

CORROSION
PREVENTIONDesorption of Oxygen From Water Using
Natural Gas for Countercurrent StrippingR. F. WEETER
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Abstract

Corrosion in the SACROC unit water flood was serious enough to warrant remedial action. A few months after installation of the flood, some injection wells were filled with 75 ft of iron hydroxides, and serious corrosion was occurring in the high-pressure pumps. The problem was studied and several methods of treating proposed, and the most promising was chosen. This method consisted of designing and constructing a tower for stripping oxygen from the injection water with countercurrent flow of natural gas.

Introduction

The SACROC unit water flood in Snyder, Tex., was initiated late in 1954, employing fresh water which was pumped from Lake J. B. Thomas, treated with lime and alum for clarification and chlorine for bacteria removal, filtered and pumped into the Canyon Reef formation. The water was received at pH of approximately 8.4, and treatment was controlled to maintain that pH. Since this water was expected to be virtually non-corrosive, bare steel was used in the injection system, consisting of 34 miles of line which ranged from 3 to 10 in. Also, the water was injected through bare casing. This information has been published in detail.^{1,2}

Within a few months, wireline work revealed fill-up of up to 75 ft in some of the injection wells, and the fill-up material proved to be iron hydroxides. Moreover, serious corrosion occurred in the high-pressure pumps. Remedial action appeared essential.

Analysis of Problem

The first remedial action taken was to raise the pH of the water to 9.3 in an attempt to reduce corrosion. Corrosion rates continued high, but the elevated pH was continued because of other operational benefits.

Next, oxygen tests were conducted throughout the system, including using a pressure bomb down hole. The tests indicated that at least half of the oxygen (approximately 5 ppm) was lost before the water reached the wellheads, and usually only traces reached the bottom of the wells. At the time, approximately 150,000 BWPD was being injected. At 10 ppm of oxygen in the water, this represented corrosion of 1,220 lb of iron per day, with formation of 2,340 lb of ferric hydroxide.

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¹References given at end of paper.

The oxygen tests down hole had some side benefits which were not anticipated.

1. Attempts were made to remove the sample from the sampler by using kerosene. To test the accuracy of the procedure, duplicate samples were taken, one with a sampler, the other caught and run as a standard Winkler method analysis. The sample was displaced from the sampler and analyzed in the same manner as the other sample. Consistently, the sample from the sampler was high in oxygen compared with the other. Finally, an oxygen determination was run on the kerosene, and oxygen content was found to be extremely high. Since that time, oil blankets have been discarded as an effective means of preventing ingress of oxygen.

2. An attempt was made to displace the sample from the sampler with natural gas, using the same procedure as above. Oxygen content of the sample was consistently quite low, indicating that natural gas was removing oxygen from the water. (Finally, the sample was chemically "fixed" in the sampler while flowing a volume of natural gas over the pipettes and sampler opening. Consistent results were obtained.)

Possible Methods of Treatment

Chemical Treatment

Removal of oxygen with chemicals was considered. The chemical most commonly used at that time was sodium sulfite (Na_2SO_3). Stoichiometric combination of sodium sulfite with oxygen requires 8 lb/lb. To make the reaction approach completion requires both a catalyst, such as cobaltous chloride, and an excess of sulfite, usually 10 ppm. To remove 10 ppm of oxygen requires approximately 90 ppm catalyzed sodium sulfite.

Depositing Scale

Another method which was considered was the deposition of a scale to protect the pipe and casing. It has been proposed that this can be accomplished by adding 10 ppm of complex metaphosphates to a stable water and precipitating a thin complex film. However, during the first few months of operation of the SACROC unit system, this treatment was used and no corrosion benefit was noted.

Stripping with Natural Gas

As a result of the observation that contact with natural gas reduced the oxygen content of water, a laboratory pilot was set up to test the practicality of removing the oxygen with natural gas. The system consisted of a small packed column. The lab pilot showed that such a pro-

cedure was possible, so a field pilot column was designed.

Two approaches were possible at this point: (1) using a packed column, which was rejected because the literature indicated that a packed column in diameters over 4 ft became less efficient than a bubble-tray column; and (2) a bubble tray column, which appeared to be a satisfactory approach.

Two agents for stripping the oxygen were considered. Exhaust gas was rejected because engine exhaust contains oxygen and because no suitable method was known at that time for generating oxygen-free exhaust gas. Moreover, exhaust gas generated as a stripping agent would have no recoverable value after use.

