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TITLE: OXYGEN STRIPPING FOR WATER FLOOD CORROSION CONTROL

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ABSTRACT: 1414-G

The corrosiveness of Lake Maracaibo water can be greatly reduced by removing its dissolved oxygen. A packed deaeration tower for this purpose was built and operated as a part of the Santa Bárbara Pilot Water Flood project. The oxygen is stripped with natural gas containing carbon dioxide. Carbon dioxide is absorbed in the process. As the carbon dioxide content of the water increases the pH decreases. Experimentally determined equations are given to show the relations between oxygen, carbon dioxide, and pH at various water throughputs and gas-water ratios.

Corrosion rates were determined on both the inlet and outlet sides of the tower. Flanged spools gave average corrosion rates over the time of the test period. Corrosometer probes were placed in different size pipe to determine the effect of water velocity.

The corrosion rates on the outlet side of the tower were only 10 to 15 per cent of those on the inlet side. The outlet piping was clean whereas the inlet piping was heavily scaled with corrosion products. Data are given to show the variation of corrosion rate with dissolved oxygen, carbon dioxide, and pH. The effect of water velocity is discussed.

It is concluded that a deaeration tower is a practical means of reducing the corrosiveness of Lake Maracaibo water.

INTRODUCTION:

Water flooding has long been recognized as a profitable means of increasing petroleum production. The payout can be especially attractive in those areas such as Lake Maracaibo where there is an abundant supply of water. The reservoirs in this area are large enough to take large volumes of water over long periods of time. This increases return on ivestment since construction and operating costs per barrel injected are less than for low volume - short life floods.

A factor that can markedly reduce the investment return on a long life flood is the expense due to equipment corrosion. The allowable corrosion rates in a 20 year flood are one half those of a 10 year flood. The nature of corrosion is such that the frequency of corrosion failures reaches a maximum in the later life of a flood near its economic limit. Repairs and replacements that would be economically feasible in the first 5 years of a 20 year flood become prohibitive in the last 5 years. Only a well planned corrosion control program started early will prevent costly corrosion failures in later years. The best time to develop corrosion prevention techniques is during the operation of the pilot flood.

Creole has 3 pilot floods operating in Lake Maracaibo. Corrosion data have been collected in one of them, the Santa Bárbara Pilot Flood, a 13,000 bpd flood in the Punta Benítez area of the Tía Juana field. Corrosion rates were determined with coupons, corrosometer probes, spools, oxygen consumption, and equipment and flowline inspection. Average corrosion rates of 75 to 80 mpy and pitting rates of over 100 mpy were measured. At these rates and with no corrosion control program the first leak would appear in a 4 inch schedule 40 pipe in roughly 2 years.

The principal contributing factor to the corrosiveness of Lake Maracaibo water is its dissolved oxygen content. There was reason to believe that removal of this oxygen would reduce the corrosiveness to a tolerable level. The decision was made to incorporate an oxygen removal experiment in the pilot flood. After looking at several alternate methods, it was decided to remove the oxygen in a stripping tower with a counter-current flow of natural gas.

A packed deaeration tower was designed by Creole Petroleum Engineers and built in the La Salina Central Shops. A schematic diagram is shown in figure 1. The tower was 30 feet high and 24 inches in diameter. There were two 5.5 foot packs of 1 inch berl saddles, a commercial packing material. The water entered the top of the tower and fell by gravity over the berl saddles. The gas entered the bottom and passed up through the pore space of the packing where it came in intimate contact with the water. The throughputs of water and gas were varied to give the desired degree of oxygen removal. The tower was usually operated at a water throughput of 3500 bpd and a gas throughput of 5250 cfpd for a gas-water ratio of 1.5 cfpb.

TOWER DESIGN:

It is well at this point to discuss some of the theoretical aspects of packed tower design. It will then be easier to understand the results of the corrosion rate studies. The sole purpose of the tower was to reduce the corrosiveness of the injection water. However there was a complicating factor; the stripping gas contained approximately 5 per cent carbon dioxide which was absorbed by the water. It was necessary to determine the relationship between oxygen removed and carbon dioxide absorbed and the effect of the dissolved carbon dioxide on the corrosiveness of the oxygen-free lake water.

Henry's law states that the quantity of gas dissolved in a given quantity of liquid is directly proportional to its partial pressure over the liquid. The Henry's law curve for oxygen is shown in figure 2. It is labeled the equilibrium curve. For any value of the partial pressure of oxygen on the ordinate the equilibrium solubility in water is given on the abscissa.

Frequently for a given sample of water, the oxygen concentration does not fall on this curve. In such cases, the dissolved oxygen is not in equilibrium with the oxygen in the gas phase. There will be a transfer of oxygen from one phase to the other until equilibrium is attained. If the point falls above the curve, there will be a transfer of oxygen from the gas to the liquid; if below, from the liquid to the gas. The latter is the case found in the deaeration tower.

The operating curve shows the actual operating conditions in the tower and falls below the equilibrium curve. The water enters the tower with an average of 3.85 ml/l oxygen and discharges with 0.05 ml/l. The gas absorbs approximately 1.5 per cent oxygen in the process.

Figure 3 shows the case for carbon dioxide. Here the operating curve lies above the equilibrium curve so that there is a transfer of carbon dioxide from the gas to the liquid. The carbon dioxide content of the gas is reduced from 5.3 per cent to about 0.6 per cent and the water absorbs 25 ppm carbon dioxide. Both figures 2 and 3 are for 3500 bpd and 1.5 cfpb.

Analyses were made for both oxygen and carbon dioxide on the outlet side of the tower. The data are shown plotted in figure 4. A least squares calculation gave the equation

$$\left[O_2\right]_{\mathrm{ml/l}} = -0.08 + \frac{3.2}{\left[CO_2\right]_{\mathrm{ppm}}} \qquad (1)$$

where $\left[O_2\right]_{\mathrm{ml/l}}$ is the oxygen concentration in ml/l and $\left[CO_2\right]_{\mathrm{ppm}}$ the carbon dioxide concentration in ppm. This equation is characteristic of the lake water and stripping gas and is independent of the tower. It will be true for any tower stripping water with 3.85 ml/l oxygen using gas with 5 per cent carbon dioxide. An equation of this form but with different constants will always be found when the stripping gas contains carbon dioxide.

