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### **Down Hole Sulphur Removal and Recovery**

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#### **Abstract**

Total and CrystaTech are developing a regenerable solvent based process to prevent the formation of sulphur deposition during production in natural gas well bores or even in the surface circuits and facilities. While producing gas from certain formations, solid sulphur has been observed to deposit on the well tubing which causes gas production to diminish and ultimately stop. Such scenarios can result in production time losses ranging from one day for batch treatment to three days for coiled tubing cleaning. In cases of severe plugging, one to two weeks could be required for a work-over. Deposited sulphur is corrosive with condensed aqueous brine phase and could have devastating effects. In addition, if not removed from the process gas stream, the elemental sulphur can also interact with the chemicals that are employed in the process treatment plants (such as amine used for gas sweetening, or Triethylene glycol (TEG) used for gas dehydration, etc.) Most of existing technologies require producers to either shut-in gas production while injecting disposable solvents to clear blocked well bores, or inject non-regenerable solvents on a continuous basis.

Down hole Sulphur Removal (DSR) is a regenerable process where solvent is continuously injected in the well to prevent the formation of solid sulphur deposits. The solvent dissolves the sulphur down hole and the sulphur rich solvent is separated from the gas in surface equipment. The separated sulphur rich solvent is regenerated and elemental sulphur is recovered by crystallization and filtration. The regenerated solvent is pumped back down into the well to dissolve additional sulphur and then can be re-utilised in subsequent cycles of the process. Unlike existing once-through technologies, DSR is designed for centralized treatment of a gas field and high sulphur throughput.

For large gas producing fields, the required amounts of sulphur solvent may be large enough in volume to be economically significant and environmentally impactful. For these reasons, it is of great importance to ensure that an efficient and reliable solvent regeneration process is always available and running such that regenerated solvent will be re-circulated continuously into the well with reduced operating expenditures.

Various solvents have been evaluated for use as the sulphur solvent for the DSR process. Solvent testing has been primarily conducted at the Gas Technology Institute in Chicago, Illinois. A dedicated screening program has been specifically designed to select the most cost effective physical solvent for this application. Sulphur solvents may be classified as either physical (such as hydrocarbons) or chemical (such as amine based formulations), whereby a chemical reaction occurs between the sulphur and the solvent. The solvents have been tested for various parameters necessary for use in the DSR process such as: sulphur solubility at well bottom and top-side conditions, solvent vapour loss, solvent separation and degradation, temperature and pressure effects, sulphur quality and reaction with H<sub>2</sub>S. Pilot scale crystallization and filtration studies have also been performed.

Total is currently pursuing a pilot scale demonstration of the DSR technology. This single well application will prove the process over long term operation and will be used to develop commercial scale-up and economic data. The preliminary design and process package of the pilot unit are underway. The final detailed design, installation and start-up will be scheduled and completed soon after a well site candidate is identified and confirmed for the pilot demonstration and once all the site specific data are integrated into the final design.

A regenerable DSR process is expected to be the only cost effective method to produce natural gas from wells that would experience solid sulphur deposition of approximately greater than 1.5 tons per day.

## INTRODUCTION

Deposition of elemental sulphur is a well established phenomenon in the production of some sour gas fields. A number of reservoirs may be listed as examples which are located in Europe (France and Germany) and North America (Alberta, Wyoming and Mississippi) [1, 2, 4, 5, 6, 8]. Sulphur deposition is a serious concern as it can result in significant operational, safety and economical issues; the problems range from nuisance issues to complete pluggage and stopped gas flow. These situations are detailed further in this paper. Given the serious impact on gas production, Total and CrystaTech have together proactively developed a regenerable physical solvent based process: the DSR (Down hole Sulphur Recovery – Patent pending). A surface pilot has recently been successfully operated in Texas and the technology will now be demonstrated in a field pilot. This single well application will be used to develop commercial scale-up and economic data. This paper presents the methodology that was adopted in this joint Research and Development Program and outlines the main advantages of the DSR process.

## BACKGROUND INFORMATION AND THEORY

Sulphur solubility in sour gas can be affected by a number of conditions including, but not necessary limited to, gas composition, pressure, and temperature and the nature and amount of condensate present in the sour gas [5, 9]. To fully understand the sulphur deposition phenomenon, it is important to be aware that sulphur is not only physically soluble in sour gas but also can be chemically bonded to  $H_2S$  [2]. The physical solubility of sulphur in a sour gas increases with the pressure and the density of the gas phase but is limited by spatial interactions between molecules. However, it decreases with the temperature because low energy interactions are broken by thermal agitation. Thus, from a pure thermodynamic perspective, the physically dissolved sulphur in a sour gas responds to changes in pressure and temperature; its precipitation will occur as soon as saturation conditions are reached along the production pathway.

