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PIPE-LINE CORROSION INHIBITION

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The present invention relates to methods for the prevention of internal corrosion in ferrous metal pipelines carrying crude petroleum and the like.

It is well known that pipelines formed of iron or soft steel are subject to severe internal corrosion and pitting them when used to convey crude petroleum oils, the rate of corrosive attack being particularly high when transporting crudes from fields in the West Texas, New Mexico and other areas where the sulfur content of the crudes is relatively great. In the past it has been assumed that the corrosive attack on ferrous metals by such crudes was due to the acidic nature of the crudes and various attempts made to reduce the corrosivity of these oils by neutralization of the crudes prior to passing the same through pipelines. These attempts have been generally unsuccessful from the standpoint of operating practicability, effectiveness of corrosion reduction or economic feasibility.

According to the instant invention it has been found that the primary cause of ferrous metal corrosion by crude oils containing relatively large amounts of sulfur is the sediment normally occurring in pipelines carrying such crudes. The exact chemical nature of the corrosive components of such sediments is difficult to determine and is variable; however, it appears that at least a major portion of the corrosive action is due to the presence of iron polysulfides with or without additional free or loosely combined sulfur. For the purpose of the present specification, the term "sulfide sediment" is intended to include sediments adhering to the interior walls of a pipeline or settled on the bottom thereof, and containing iron polysulfides with or without additional loosely combined sulfur, and/or free sulfur or other corrosive compounds containing sulfur. Other components of crude oil such as brine and various compounds of hydrogen and sulfur appear to be but minor factors in the corrosive attack of such crudes on ferrous metals, these compounds however tending to accelerate the corrosive rate of sulfide sediments.

It is an object of this invention to provide methods for reducing the corrosive attack of sulfide sediments on ferrous metals to a satisfactory minimum in an effective and economical manner.

It has now been found that the corrosive sulfur components and sulfide sediments may be converted to non-corrosive sulfides by the action of substantially hydrocarbon-insoluble non-oxidizing alkaline agents capable of converting iron polysulfides to lower sulfides. For convenience

these materials may be called "desulfurizing agents." Suitable examples of such agents include the alkali metal hydroxides, monosulfides, hydrosulfides, selenides, tellurides, hyposulfides ($\text{Na}_2\text{S}_2\text{O}_2$) and their formaldehyde complexes, silicates, aluminates, arsenites, etc., particularly the sodium and potassium compounds of the foregoing, the monosulfides and hydroxides of calcium, the monosulfides of ammonium, etc. Strong oxidizing agents such as alkali nitrites, chromates, etc., which normally serve to passivate iron and thus render it resistant to corrosion, are generally unsatisfactory for the purpose of this invention and, on the contrary, as they react with hydrogen sulfide normally contained in sour crudes to release sulfur and/or corrosive sulfur compounds they would defeat their useful purpose in such applications.

It has been found that the action of the above group of desulfurizing agents on sulfide sediments is ineffectual in solutions having a pH of less than 9. It is therefore necessary in treating sulfide sediments with desulfurizing agents to maintain the solution throughout the entire section of line under treatment and in which the reaction takes place at a pH of at least 9 and preferably at a pH of 10 or more.

One method of applying the above principles to the problem of preventing corrosion of ferrous metal pipelines, according to the instant invention, comprises the injection into a pipeline at intervals of unit volumes, or "slugs," of an aqueous solution of a suitable desulfurizing agent, the quantity and pH of the solution injected being sufficiently high to maintain a pH of at least 9 in the injected solution as it passes through the section of pipeline under treatment. For purposes of illustration, it may be stated that when sodium hydroxide is used as the desulfurizing agent, the size of the unit volume injected may vary from 2 to approximately 100 gallons, the concentration of sodium hydroxide in the injected solution being at least approximately 15% by weight and preferably of the order of 30% by weight or higher. The optimum concentration of the sodium hydroxide solution, quantity injected and frequency of injections will be found to vary considerably, depending upon the particular conditions at hand, as will be discussed below. Generally speaking, it has been found that from approximately .5 to 10.0 gallons of a 30% by weight sodium hydroxide solution provide satisfactory protection for 1000 feet of pipeline under average conditions, the unit volume injected

tion being repeated for each 500 to 2000 barrels of crude oil passed through the pipeline.

