Corrosion Control in a Waterflood by Removal of Hydrogen Sulfide and Carbon Dioxide from the Injection Water by a Hydrocarbon Gas Cycling Process

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INTRODUCTION

Equipment handling water containing relatively large quantities of carbon dioxide and hydrogen sulfide is susceptible to excessive corrosion which may attain conditions not economically controllable using corrosion inhibitors. One such extreme condition developed in a waterflood where selective injection into multiple zones through common wellbores necessitated annular injection which eliminated the feasibility of using downhole protective coatings.

Severe tubing corrosion was observed and continued even after inhibitor treatment had been increased to as much as 72 parts per million. This relatively expensive inhibitor program justified removing the corrosive constituents - - hydrogen sulfide and carbon dioxide. A process developed for this purpose consisted of stripping these gases from the water by cycling sweetened hydrocarbon gas counter-current to the water flow in a contact tower. This treatment rendered the water quite suitable for use as injection water in bare tubing and casing with the addition of corrosion inhibitor in economical quantities.

SUMMARY

Since the start of the Wickett Waterflood in May 1963, sour El Capitan Reef water mixed with sour produced water has been used for flooding at a rate as high as 40,000 BPD. The mixed water was severely corrosive; however, tests indicated that a prudent inhibitor program could successfully control corrosion in this waterflood. Since the water was injected into 76 injection wells with 175 injection streams, it was necessary to use annular injection to attain selectivity. Corrosion inhibition of the injection waters was most essential because downhole protective coatings could not be used effectively. Experience using corrosion inhibitors at this flood reveals that corrosion control was not satisfactory even after increasing inhibitor concentration from 13 to 72 parts per million over a period of two years. A decision was made to remove the hydrogen sulfide and carbon dioxide from the water, and a process for stripping these gases by cycling sweetened hydrocarbon gas counter-current to the waterflow in a contact tower was developed. Since April 1965 this process has been used to effectively control corrosion in tubing and casing with the addition of economical amounts of corrosion inhibitor.

Sweetening water at the Wickett plant (handling 40,000 BWPD) costs about 4.0 mils per bbl. In plants flaring hydrogen sulfide in volumes economically attractive for conversion to sulfur or its allied products for sale, the net income from this operation will defray water treating costs to some degree. Sulfuric acid manufactured from flare gas often provides a more economical water treating chemical than commercially purchased acid.

CORROSION EXPERIENCE AT WICKETT WATERFLOOD

The Wickett waterflood began injection of 39,000 BPD in May 1963 into 62 injection wells with 175 injection streams. Chemical treatment began, using 13 parts per millions of water soluble organic amine inhibitor; the produced water was treated with 25 parts per million of a combination corrosion-bactericide.

After three months' operation of this waterflood some meter runs were severely corroded; water backflowed from injection wells contained large quantities of iron sulfide. During October 1963 a second amine-base corrosion inhibitor at the same concentration was used to replace the original corrosion inhibitor. The following month, after corrosion coupon tests at the wellheads of water source wells indicated corrosion rates of 60 mils per year, inhibitor concentrations were increased from 13 to 21 parts per million. At this time also, injectivity of several wells had decreased to a level which required workovers to clean up wells to replace badly corroded tubing. Following these workovers and experiencing an increasing incidence of corrosion, the inhibitor concentration was increased from 21 to 26 parts per million.

Since the start-up of the flood, bacterial analysis of the injection water had indicated the absence of sulfate-reducing bacteria and low total bacterial populations. In March 1964 injection of the bactericide was discontinued and corrosion inhibitor concentration was increased to 72 parts per million or 106 gal. of corrosion inhibitor per day.

By May 1964 a majority of wells had experienced reduced injectivity as a result of iron sulfide plugging and extensive workovers were required. Since even inhibitor concentrations up to 72 parts per million had not satisfactorily controlled corrosion rates, and observation program was conducted to critically survey inhibiition operations. During the workovers all the tubing to be run was sandblasted and dipped in corrosion inhibitor to establish an initial film which would be continuously treated using 72 parts per million inhibitor. Annular injection was temporarily suspended, except on four wells, until data on the dipped tubing could be evaluated. The four "key" wells that had been kept on annular injection were pulled after one month, and visual inspection of the tubing revealed that approximately 50 per cent of the initial inhibitor film had been washed away. Also, a layer of iron sulfide and many small shallow pits had begun to form. This indicated that the corrosion inhibitor, even when added at a concentration of 72 parts per million, was not repairing the initial film or forming a new film under the injection conditions.