Natural gas was chosen because it is recoverable for use as fuel. It was decided to base the design of the pilot plant on the amount of fuel used at the treating plant. This was 1.75 cu ft/bbl of water treated. Unfortunately, the engines in the treating plant site operated on 60 psig fuel gas pressure. This represents more than 5 atm absolute pressure, and, if stripping is carried out at that pressure, the amount of gas required would be approximately five times that required at atmospheric pressure.

Field Test

The pilot equipment was built to operate at 60 psig and a 1.75 cu ft/bbl gas-water ratio. It consisted of a section of 10-in. diameter pipe with 10 trays on 18-in. centers. The downcomers were placed outside to give higher flow rates. The tower was made with three water inlets so that it could be operated with six, eight, or 10 trays. A detailed section of the tower is shown on Fig. 1.

The efficiency of the column was 7.25 per cent, much lower than anticipated. A formula to extrapolate the test

results was developed as follows. Given time, the quantity of any gas in any liquid will reach equilibrium with the partial pressure of that gas in the atmosphere surrounding the liquid. This is expressed by Henry's law,

$$p_a = HX_a$$

where p_a = the partial pressure of the gas under investigation, atm.

H = Henry's constant for the gas at the existing temperature,

X_a = the mol fraction of the gas in the liquid.

The conditions under which the tests were run were: pressure 54 psig, 5 atm (app.); temperature, 50F; H , 3.27×10^4 ; oxygen content of water, 10.56 ppm at 50F; and gas-water ratio, 1.75 cu ft/bbl.

The efficiency was calculated as follows:

$$p_a = HX_a = \frac{3.27 \times 10^4 \times 18.02 \times \text{ppm } O_2}{32 \times 10^6 \times 5 \text{ atm}}$$

$$= 3.67 \times 10^{-3} \times \text{ppm } O_2$$

$$\frac{\text{Total weight gas (expressed as } O_2)}{1 \times 10^6 \text{ lb H}_2O}$$

$$\frac{1.75 \text{ (cu ft/bbl)} \times 32 \text{ (lb/mol)} \times 1 \times 10^6}{379 \text{ (cu ft/lb mol)} \times 350 \text{ (lb H}_2O/\text{bbl)}} = 422 \text{ lb.}$$

$$\text{Total oxygen removed}^* = T = R(1 + eK)$$

$$[1 + e(K - 1)]^{n-1}$$

where R = residual O_2 , in ppm.

e = tray efficiency.

$$K = \frac{\text{Total weight } O_2}{1 \times 10^6 \text{ lb H}_2O \times \text{ppm } O_2}$$

$$\text{Total weight } O_2 = K \times \text{ppm } O_2 =$$

$$422 \times 3.67 \times 10^{-3} \times \text{ppm } O_2 =$$

$$1.55 \times \text{ppm } O_2$$

$$K = 1.55.$$

The efficiency was established experimentally in the pilot column using 4.47 cu ft/bbl, which gave a K value of $1.55 \times 4.47/1.75 = 3.96$. Residual oxygen was 1.42 ppm (see Table 1).

Using Operating Formula

$$[1 + e(K - 1)]^{n-1} = \frac{T}{R(1 + eK)}$$

$$(1 + 0.725 \times 2.96)^n = \frac{10.56}{1.42(1 + 0.0725 \times 3.96)}$$

$$= 1.217^n = 5.9 \text{ (Check).}$$

Thus an efficiency of 0.0725 was used in design calculations.

Design Considerations

A high-pH water (pH above 8.4) can be stripped with natural gas without any possibility of supersaturating the water with calcium carbonate.

A water with a pH lower than 8.4 tends to become supersaturated with calcium carbonate, and the lower the pH the worse the tendency. This is due to removal of carbon dioxide from the water, upsetting the chemical balance. Within limits, the effect can be countered with complex metaphosphates.

Four-cycle, naturally aspirated engines are most convenient for use in a plant where oxygen desorption with natural gas is being practiced, because the gas can be used as fuel without repressuring. However, extra initial cost and operating cost of such engines often exceed the costs of installing and operating a compressor to increase the gas pressure to that necessary to fuel two-cycle engines.