Crude oil pipelines may roughly be divided into three groups: gathering lines, laterals and trunk lines. Most serious corrosion is usually experienced in gathering lines, and this is probably due in part at least to their being used quite irregularly. A link of a gathering line may be operated a few hours per day or per week and during the remaining period remains idle. It is during the idling period that corrosion usually proceeds at the most accelerated rate. Gathering lines moreover are relatively short, generally only a few miles in length at the most. For these reasons, the present treatment is particularly applicable to gathering lines.

As has already been indicated, the size of the unit volumes of desulfurizing agent injected, the concentration of desulfurizing agent in the solution injected and the frequency of injections, may vary rather widely, and recommendations regarding the magnitude of these variables can be made only in general terms. In many cases they can only be determined by experimental trial methods. It may be stated, however, that in all instances the desulfurizing solution should be injected as rapidly as possible in order that the ideal condition is approached wherein the unit volume of treating solution is entirely separated from the crude oil except at its ends. In those instances where it is not impractical to interrupt the flow of crude oil through the pipeline for a period of time sufficient to inject the required quantity of desulfurizing solution, such procedure may be followed. On the other hand, in those cases where it is either undesirable or impractical to interrupt the flow of crude oil through the pipeline the unit volume of desulfurizing solution is introduced into the oil stream as rapidly as possible, preferably at a rate such that the crude oil immediately after the point of injection contains not less than about 1% to 2% by weight of water in excess of its natural water content. As the oil moves through the pipeline, the desulfurizing solution may spread through a further portion of the moving column of oil, thereby neutralizing or alkalinizing acidic brines which may be present. The acidic brines present in that portion of the oil into which the desulfurizing solution is injected will, of course, also be neutralized or rendered alkaline to a large extent. However, the main portion of each unit volume injected should remain substantially intact, distributed through a relatively small portion of the moving column of oil, and if several unit volumes are injected at short intervals they should form a train in the moving column of oil, each unit of desulfurizing solution in the train extending over as small a length of pipeline as possible in order to minimize reaction with the acidic constituents of the crude oil.

The method of injection will also depend on the emulsifying tendency of the crude oil. If the crude emulsifies very readily, the desulfurizing solution is advantageously injected into the line, while the flow of the crude has been stopped momentarily. If there is some tendency to emulsify which is not excessive, the treating solution may be injected into the flowing stream of the crude at any desired point. If the oil emulsifies with difficulty the treating solution may be advantageously introduced into the suction side of the crude oil pump—if a pump is used—to effect thorough mixing in the pump, otherwise the caustic may drop out and accumulate in bends

and low places; if a pump is not employed, the treating solution may be premixed with a quantity of the crude. Thus the topography of the pipeline is also an important factor in its bearing on the most suitable point of injection. In pipelines including sharp rises and dips, emulsification is preferably induced in order to avoid settling out of bodies of desulfurizing solution in low points along the line. In level or gently sloping lines, on the other hand, emulsification is not necessary to carry the desulfurization agent and is generally avoided in order to minimize reaction between the treating agent and acidic constituents of the crude.

Since most crude oils contain some water which is usually acidic, the spreading of the desulfurizing solution through the crude as the latter moves through the pipeline reduces the concentration and potency of the solution. This spreading is a complicated function of several factors including the tendency of the crude to emulsify with the aqueous desulfurizing solution, the velocity of the crude through the pipe, the diameter of the pipe, the rate, method and location of the solution injection, etc. Spreading, while undesirable, cannot be completely avoided, particularly because, as has been stated already, a certain degree of emulsification is often essential in order to carry the aqueous desulfurizing solution along with the crude. In some instances, where the desulfurizing solution and crude emulsify with difficulty only, it was found that the desulfurizing solution settled out in low places of the pipeline, the crude merely passing over it.

