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Assistant Secretary, Conservation
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DEVELOPMENT OF THE UTILIZATION OF COMBUSTIBLE GAS PRODUCED IN EXISTING SANITARY LANDFILLS: EFFECTS OF CORROSION AT THE MOUNTAIN VIEW, CA LANDFILL GAS RECOVERY PLANT

United States
Department of Energy

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Prepared by:
Pacific Gas and Electric Company
San Francisco, CA
Under Contract No. DE-FG01-79CS20201

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ABSTRACT

Corrosion of equipment has occurred at the Mountain View, California Landfill Gas Recovery Plant. Corrosion is most severe on compressor valve seats and cages, tubes in the first and second stages of the interstage gas cooler, and first and second stage piping and liquid separators. Corrosion occurs because the raw landfill gas contains water, carbon dioxide, and oxygen. Some corrosion may also result from trace concentrations of organic acids present in the landfill gas. Corrosion of the third stage compressor, cooler, and piping does not occur because the gas is dehydrated immediately prior to the third stage. Controlling corrosion is necessary to maintain the mechanical integrity of the plant and to keep the cost of the gas competitive with natural gas. Attempts to reduce corrosion rates by injecting a chemical inhibitor have proved only partially successful. Recommendations for dealing with corrosion include earlier dehydration of the gas, selection of special alloys in critical locations, chemical inhibition, and regular plant inspections.

EXECUTIVE SUMMARY

The Mountain View, California Landfill Gas Recovery Plant has been operating since May 1978. Raw landfill gas from an area of the Mountain View Shoreline Regional Park Sanitary landfill is extracted under vacuum through 33 wells, compressed and cooled in two stages, dehydrated and stripped of CO_2 and trace organics, compressed and cooled a third time and injected into PGandE's natural gas transmission line L-101 which services the San Francisco peninsula. Corrosion of plant equipment in contact with the gas prior to dehydration and CO_2 removal is a problem. Corrosion occurs because the gas contains water, CO_2 and O_2. Without water, corrosion would not occur. Compressor valve seats and cages, tubes in the first and second stage coolers, and first and second stage piping and liquid separators have been severely corroded. A uniform rust-type coating has been observed on most internal surfaces of the first and second stages, but localized pitting on tubes and pipes and velocity related erosion-corrosion on pipe bends and compressor valves are responsible for major loss of mechanical integrity in plant equipment. Corrosion must be controlled to preserve employee safety around high pressure piping and to avoid high maintenance costs which would make the gas economically uncompetitive with other forms of gas.

Corrosion is monitored on ten corrosometer probes located throughout the plant. The probes are useful for detecting general changes in corrosion but cannot detect localized pitting. Removal and inspection of cooler tubes, process piping, and compressor valve seats and cages was done to determine the extent and nature of corrosion attack.

Injecting a chemical corrosion inhibitor proved only partially successful in reducing corrosion. Keeping all internal surfaces coated with inhibitor is extremely difficult in a plant of this type. Other problems were experienced with the inhibitor including gumming of compressor valves and plugging of pipes.

Recommendations to control corrosion at the existing plant include selection of corrosion and stress corrosion cracking resistant alloys in critical areas, continued testing and use of corrosion inhibitors, and regular plant inspections to check for corroded parts. Future plants should be designed to wash the gas of chlorides and sulfides so that regular stainless alloys can be used without stress corrosion cracking occurring, and to dehydrate the gas as early as possible. Routine inspections for corrosion should also be conducted.

INTRODUCTION

This report is part of a program conducted by PGandE and the Department of Energy (DOE) to determine how to most efficiently utilize combustible from gas existing landfills. Using the Mountain View, California landfill as the model, the following tasks form the basis of the "Utilization of Combustible Gas" Program:

- Corrosion Evaluation
- Gas and Condensate Analyses
- Investigation of Effects of Air Inclusion
- CO_2 utilization

One of the more serious problems related to landfill gas utilization is that of corrosion. Corrosion may occur in equipment in the presence of hydrogen sulfide, oxygen, water, and carbon dioxide. Corrosion may take place in the piping network used to draw the gas from the landfill, in the gas compression and treatment systems, or in pipelines used to transport the treated gas to customers. This report details operational problems related to corrosion and why they occurred at the existing PGandE landfill gas recovery plant at Mountain View and discusses methods to control or eliminate corrosion.

OBJECTIVES OF THE CORROSION INVESTIGATION

In determining the overall feasibility of a landfill gas utilization project, the problem of corrosion must be considered. The main objectives of the corrosion investigation are the determination of how much corrosion will occur, and the choice of the proper materials and systems to be employed to eliminate or control corrosion. Specifically, the objectives are:

1) Determine what chemical compounds in the extracted gas cause corrosion and in what concentrations they occur in the gas.
2) Determine the degree of corrosion resulting from present concentrations of corrosive compounds.
3) Select proper systems to eliminate corrosive agents or select proper materials and inhibitors to reduce the effects of corrosive agents not eliminated.