WATER SWEETENING PROCESSES

Since corrosion control could not be obtained even when using excessive inhibitor concentrations, it was necessary to remove the corrosive constituents from the water before it could be used for flooding and means to sweeten the water were investigated.

Various methods have been used to remove hydrogen sulfide from source water prior to injection: (1) aeration with forced draft aerators, (2) stripping the hydrogen sulfide wtih conditioned engine exhaust gas in a contact tower and (3) stripping the hydrogen sulfide in a contact tower with exhaust gas produced by a submerged combustion burner.[1] All have had varied degrees of success. The "Tenex" process in which engine exhaust gases are converted to near oxygen-free gas by use of a platinum catalyst is being done at the Pembrook Spraberry Unit. At Wickett the injection engines are turbocharged and have a valve overlap of 54° which results in excess oxygen in the exhaust gases. Due to this excess oxygen, the catalyst could not convert the exhaust gases to near oxygen-free gas. A modification of this process would generate inert gas by burning natural gas under controlled conditions. This process would have required less investment; however, the anticipated operating costs would have been relatively more costly. The manufacturer of the unit would not guarantee an oxygen content of the gas lower than 0.25 per cent, which would have exceeded the desired maximum oxygen content of not more than one part per million in the conditioned gas. Residual oxygen reacting with the hydrogen sulfide would precipitate free sulfur to make the water about as corrosive as it was originally. The stripping gas generated by the burner contains a low per cent combustible, which is principally carbon monoxide. Instrumentation is provided to analyze the burner exhaust gas and control the air-fuel ratio so that no excess air is fed to the burner. This control is critical and must attain high precision for the system to produce the desired quality water for injection purposes. The pH of the water being treated must be maintained acidic to prevent the formation of alkaline sulfides and to enhance the removal of hydrogen sulfide. Therefore, the water being treated must contain sufficient carbon dioxide to maintain this acid pH or acid must be added. This type of plant is being used at the Spraberry Driver Unit and the Pegasus Field to remove hydrogen sulfide from the San Andres water. The water-sweetening process selected for Wickett was one which Humble developed during 1962 using a pilot plant treating San Andres water.

THE HUMBLE PROCESS

The process developed by Humble to remove hydrogen sulfide and carbon dioxide from sour water is shown schematically in Fig. 1 and is made up primarily using conventional oil field equipment and controls. Sweet hydrocarbon gas contacts the sour water to pick up the acid gases and is recycled by a compressor through a sweetening reclamation using typical monoethanolamine (MEA) unit. The sour gas discharged from the MEA reactivator is concentrated to the point that it combustible; in sufficient concentrations and volumes this could make the recovery of sulfur or its allied products, sulfur dioxide or sulfuric acid, economically attractive. In this water-sweetening process, acid has to be added to lower the pH to about 5.4 so that the sulfide can be effectively stripped from the water.

