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INHIBITING WELL CORROSION

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This invention relates to a method of inhibiting the corrosive action of natural gas and oil containing soluble sulfides. More particularly, the invention relates to means for inhibiting the rapid corrosion of well equipment which has heretofore occurred in producing wells where the hydrocarbon contains both brine and hydrogen sulfide.

Crude oil containing soluble sulfides is produced in the major producing areas of the United States, and corrosion of oil field equipment is especially severe in areas where brines are produced with sour crudes. These corrosive sulfide brines include alkali sulfides, alkaline earth metal sulfides and acid sulfides such as hydrogen sulfide. Hydrogen sulfide is very soluble in water and brines, causing the brines to become very corrosive to equipment due to the active formation of iron sulfide. Hydrogen sulfide corrosion will take place in both acidic sulfide brines and in alkaline sulfide brines with pH below 9. This range embraces virtually all natural brines.

In some areas, the production is so corrosive that, after the tubing has been in use for a relatively short time, it has been necessary to pull the tubing once a week to inspect for failure. In one case, it was necessary to replace eleven joints in one string of tubing within eight months because of leaks; in another, a new string of pump rods began parting after thirty-six days of service. It will be apparent, therefore, that the cost of replacing equipment made useless by corrosion and the cost of labor involved are major factors in the future economic operation of many oil fields producing sour crude and brine.

One object of this invention, therefore, is to provide a means for inhibiting the attack of metals by sour crudes containing brine. Another object is that of providing a class of materials for preventing chemical attack of metals by fluids in both the liquid and vapor phases. A further object of this invention is to provide an effective inhibitor for use in treating produced well fluids before they enter the well tubing. Another object is to provide a system for treating the surface of metal to inhibit corrosion. The above and other objects of my invention will become apparent to those skilled in the art as the description thereof proceeds.

For many years generally ineffective efforts have been made by equipment manufacturers and corrosion experts to develop materials capable of withstanding hydrogen sulfide corrosion of the type to which this invention is directed. Various steel alloy tubings were tried under these

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corrosive conditions without apparent success, since the additional cost of the alloy did not give a corresponding additional length of service. Likewise, coatings of paint and synthetic rubber have failed to prevent metal from attack when the equipment was put in field use. Zinc plates have been installed on pump rods and in treaters as a form of cathodic protection, but this has also failed to prevent damage. Chemical treatment with sodium hydroxide, tannin, and sodium silicate, and the like involving the attempted neutralization of the hydrogen sulfide has been tried in wells without avoiding this type of corrosion.

In carrying out the present invention, an amount of a soluble-inhibiting substance as for example a cyanide, and preferably sodium or potassium cyanide, is introduced into the producing well. The cyanide apparently reacts with the hydrogen sulfide in the presence of the brine to produce a thin protective film on the exposed metal surfaces. Various methods of introducing the inhibitor may be used, but in each case the inhibitor is supplied to the fluids being produced and is carried upwardly through the tubing. A protective film is thereby applied to the inner surface of the tubing and this film apparently acts to prevent the corrosion by the brine and hydrogen sulfide while producing the well.

Reactions are known to take place to produce traces of new compounds, only a relatively minor proportion of the original agents reacting. This appears to be the case with the soluble cyanide and hydrogen sulfide in brines, since the major portion of the hydrogen sulfide content is unaffected but apparently does not retain its corrosive properties. Without being limited to any theory of operation, it appears that by the slow reaction of cyanide with the hydrogen sulfide in brine a new compound is produced which in turn reacts to form a molecular film on the iron which corresponds to the theoretical mechanism by which pickling agents operate.

The phenomenon was studied in the laboratory and when sodium cyanide was added to alkaline hydrogen sulfide brines there appeared to be visible signs of chemical reaction and a very small amount of insoluble precipitate formed, the reaction drifting slightly toward neutral. The cyanide reacted, but only a small portion of the dissolved hydrogen sulfide was consumed, since the brine still showed a high content of hydrogen sulfide following the treatment.

Panels of mild steel were cleaned of mill scale and smoothed with the finest grade of emery cloth. These panels were dried and weighed then

suspended in the sulfide brine on glass hooks. After immersion for a known time, the panel was removed from the brine, washed quickly in a 1% hydrochloric acid solution, wiped free of corrosion products with a soft cloth, washed with distilled water, dipped in alcohol, dried rapidly and reweighed. The weight loss was assumed to be due to hydrogen sulfide corrosion.