Equation (1) has a practical use. Inexperienced personnel have difficulty obtaining accurate results with the analytical procedure for oxygen. The procedure for carbon dioxide is simple, rapid, accurate, and easily performed by non-technical people. Using a conversion chart drawn from Equation (1) the tower operators maintain control over the outlet oxygen concentration by analyzing for carbon dioxide.

Carbon dioxide forms carbonic acid in water; hence the pH of the lake water decreases as carbon dioxide is absorbed. A plot of the pH data is shown in figure 5. The equation for this curve is

$$\mathrm{pH} = 7.7 - \mathrm{Log}_{10}\left[CO_2\right]_{\mathrm{ppm}} \qquad (2)$$

This equation is characteristic of the lake water and will be found for any tower stripping lake water. Of course no change in pH will be observed unless the stripping gas contains carbon dioxide.

When combined with equation (1), equation (2) also has a practical use. It is possible to regulate the oxygen content of the water by the use of pH recording controllers. The controller actuates a valve to vary the inlet gas flow maintaining the correct gas-water ratio and outlet pH. The same control could be accomplished with automatic dissolved oxygen analyzers but these instruments are more expensive and require considerably more attention.

CORROSION STUDIES:

Figure 6 is a schematic of the tower and the piping used in the corrosion studies. Corrosometer probes were placed in 2 inch and 4 inch elbows on both the inlet and outlet sides of the tower; CP-1 through CP-5 on the inlet side and CP-6 through CP-11 on the outlet side. Spools S-1 through S-3 were on the inlet side and S-4 through S-6 on the outlet side. Outlet water samples were taken at valve SO-2 and inlet samples at SO-1.

The corrosion rate data were complicated by erratic tower operation due to clogging. The filter did not operate properly so that algae, scum, debris, and even small crabs lodged in the pore space of the packing. As the pore space filled, the efficiency of the tower decreased resulting in a smaller oxygen removal. The tower finally flooded six weeks after startup. It was partially chemically cleaned and put back in service but flooded at 2 to 4 week intervals after that.

The decreasing efficiency of the tower was compensated for by decreasing the water throughput. The corrosion rates were affected by two changing variables; changing oxygen content and changing water velocity. The spools were put into the piping at the beginning of the test and not removed until the end. They were subject to the corrosion rate variations and integrated the different corrosion rates to an average value of 10 mpy over the total time of the test. This rate corresponds to 80 per cent protection. Although the tower was giving poor performance in oxygen removal, the corrosion rates were significantly less than for aerated lake water.

The most striking evidence of the effectiveness of the tower was afforded by the appearance of the spools. In 62 operating days the inlet spools has acquired a 1/8 inch hard scale; the outlet spools were clean. Thus deaeration greatly reduces scaling or possibly eliminates it entirely. This in itself is an important benefit since insoluble corrosion products that pass downhole plug the injection sands and reduce injectivity.

No pitting was found but because of the short duration of the test this does not necessarily mean that deaeratiion eliminates pitting. However, since pitting is associated with oxygen corrosion it would be expected that deaeration would greatly reduce or eliminate pitting.

The corrosometer measures corrosion by following the increase in electrical resistance of a probe immersed in the corroding medium. The corrosion rate is a differential rate obtained on a day-to-day basis without requiring equipment shutdown. Although the corrosion rates varied in the tower due to the clogging and flooding, with the corrosometer it was possible to get a correlation between corrosion rates and oxygen content. The data are shown in figure 7. Plotted on the ordinate is the ratio of the outlet corrosion rate to inlet corrosion rate rather than the actual outlet corrosion rate. This was done because the inlet and outlet corrosion rates varied with water throughput but their ratio did not. This procedure eliminated the effect of changing water velocity.

The corrosion curve in figure 7 appears anomalous at first analysis. Most investigators have reported a linear decrease in corrosion rate with decrease in oxygen. Figure 7 shows an increasing corrosion rate with decrease in oxygen, passing through a maximum at 0.13 ml/l oxygen and then decreasing to a minimum value at zero oxygen. It is believed that **this** behaviour is due to the effect of the absorbed carbon dioxide. Figure 8 is postulated as an expansion of figure 7. No measurements were made in the areas of the dotted part of the curve but there are data reported in the literature (1) (2) (3) that indicate that the shape of the curve as proposed here is not far wrong.

The lake water in the Punta Benítez area usually has a pH of 8.3. As it passes through the tower, oxygen is removed, carbon dioxide is absorbed, and the pH decreases. At first the corrosion rate decreases linearly with decreasing oxygen. At pH 7, oxygen 0.56 ml/l, the water passes to the acid side and the corrosion rate starts to increase. This trend continues down to pH 6.3, oxygen 0.13 ml/l, at which point the decrease in oxygen again becomes the more important factor and the corrosion rate begins to decrease. The lowest corrosion rates of the test were observed at zero oxygen, pH 6.0. No corrosion rate data were taken at higher gas-water ratios but pH's were measured as low as 5.5 at 4 cfpb. Slightly higher corrosion rates are to be expected at these lower pH's.

Figure 8 indicates that to obtain the maximum reduction in corrosion rate a tower must be operated over a narrow range of gas-water ratios. The lowest corrosion rates in the Santa Bárbara tower were obtained with gas-water ratios giving zero oxygen, 48 ppm carbon dioxide, and pH 6.0. The lowest rate measured was 8 mpy at 2.5 fps water velocity for 90 per cent protection.

WATER VELOCITY EFFECT:

If not properly evaluated changes in water velocity will obscure trends in corrosion rate data. To specify a corrosion rate without stating the water velocity is meaningless. This is the reason Figures 7 and 8 have plotted on the ordinate the ratio of outlet and inlet corrosion rates rather than absolute outlet corrosion rates. This was the only way to eliminate the effect of varying water throughput in the piping.