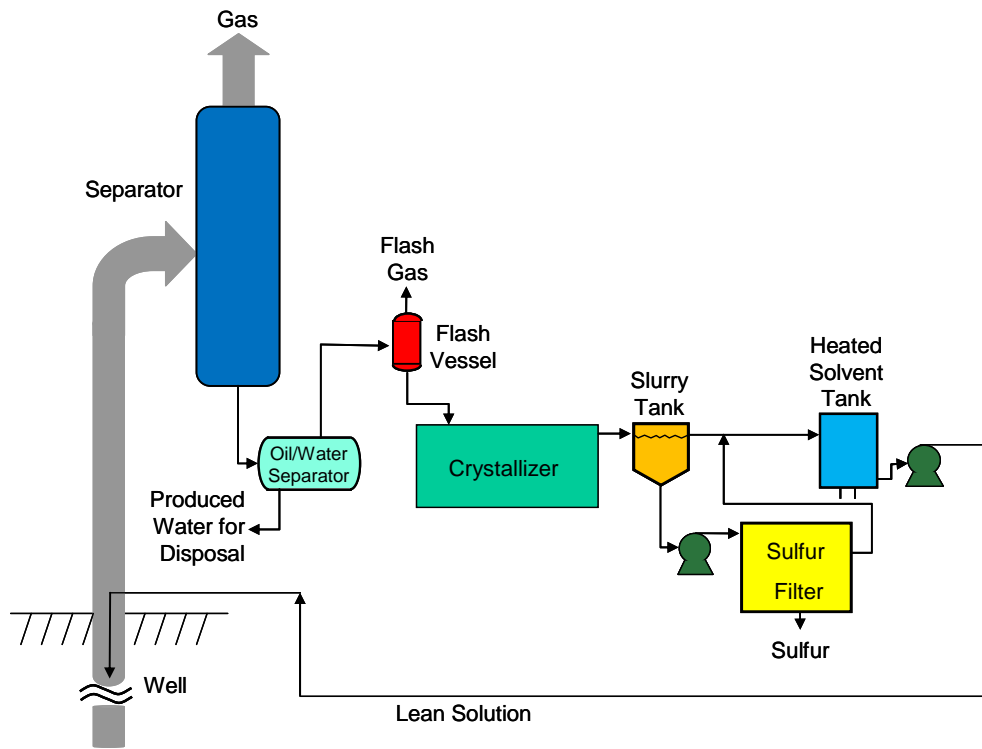
The chemical solubility of sulphur in a sour gas is associated with the formation of hydrogen polysulphides ( $H_2S_x$ ), called polysulphanes or sulphanes [2, 7]. This chemical solubility is even more pronounced at very high concentration of  $H_2S$  that can significantly depress the sulphur precipitation temperature. Therefore, the attainment of sulphur gas saturation conditions involves the chemical decomposition of sulphanes, a rather slow reaction, which may be associated with a delay in sulphur precipitation and deposition. Thus, if a source of elemental sulphur exists, the produced sour gas may contain a mixture of hydrogen sulphide, physically dissolved elemental sulphur and a mixture of hydrogen polysulphanes. The hydrogen sulphide is stable unlike the dissolved sulphur and the sulphanes that respond to pressure and temperature changes.

As described above, depending on reservoir and flowing conditions, sulphur may precipitate and deposit. However, non-thermodynamic factors such as kinetics or hydrodynamics can influence the ability of the gas to carry free elemental sulphur and may delay precipitation. When sulphur precipitates and deposits, the consequences can vary in importance from being a nuisance to a situation where production is shut down due to the obstruction of the well string, gathering lines or surface equipment or even to reservoir impairment. In addition, sulphur deposition can pose significant asset integrity issues as deposited sulphur can be very corrosive with condensed aqueous brine. Exposed lines made of carbon or stainless steel can undergo severe damage and surprisingly, local pitting has been observed on corrosion resistant alloys. If not removed from the process gas stream beforehand, the elemental sulphur can also have a detrimental effect on the downstream treating units, such as the amine unit used for gas sweetening, or triethylene glycol unit used for gas dehydration.

Because of all of the operational and economic adverse effects described above that are caused by sulphur deposition, it can be crucial for operated assets to implement a reliable mitigation strategy throughout the entire production life. Some control of sulphur deposition is possible to a limited extent by limiting pressure and/or temperature changes, but such solutions may affect production volumes and subsequently reduce associated revenues. The existing technologies require producers to either shut-in gas production while injecting disposable solvents to clear blocked well bores, or continuously inject non-regenerable solvents or use chemical regeneration processes. For large producing sour gas fields, the required amounts of sulphur solvent may be large enough to be economically unfeasible and environmentally detrimental. The use of a sulphur solvent regeneration process shall be seriously envisaged as it can be the only realistic and cost-effective option.

## DSR PROCESS PRINCIPLE

The objective of the DSR project is the development of a novel and safe technology capable of providing operators with an easy and reliable solution for the efficient mitigation of sulphur deposition and resulting adverse operational, safety and economical consequences. The DSR technology is designed to employ a non-aqueous, thermally regenerable physical solvent capable of preferentially removing sulphur from a sour gas. The process can be described as follows and is represented in Figure 1.