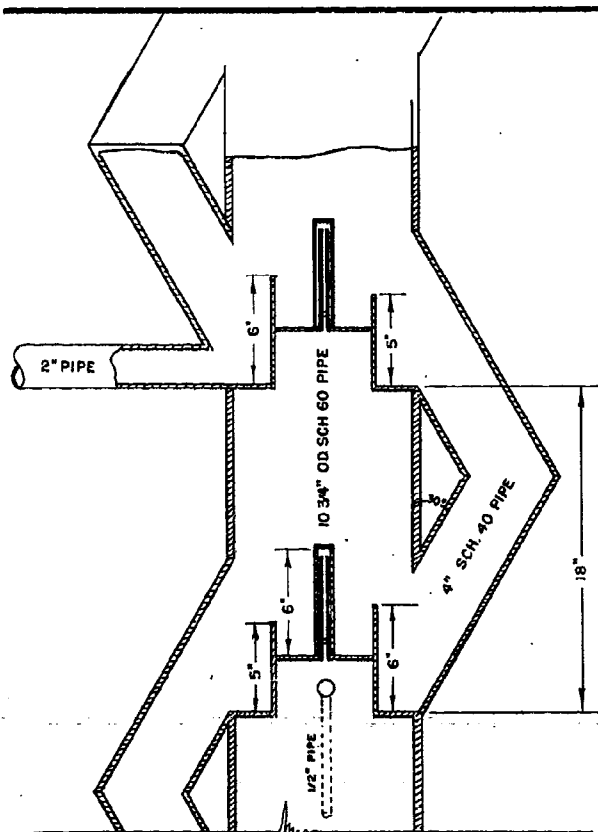


Fig. 1—Cross-section of pilot tower showing internal detail.

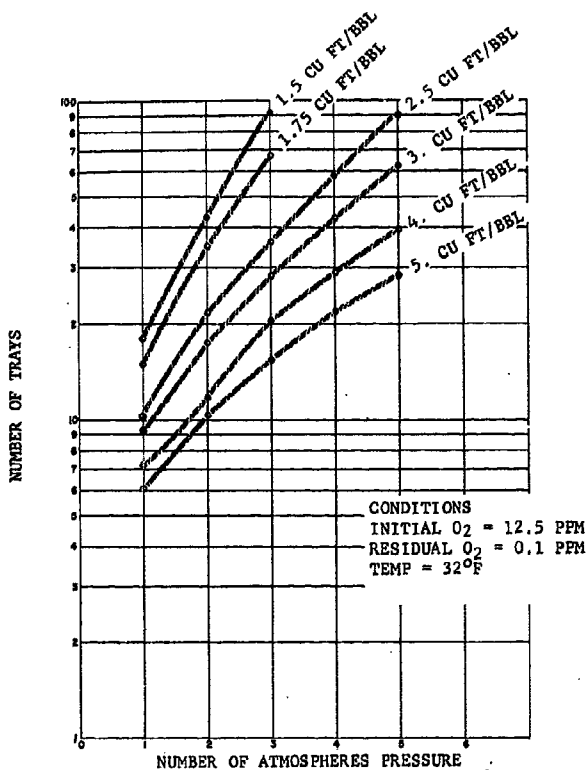


Fig. 2—Relationship of gas-water ratio to number of trays and pressure.

If gas is available and it is needed for fuel, the highest gas-water ratio which is possible should be used. Figs. 2, 3 and 4 show the calculated relationship of gas-water ratio, pressure and number of trays, based on an efficiency of 7.25 per cent. From these figures, the most economical combination of the three can be calculated.

Henry's constant is larger for water at low temperatures, being greatest at 32F. Moreover, the solubility of