PLANT RECOVERY DESCRIPTION

The Mountain View Landfill Gas Recovery Plant began operation in May, 1978, following four years of development work by PGandE, the City of Mountain View, California, and the U.S. Environmental Protection Agency. The plant recovers and treats landfill gas produced by the natural decomposition of municipal solid waste from a 30-acre site within the Shoreline Regional Park landfill in Mountain View.

The Mountain View Landfill Gas Recovery Plant consists of 33 shallow wells and a collection system, all constructed of plastic pipe, feeding gas into a central gas treatment facility (Figure 2). The gas enters the plant at a slight vacuum, goes through a liquid separator, is compressed to about 45 psig, and cooled in a single pass forced air gas cooler. The cooled gas goes through a second liquid separator, is compressed to 160 psig and cooled in a three-pass cooler. The cooled gas goes into a third liquid separator before going to the treatment section which consists of 3 parallel adsorption columns containing beds of activated alumina, activated carbon, and molecular sieves which remove organic materials, water, and carbon dioxide. The treated gas is compressed to 350 psig for injection into the nearby PGandE transmission line L-101. The adsorption beds are regenerated by vacuum at atmospheric temperature. A schematic flow diagram is given in Figure 3. With the exception of a few minor equipment items, the process equipment in contact with the gas within the plant area is made of carbon steel.