To evaluate the water velocity effect the corrosometer probes were placed in both 2 inch and 4 inch pipe. Although the absolute velocity varied during the time of the tests the ratio of velocity in the 2 inch pipe to that in the 4 inch pipe was always 4.

Corrosion at a pipe wall is an example of mass transfer just as were the oxygen and carbon dioxide transfer in the tower. The same mathematical approach is valid for either case. For oxygen corrosion, the corrosion rate at a metal surface is directly proportional to the rate of diffusion of oxygen to that surface. A theoretical equation (4) (5) that has been successfully used to explain such a corrosion mechanism in the case of water flowing in a pipe is

$$k_c = K \frac{D_v}{D} R_e^{0.83} \qquad (3)$$

where kc is the mass transfer coefficient in lb. moles/(hr) (ft) (lb. mole/ft), K a constant, Dv the molecular diffusivity in ft/hr, D the diameter of the pipe, and R_e the dimensionless Reynolds number. For a constant mass rate of flow only R_e and D vary between 2 inch and 4 inch pipe so that for a constant oxygen concentration

$$\frac{\text{(CORROSION RATE IN 2" PIPE)}}{\text{(CORROSION RATE IN 4" PIPE}} = 2 \left(\frac{R_e \text{ (2" PIPE)}}{R_e \text{ (4" PIPE)}} \right)^{0.83} \qquad (4)$$

For constant mass rate of flow

$$R_e \text{ (2" PIPE)} = 2\, R_e \text{ (4" PIPE)} \qquad (5)$$

Putting (5) into (4) gives

$$\frac{\text{(CORROSION RATE IN 2" PIPE)}}{\text{(CORROSION RATE IN 4" PIPE)}} = (2) \times (2)^{0.83} = 3.56 \qquad (6)$$

Corrosion rates found in practice seldom fit equation (3). Usually the exponent on R_e is much less than 0.83. This was found to be the case on the inlet side of the tower. The ratio of the corrosion rates in the 2 inch pipe to those in the 4 inch pipe were 2.58, much less than the theoretical 3.56. Equation (3) refers to one variable, water velocity at a constant oxygen concentration but the oxygen diffusion rate is depended on 3 variables; the total oxygen content, the water velocity, and the thickness of corrosion product. Apparently in the oxygen saturated water on the inlet side of the tower, the diffusion rate of oxygen through the scale is not as sensitive to turbulence as implied by Equation 3.

The average ratio of corrosion rates in the outlet piping was 3.43, much nearer the theoretical value. This is believed to be due to the absence of scale.

For a given mass rate of flow R_e is proportional to (1/D). Using this relation in Equation (3) gives

$$\frac{\text{(CORROSION RATE AT DIAMETER } D_2\text{)}}{\text{(CORROSION RATE AT DIAMETER } D_1\text{)}} = \left(\frac{D_1}{D_2}\right)^{1.83} \qquad (7)$$

This relation is shown in Figure (9)

Figure 9 illustrates the importance design plays in reducing corrosion rates. For a flood injecting deaerated lake water, the corrosion rate in a 6 inch injection line will be 50 per cent that in a 4 inch line; that in an 8 inch line 28 per cent of that in a 4 inch line. Injection lines should be designed as large as economically practical to reduce the velocity effect.

CONCLUSIONS:

The Santa Bárbara deaeration tower experiment was done to determine if deaeration is a practical means of reducing corrosion in Lake Maracaibo water flood, to determine the effect of water velocity on corrosion rates, and to gain experience in operating a deaeration tower. The conclusions were:

1. Deaeration towers are a practical means of reducing lake water corrosiveness. Corrosion rates are reduced as much as 90 per cent.

2. Deaeration greatly reduces or eliminates scaling. No pitting was observed.

3. A packed tower is subject to clogging and flooding. Future towers will be tray towers.

4. For best results a tower should be operated over a narrow range of gas-water ratio. Towers may be controlled by pH recording controllers.

5. Water flood piping should be designed with as large a diameter as practical.

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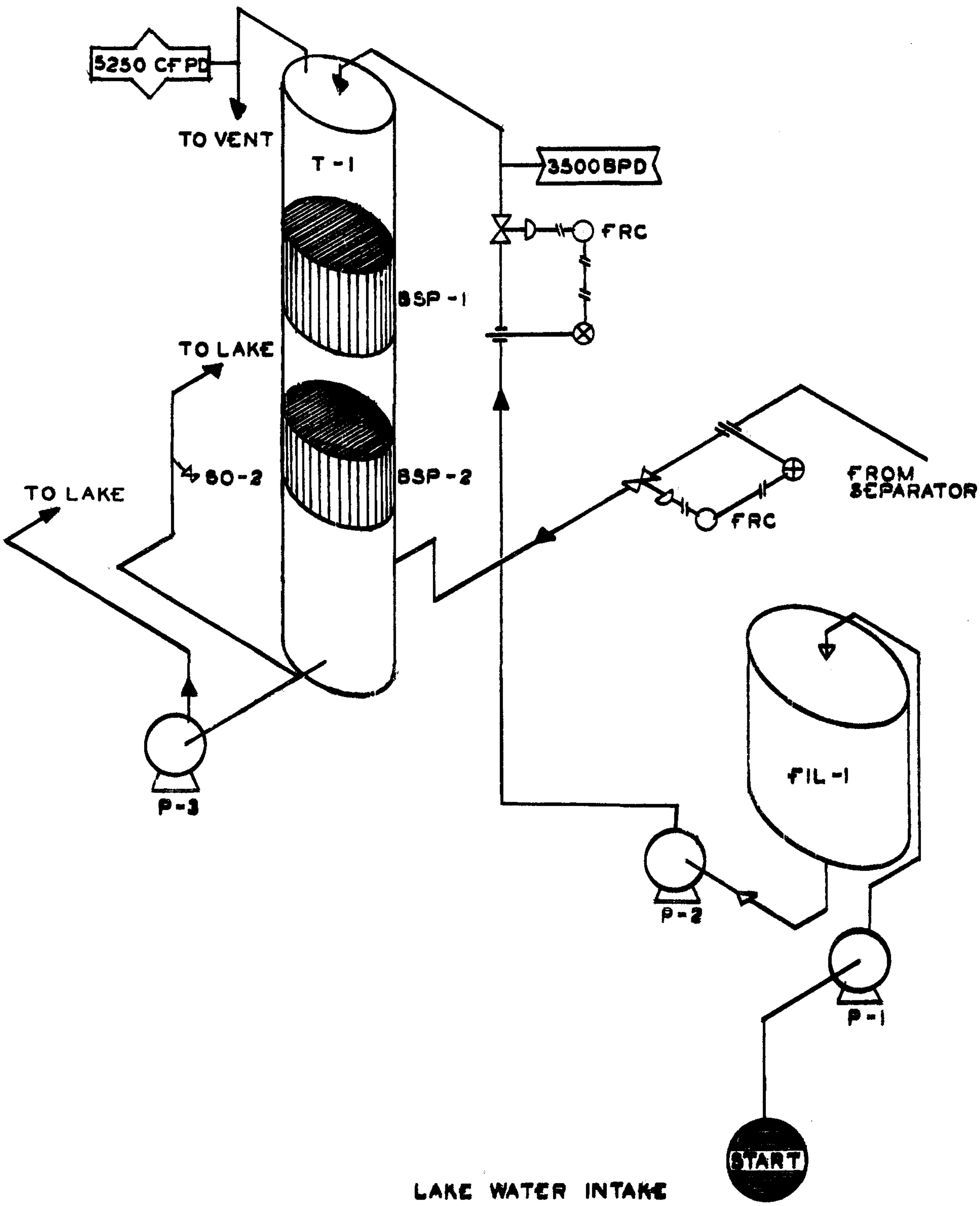