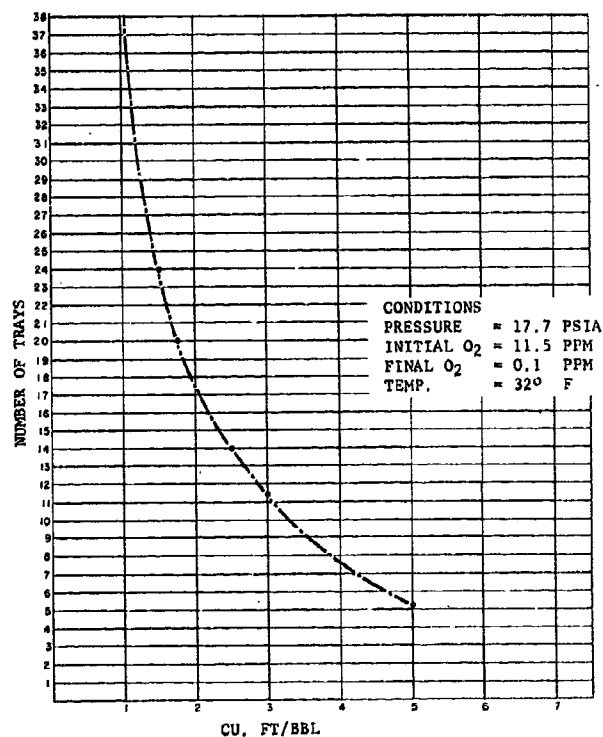


Fig. 3—Relationship of gas-water ratio to number of trays.

oxygen is greatest at 32F. For that reason, desorption should be designed for the lowest temperature which the water can be expected to reach in the area for which the plant is being designed. The effect of temperature on number of trays is shown graphically in Fig. 5.

Every effort should be made to keep a positive pressure on the water at all points downstream from the desorption tower. The installation of a back pressure valve in the top of a tubing or casing string through which water is being injected should be considered if the well

TABLE 1—SACROC UNIT—PILOT PLANT OPERATING DATA.

Date	Number of Trays	Gas Temp In	Gas Temp Out	Water Temp In	Water Temp. Out	Gas Pressure In	Gas Pressure Out	Water Pressure In	Water Pressure Out	Gas Out (scf/day)	Water In (B/D)	Oxygen In (ppm)	Oxygen Out (ppm)
12-14-55	10	50	46	50	48	3.75	2.0	12.0	2.25	10800	2000	10.50	1.86
	10	50	46	50	48	3.75	2.0	12.0	2.25	10800	2000	10.50	1.86
	8	50	46	50	48	3.75	2.0	12.0	2.25	10800	2000	10.50	2.88
	8	50	46	50	48	3.75	2.0	12.0	2.25	10800	2000	10.50	2.92
	6	50	46	50	48	3.75	2.0	12.0	2.25	10800	2000	10.50	3.58
	6	50	46	50	48	3.75	2.0	12.0	2.25	10800	2000	10.50	3.84
12-16-55	10	55	60	50	47	55	53	57	52	9600	2420	11.26	1.44
	10	55	60	50	47	55	53	57	52	9600	2420	11.26	1.44
	6	55	60	50	47	55	53	55	52	9600	2420	11.26	3.90
	6	55	60	50	47	55	53	55	52	9600	2420	11.26	3.90
12-19-55	10	55	45	54	45	54	51	57	50	10000	2240	10.56	2.05
	10	55	45	54	45	54	51	57	50	10000	2240	10.56	1.41
	10	55	45	54	45	54	51	57	50	10000	2240	10.56	1.42
	8	55	45	54	45	54	51	56	50	10000	2240	10.56	2.46
	8	55	45	54	45	54	51	56	50	10000	2240	10.56	1.95
	8	55	45	54	45	54	51	56	50	10000	2240	10.56	2.08
12-20-55	6	55	45	54	45	54	51	55	50	10000	2240	10.56	3.33
	10	58	57	55	47	56	55	55	54	10000	2200	10.56	1.34
	10			55	47	56	55	55	54	10000	2200	10.56	1.82
	10			55	47	56	55	55	54	10000	2200	10.56	1.82
	10			55	47	56	55	55	54	10000	2200	10.56	1.93
	10			55	47	56	55	55	54	10000	2200	10.56	1.54
	10	80	80	55	47	56	55	55	54	10000	2200	10.56	1.70
	10	80	80	55	47	56	55	55	54	10000	2200	10.56	1.30
	10	80	80	55	47	56	55	55	54	10000	2200	10.56	1.50
	10	80	80	55	47	56	55	55	54	10000	2200	10.56	1.63
	10	80	80	55	47	56	55	55	54	10000	2200	10.56	1.66
	8	80	80	55	47	56	55	55	54	10000	2200	10.56	3.01
	8	80	80	55	47	56	55	55	54	10000	2200	10.56	2.90
	8	80	80	55	47	56	55	55	54	10000	2200	10.56	2.70
	8	80	80	55	47	56	55	55	54	10000	2200	10.56	2.75
	6			55	47	56	55	55	54	10000	2200	10.56	4.27
	6			55	47	56	55	55	54	10000	2200	10.56	4.41
	6			55	47	56	55	55	54	10000	2200	10.56	4.38
	6			55	47	56	55	55	54	2090	2000	10.56	6.18
	10	47	51	48	47	66	63	70	65	8750	2000	10.56	1.45
	10	47	51	48	47	66	63	70	65	7200	2000	10.56	1.71
	10	47	51	48	47	66	63	70	65	9600	2000	10.56	1.28