**Figure 1: DSR Process Block Diagram**

The solvent dissolves the sulphur down hole and the sulphur-rich solvent is separated from the gas in surface equipment. The separated sulphur-rich solvent is regenerated and elemental sulphur is recovered by crystallization and filtration. The regenerated solvent is pumped back down into the well to dissolve additional sulphur and then can be re-utilised in subsequent cycles of the process. As represented in Figure 1, the system features standard equipment, mainly injection pumps, separation vessels, a crystalliser, and a sulphur filter system. The core feature of the process lies in the solvent and associated characteristics.

### DSR PROCESS DEVELOPMENT

To achieve the above objective, it was decided to direct the DSR Project through a phased approach. Overall, the project can be described as a 3-stage program, as follows:

#### Stage 1 – DSR sulphur solvent screening and selection

The DSR solvent selection is certainly one of the most important and time consuming activities and is basically the most critical item in the project agenda. With this in mind, a certain number of technical criteria have been established for the solvent screening program. These are, but not necessary limited to:

1. High sulphur pick-up capacity
2. Thermally regenerable (by cooling)
3. Chemically and thermally stable under well and surface conditions
4. Low solvent losses (i.e. low vapour pressure at plant inlet conditions)
5. Not corrosive
6. Suitable physical characteristics (viscosity, density, vapour pressure at well conditions)
7. Health, Safety & Environment requirements (e.g. toxicity)
8. Commercial availability at acceptable cost

The experimental program associated with this first step of the process development was itself divided into laboratory and bench scale sub-activities that helped compare the solvents to each other with regard to the above criteria. All the experimentation was performed at the Gas Technology Institute (GTI) in Chicago under realistic sour gas environment. The plan focused initially on the following tasks:

1. Determining a pool of candidate solvents based on theoretical performance expectations (initial candidates).
2. Solvent screening for sulphur solubility at low pressure

3. Solvent screening for sulphur solubility over a range of conditions including down hole conditions
4. Chemical and thermal stability measurements at down hole and surface conditions
5. Physical and Chemical properties measurements at various conditions.

To assess the overall performance of a solvent, under given conditions of temperature  $T$  and pressure  $P$ , and from purely a sulphur pick-up and/or regeneration capacity perspective, we have defined the parameter Delta Sulphur as follows:

$$\Delta S_{\text{Solvent}}(T, P) = S_{\text{Solvent}}(T_0, P_0) - S_{\text{Solvent}}(T, P); S \text{ being measured in weight percentage.}$$

This parameter compares the solubility  $S_{\text{Solvent}}$  of sulphur in the solvent at  $T$  and  $P$  conditions to its solubility at reference conditions  $T_0 > T$  and  $P_0 > P$ .  $T_0$  and  $P_0$  can represent, for example, down hole conditions. A large solubility difference value indicates that the solubility of sulphur decreased at low temperature and therefore elemental sulphur precipitated from the solvent and the sulphur is not bound in the solution. A low difference indicates either the overall solubility of sulphur is low or the sulphur is bound in the solution and regeneration of the solvent will be more difficult.

The apparatus used at GTI for performance of the high-pressure tests to simulate down hole conditions is shown in Figure 2. The unit is from Autoclave Engineers and is a high pressure cell which features a mixer, heating control and the ability to gather liquid and gas samples. The test apparatus is qualified to be used at pressure of 340 bars and 300 °C. For this testing the routine operation was at 238 bar, a temperature range of 80 – 150 °C, containing a gas mixture of 30% hydrogen sulphide ( $\text{H}_2\text{S}$ ), 3% carbon dioxide ( $\text{CO}_2$ ), a slight excess of water in a balance of methane. The sulphur solvent occupied approximately  $\frac{1}{2}$  of the volume of the reactor cell and the gas occupied the other half. Shown in Figure 2 is the high-pressure test unit as assembled for testing. Significant care was taken to ensure that the liquid sample lines were heat traced so that the samples taken would flow freely and that solid sulfur would not form and plug the lines during sampling.