DEAERATION TOWER
FIGURE - 1

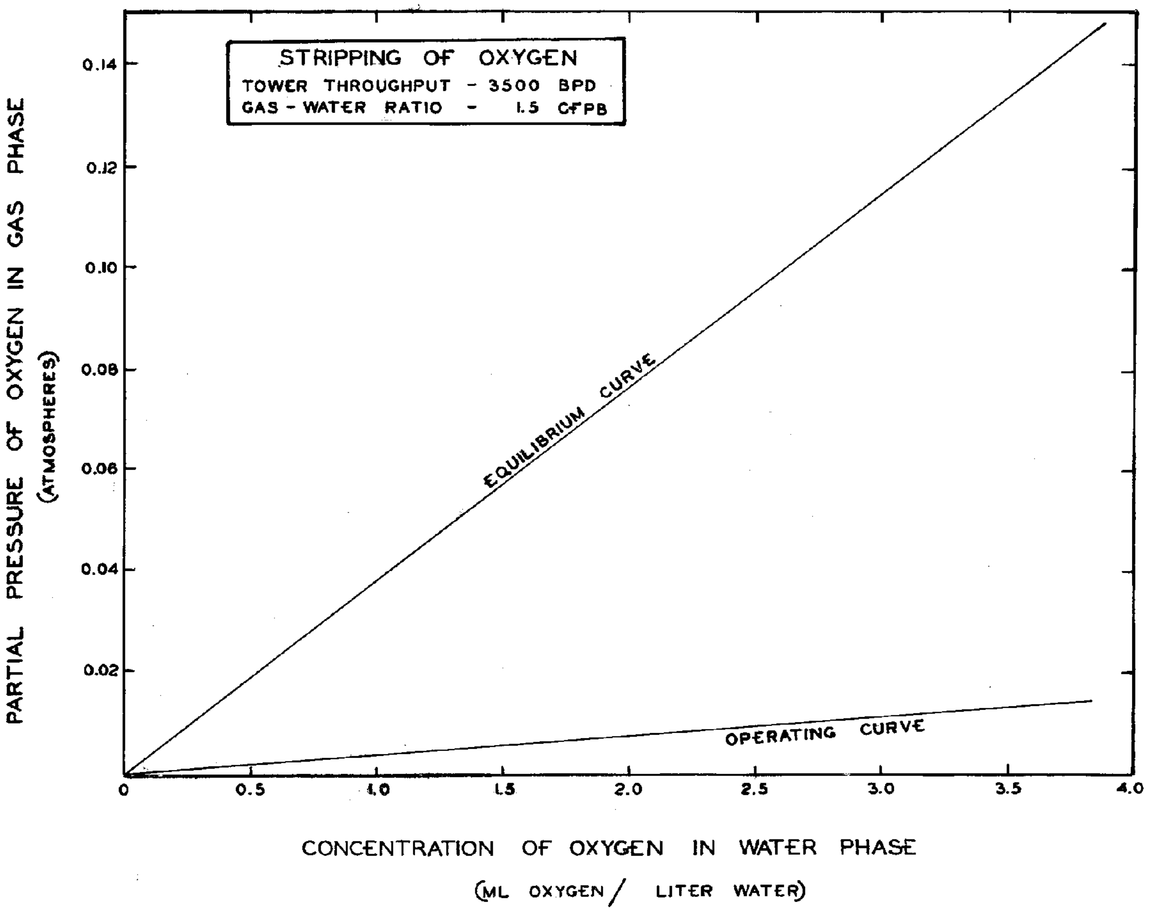


FIGURE - 2

