METHOD OF PREVENTING HYDROGEN SULFIDE CORROSION AND EMBRITTLEMENT

Theodore M. Swanson, El Cerrito, Calif., George H. Calhoun and William E. Bingman, Midland, Tex., and Richard S. Treseder, Oakland, Calif., assignors to Shell Oil Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed Jan. 25, 1967, Ser. No. 611,547

Int. Cl. C25F 15/00, 11/04

U.S. Cl. 21—2.5

5 Claims

ABSTRACT OF THE DISCLOSURE

A method of preventing sulfide stress corrosion cracking of metals in contact with hydrogen sulfide containing fluids by contacting said metals with hot sour gases at a temperature of at least 150° F.

The present invention is directed to inhibiting and preventing corrosion cracking and embrittlement, and particularly sulfide stress corrosion cracking of metallic equipment used in recovery of sour effluents, e.g., sour gas and/or oil, from underground formations which products are thereafter processed in refinery equipment to produce sweet natural gas and oil products as well as sulfamic and sulfur-containing products such as organic sulfides and the like.

In the production and refining of sour gas and/or oil the large amounts of hydrogen sulfide, carbon dioxide, water and corrosive acids present in such products renders the metal equipment such as casing, tubing, sucker rods, lead lines and refinery equipment susceptible to hydrogen sulfide corrosion and damage such as blistering, cracking and the like.

Sulfide corrosion, cracking and brittle transverse fracturing of steel under stress in hydrogen sulfide environments, is a serious problem in sour gas-condensate and sour oil production. Thus, the mechanism of such failure has not been satisfactorily established, it is considered to be a form of stress corrosion cracking modified by the embrittling action of occluded hydrogen resulting from corrosion by hydrogen sulfide. Failures due to corrosion and cracking have been experienced with tubing, casing, drill pipe, tool joints, and equipment such as valves and related equipment items. Such failures are extremely costly and hazardous to personnel.

Sulfide stress corrosion cracking is a particularly serious corrosion problem in the oil and gas production industry since the failure of alloy tubing in well in a sour gas-condensate field can be a major problem in view of the magnitude of the hazard caused by this type of failure. That is, failure of the casing or tubing or tool joints in such high pressure wells can result in loss of the well content and extensive damage to the producing formation which would entail severe economic loss.

Various means have been proposed to protect metals in this corrosive environment from corrosion and cracking, such as by use of protective coatings, additive inhibitors or by metallurgical means as described in U.S. Patents 2,560,351, 2,593,057 and 3,127,932 or by methods described by Treseder et al. in a paper entitled "Cracking of High Strength Steel in Hydrogen Sulfide Solutions" and NACE Report TP-16 of October 1952 on "Field Experience with Cracking of High Strength Steels in Sour Gas and Oil Wells." Most of the proposed methods are essentially ineffective for one reason or another or are impractical because the costs are too high.

It is an object of the present invention to protect metals from corrosion and embrittlement and sulfide stress corrosion cracking by sour effluents. Another object of the present invention is to inhibit and prevent hydrogen sulfide corrosion of metal equipment used in well recovery of sour gas. Still another object of the present invention is to inhibit corrosion, embrittlement, cracking and damage to refinery equipment processing sour gas. Other objects of the present invention will be apparent from the following description of the invention.

It has now been discovered that equipment used in recovery of sour effluents, e.g., sour gas and oil, from sour wells, as well as refinery equipment and pipelines handling such sour products or where hydrogen sulfide is generated in refinery processes, can be effectively protected against corrosion, embrittlement, cracking and general damage, such as is generally known in the art as sulfide stress corrosion cracking, by contacting such metals with hot sour gas or oil or generated hydrogen sulfide containing hydrocarbons at a temperature of at least 150° F, and preferably between 200° F. and 450° F. Thus, equipment used in well recovery of sour gas or oil, e.g., tubing, casing and sucker rods and the like, can be effectively protected against corrosion by circulating through and around such equipment, e.g., casing and tubing, hot sour gas or oil within a temperature range of from about 200° F. to about 450° F., which may be a non-processed recovery sour gas or oil from the well well being produced or the hot sour gas oil may be obtained from any suitable source.