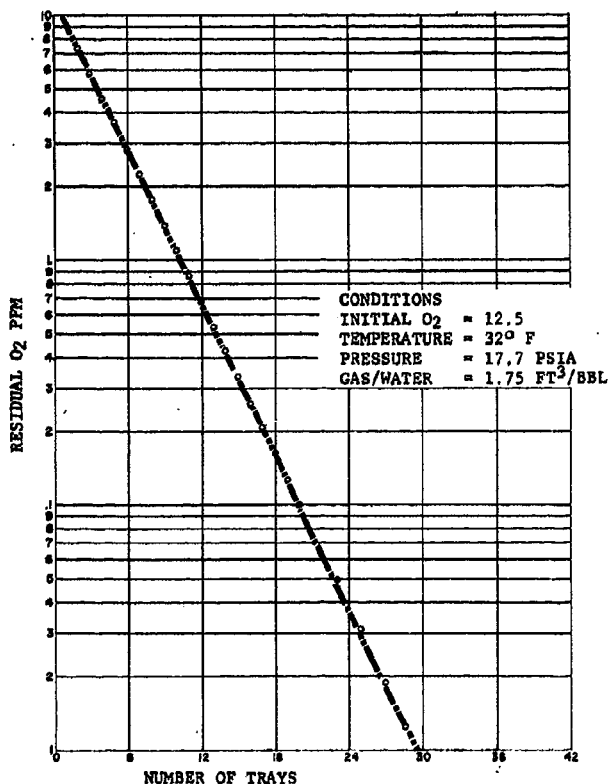


Fig. 4—Residual oxygen in ppm vs number of trays.

takes water on vacuum or goes on vacuum when shut in. A system which shows no water leaks even under considerable pressure quite probably will permit ingress of oxygen when placed under vacuum.

Design of SACROC Column

If oxygen content could be reduced to 0.1 ppm, satisfactory corrosion control probably would be obtained. (Removal to zero is theoretically impossible.) The number of trays necessary to do this at 60 psig and with a 1.75 cu ft/bbl gas-water ratio was calculated under the following conditions: pressure, 60 psig, 73.7 psia; H , 2.55×10^4 at 32F; gas-water ratio, 1.75 cu ft/bbl; $e = 0.0725$; and $T = 12.5$.

$$K = \frac{2.55 \times 10^4 \times 18.02 \times 1.75 \times 13.7}{73.7 \times 379 \times 350} = 1.13.$$

$$[1 + e(K - 1)]^{n-1} = \frac{12.5}{0.1(1 + eK)}$$

$$(1 + 0.0725 \times 0.13)^{n-1} = \frac{12.5}{1 + 0.0725 \times 1.13}$$

$$1.0094^{n-1} = \frac{125}{1.082} = 115$$

$$n - 1 = \text{Approximately } 700$$

$$n = 700$$

Thus it is impractical to operate at 60 psig or 73.7 psia. Now assume the same conditions but 4 psig or 17.7 psia.

$$K = \frac{1.13 \times 73.7}{17.7} = 4.7$$

$$(1 + 0.0725 \times 3.7)^{n-1} = \frac{125}{1 + 0.0725 \times 4.7}$$

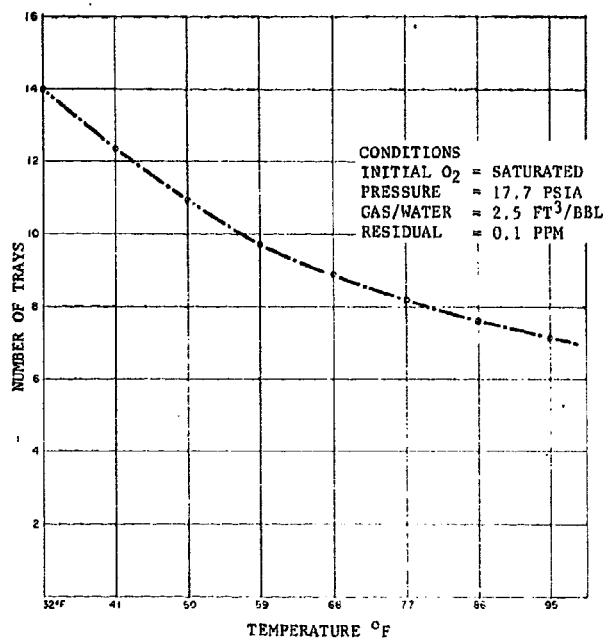


Fig. 5—Temperature vs number of trays.