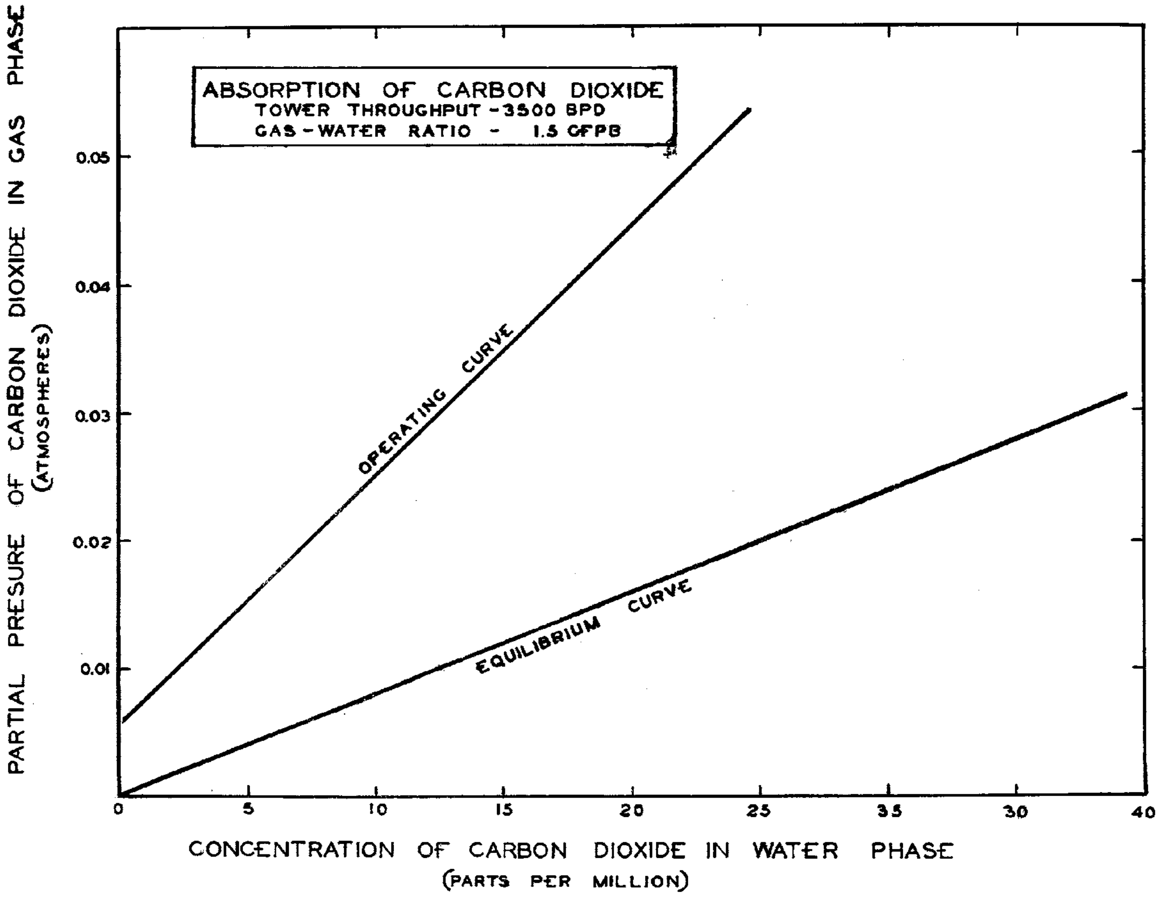


FIGURE - 3

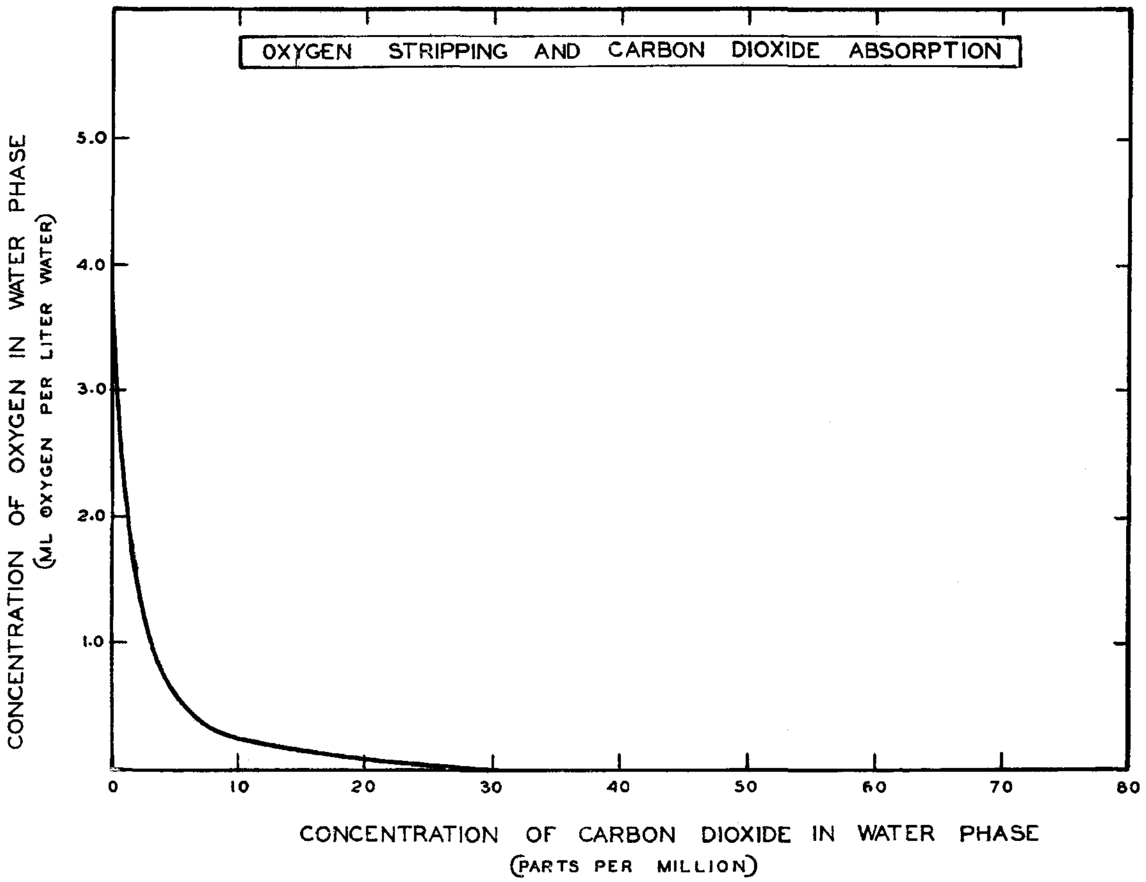