Data obtained by these tests are set out in the following table:

Corrosion of iron by sulfide brine	Loss in lbs. per sq. ft. per day	Inhibiting power
		Per cent
West Texas brine (control)	.00286	none
West Texas brine+.02% NaCN	.00016	95
West Texas brine+.04% NaCN	.00000	100
West Texas brine+.06% NaCN	.00000	100
New Mexico brine (control)	.0022	none
New Mexico brine+.02% NaCN	.0005	80
New Mexico brine+.04% NaCN	.00016	95
New Mexico brine+.06% NaCN	.00016	95

It will be apparent that if a soluble cyanide such as sodium cyanide is added to a brine containing hydrogen sulfide, such treated brine has little or no corrosive property on metal. Iron that has been immersed in brine treated with sodium cyanide shows a resistance to corrosion by untreated hydrogen sulfide brines for about twenty-four hours. These data demonstrate the effectiveness of a cyanide in the inhibition of sulfide corrosion of metals in the presence of brine. Thus the invention is useful in the protection of subsurface equipment of oil wells. It is also contemplated that the treatment may be applied to pipe lines, storage tanks, and refinery equipment where attack by sour crude can be expected. Where smaller percentages of water are present, proportionately smaller amounts of inhibitor may be effective.

In another example, potassium cyanide was added to alkaline sulfide brine of pH 7.5 in the ratio of 250 P. P. M. This was found to prevent hydrogen sulfide corrosion. The cyanide salt is most effective in preventing corrosion of alkaline brines and a suitable neutralizing agent, such as sodium hydroxide or ammonium hydroxide, can be added to bring the pH above about 7.

The foregoing description has been with particular reference to the use of sodium cyanide as an example of the class of materials contemplated by this invention. It is to be understood, however, that soluble cyanide salts as a class or materials producing cyanides under conditions existing within a producing well are contemplated.

The preferred embodiments of my invention described herein are for the purpose of illustration and are not intended to limit the scope of the invention, since it is apparent that the principles of my invention may be applied to analogous situations by those skilled in the art in view of the foregoing description.

What I claim is:

1. The method of inhibiting hydrogen sulfide corrosion of metal in the presence of water comprising the step of commingling a small amount of a water-soluble cyanide with said water and hydrogen sulfide.

2. The method of inhibiting the attack of metals by well fluids including sulfur compounds which comprises mixing with the well fluids a small amount of an at least partially water-soluble cyanide salt in the presence of said metal.

3. The method of treating hydrogen sulfide-containing well fluid to inhibit its tendency to cause corrosion in the presence of brine which includes the step of mixing with the producing well fluids a small amount of a metal cyanide at least partially soluble in said well fluids.

4. The method of inhibiting the corrosion of ferrous metals by well fluids containing hydrogen sulfide and brine which comprises supplying a small amount of sodium cyanide to the well fluids in a lower region of a producing well.

5. The method of inhibiting the corrosion of ferrous metal well equipment by produced well fluids containing hydrogen sulfide and water the step which comprises treating the well at frequent intervals with a small amount of an alkali metal cyanide whereby the produced well fluids distribute a protective film over the metal surfaces.

6. The method of inhibiting the tendency of well fluids containing hydrogen sulfide and water to corrode metal surfaces which comprises the steps of introducing a small amount of a water-soluble metal cyanide near the base of the well at spaced intervals of time while producing said well.

7. The method of coating well equipment with a protective film to inhibit corrosion thereof by brine and sulfur-containing hydrocarbon well fluids which includes the step of introducing into the well a small amount of a cyanide at least partially soluble in said well fluids thereby depositing a protective film on the metal surfaces and reducing the hydrogen sulfide content of the well fluids.

8. The method of rendering metal surfaces resistant to hydrogen sulfide corrosion in the presence of brines which comprises the steps of contacting the metal surfaces with an alkaline solution of the reaction products of hydrogen sulfide and a metal cyanide at least partially soluble in said brine.

9. The method of inhibiting corrosion of metals by fluids containing soluble sulfides which includes the addition to said fluids of a small amount of a cyanide salt which is at least partially soluble in said fluids.

10. The method of inhibiting hydrogen sulfide corrosion of metal in the presence of water, comprising the step of commingling a small amount of a water soluble salt of hydrocyanic acid with said water and hydrogen sulfide.

11. The method of inhibiting the attack of metals by well fluids including sulfur compounds which comprises dispersing in the well fluids a small amount of a water soluble salt of hydrocyanic acid.

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