$$1.269^{n-1} = \frac{125}{1.341} = 92.7$$

$$n - 1 = 19$$

$$n = 20.$$

Figs. 2 through 5 show the calculated data upon which bubble-tray columns can be designed and are determined by the above formula.

Calculations showed that two 6-ft diameter, two-pass columns would be adequate to handle 200,000 BWPD and 350,000 scf/day natural gas. Because it was a new type of installation, cost evaluation was made on the basis of three such columns. Because of the many unknowns, it was decided to install one column initially and after it had been evaluated, to install an additional column or columns. The initial pump, however, was sized to pump up to 200,000 BWPD, and the gas compressor was designed to compress up to 350,000 scf/day of gas from atmospheric pressure to 60 psig.

Internal details of the column are illustrated in Fig. 6, showing an edge-to-center flow tray between two center-to-edge flow trays. The column contains 20 trays on 22-in. centers, with all of the internals made of mild steel, except for the caps which are made of 304 stainless steel. The caps are insulated from the trays with shaped polyethylene gaskets to prevent electrolytic attack on the trays. The bubble caps are designed for a riser flow rate of 10 ft/sec when the column is handling 140,000 scf/day of gas. A picture of the plant, itself, is shown in Fig. 7.

Since it would be difficult to apply a successful coating to the intricacies of such a vessel's internals, $\frac{1}{8}$ -in. corrosion allowance was used on the shell and it was designed $\frac{3}{8}$ -in. thick. Internal manways were made removeable from either top or bottom. To permit adequate accessibility, the trays were spaced on 22-in. centers.

Operating Information

The first tower was placed in operation in June, 1957, and was checked to determine its efficiency. The plant was not designed to measure either water or gas accurately; therefore, the exact efficiency of the column has

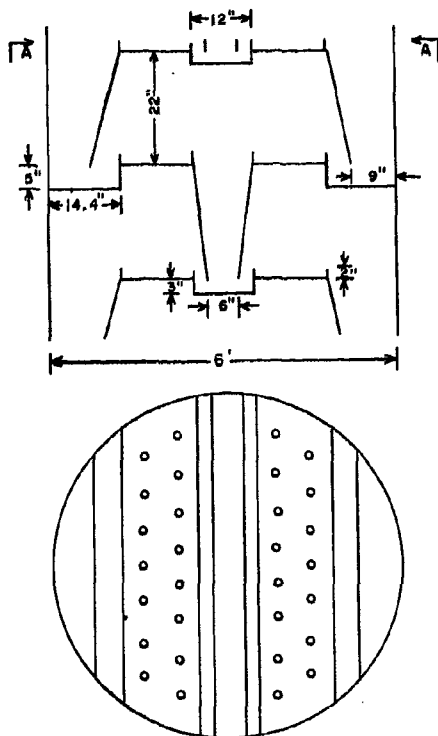


Fig. 6—Tray details, 6-ft diameter, two-pass column.

never been determined. The approximate rates were calculated. Tests under design conditions of 1.75 cu ft/hbl gas-water ratio, temperature near freezing and dissolved oxygen contents up to 14 ppm, consistently indicated oxygen residuals of 0.1 ppm or less. Thus, within the measuring accuracy of the equipment, the efficiency of the column was 7.5 per cent based on inlet gas pressure of 4 psig.

Column Capacity

Meanwhile, tests were run to establish the capacity of the column. Calculations showed the capacity to be in excess of 150,000 BWP/D if bubble-cap riser velocities were kept below 10 ft/sec. Since the expected capacity was approximately 80,000 BWP/D, the riser design was for only 140,000 scf/day. Experiments proved that carry-over of water with the gas occurred when the gas rate became too high or when the water rate and gas rate exceeded 134,000 B/D and 200,000 cu ft/day, respectively.