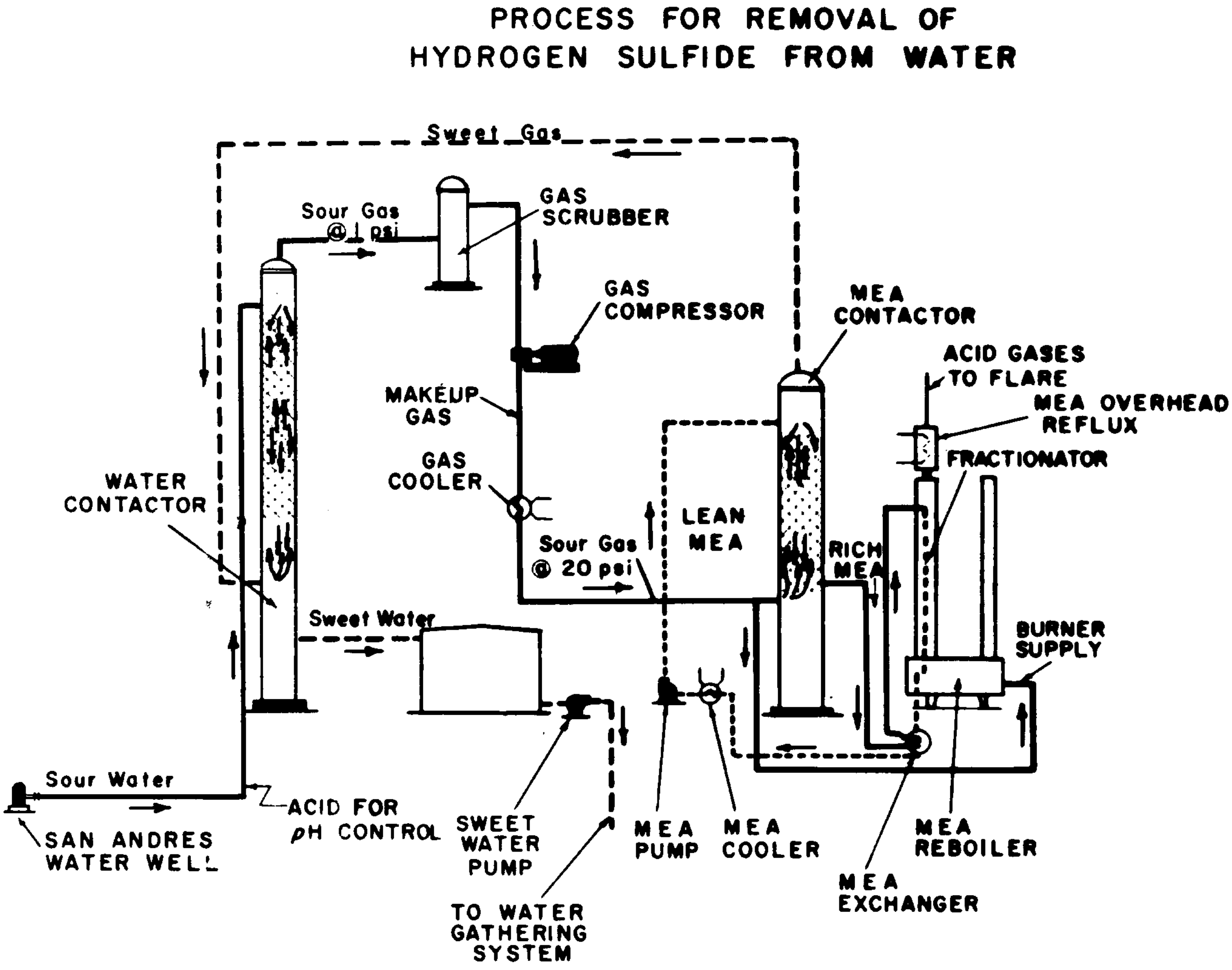

Figure 1

Approximately eight gal. of sulfuric acid per 1000 bbl. of water are required for pH control at Wickett; the amount of acid required is dependent upon the alkalinity of the water being processed.

DESIGN CRITERIA

The contactor column used for stripping acid gases from water is designed according to Henry's law, which states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas in the surrounding atmosphere at a given temperature. Thus, if the partial pressure of hydrogen sulfide and carbon dioxide in the surrounding atmosphere approaches zero under conditions when the hydrogen sulfide and carbon dioxide are given adequate opportunity to escape from the water, the dissolved hydrogen sulfide and carbon dioxide will approach zero. Counter-current stripping of gases from water with a hydrocarbon gas readily provides these conditions.

Most sour waters contain both free hydrogen sulfide and un-ionized sulfides; the pressure of the latter reduces the effectiveness of counter-current stripping of hydrogen sulfide unless the pH of the water is adjusted to between 5.0 and 5.4. Table I shows the percentages of hydrogen sulfide at various pH levels with the remainder of the total sulfides being present as the alkaline sulfides. This demonstrates that the pH must be lowered for satisfactory removal of sulfides from water.

TABLE I

Percentage of Total Sulfide Present as Hydrogen Sulfide[2]

PH	Percent H_2S
5.0	98
5.4	95
5.8	89
6.0	83
6.5	61
7.0	33
7.5	14
8.0	4.8
9.2	0.32

WICKETT WATER SWEETENING PLANT

The produced water passes through a coalescer into a 500 bbl tank to be mixed with reef water and sulfuric acid to lower the pH from approximately 7.1 to 5.4. A high level equalizing line transfers the mixed water to a tank from which it is pumped to the top of the water contact tower. Water entering the contact tower with a pH of 5.4 and approximately 360 parts per million hydrogen sulfide and 720 parts per million carbon dioxide flows downward over 35 nutter valve trays with double downcomers. Hydrocarbon gas circulated upward through the tower at a rate of 2.5 MMCF per day. The sweetened water leaving the tower with a pH of 7.4 and containing approximately three parts per million hydrogen sulfide and four parts per million carbon dioxide goes to the unfiltered, treated water tank and is pumped from there to the filters. After filtration the water is stored in treated water tanks awaiting transfer by centrifugal pumps to the suction of the injection pumps.