It is apparent that a small unit volume of caustic will be more quickly dissipated and rendered too weak for effective protection than a larger one. Therefore, other factors being equal, a relatively large unit volume of equivalent concentration will protect a longer section of pipe line. However, as long as the pH of the effluent water that is carried by that portion of the crude oil to which the desulfurizing solution has been injected is maintained at 9 or higher, satisfactory inhibition will be attained.

In favorable cases it is possible to protect lengths of line between points of injection as much as 30 miles apart, although the maximum practical length may vary a great deal with various circumstances.

The requirement for a reserve alkalinity for brine neutralization purposes also makes it clear that when the treatment of a pipeline is begun for the first time, the original unit volume of treating solution may have to be much larger than the volumes following, at times as much as 5 or 10 times as large. This is particularly true in the case of an old line which contains accumulated sulfide sediment and often other salts or acids. Thus, while it was previously stated that the intermittent unit volumes of aqueous desulfurizing solution may be as much as about 100 gallons each, the initial unit may be several times that size, possibly 500 gallons or more. It is of course understood that the unit volumes following the first large injection need not all be of the same size. Depending on the condition of the pipeline, the sourness of the crude, its salt content, variations in source and composition, and other factors, the volumes of the injections may be varied and be adjusted from time to time. The important consideration is to maintain considerable excess alkalinity in the moving train of local mixtures to provide an effluent water pH of at least 9, as has been

pointed out before, and the smallest volumes and concentrations of desulfurizing solutions which will achieve this are obviously the most desirable.

If desired, the treatment may be augmented by one or several mechanical scrapings to remove deposits which are not readily removed by chemical treatment alone. In cases of very severe sulfide accumulation, a scraper may be passed through the line immediately behind a slug of desulfurizing solution.

The frequency of the injection can be estimated on the basis of at least one injection in each time interval represented by the passage of about 1,000 barrels of oil through the section of the line being treated, although considerable leeway is permissible. Since the flow of crude oil through various gathering line networks is normally an intermittent affair, influenced by a variety of uncontrollable factors, this figure would be subject to modifications in each particular case, for the sake of convenience in operation.

Assuming that sodium hydroxide is to be used in the treatment of a 6000 foot section of a four-inch pipe line through which the normal rate of flow is about 1 foot per second, about six gallons of 25% to 30% by weight sodium hydroxide in aqueous solution would be injected approximately every 18 hours exclusive of the idling time of the line.

As a specific example of the operating details of the invention, the treatment of a section of gathering line in the Roberts field in West Texas, adjacent to New Mexico, was carried out. The crude from this field is very sour and corrosion of the gathering lines was very severe prior to the treatment. In order to provide quantitative results for comparative purposes, the following method for determining the rate of corrosive attack of pipeline sediment on steel was devised. A weighed piece of polished, low carbon steel approximately 0.75 inch square and 0.05 inch thick is placed in a container and a known weight of pipeline sediment is evenly distributed over the steel specimen, entirely covering the same. Sufficient brine solution is then placed in the container to nearly fill the same and the top of the container is stoppered, leaving a small air space. After a given period of time has elapsed, the steel specimen is removed, washed, dried and weighed, the corrosion rate in inches per year being calculated from the weight loss over the period of the test. Using this method, a sample of sediment from the gathering line described above was tested and a corrosion rate of 0.13 inch per year noted.

The section of pipeline treated was 4 inches in diameter, 2000 feet long, and the average daily throughput of crude oil was 1000 barrels. Over a period of 25 days, 3 injections of 15 gallons and 18 injections of 10 gallons each of approximately 30% by weight aqueous sodium hydroxide were made. The average pH of effluent water carried by those portions of the crude oil in which treating slugs had been injected was approximately 10. At the end of the 25-day treating period a sample of sediment removed from the line was found to have a corrosive rate of 0.025 inch per year when tested in the above described manner.

Further decreases in the quantity and/or frequency of treating solution injected may be made as the corrosion rate of sediment contained within the pipeline continues to decrease, the essential criterion being to maintain a pH of at least 9

and preferably 10 or more in the treating solution as it exits from the pipeline.

Incidental to the elimination of corrosive components from sulfide sediments, the present treatment assists in breaking down sulfide deposits which tend to obstruct the free passage of oil through the pipeline. Thus, when operating according to the present invention the capacity of crude oil pipelines is often restored to a throughput at or near the original capacity before impairment by the gradual formation of sulfur containing scale deposits and the like.