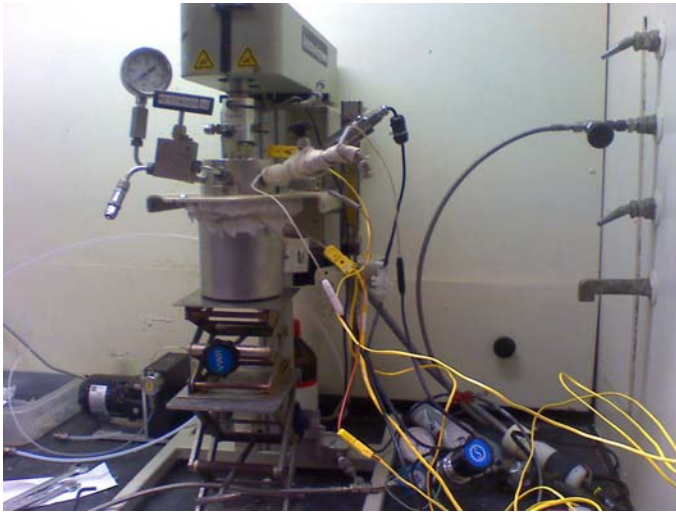


Figure 2: High-Pressure Reactor as Assembled for Testing

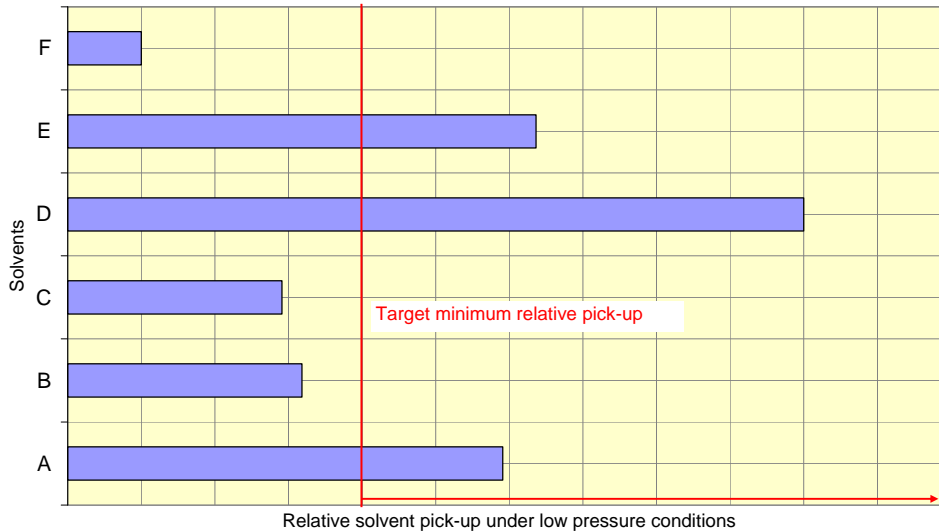
### ***Solubility Test Results and discussion***

Solvents were initially screened at low pressure conditions to determine a baseline for elemental sulphur solubility. Each solvent was tested for sulphur solubility at two temperatures. These represent respectively the anticipated temperature ( $T_{\text{feed}}$ ) of the sulphur loaded solvent feeding the crystalliser unit and the solvent regeneration temperature itself ( $T_{\text{regen}}$ ). The pressure being low at both locations and reasonably unchanged, the experiments were conducted under atmospheric pressure conditions  $P_{\text{atm}}$ .

Each solvent was also tested for its ability to be regenerated by cooling, i.e. by verifying that solid sulphur forms in solution in every solvent that is cooled to  $T_{\text{regen}}$ . For each solvent “i”, we have calculated the parameter  $\Delta S_i$  at the regeneration conditions, with the feed conditions taken here as the reference conditions, i.e.:

$$\Delta S_i(T_{\text{regen}}, P_{\text{atm}}) = S_i(T_{\text{feed}}, P_{\text{atm}}) - S_i(T_{\text{regen}}, P_{\text{atm}})$$

The calculated  $\Delta S_i$  is a measure of the sulphur pick-up of solvent “i” in the low pressure tests. For the purpose of this initial screening, a minimum target pick-up performance was set in comparison with the best performer. Figure 3 shows the relative sulphur pick-up of the solvents (ratioed to the best pick-up) and illustrates how the solvents are compared to the best performer: candidates A, D and E are the top three performers with a clear advantage for solvent D. The solvent F has clearly very low sulphur solubility. All tests have been repeated to confirm these results.

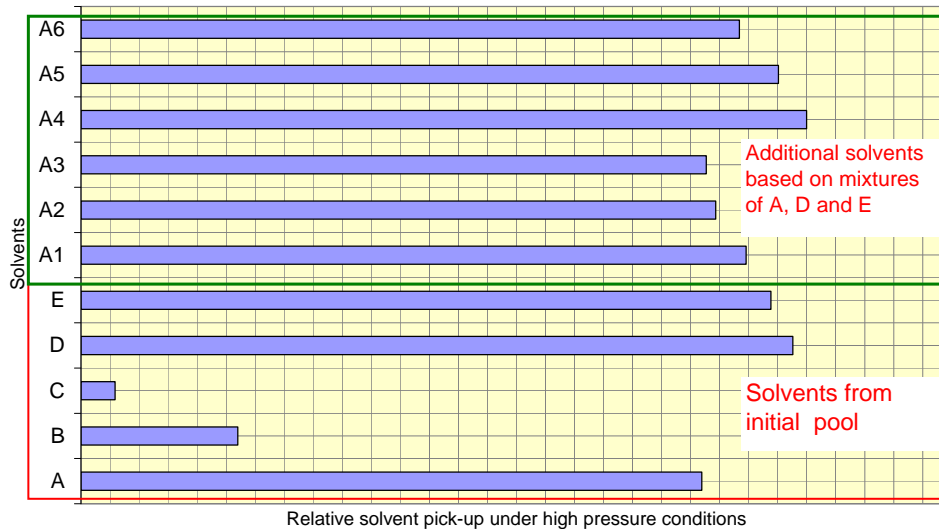


**Figure 3: Solvent Screening for Sulphur Solubility at Low Pressure**

In addition, each solvent was tested for the effect of water addition and also in presence of  $H_2S$  to evaluate the effect of water and  $H_2S$  on sulphur solubility at atmospheric pressure. After those tests were complete, amounts of additives were added to each solvent with continuing saturation of the mixture with  $H_2S$ . These tests were performed to determine if these additions would cause the mixture to increase sulphur solubility due to the formation of polysulphanes, i.e. if the mixture becomes a chemical solvent. The results are the following:

- The addition of water did not have a significant effect on the solvent sulphur solubility.
- The addition of  $H_2S$  did not have a significant effect on the solvent sulphur solubility, nor did the addition of  $H_2S$  to the liquid interfere with the analytical measurement of solid sulphur in the liquid.
- The additives may have a slight negative impact upon sulphur solubility, indicating no formation of polysulphane under atmospheric conditions. It was expected that their addition would promote polysulphane formation. The “slight negative impact” on sulphur solubility is probably due to addition of components, which have lower sulphur solubility than base sulphur solvent in the test.