The hydrocarbon stripping gas cycle begins at the compressor. The sour gas from the inlet scrubber enters the compressor at one psi and is discharged at 20 psi with a circulation rate of 2.5 million cu ft/day. From the compressor the gas flows through a heat exchanger, lowering the gas temperature from 200° F to 95° F. Gas entering the bottom of the amine contact tower contains approximately 875 grains/100 cu ft of hydrogen sulfide or 1.4 mol per cent hydrogen sulfide, and 1.8 mol per cent carbon dioxide. Sweetened gas leaving the amine contact tower has less than one grain/100 cu ft of H_2S. The sweetened gas from the amine scrubber enters at the bottom of the water contact tower and passes upward to strip the acid gases from the water. The soured gas leaving the top of the water contact tower passes through the compressor inlet scrubber into the compressor to complete the gas cycle. The step described for reclaiming the sweet hydrocarbon gas is the conventional monoethanolamine process used throughout the gas processing industry. Makeup gas as required is introduced to the hydrocarbon stream leaving the discharge of the compressors. Makeup gas and fuel consumption average about four MCF per 1000 bbl of water processed.

The efficiency of the water-sweetening process is affected by several variables. These include stripping gas flow rate, sweetness of the stripping gas, and pH of the unsweetened water as it enters the top of the water contact tower. As shown by the graph of Fig. 2, the efficiency

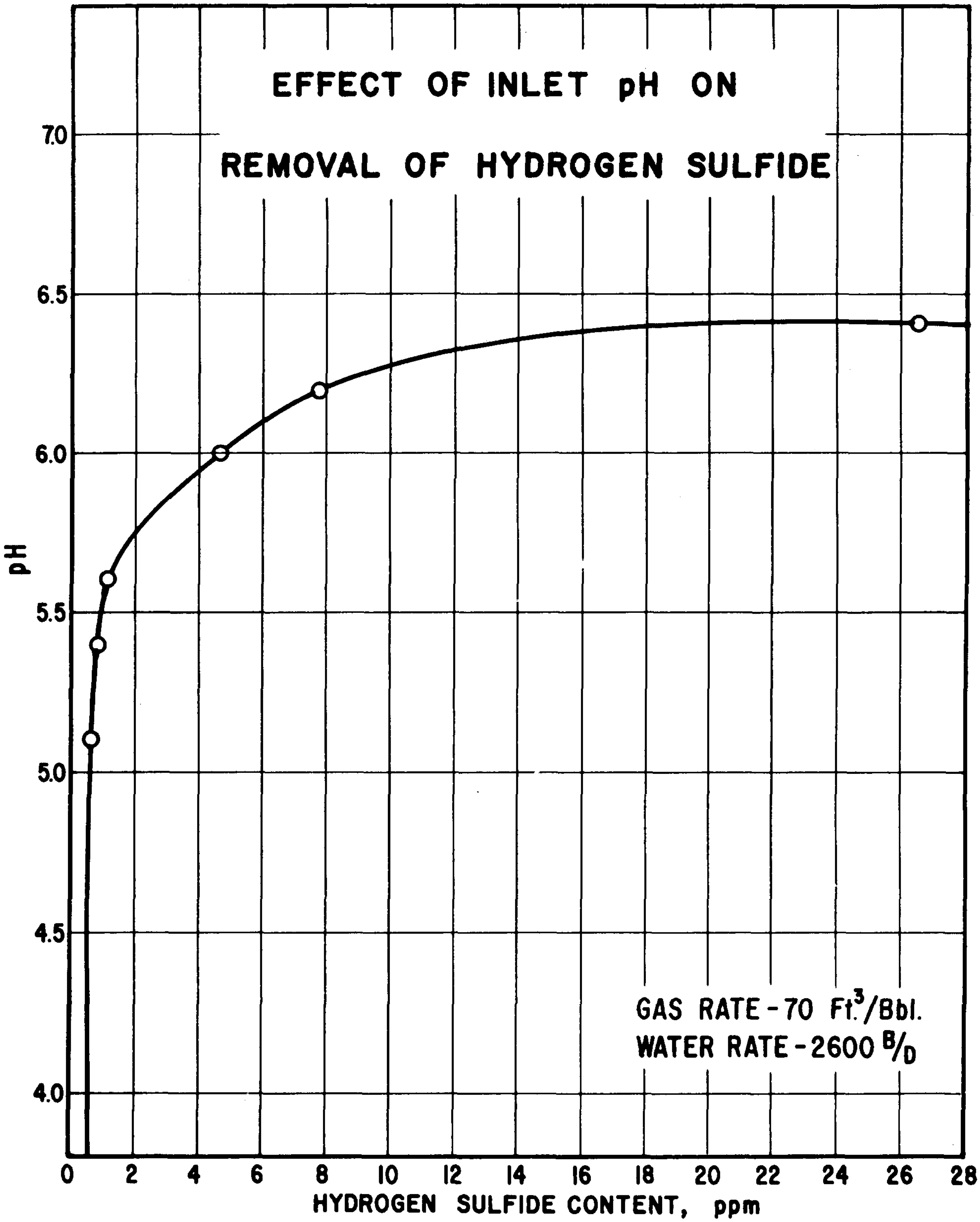
EFFECT OF INLET pH ON
REMOVAL OF HYDROGEN SULFIDE
7.0
6.5
6.0
5.5
5.0
4.5
4.0
pH
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
HYDROGEN SULFIDE CONTENT, ppm
GAS RATE - 70 Ft.^{3}/Bbl.
WATER RATE - 2600 B/D