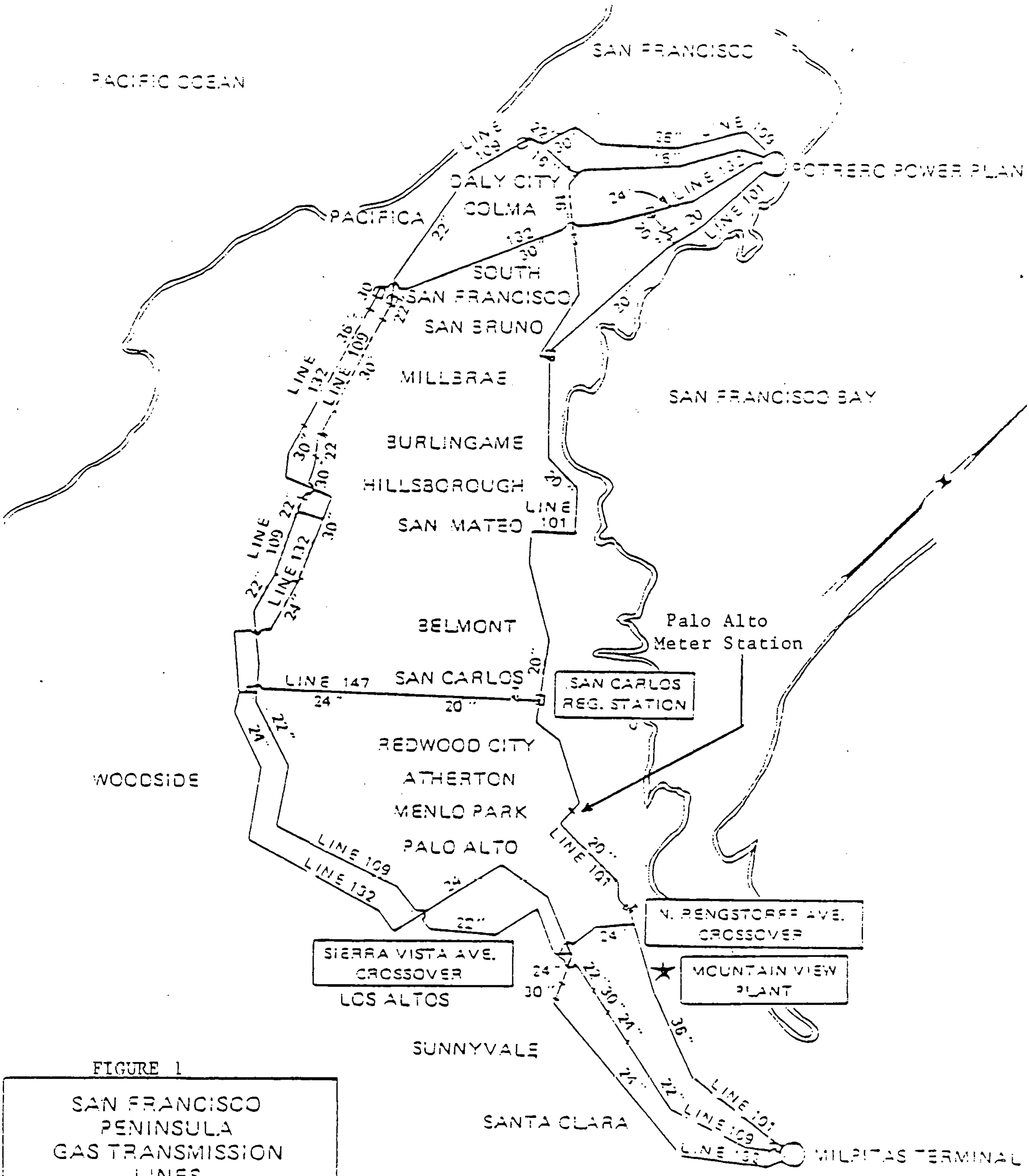
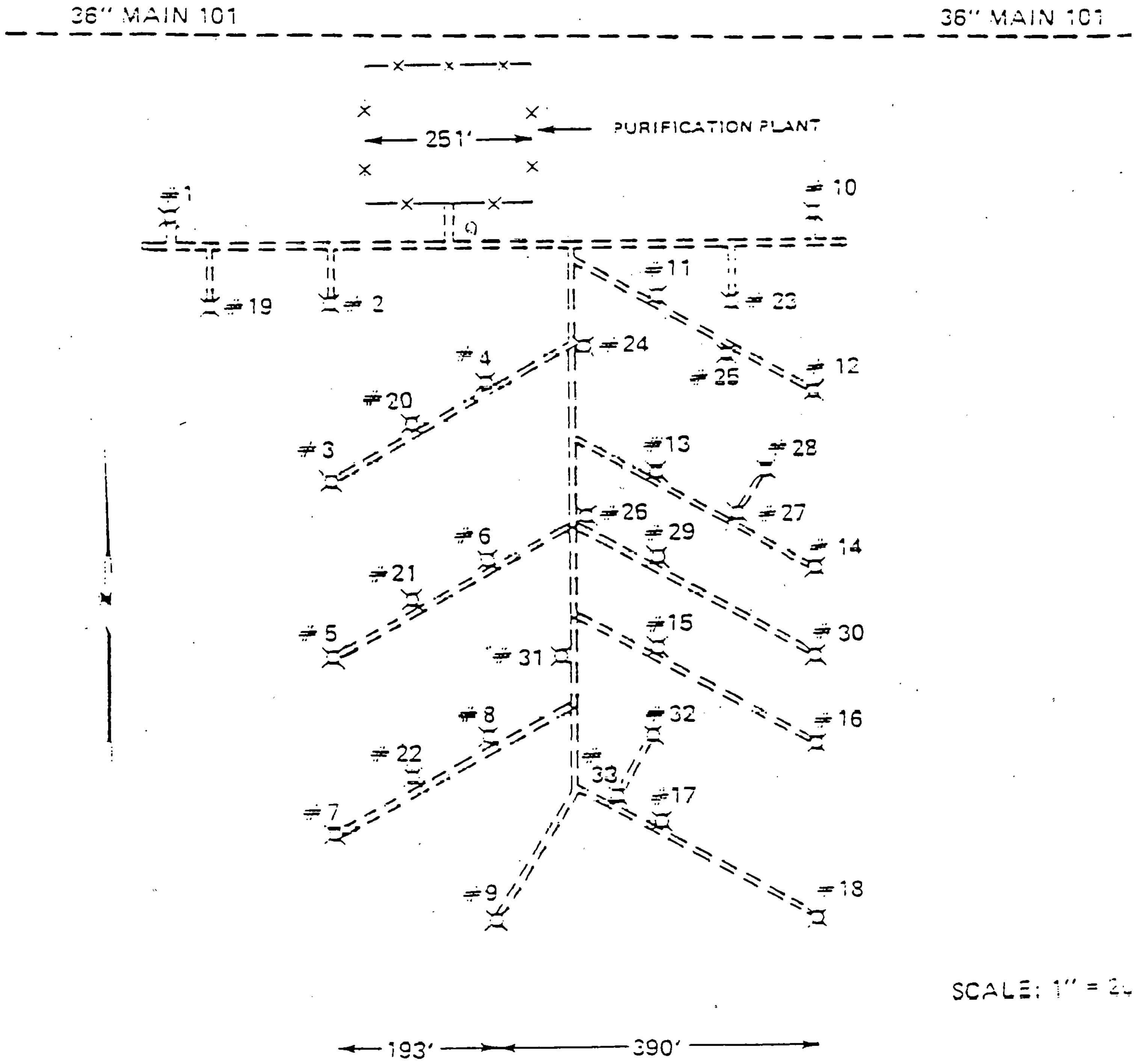


FIGURE 1

SAN FRANCISCO
PENINSULA
GAS TRANSMISSION
LINES



SCALE: 1" = 2

NOTE:

WELLS 19 THROUGH 3
ADDED SEPTEMBER 19

FIGURE 2

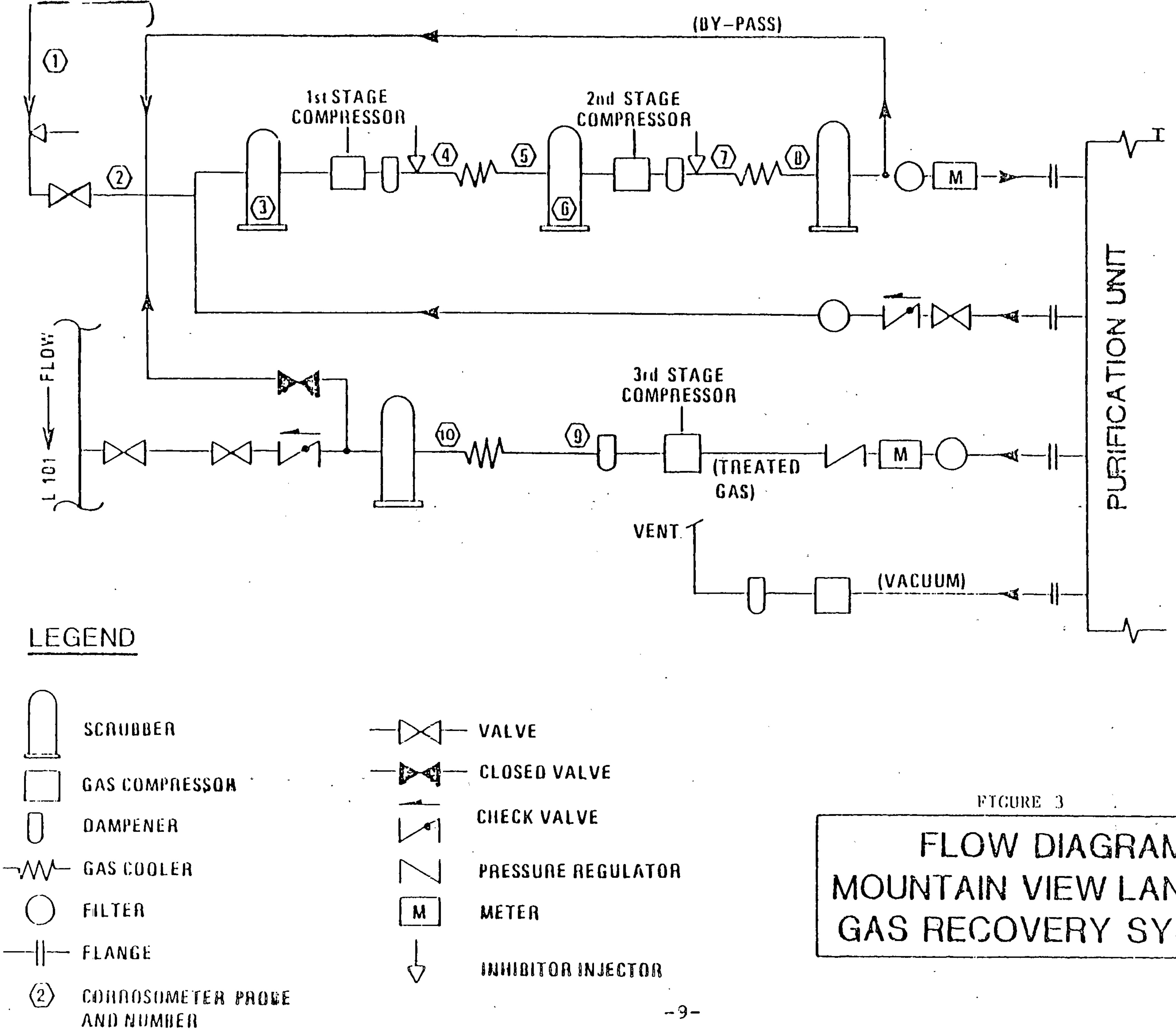


FIGURE 3

FLOW DIAGRAM MOUNTAIN VIEW LANDFILL GAS RECOVERY SYSTEM

The typical gas compositions, pressures, and temperatures for each compression stage are given in Table 1. The plant is designed for processing 1 MMSCF/D of raw gas and has been operating at about half that value for the approximately 9,000 hours of operation since startup in June, 1978 (Figure 4). A total of over 100 MMSCF of treated gas has been injected into L-101 (Figure 5).

When a landfill is covered, a limited amount of air is trapped in the landfill with the municipal solid waste (MSW). Aerobic microorganisms convert MSW to CO_2 and water until oxygen is depleted. Anaerobic microorganisms produce the principal gaseous constituents of landfill gas, CH_4 and CO_2.

When gas is extracted from a landfill at a rate greater than the gas is produced, air will intrude into the landfill across the cover. Under limited air intrusion near the surface of the landfill, aerobic microorganisms convert the oxygen to carbon dioxide. Excessive air intrusion will poison the anaerobes and cause methane production to cease. The nitrogen in the intruding air is not toxic to the microorganisms but does depress the heating value of the product gas. Additionally, oxygen drawn into the landfill amplifies the corrosion potential of the landfill gas drawn into the gas recovery plant.