FIGURE - 4

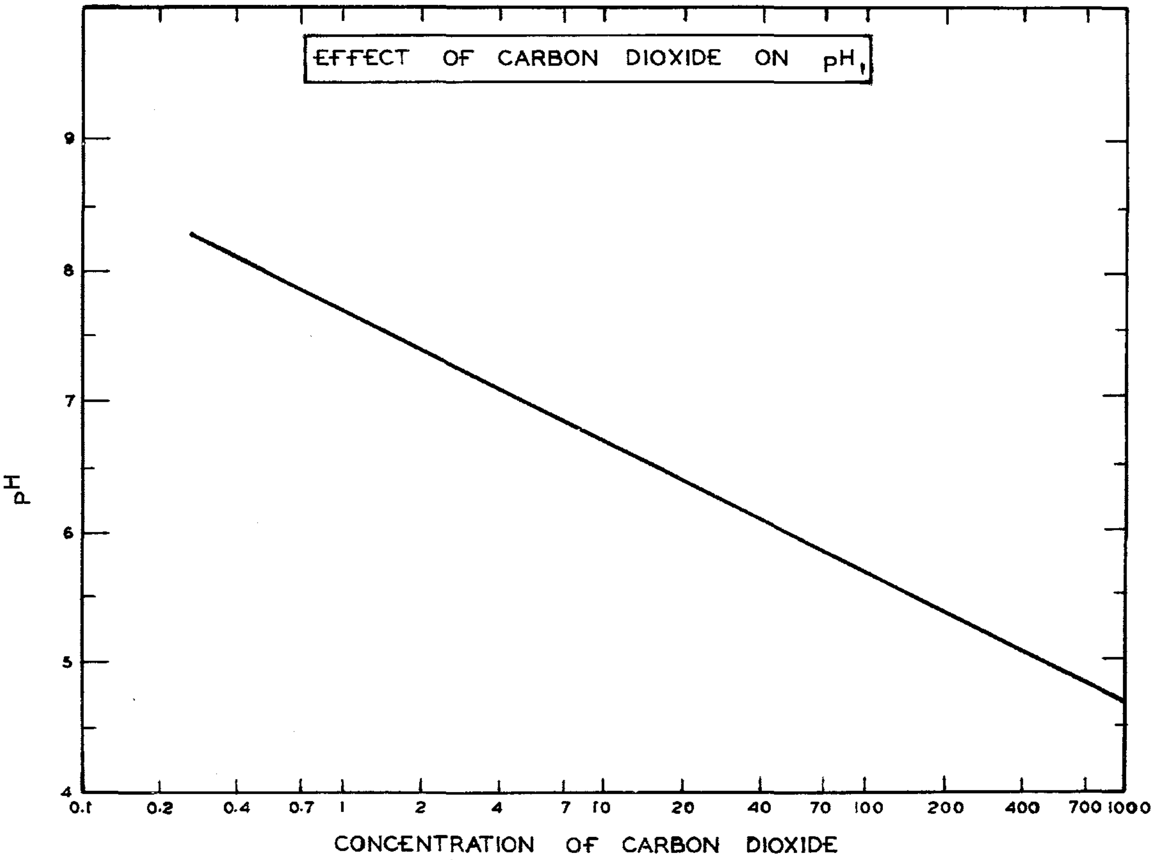
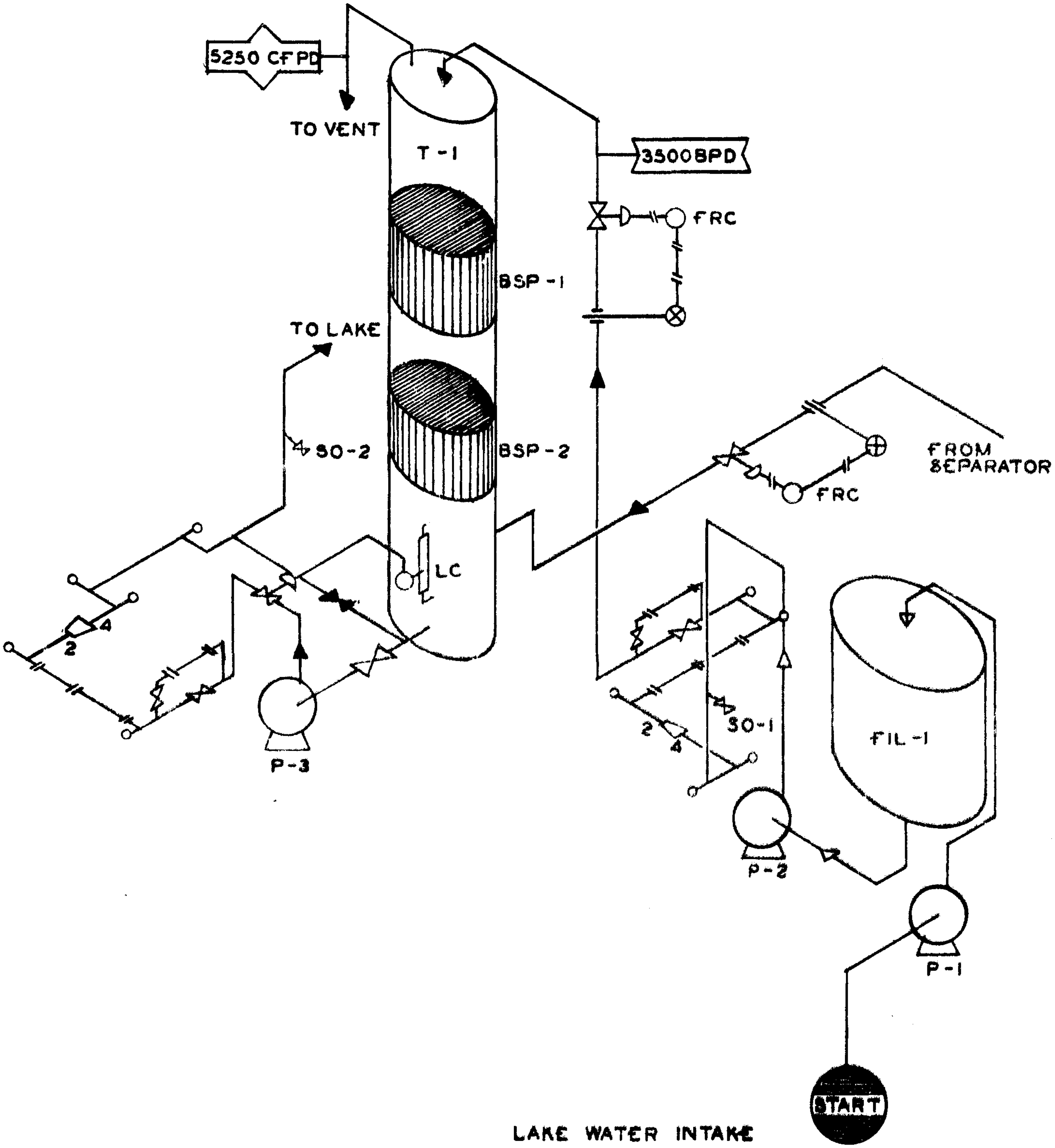