Although the preceding specification deals primarily with the problem of corrosion of crude oil pipelines, it will be understood that certain other hydrocarbon oils, such as semi-refined distillates from various sources including petroleum oil, coal tar distillates, etc., may cause a similar type of corrosion. Regardless of the type of hydrocarbon oil, where the corrosion in a pipeline is of the type described above, treatment according to the present invention will be found suitable as a remedy.

We claim as our invention:

1. A method of decreasing sulfide sediment corrosion in a ferrous metal pipeline carrying a stream of liquid hydrocarbons, comprising the step of intermittently injecting into said pipeline a relatively concentrated aqueous solution of non-oxidizing hydrocarbon-insoluble desulfurizing material, which solution has a pH in excess of 9, to form columns of liquid containing said concentrated solution, said columns being separated from each other by columns of said hydrocarbons.
2. The methods of claim 1, wherein from approximately 2 to approximately 100 gallons of said concentrated aqueous solution is introduced in each injection step.
3. The method of claim 1, wherein the pH of the solution is in excess of 10.
4. A method of decreasing sulfide sediment corrosion in a ferrous metal pipeline carrying a stream of liquid hydrocarbons, comprising the step of intermittently injecting into said pipeline a relatively concentrated aqueous solution of non-oxidizing hydrocarbon-insoluble desulfurizing material, which solution has a pH in excess of 9, to form a train of columns of a mixture of said hydrocarbons and at least 1% by weight of said concentrated solution, said columns being separated from each other by columns of said hydrocarbons, the magnitudes of said columns being sufficient to maintain a pH of at least 9 in said columns while passing through the section of said pipeline under treatment.
5. A method of decreasing sulfide sediment corrosion in a ferrous metal pipeline carrying a stream of liquid hydrocarbons, comprising the step of intermittently injecting into said pipeline a relatively concentrated aqueous solution of non-oxidizing hydrocarbon-insoluble desulfurizing material in approximately 2 to 100 gallon portions to form columns of a mixture of said hydrocarbons and at least 1% by weight of said concentrated aqueous solution, said columns being separated from each other by columns of said hydrocarbons, the concentration of said desulfurizing material being at least about 15% by weight and sufficient to maintain a pH of at least 9 in the aqueous phase of said mixture while passing through the section of said pipeline under treatment.
6. The method according to claim 5 wherein the desulfurizing agent is an alkali metal hydroxide.
7. The method according to claim 5 wherein the desulfurizing agent is an alkali metal sulfide,

8. The method according to claim 5 wherein the desulfurizing agent is sodium hydroxide.

9. The method according to claim 5 wherein the desulfurizing agent is sodium sulfide.

10. The method of claim 5 wherein said concentration of said desulfurizing material is at least 30% by weight.

11. The method of claim 5 wherein said stream of liquid hydrocarbons is of crude petroleum oil and the injection step is repeated for approximately each 500 to 2,000 barrels of crude oil passed through the pipeline.

12. A method of decreasing sulfide sediment corrosion in a ferrous metal pipeline carrying a stream of crude petroleum oil, comprising the step of injecting into said pipeline approximately 0.5 to approximately 10 gallons of an aqueous solution containing at least approximately 30% by weight of sodium hydroxide for each 1,000 feet of said pipeline to form a column containing said aqueous solution.

13. A method of decreasing sulfide sediment corrosion of a ferrous metal pipeline carrying a continuous stream of liquid hydrocarbons conveyed by a pump, comprising the step of intermittently injecting into said pipeline on the suction side of said pump a relatively concentrated aqueous solution of non-oxidizing hydrocarbon-soluble desulfurizing material in approximately 2 to 100 gallon portions to form columns of a mixture of said hydrocarbons and at least 1% by weight of said concentrated aqueous solution, said columns being separated from each other by columns of said hydrocarbons, the concentration of said desulfurizing material being at least about 15% by weight and sufficient to maintain a pH of at least 9 in the aqueous phase of said mixture while passing through the section of said pipeline under treatment.

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