TABLE 1 AVERAGE GAS COMPOSITIONS
AND
PROCESS CONDITIONS AT VARIOUS PLANT LOCATIONS

	Average Composition						
	CH_4(%)	CO_2(%)	N_2(%)	O_2(%)	H_2(%)	H_2S(ppm)	H_2O(#/MMSCF)
Raw Gas	50	35	13	1.7	0.3	9-500	(Sat.)
Treated Gas	73	5.5	19.5	1.75	0.25	0.2	7

Location	Temperature °F	Pressure psig	CO_2 psia	O_2 psia
1st Stage Compressor Discharge	250.	45	21.	1.0
1st Stage Cooler Discharge	70.	45	21.	1.0
2nd Stage Compressor Discharge	300	160	61.	3.0
2nd Stage Cooler Discharge	70	160	61.	3.0
3rd Stage Compressor Discharge	220	350	20.	6.4
3rd Stage Cooler Discharge	70	350	20.	6.4

Figure 4

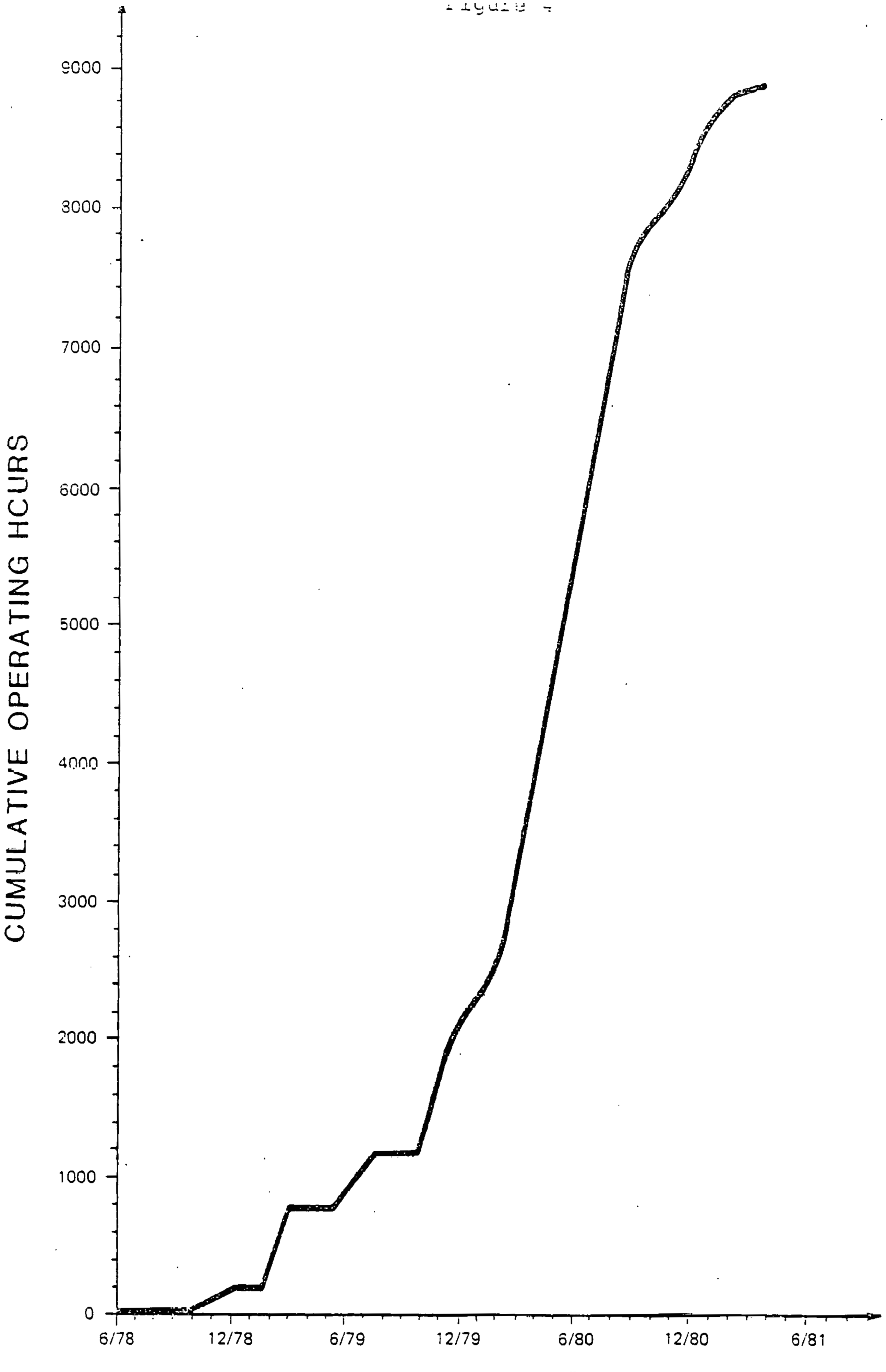
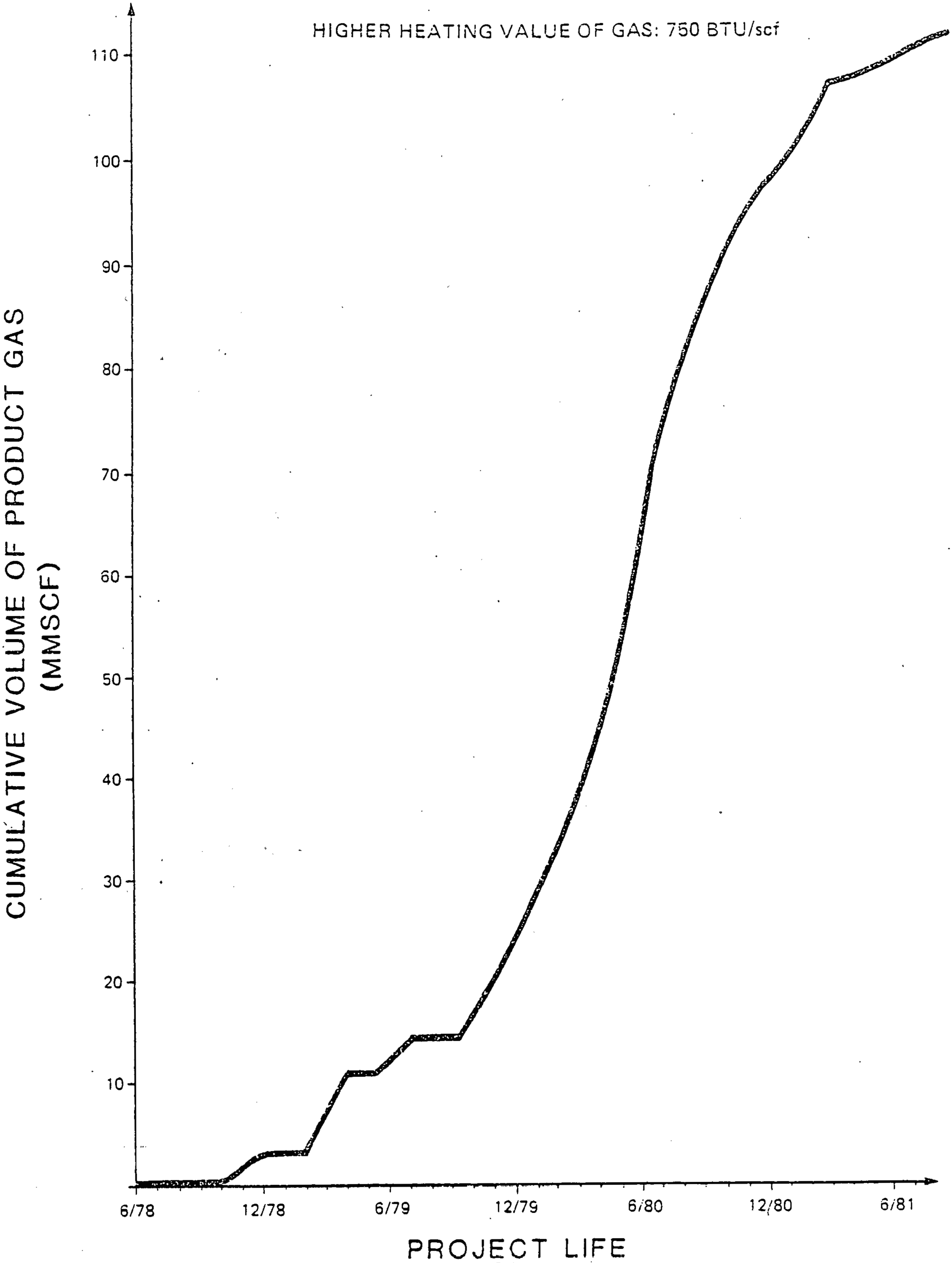

