institute of PetroChina Southwest Oil and Gas Field Company. The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. The Exploration and Development Research Institute of PetroChina Southwest Oil and Gas Field Company had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

## References

- Huang, L. New progresses in safe, clean and efficient development technologies for high-sulfur gas reservoirs. *Nat. Gas Ind. B* **2015**, *2*, 360–367. [[CrossRef](#)]
- Hu, Y.; Peng, X.; Li, Q.; Li, L.; Hu, D. Progress and development direction of technologies for deep marine carbonate gas reservoirs in the Sichuan Basin. *Nat. Gas Ind. B* **2020**, *7*, 149–159. [[CrossRef](#)]
- Ma, X. A golden era for natural gas development in the Sichuan Basin. *Nat. Gas Ind. B* **2017**, *4*, 163–173. [[CrossRef](#)]
- Hu, Y.; Peng, Y.; Zhang, W.; Song, M. Corrosion Inhibition Performance on Tubing Steel in Oil Wells Based on Schiff Base Surfactants. *Int. J. Electrochem. Sci.* **2017**, *12*, 4360–4369. [[CrossRef](#)]
- Hu, Y.; Peng, Y.; Hu, F.; He, F.; Guo, P. Anti-corrosion Performance of Chromium-coated Steel in a Carbon Dioxide-saturated Simulated Oilfield Brine. *Int. J. Electrochem. Sci.* **2017**, *12*, 5628–5635. [[CrossRef](#)]
- Hu, Y.; Peng, Y.; Zhao, J.; Guo, P.; Long, S. Electrochemical Analysis of the Corrosion Behavior of Drill Pipe Steel under Oil/Water Emulsion Condition. *Int. J. Electrochem. Sci.* **2017**, *12*, 8526–8534. [[CrossRef](#)]
- Yong, H.; Dong, H.; Xian, P. Key development technologies for high-sulfur gas reservoirs: New progress, challenges and key research directions. *Nat. Gas Ind.* **2022**, *42*, 23–31.
- Peng, Y.; Luo, A.; Li, Y.; Wu, Y.; Xu, W.; Sepehrnoori, K. Fractional model for simulating Long-Term fracture conductivity decay of shale gas and its influences on the well production. *Fuel* **2023**, *351*, 129052. [[CrossRef](#)]
- Li, J.; Cao, K.; Duan, Y. Seepage mechanism and productivity decline of shale-gas well. *Nat. Gas Explor. Dev.* **2011**, *34*, 10.
- Peng, H.; Zhang, M.; Liang, X. Establishment of material balance equation for a gas reservoir considering sulfur deposition. *Nat. Gas Explor. Dev.* **2011**, *34*, 9.
- Peng, Y.; Ma, H.; Li, Z.; Zhou, L.; Zhao, J.; Wen, X. Material balance evaluation method for water-bearing gas reservoirs considering the influence of relative permeability. *Pet. Sci. Technol.* **2024**, *1*–16. [[CrossRef](#)]
- Li, H.; Liu, P.; Liu, C.; Wu, L.; Chen, J. Technologic bottleneck of effectively developing high-sour gas fields in eastern Sichuan basin and its countermeasure effect. *Nat. Gas Explor. Dev.* **2015**, *38*, 10.
- Zhou, M.; Xiang, Y.; Zhang, W.; Zhang, N.; Wang, Y.; Chen, Z.; Wang, H. Develop features of Chuangxing bioreef gas reservoirs in eastern Sichuan Basin and technical countermeasures. *Nat. Gas Explor. Dev.* **2020**, *43*, 7.
- Kennedy, H.T.; Wieland, D.R. Equilibrium in the Methane-Carbon Dioxide-Hydrogen Sulfide-Sulfur System. *Trans. Aime* **1960**, *219*, 166–169. [[CrossRef](#)]
- Roof, J.G. Solubility of Sulfur in Hydrogen Sulfide and in Carbon Disulfide at Elevated Temperature and Pressure. *Soc. Pet. Eng. J.* **1971**, *11*, 272–276. [[CrossRef](#)]
- Swift, S.C.; Manning, F.S.; Thompson, R.E. Sulfur-Bearing Capacity of Hydrogen Sulfide Gas. *Soc. Pet. Eng. J.* **1976**, *16*, 57–64. [[CrossRef](#)]
- Brunner, E.; Woll, W. Solubility of Sulfur in Hydrogen Sulfide and Sour Gases. *Soc. Pet. Eng. J.* **1980**, *20*, 377–384. [[CrossRef](#)]
- Brunner, E.; Place, M.C.; Woll, W. Sulfur Solubility in Sour Gas. *J. Pet. Technol.* **1988**, *40*, 1587–1592. [[CrossRef](#)]
- Gu, M.; Li, Q.; Chen, W.; Guo, T. Solubility of solid sulfur in super/near-critical H<sub>2</sub>s-containing sour fluid mixtures (II) The thermodynamic model. *J. Chem. Ind. Eng.* **1993**, *3*, 321–327.
- Gu, M.; Li, Q.; Chu, X.; Chen, W.; Guo, T. Solubility of solid sulfur in super/near-critical H<sub>2</sub>s-containing sour fluid mixtures (I) The thermodynamic model. *J. Chem. Ind. Eng.* **1993**, *3*, 315–320.
- Fu, D.; Guo, X.; Du, Z. Sulfur deposition mechanism of the gas reservoir with high sulfur content. *J. Southwest Pet. Univ. (Sci. Technol. Ed.)* **2009**, *31*, 109–111.
- Yang, X.F.; Huang, X.P.; Zhong, B. Experimental Test and Calculation Methods of Elemental Sulfur Solubility in High Sulfur Content Gas. *Nat. Gas Geosci.* **2009**, *20*, 416–419.
- Serin, J.; Jay, S.; Cézac, P.; Contamine, F.; Mercadier, J.; Arrabie, C.; Legros-Adrian, J. Experimental studies of solubility of elemental sulphur in supercritical carbon dioxide. *J. Supercrit. Fluids* **2010**, *53*, 12–16. [[CrossRef](#)]
- Cloarec, E.; Serin, J.; Cézac, P.; Contamine, F.; Mercadier, J.; Louvat, A.; Lopez, A.C.; Caneghem, P.V.; Forster, R.; Kim, U. Experimental Studies of Solubility of Elemental Sulfur in Methane at 363.15 K for Pressure Ranging from (4 to 25) MPa. *J. Chem. Eng. Data* **2012**, *57*, 1222–1225. [[CrossRef](#)]

25. Zhang, G. *Study on Feature of Phase Behaviors and Seepage Mechanism in High Sour Gas Reservoir-Take Samples from Changxing Gas Reservoir in Yuanba as Study Object*; Chengdu University of Technology: Chengdu, China, 2014.
26. Zeng, D.; Peng, X.; Fu, D.; Hu, J.; Wu, X.; Zhang, J. Development dynamic monitoring technologies used in the Puguang high-sulfur gas field. *Nat. Gas Ind. B* **2019**, *6*, 191–197. [[CrossRef](#)]
27. Wu, Y.; Wang, N.; Zhang, G.; Zhang, M.; Mo, C. Testing Method and Prediction Model of Elemental Sulfur Solubility in Sour Gas Reservoirs. *Spec. Oil Gas Reserv.* **2022**, *29*, 104–109. [[CrossRef](#)]

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