In parallel to the above experimental work, an investigation of the commercial availability of pre-selected solvents indicated potential serious difficulties in procuring some of the solvents in large quantities, most notably solvents D and E, unlike solvent A. This is a non-negligible factor affecting the solvent ranking in favour of A, providing subsequent tests do not reveal any disadvantage in using this solvent. To move forward with the experimental program, i.e. high-pressure testing, it has been decided not to fully discount solvents D and E given their high performance. A new pool of nine solvent candidates has therefore been created with the inclusion of new formulations (solvents A1- A6) well concentrated in solvent A with additives of various mixtures from D and E. The intent of these new formulations was to improve the performance of A with small additions of solvents D and/or E since they have exhibited higher sulphur pick-up capabilities at low pressure conditions in the first round. Solvents B, C and F were also tested for final confirmation of their low performance.



**Figure 4: Solvent Screening for Sulphur Solubility at High Pressure**

The second round of tests confirmed the expectations, as it can be seen in Figure 4, under the high pressure conditions:

- Solvents B and C continue to have the lowest performance.
- Solvent F exhibited a very high viscosity to an extent that the test was not continued.
- Solvents D and E perform better than A, with solvent D being the best performer. All solvents A1- A6 have also better performance than A.
- A4 revealed to be the best sulphur solvent, followed by D and A5, indicating the benefits of the selected formulation.

It has now been confirmed that the best solvent formulation arrived at was derived from a suitable mixture of A, D and E. At an industrial scale, from a logistics point of view, and to achieve the above performance, it is important to secure the required volumes of D and E to maintain rigorously the appropriate relative proportions of the three components; otherwise the performance can significantly be affected. To be conservative, and in the remainder of this paper, it is assumed that A is the selected solvent for the DSR process design, with potential improvements by minor quantities of solvents D and/or E.

It has also been established that the sulphur pick-up capacity of a solvent is affected by the presence of heavy hydrocarbons present in the well stream. These are known to have a limited sulphur pick-up capacity and therefore, if present, reduce the circulating solvent sulphur removal efficiency.

#### ***Degradation Tests Results and discussion***

The DSR solvent must be thermally stable and resistant to degradation when subjected to the process operating conditions; otherwise the process will not be economically viable. Therefore, the best DSR solvent formulation was subjected to degradation testing. The DSR solvent degradation tests were performed in the high pressure cell shown in Figure 2, at 238 bar, in a methane, water, CO<sub>2</sub> (3%), and high H<sub>2</sub>S (30%) environment. The best solvent formulation was heated to 80, 120 and 150 °C, and sampled at intervals across approximately 340 hours to determine the effects of the environment on the solvent, i.e., the degradation rate of the solvent at down hole conditions.

For each degradation test, the samples were analyzed by gas chromatography. The analytical results of each component of the DSR solvent formulation for the samples gathered after the t = 0 hour sample were ratioed to the t = 0 hour sample for comparison. By this method all changes in amount from the starting concentrations of each component of the DSR formulation can be measured, i.e., degradation can be determined.

Using the data from the test at 150°C and considering a worst case scenario of a degradation rate of  $2.0 \times 10^{-5}$  (hour<sup>-1</sup>), then a degradation of no more than 2-3% of the inventory of DSR solvent can be expected for a full year. This degradation rate is calculated by determining that the DSR solvent will only spend a limited time at the elevated 150 °C temperature subjected to harsh conditions causing degradation. However, in a more realistic scenario, many applications of the DSR process the solvent degradation rate will be much lower. This is because there is no sulphur precipitation at locations where the temperature exceeds 120 °C and therefore there is no requirement for solvent injection near bottom hole but at a depth where the temperature is around 120°C, temperature at which the solvent degradation rate is reduced. This degradation rate will be better determined in the field pilot unit due to the sampling and analytical variability associated with lab data. For example, the field pilot will operate for months on a real gas stream whereas the lab data was only operated for 340 hours in a simulated gas atmosphere, i.e., a greater degree of confidence will be gained from the pilot data.

### Viscosity Results and discussion

The final samples of the degradation tests from above were also analyzed for viscosity. A Brookfield Engineering Viscometer was used to analyze the final solvent after the degradation test was performed to determine the effects of degradation on the viscosity of the solvent. The results are shown in Figure 5.