9000
8000
7000
6000
5000
4000
3000
2000
1000
0
CUMULATIVE OPERATING HOURS
6/78
12/78
6/79
12/79
6/80
12/80
6/81
PROJECT LIFE

Figure 5


HIGHER HEATING VALUE OF GAS: 750 BTU/scf
CUMULATIVE VOLUME OF PRODUCT GAS (MMSCF)
110
100
90
80
70
60
50
40
30
20
10
6/78
12/78
6/79
12/79
6/80
12/80
6/81
PROJECT LIFE

IDENTIFICATION OF THE PROBLEM

Corrosion Mechanism

Corrosion is the deterioration of a metal as it reacts with its environment. Corrosion at Mountain View occurs because water vapor condensed water, CO_2, and O_2 are present in the process piping. Corrosion caused by the presence of acid gases and organic acids may also exist.

An active metal, a corrosive agent, and an electrolyte are all necessary for corrosion. The corrosive agent becomes disolved in the electrolyte, and an oxidation/reduction reaction occurs between the metal and the electrolyte. Over time the mechanical integrity of metal parts is impaired.

Carbon dioxide and hydrogen sulfide will dissolve in water, causing the water to become acidic, and thus corrosive. In the presence of oxygen, carbon dioxide and hydrogen sulfide become more corrosive. H_2O, CO_2 and O_2 are the principal corrosive agents in landfill gas. H_2S has not been detected at significant level. Elevated temperatures due to compression of the gas can also increase the corrosion rate.

If there were no water associated with landfill gas, carbon dioxide, hydrogen sulfide, and oxygen would not have a corrosive effect on gas piping.

HISTORY OF PROBLEMS

The landfill gas recovery plant was not designed with any special allowances for corrosion. The extent of potential corrosion induced damage to the plant was not known in advance. As a demonstration plant, corrosion problems had first to be identified. Corrosion inhibition was thought to be sufficient for controlling corrosion problems that might arise.

Prior to the construction of the present demonstration plant at Mountain View a test well was inserted into the landfill to examine the landfill gas.

To investigate initial concerns over corrosion, corrosometer probes were installed in a liquid separator tank attached to the well to evaluate the corrosion characteristics of various metals to landfill gas condensate.

Four alloys were exposed to the condensate and corrosion rates were monitored for approximately one year (see Reference 2). The measured corrosion rates are as follows:

Metal	Corrosion Rate (mils/year)*
Mild steel	up to 17
316 stainless	-0-
304 stainless	-0-
Copper	7.0

*1 mil = 0.001 inch

It should be noted that the indicated corrosion rates resulted from exposure to condensates at ambient temperatures and do not reflect actual plant operating conditions.

The corrosion rate of mild steel determined by corrosometer probe measurements was verified by laboratory tests in 1977. A Petrolite corrosion rate recorder and Princeton Applied Research potentiostat were used to record corrosion rates. This test procedure utilizes an electrochemical linear polarization method, which is an accelerated test to determine probable corrosion rates of metals in a specific environment. These tests indicated that the expected general corrosion rate could be 8 to 12 mils/year (MPY). In addition, the tests showed corrosion could be controlled effectively with the use of a inhibitor.

Corrosometer probes were also installed in the natural gas pipeline L-101 downstream from the Mountain View facility. The probes installed at the Palo Alto meter station and at the Sierra Vista Crossover (Figure 1) have been monitored since 1976 and there has been no evidence of internal corrosion at these locations.

During the fall of 1978, four corrosometer probes were installed in the Mountain View plant equipment to monitor possible on-line corrosion. At this time the plant was undergoing mechanical shakedown prior to continuous operation. These probe locations were selected because existing fittings were available, and installation could be easily completed.

Corrosometer probe locations and indicated corrosion rates were as follows:

Probe Number	Location (Refer to Figure 3)	Corrosion Rate (mils/year)
(#5)	First stage cooler	2.6
(#3)	First stage scrubber	2.4
(#7)	Second stage discharge	15.0
(#10)	Third stage cooler	-0-

Higher corrosion rates were indicated sporadically but this data was later proven to be erroneous. Corrosometer readings (used to calculate corrosion rates) are temperature sensitive and vary during transients in plant operation.

Corrosometer probes were monitored using a Rohrback Magna Instruments portable corrosometer. There was a substantial difference between readings when the compressor was operating and when it was shut down. A chronology of corrosion related problems at the plant is included in Table 2.

In light of high corrosion rates, PGandE decided to use a chemical inhibitor to reduce corrosion. The manufacturer describes this inhibitor as "--a reaction product of amide amine, alcohol, epichlorohydrin amine adduct with diethylamine." This inhibitor controls corrosion by coating the internal surfaces of the pipe by adsorption, thus providing a chemical barrier between the metal and the corrosive liquid. To achieve and maintain this barrier, sufficient quantities of the inhibitor must be injected.

In the Fall of 1978, a corrosion inhibitor treatment system employing a gravity-drip feed applicator upstream of the first stage compressor was tested with little success.

During December 1979, six additional probes were installed. At the same time, a positive displacement high-pressure corrosion inhibitor pump with an injection atomizer was installed in the piping system upstream of the first stage compressor.

The six additional probes were located at: (1) first-stage compressor suction (before inhibitor injection probe), #1 (Refer to Figure 3); (2) first-stage compressor suction (after inhibitor injection), #2; (3) first-stage compressor discharge, #4; (4) second-stage cooler discharge, #8; (5) second-stage scrubber, #6; and, (6) third-stage discharge, #9. The ten probes were connected to an Automatics recording corrosometer and changes in electrical resistance were measured sequentially with a programmer.