Since the water being handled was in the range of 150,000 B/D, some water had to be left untreated, and this was mixed with the treated water for injection. To bring the oxygen content to zero, sodium sulfite was added. This treatment, however, made sulfate-reducing bacteria, which had always been present in the system, grow furiously. These created a corrosion problem which, to a large extent, offset any beneficial effect of oxygen removal. The pH of the water was raised to 11, but, although it drastically reduced the bacteria count, the result was not lasting. The treatment was too expensive to be used continuously. Periodic slug treatment with an organic bactericide was then used, with limited effect. Use of sodium sulfite was discontinued early in 1959, and the sulfate-reducing bacteria problem appeared to lessen with decreased corrosion rates, resulting.

The following benefits were noted:

1. Workovers to remove ferric hydroxide from injection wells were eliminated.

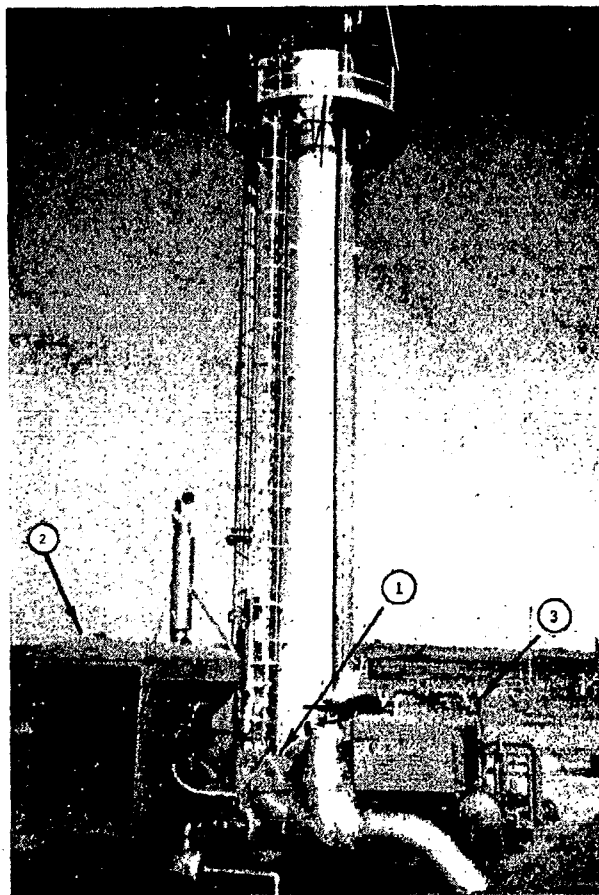


Fig. 7—SACROC unit oxygen stripping plant: (1) pump; (2) pump engines; and (3) compressor engine.

2. Valve failures in pumps decreased.
3. High-pressure pump working barrel failures decreased.
4. Pigging injection lines has not been necessary.
5. Projected injection pressures were reduced because of reduced formation plugging.
6. Major injection-well workovers have been less frequent due to less formation damage.
7. Casing failures, with resulting expense of installing tubing in the injection wells, will be postponed or eliminated.
8. Failures of surface lines will be postponed if they occur at all.

State allowables have been reduced for the past six years to a point at which the rate of injection has been below 134,000 BWP/D, and all of the water is being de-oxygenated.

The column has been in operation for approximately eight years. No serious difficulties have arisen in its operation in that time. Corrosion coupon reports show a decrease of 50 per cent in corrosion rates; however, since negligible fill-up of wells is occurring, much greater corrosion reduction is indicated. It is probable that sufficient oxygen was introduced into the corrosion coupon port to create rapid corrosion for a short period. These ports were in high points in the line where air might remain trapped. Since coupon exposures were for approximately 30 days, the indicated corrosion rates were high. Repair costs on pumps have declined considerably, which is probably due to oxygen removal. All of the scale deposits re-

moved from the lines or wells have been analyzed as primarily Fe_2O_3 or $\text{Fe}(\text{OH})_3$. If 134,000 bbl of water containing 0.2 ppm of oxygen loses all of its oxygen, it can contribute only 46 lb of $\text{Fe}(\text{OH})_3$ /day to the system, whereas 10 ppm could contribute 2,340 lb/day. As mentioned earlier, oxygen tests indicated that most of the 2,340 lb, representing 1,100 lb of corroded iron, actually was being formed. It must be concluded, therefore, that overall corrosion was reduced much more than 50 per cent.