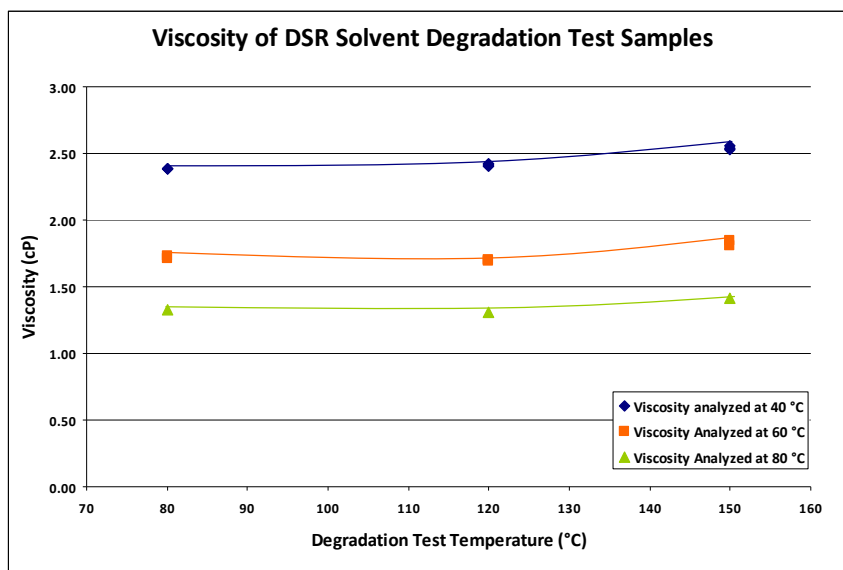


Figure 5: Viscosity of the Final Solvent Sample from Each Degradation Test.

The viscosity results indicate that after over 340 hours of degradation testing, the sample that was subjected to the highest degradation temperature, i.e., 150 °C, shows a slight increase in viscosity. This increase in viscosity is very minor and will not present a problem for pumping and process flow considerations. In addition, during the operation of the process, the sulphur solvent will have a makeup rate that will be larger than the degradation rate due to various loss mechanisms of the solvent. These other potential solvent losses are in the vapour phase with the gas at the inlet separation vessel located upstream of the crystalliser, in the separated water, and in the filtered sulphur. The losses will be replenished with a fresh makeup stream of sulphur solvent. The sulphur solvent makeup rate will maintain the viscosity level and prevent it from consistently increasing overtime, i.e., a steady state will be achieved. Even though all viscosity tests performed in the lab work have indicated that the DSR process should not suffer from problems due to increased viscosity of the circulating solvent, Total and CrystaTech are prepared to take steps to add viscosity modifiers to the process in the field pilot test unit if necessary.

### Health, Safety and Environment (HSE) Requirements

Unlike the existing commercially available sulphur solvents used in other technologies such as amines, hydrocarbon oils or organic disulphides, the selected solvent for the DSR process is a more “operator friendly” solvent due to its physical and chemical properties: it does not exhibit a strong odour and is easily handled in operation as confirmed during the surface pilot testing program, which is described later in this paper. In addition, and as shown in Figure 1, the DSR design features standard equipment and is inherently safe. The DSR unit will be typically required for sour gas reservoirs and therefore will be installed at sour gas plants, requiring no special or extra HSE precautions other than those covered by routine HSE already associated with high-pressure sour gas plants. Depending on the intended sour gas plant design, the sulphur filters may be the

only equipment that would potentially involve dedicated operational procedures and precautions that are not required for the other equipment.

## Stage 2 – DSR process design – Key considerations

The efficiency of the Down hole Sulphur Recovery design is governed by a number of important aspects that will be carefully investigated, these can be summarised as follows, but are not necessary limited to:

- The quality of the thermodynamic representation and the predictions of the well stream conditions and properties:  
An important and complex piece of work has been conducted to carefully include the elemental sulphur in the well-stream composition and to represent the thermodynamic properties of various sulphur species, and more particularly the sulphanes as it is almost impossible to determine experimentally their speciation. In the case of a sour gas condensate, the phase behaviour is complex: the sulphur is partially soluble in the liquid condensate and H<sub>2</sub>S is partially soluble in the sulphur liquid phase. Therefore the liquid/solid transition in the sulphur phase is shifted to lower temperatures compared to pure sulphur under the same P&T conditions. Rigorous calculation requires taking into account all the sulphanes and sulphur allotropes. Chemical and phase equilibrium must be modelled simultaneously in the reservoir but most of the reactions are quenched along the production pathway. Therefore the precipitation of elemental sulphur in a sour gas during production can be obtained from a simple phase equilibrium calculation. The sulphanes are considered to be stable species at the production timescale. The transition between liquid and solid sulphur phase can also be obtained from thermodynamic calculation but there is a lack of reliable data on the mutual solubility of sulphur and hydrocarbons under high H<sub>2</sub>S partial pressure. The sulphur solubility in a sour gas depends mainly on H<sub>2</sub>S content, pressure and temperature.
- The sulphur pick-up capacity of the solvent throughout the well up to surface:  
This is determined from a correlation that has been obtained from the experimental program. The calculated solubilities are measured over a range of temperatures and are underestimated at higher temperatures. This means that the calculated pick-up capacity may lead to over estimated solvent injection rates depending on the well pressure and temperature profiles. This is a conservative approach from a sulphur pick-up perspective.
- The thermal regeneration of the solvent by cooling in the crystallisation unit:  
The regeneration temperature is one key process parameter that can affect not only the overall performance of the system but also the size of some of the DSR equipment. Careful attention should also be paid to the sensitivity to condition changes throughout the entire production life. Minimising the regeneration temperature helps reduce the solvent injection rate requirements; however site conditions such as the nature and the availability of cooling medium may represent limiting factors.
- Filtration performance and generated sulphur management:  
For large sour gas fields where sulphur deposition is a problem, the quantities of separated sulphur may be relatively important and may require appropriate treatment or disposal solutions. Consideration will be given to growth of sulphur particles in the crystalliser as it may affect the performance of the downstream filters. Particularly, the solvent residence time in the crystalliser is a parameter that needs to be optimised and could affect, for example, the number and the arrangement of the crystallisation units.