Although the mechanism of why hot sour gas at between about 150° F. and 450° F. protects metals against corrosion and sulfide stress corrosion cracking is not clearly understood, nevertheless it has been found that various ferrous metals and alloys can be effectively inhibited against corrosion in such corrosive environments as is normally encountered in recovering and processing sour gas and oil, namely by maintaining the temperature of the metal and contacting sour effluent at a temperature between 150° F. and 450° F. Metals effectively protected against corrosion and hydrogen embrittlement by this means include conventional metal produced used in well equipment such as casing, tubing, drill pipe, etc., including steels of API grades N-80, P-110, etc., casing and tubing, P-105 tubing, and grade E and stronger drill pipe and tool joints, and conventional refinery steel equipment used in processing sour gas and oil. As defined and referred to in this invention, hot sour gas or hot sour oil contain at least 0.005 of one mole percent and generally between about 0.05 of one percent and about 45 mole percent hydrogen sulfide and the balance can be essentially hydrocarbons. Impurities naturally present in such sour products are normally present in amounts of up to 10% but are sometimes as high as 55 mole percent and include acidic products, e.g., CO₂, organic acids and the like. It is preferred that these impurities be removed prior to using the hot sour product as a corrosion inhibitor. A sour gas which on heating to above 150° F. and used as an inhibitor can be obtained from any suitable source and by numerous drilling recovery means. Generally, in drilling in sour gas fields for recovery of the gas for further processing to remove carbon dioxide, sulfur, hydrogen sulfide and the like in order to obtain on processing a suitable sweet gas, a portion of the sour gas as recovered can be heated to at least 150° F. and used as the corrosion inhibiting agent.

The hot sour gas or oil can be used per se or as an additive in a suitable hydrocarbon vehicle such as an oil base and the entire mixture heated to above 150° F. and used as a corrosion inhibiting composition. In addition, if desired, conventional oil additives such as foaming agents, surfactants and the like can be added to the hot sour gas or oil.
Hot sour gas is particularly applicable in protecting well equipment such as tubing, casing and drill pipe against corrosion and cracking by contacting such equipment with hot sour gas at between 200° F. and 450° F.

The pronounced effect of temperature on hot sour gas in reducing its tendency to embrittle and crack metals such as P-grade tubing and casing and tool joint (i.e., drill pipe) steel is shown in Table I.

**Table I.** - Effect of Temperature on Sulphide Corrosion Cracking of High Strength Steels

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature, ° F.</th>
<th>S.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tool joint steel (low alloy steel) with hardness of 255 Brinell</td>
<td>200</td>
<td>0.06</td>
</tr>
<tr>
<td>70</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>P-100 casing (276 Brinell)</td>
<td>200</td>
<td>0.06</td>
</tr>
<tr>
<td>100</td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>

*Materials having values of about 10 or greater are considered satisfactory for use in sour service.

Additional advantages of the present invention are evidenced from the following examples, in which a total of 96,000 feet of hole have been drilled:

(a) Heated sour gas to 150-200° F. (three grains of hydrogen sulfide per 100 c.c.f.) was used to drill the 14,000 to 15,000 foot area Ellenburger gas wells, Crockett County, Tex. Drilling conditions in the area were such that no water intrusion from surface to top of the Ellenburger at approximately 12,200 feet was encountered. The use of hot sour gas in this manner has drilled seven wells in this field yielding an approximate savings of $175,000 as compared with the best alternative, air drilling.

(b) Heated sour gas at 150°-200° F. (99 grains of hydrogen sulfide per 100 c.c.f.) was used to drill 2537 feet of 6½ inch diameter borehole in an 18,000-foot well, West Waha Field, Reeves County, Tex. This test further confirmed the advantage of using heated sour gas as a drilling fluid for the 13,090 to 15,627-foot interval. A saving of approximately $37,000 was realized from this procedure, compared with the cost of conventional mud drilling.

(c) Hot sour gas was also used in drilling Mitchell 110-1, Brown-Bassett Field, Crockett County, Tex., in which some 6,700 feet have been drilled by this procedure. Drilling cost reductions of some $15,000 have been realized in this well both because of the much faster drilling rate and the equipment protection (from H₂S corrosion and embrittlement) afforded by the hot sour gas.

We claim as our invention:

1. A method of protecting metal surfaces against hydrogen sulfide corrosion and embrittlement used in the recovery and processing of our fluid, the improvement comprising heating said sour fluid to above 150° F. and thereafter contacting said metal surfaces with the hot sour fluid and maintaining the temperature of the hot sour fluid at above 150° F.

2. The method of claim 1 wherein the metal surfaces are metallic equipment used in recovery and refining processes and the hot sour fluid is sulfur gas consisting essentially of a mixture of hydrogen sulfide and hydrocarbons heated to 150-450° F. and maintained at said temperature while in contact with the metal surface.

3. The method of claim 2 wherein the hot sour gas temperature is heated to and maintained at between 200-400° F.

4. The method of claim 3 wherein the hot sour gas contains 20-45 mole percent hydrogen sulfide.

5. The method of claim 1 wherein the hot sour fluid is added to an oil base and the mixture heated to above 150° F. and maintained at said temperature while in contact with the protective metal surface.

References Cited

UNITED STATES PATENTS

2,461,359 2/1949 Viles et al. 252—8.55

LEON D. ROSDOL, Primary Examiner

I. GLUCK, Assistant Examiner

U.S. Cl. X.R.

203—7; 208—47; 252—8.55, 387, 388, 399