General Comments

The design of a plant to mechanically strip oxygen from water must take a number of things into consideration.

1. Exhaust gas can now be generated sufficiently oxygen-free, as described in an earlier report,⁷ to be suitable for oxygen removal, and will not reduce the carbon dioxide content of the water if handled properly.

2. Although small-diameter packed columns can be built to handle small quantities of water (up to 20,000 B/D) for less investment than can bubble-tray columns, they are not recommended for the following reasons: (a) any suspended matter will plug the packing; (b) the packing is an excellent culture medium for bacteria, which will also plug the packing; and (c) any supersaturated salt will be precipitated on the packing. All three of these cause carry-over of water in the gas and can sharply reduce water through-put.

It is well to have a surge vessel between the column and any pump downstream because, at high through-put rates, gas is entrained in the water and will cause gas-lock in a centrifugal pump or hammer in a positive-displacement pump. This should be a gas-blanketed vessel with the pressure-reducing valve in a horizontal run on top of the tank. Since only ounces of pressure can be placed on a tank, inches of water or oil collecting on top of a pressure reducing valve in a vertical run can prevent opening of the valve and create a vacuum on the tank.

4. No water is non-corrosive, but dissolved gases in water contribute heavily to corrosion. Oxygen is one of the worst offenders. It is the opinion of the author that oxygen, if present in more than trace quantities, can profitably be removed. The most economical removal, in many cases, is with natural gas if the gas can then be used in some process rather than be wasted.

Acknowledgments

The author wishes to express his appreciation to the management of Mobil Oil Co. for permission and encouragement leading to publication. Much of the initial work was carried out while the author was employed by SACROC unit, and the assistance of H. H. Allen, former unit manager, M. L. Broman, unit manager and Robert Melton, unit office manager, is very much appreciated.

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APPENDIX

Design of Trays

Since the efficiency of the column was not improved by dropping the flow rate below 10 ft/sec in the trial runs, a design gives a minimum gas rate of 5 and a maximum of 10 ft/sec. Then

$$\frac{350,000 \times 144}{10 \times 86,400 \times 3} = 19.45 \text{ sq in.}$$

A 1-in. riser has a cross-sectional area of 0.71 sq in., and 26 such risers, or 13 per section, would be required. Place six in one row in seven spaces, and seven in another row in eight+ spaces. The distance between centers of caps on first row will be 1/7 width of tray at the point. Place these caps 4 in. from the edge downcomer, or 1 ft 5.6 in. from center. From Perry,⁸ width at this point is 5.16 ft = 62 in.

Thus, if the caps are placed on 9-in. center, and 4 1/2 in. from the edge wall—i.e., the wall at right angles to the weir—they will be satisfactory.

If the other caps are placed 4 in. from the central weir, they will be on equal spacing—9 in. and equidistant from the two closest caps on the first row. The end caps would be 3 in. from the edge of the tray. The rows would be 1 ft 5.6 in., 10 in., 7.6 in. apart. This would appear to be a reasonable design.

Design of Downcomers

Edge downcomers will have an area of $4/2 = 2$ sq ft at the bottom. This is the seal-pot cross-sectional area. Since the length of the weir is 4.8 ft, or 58 in., the height of the downspout above the bottom of the seal pot will be $(2 \times 144)/58 = 5$ in.

To obtain 2-in. seal, it is necessary to suspend the seal pot 5 in. below the tray level.

The central downcomer will have an area of 5.9 sq ft and the seal-pot cross-section will be 2.95 sq ft. Length of weirs is 142 in., and height of a downcomer above bottom of seal pot is $(144 \times 2.95)/142 = 3$ in.

To obtain a 2-in. seal, it is necessary to suspend the central seal pot 3 in. below the tray level.

Location of Details

Bottom of side downcomers will be 8.9 in. from edge of column. Central downcomer will have its bottom edge centerlines 6 in. apart and centered in the column. An impingement plate will be placed 1 ft from top of straight portion of column, another 18 in. below gas inlet. The top plate will have 1-in. holes on 3-in. centers and the bottom plate 1 1/2-in. holes on 4-in. centers. ★★★

EDITOR'S NOTE: A PICTURE AND BIOGRAPHICAL SKETCH OF R. F. WEETER APPEAR ON PAGE 570.