Figure 2

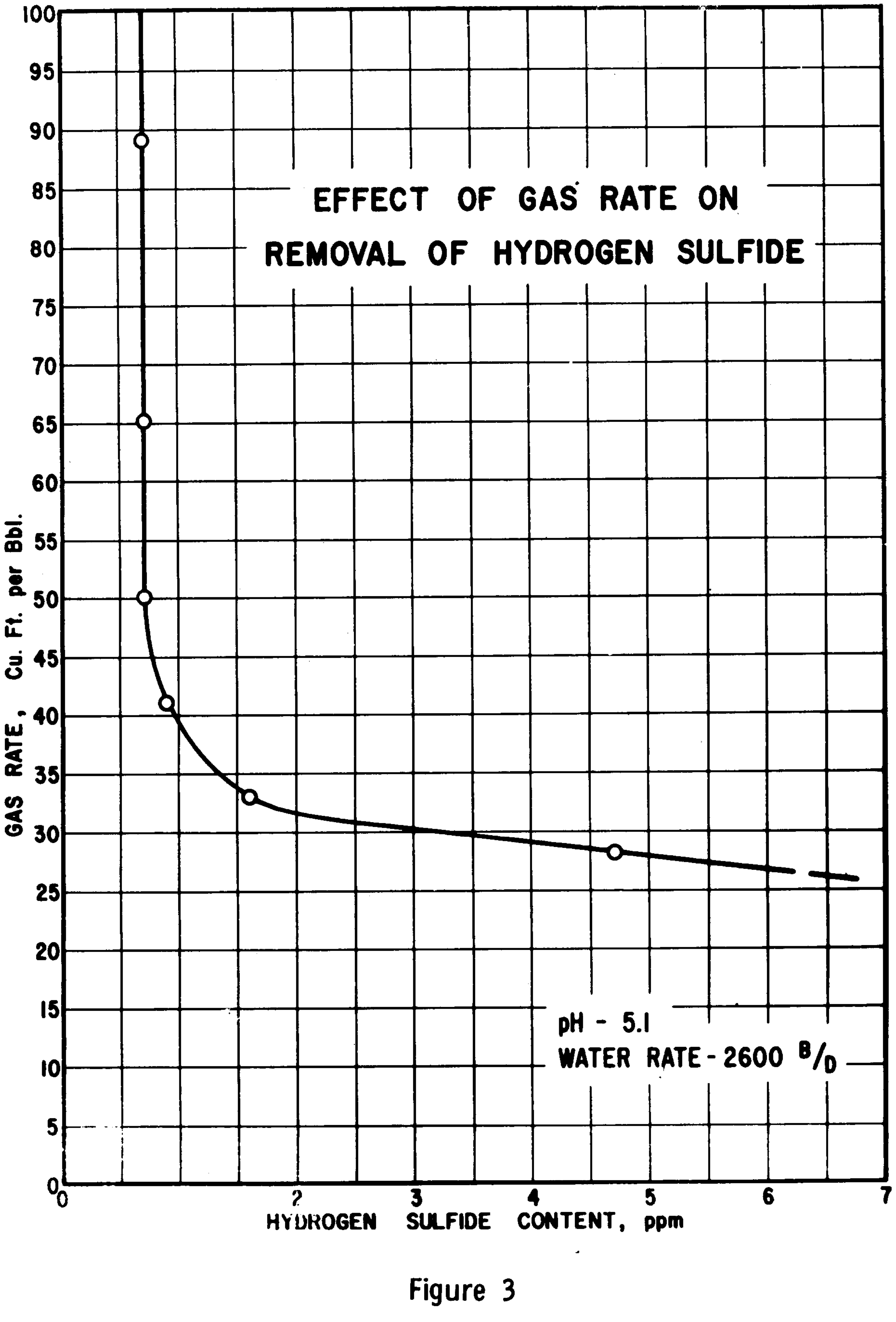
EFFECT OF GAS RATE ON
REMOVAL OF HYDROGEN SULFIDE
pH - 5.1
WATER RATE - 2600 B/D
GAS RATE, Cu. Ft. per Bbl.
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
0
2
3
4
5
6
7
HYDROGEN SULFIDE CONTENT, ppm