As it can be understood from above, it may be challenging and complex to determine the required sulphur solvent injection rate in a given well. As a proposed methodology for a given case, it is necessary to answer the following questions:

1. Is there a risk of sulphur precipitation in the well and what are the associated conditions?  
For a given well design and architecture, pressure and temperature profiles shall be determined from bottom hole up to wellhead. As a first approximation, presence of solvent may be ignored. These profiles are then used to check for sulphur precipitation in the well, taking into account the effect of presence of H<sub>2</sub>S and the thermodynamic equilibrium between all sulphur species at regular locations in the well. Using the appropriate thermodynamic representation as discussed above, it is possible to predict the location where the sulphur starts to precipitate, its phase (liquid or solid), the associated conditions and quantities.

It is prudent to mention that these complex calculations do not take into account any kinetic or hydrodynamic sulphur precipitation retarding effect. Additionally, the content of sulphur in the reservoir natural gas needs to be validated by actual sampling and measurement.

2. Is there a risk of sulphur precipitation in the flow lines and surface facilities? This is obviously answered when typical process conditions are determined.

If the answer to either or both questions confirms the potential for sulphur deposition then the solvent is required and its minimum injection rate can be determined from the lowest operating temperature,  $T$ , upstream the DSR unit and the solvent regeneration temperature,  $T_{\text{regen}}$ . It is important to note that once regenerated, the solvent will always contain residual sulphur that corresponds to the solvent saturated with sulphur at  $T_{\text{regen}}$  and therefore the solvent rate shall account for both this residual sulphur and the sulphur coming from the well stream. In addition, the effect of this residual sulphur in the solvent once injected in the well shall be carefully examined as its content may be, in some cases, important enough to approach or exceed the sulphur in the well stream and to contribute to the sulphur deposits. The solvent regeneration temperature,  $T_{\text{regen}}$ , needs to be suitably selected to minimise the residual sulphur content and therefore the solvent circulation rate. However, credit shall be given to other factors as well, such as the specific site conditions (nature and availability of cooling medium, or presence of buried sections of lines that can lead to high temperature drops from wellhead to Gas Plant Treatment, etc.).

All the above considerations will yield a minimum solvent rate that could be further reviewed for some other considerations that include but are not necessary limited to:

- Impact of the solvent on the pressure and temperature profiles, especially when the solvent rate is important.
- Solvent behaviour throughout the well; especially when the solvent rate is low enough to disperse the solvent in the well stream.
- Solvent dilution with hydrocarbon species that will modify the pick-up capacity and will require higher solvent injection rates.
- Solvent ageing, etc.

To complete a proper design, it is important technically and economically to integrate the solvent make-up requirements taking into consideration all potential solvent losses' possibilities: in gas/liquid/water separation, in the filtration, in produced sulphur or by degradation. To summarise, the whole design of the DSR can be a complex problem solving exercise that requires a designer to integrate the knowledge of sulphur species thermodynamics, the reservoir conditions, the well stream data, the well design architecture and the surface conditions.

### Stage 3 – DSR surface pilot testing

A key mechanical element of the DSR process is associated with the crystallisation and separation of elemental sulphur from the solvent once separated from the gas stream. Various crystallisation techniques have been investigated to ensure a robust method is selected since crystal formation is basically the heart of DSR. One key to good crystallisation is to have adequate nucleation sites of which are mainly sulphur and to reduce the crystal growth on unwanted surfaces, like vessel walls and piping. Numerous crystallisation methods are used in the industry and more particularly in the pharmaceutical sector. These approaches involve for example evaporative, direct refrigeration, and mixed suspension techniques. Batch crystallisers are not feasible for use in the DSR process as the overall volume of the system would increase dramatically due to the need for accumulation tanks. Furthermore evaporative crystallisers are not an option due to the very low vapour pressure of the DSR solvent, i.e., it does not readily evaporate. Over the years, CrystaTech has evaluated mixed suspension, spouted-bed and surface cooled techniques for removing solid sulphur from hydrocarbon based solvents.