FIGURE - 5



FLOW DIAGRAM
DEAERATION TOWER

FIGURE - 6

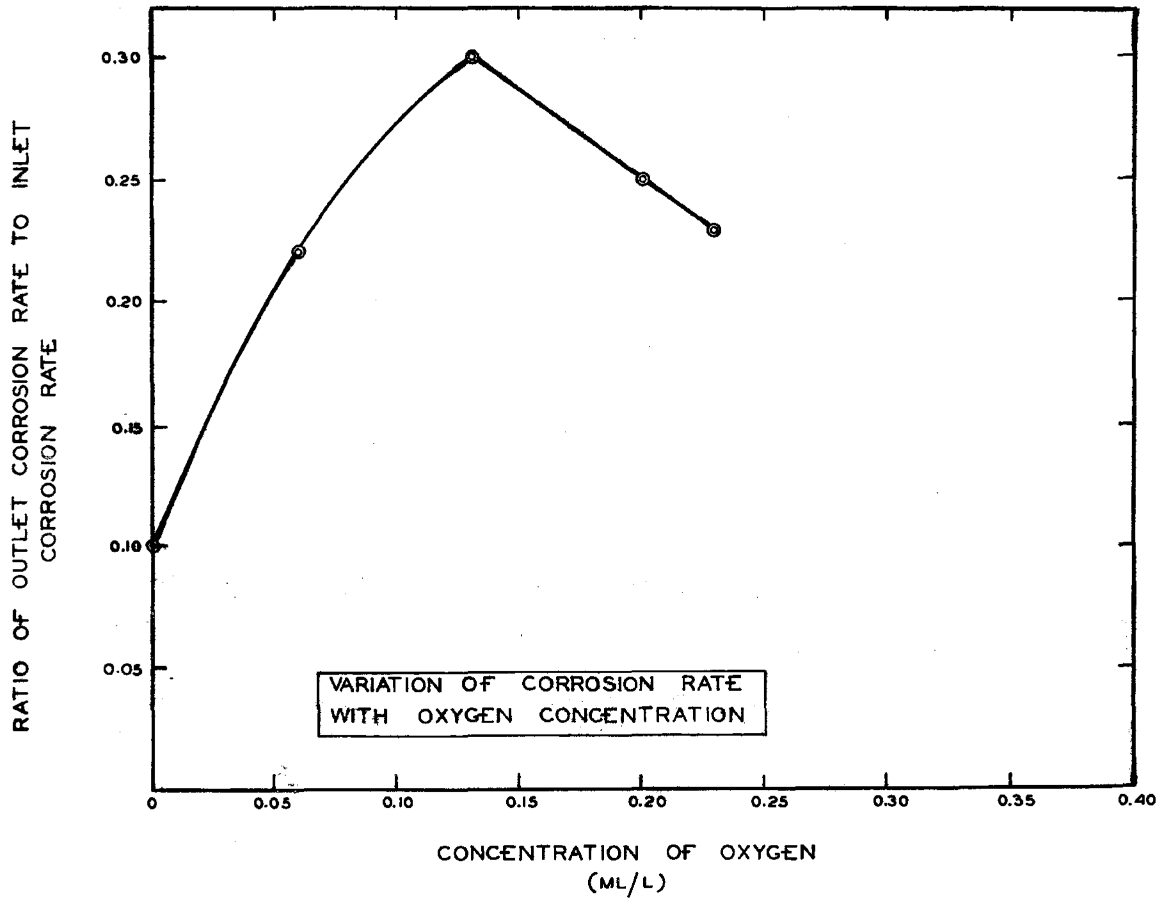


FIGURE - 7

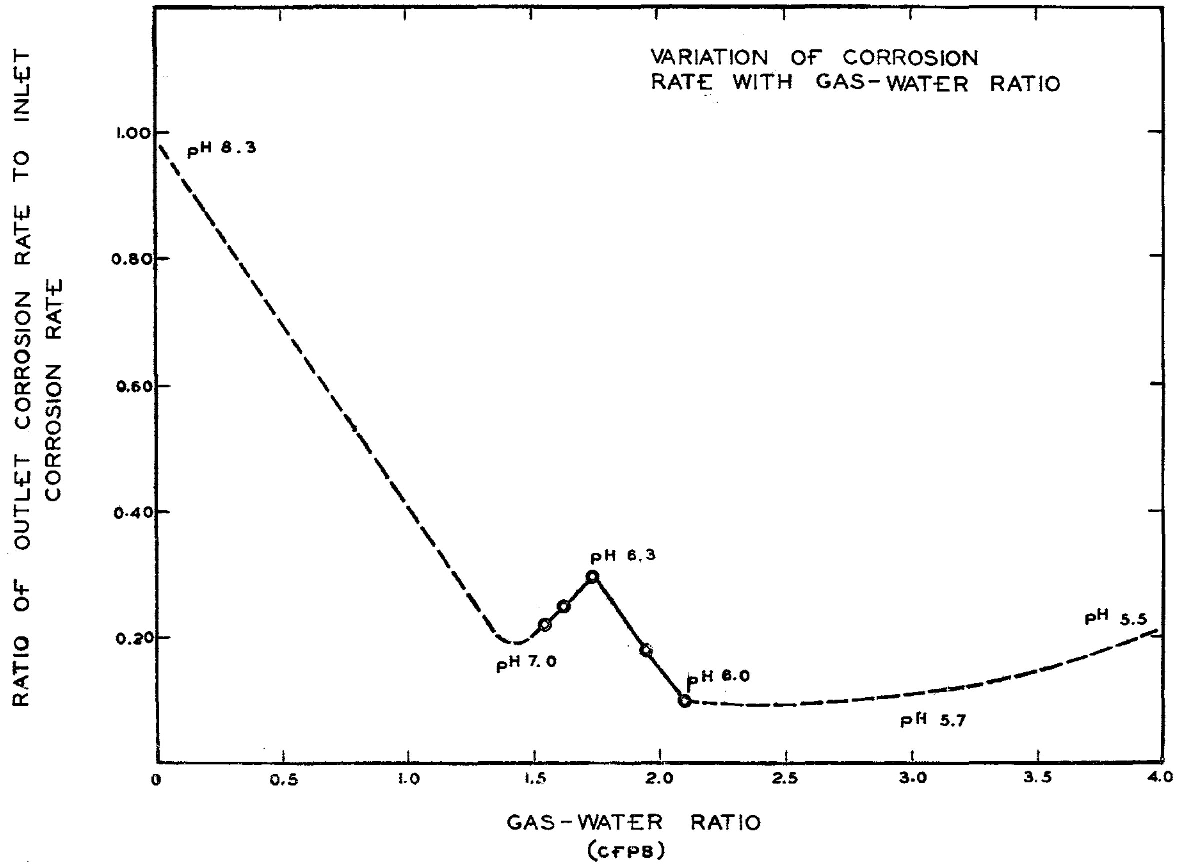


FIGURE - 8

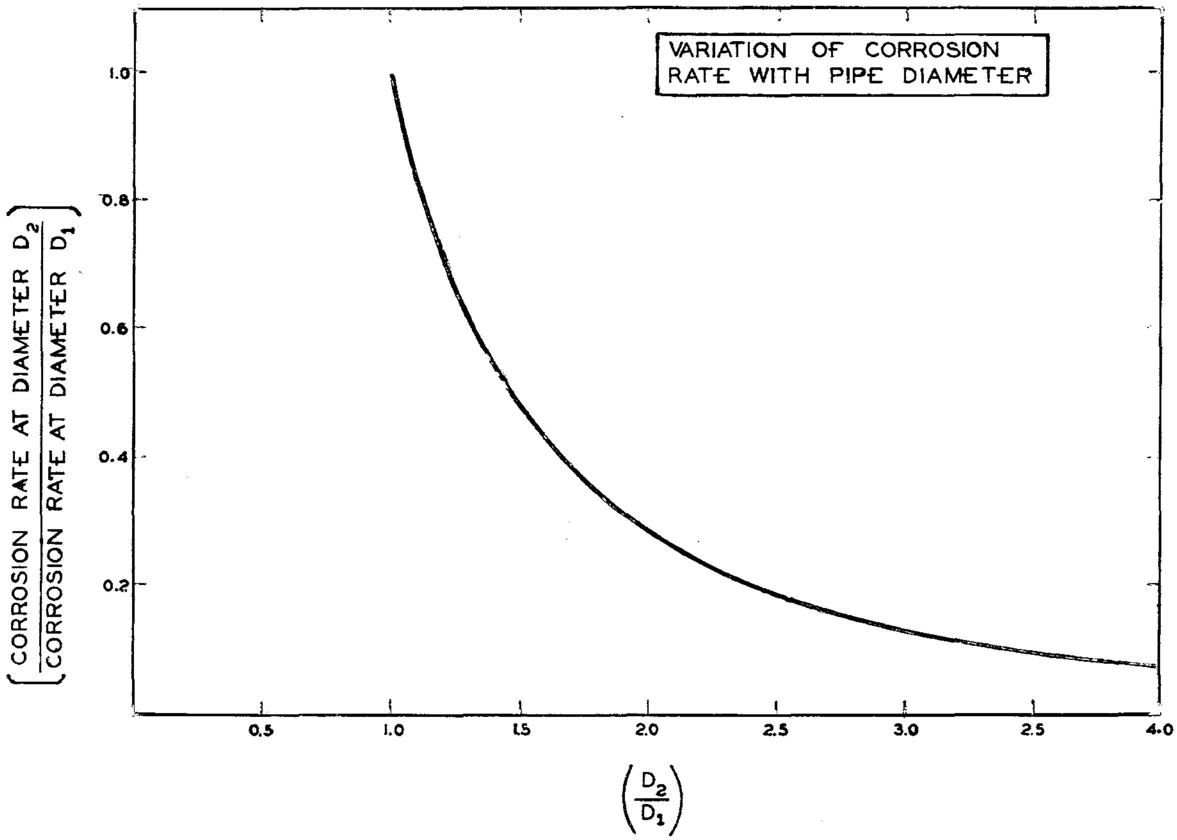

VARIATION OF CORROSION RATE WITH PIPE DIAMETER
1.0
0.8
0.6
0.4
0.2
0.5
1.0
1.5
2.0
2.5
3.0
2.5
4.0
$\left(\frac{\text{CORROSION RATE AT DIAMETER } D_2}{\text{CORROSION RATE AT DIAMETER } D_1}\right)$
$\left(\frac{D_2}{D_1}\right)$

FIGURE - 9