Figure 3

of the sweetening process is directly dependent upon pH of the inlet water; Fig. 3 relates the effect of the gas rate to this efficiency. From these illustrations, the optimum pH is shown to be about 5.4 and a preferred gas rate should be at least 50 cu ft per bbl. The Wickett Plant was designed to provide approximately 70 cu ft of gas per bbl of water for a maximum of 40,000 BWPD and is operated currently at a rate of 60 cu ft per bbl.

CORROSION CONTROL WITH SWEETENED WATER

The comparison of the composition of water before and after sweetening by hydrocarbon gas, shown in Table II, indicates that hydrogen sulfide was reduced from 360 to 3 ppm, while the carbon dioxide was reduced from 160 to 4 ppm. After removal of these acid gases, the water pH increased from 5.4 to 7.4, while the calcium carbonate stability attained the desirable value of +13. Tests by coupons, corrator and corrosometer have indicated a corrosion rate of less than 1.5 mils per years for the sweetened water.

TABLE II
COMPARISON OF COMPOSITION OF WATER AT VARIOUS STAGES IN THE SWEETENING PROCESS

Component PPM	**As Produced**	**After pH Adjusted**	**After Gas Stripping**
Sodium	3150	3150	3150
Calcium	1022	1022	1022
Magnesium	288	288	288
Chloride	5100	5100	5100
Sulfate	2639	2639	2639
Bicarbonate	561	48	48
Total Solids	12760	12247	12247
pH	6.8	5.4	7.4
Hydrogen Sulfide	360	360	3.0
Carbon Dioxide	160	720	4.0
Calcium Carbonate Stability	+44	-260	+13

The water-sweetening plant was placed in operation in April 1965, and periodic inspection of tubing in two key injection wells at four to six-month intervals indicate satisfactory corrosion control since that time. The current program started treating the sweetened water using 50 parts per million of corrosion inhibitor; after six months an inspection indicated this inhibitor concentration could be reduced, and it was lowered to 25 parts per million. Subsequently, it has been reduced to 15 parts per million because all inspections showed that both inside and outside surfaces of tubing are being adequately protected from corrosion.

CONCLUSIONS:

1 The cycling of hydrocarbon gas in a water contact tower can be effectively used to remove the acid gases, hydrogen sulfide and carbon dioxide from sour waters.

2. The water sweetening process used at the Wickett Waterflood rendered the water quite suitable for injection into bare tubing and casing with the use of economical quantities of corrosion inhibitor.

3. The Humble process for sweetening water can provide a source for recovery of sulfur or its allied products from the flare gas where hydrogen sulfide concentrations are high enough in sufficient volumes to make such recovery economically attractive.

REFERENCES

1. Exhaust Gases Strip H_2S from Sour Flood Water, by R. F. Weeter, Petroleum Engineer, May 1963, P. 51-58.

2. Standard Methods for the Examination of Water, Sewage and Industrial Wastes, Tenth Edition 1955, p. 274.