In the mixed suspension design, a cool, sulphur solid containing slurry is recirculated in a loop to and from a slurry tank. The hot dissolved sulphur solvent from the flash tank is added to this loop, is cooled and the sulphur grows onto the existing solids circulating in the loop. The sulphur solids are removed from the tank by filtration.

In the spouted-bed crystalliser design, a cool lean solvent flows from the overflow weir from the top of the crystalliser tank where the hot dissolved sulphur solvent from the flash tank is added to that stream and then the combined stream flows through a Teflon® heat exchanger to reduce the solvent temperature; the stream flows back into the bottom of the same crystalliser, i.e., a spouted-bed crystalliser. The combined stream (from the flash tank and the crystalliser overflow) cools and becomes super-saturated in sulphur content; the combined stream enters the bottom of the spouted bed crystallizer where the sulphur contacts existing sulphur solids inside the spouted-bed crystalliser and grows onto those existing solids. The sulphur solids are removed from the crystalliser by filtration.

In the surface cooled crystalliser design, the hot sulphur rich stream flows from the flash tank through a scraped surface crystalliser. This crystalliser is a shell and tube heat exchanger and inside that crystalliser the temperature of the surface of the pipe is reduced where sulphur solids form. A rotating scraper passes over the surface of the pipe and scrapes the formed sulphur off the surface into the flowing solvent stream inside the pipe. The sulphur slurry then flows into a slurry tank. The sulphur solids are removed from the slurry tank by filtration and the lean solvent overflow of the tank is returned to the process.

The crystalliser that is best suited for the DSR application must have the following features and characteristics:

- Suitable for high solids throughput
- Suitable for large process fluid-coolant temperature differences
- Limited footprint
- Modular in design and flexible in operation

A preferred crystalliser design has been chosen and has been evaluated in a surface pilot test in Texas, USA. The results of the testing are described below.

Various sulphur filtration and purification techniques have been researched for the DSR application and three main technologies have been pre-selected for DSR for their solvent separation performance and for the expected sulphur quality. The filtration of DSR solvent can be problematic due to the presence of hydrocarbon vapours, both light and heavy hydrocarbons, and dissolved H<sub>2</sub>S in the circulating solvent. Therefore minimum requirements for the filtration devices are:

- Filtration must be performed in a closed system.
- Purging of hydrocarbons and H<sub>2</sub>S from the filtered sulphur must be possible.
- Ability for multiple solids washing steps.
- Vapour handling available for when product is discharged.
- Containment of liquids away from final product to minimize contamination if there are mechanical problems during filtering or during filter cleaning steps.

The three styles of filters selected are filter press (vertical or horizontal), pressure filters, and centrifuge. One representative from each filter style was tested at the surface pilot and operational and performance data was gathered. The filters tested were test or rental filters, but were intended to provide the necessary data collection to design and size the filters for the field pilot and commercial applications. A summary table of the filters tested is provided in Table 1 below:

**Table 1: Filters tested at the surface pilot**

	<b>Filter Press</b>	<b>Pressure Filter</b>	<b>Centrifuge</b>
<b>Manufacturer</b>	Andritz	Oberlin	Western States
<b>Design comments</b>	Vertical membrane	Indexing belt pressure filter	Perforated bowl centrifuge
<b>Tested filter area</b>	4135 cm <sup>2</sup>	290 cm <sup>2</sup>	1700 cm <sup>2</sup>
<b>Filter media</b>	Woven polypropylene	Woven polypropylene	Woven polypropylene
<b>Average Cake thickness</b>	25 mm	50 mm	50 mm
<b>Cycle time</b>	50 min	20 min	30 min

Each of the filters tested worked well from a solid separation standpoint and did not pose any mechanical problems during the test. A picture of the produced sulphur generated from the centrifuge tests is presented in Figure 8. The other filtration techniques provided similar products at completion of their filtration cycle.

The surface pilot testing program provided valuable insight and proper design and operational information that will translate well to a field pilot unit and therefore to a commercial unit. The main purpose of this testing was to validate laboratory results, optimise and operate the technologies that were pre-selected for the DSR unit. It also covered analysis of the produced sulphur and validation of the sulphur purification process.

For this purpose and as illustrated in Figure 6 below, a closed loop system was designed accordingly whereby rich solvent was chilled in the crystalliser and sulphur was separated and filtered.





Figure 7: Surface Pilot Unit and Produced Sulphur.



Figure 8: Produced Sulphur from the Surface Pilot Unit.

## CONCLUSIONS

While producing sour gas from certain formations, solid sulphur has been observed to deposit on the well tubing, causing gas production to diminish and ultimately stop. Total and CrystaTech have developed a regenerable solvent-based process to prevent the formation of sulphur deposits in natural gas production wells and in the surface circuits and facilities. Unlike existing once-through technologies, DSR is designed for centralised treatment of a gas field and high sulphur throughput. A successful surface pilot was recently operated in Texas, and the technology is now ready to be implemented in a field pilot. This single well application will be used to develop commercial scale-up and economic data.

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## NOMENCLATURE

*DSR* = Down hole Sulphur Recovery

*T* = Temperature

*P* = Pressure

*S* = Sulphur solubility in a solvent (expressed in weight %)

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