Table 2 Chronology of Corrosion and Related Events

Date	Operational Event	Corrosion Event
6- -78	Plant start-up	-
8- 8-78	-	Rust observed, compressor valve seat guard, suction side
9-26-78	Drip feed inhibitor system installed upstream of 1st stage. 4 corrosometer probes installed	Corrosion, valve guard assembly, suction side; particles in seats, head end of vacuum cylinder.
11- 2-79	-	Bottom suction valves, crank, head ends, second stage were badly corroded. Top suction valves were split and corroded.
11- 3-79	-	Corroded seats on top inlet valves, second stage, guards lightly for cleanup.
11-13-79	-	Replaced seats, inlet suction side, 2nd stage.
11-20-79	Started atomizing inhibitor injection via pump at 1st stage suction. Two quarts per day of GAS-COR 970.	-
11-26-79	-	Leaking tubes, 1st stage heat exchanger.
11-27-79	-	Leaking tubes, 1st stage h.e.
11-28-79	-	Corrosion (pitting) on two compressor head end valves; 2nd stage.
12- 4-79	Inhibitor rate 1 quart/day. 6 additional corrosometer probes installed.	-
12-31-79	2,319 hours operating time to date	-
2-27-8	Installed bypass valve	-

Table 2 (continued)

Date	Operational Event	Corrosion Event
3-18-80	-	1st stage cylinder gummed with inhibitor, probe #8 recorded high corrosion rates.
4-16-80	-	3 leaking tubes, 2nd stage h.e.
6- 2-80	-	Leaking tube, 2nd stage h.e.
7-15-80	Inhibitor injection point moved to 2nd stage discharge.	-
7-21-80	-	4 leaking tubes, 2nd stage h.e.
8-15-80	-	2 Leaking tubes, one in 1st stage and one in 2nd stage h.e.
9- 5-80	-	2nd stage cylinder gummed up.
9-12-80	-	7 leaking tubes, 1st stage h.e.
9-24-80	Additional inhibitor injection point at 1st stage suction. 0.75 quart/day at 1st stage, 0.5 quart/day at 2nd stage	
10- 9-80	-	Leaking tubes
12-10-80	Moved inhibitor injection from 1st stage suction to 1st stage discharge.	-
12-30-80	-	Leaking tube, 1st stage h.e.
12-31-80	7,970 hours operating time to date.	-
1-20-80	-	Replaced corroded suction valves (4) 2nd stage cylinder. New seats and springs in discharge valves (4).
1-28-81	-	Leaking tube
2- 5-81	-	Leaking tube, 1st stage h.e.

Table 2 (continued)

Date	Operational Event	Corrosion Event
2-17-81	-	Leaking tube, 1st stage h.e.
2-18-81	-	Leaking tubes (2)
2-23-81	Inhibitor injection rate changed to 0.25 quart/day each location.	-
3- 8-81	9,239 hours operating time to date	-
3-18-81	-	Leaking tube, 1st stage h.e.
3-10-81 4-16-81	Plant already shutdown due to previous mechanical problem. Corrosion inspection of process piping and equipment.	

At this time, the corrosion rate indicated by the probe located at the second-stage compressor discharge increased from 2.3 mils per year (MPY) to 27 MPY and subsequently increased to 55.8, 84.5 and 129.5 MPY during successive weeks. During the same period, no other probes downstream from the inhibitor injection point indicated an increased corrosion rate (Table 3).

A second corrosion inhibitor injection pump has since been installed downstream of the second stage discharge. Subsequent to this installation, the corrosion rate on probe #8 has been reduced to less than 1 MPY.

There are two conditions existing in the compressor system that affect the performance of the corrosion inhibitor. A liquid separator exists between each compression stage, designed to remove water and other liquids that condense with increased pressure. Since portions of the inhibitor are soluble in water, they also are removed at the separator. The second problem occurs inside the compressor cylinder where, because of elevated temperature, the alcohol carrier in the inhibitor evaporates, and a deposit is left on the exhaust valves. The inhibitor thus does not reduce corrosion occurring on the valve seat. Therefore, both the first stage and second stage injection is currently being performed downstream of the compression cylinders. This leaves the first stage compressor and upstream piping unprotected.

CORROSION RATE (MILS PER YEAR) FOR TIME PERIOD INDICATED

CORROSOMETER PROBES NO.	LOCATION	Prior 12-14-79*	12-14-79 1-15-80	1-15-80 1-29-80	1-29-80 2-11-80	2-11-80 3-12-80	3-14-80 4-11-80	4-11-80 5-12-80	5-12-80 6-11-80	6-11-80 7-14-80**	7-14-80 8-18-80	8-18-80 9-15-80	9-15-80 10-9-80
1	Suction Line - Upstream Inhibitor Pump		32.	7.4	12.	6.5	6.8	2.0	1.0	5.2	9.2	5.0	11.6
2	Suction Line - Downstream Inhibitor Pump		1.0	0	0	0	0	1.0	1.0	0	0	0	0
3	1st Stage Compressor Scrubber	2.4	0	0	0	0	1.3	2.0	1.8	2.2	0	0	0
4	1st Stage Compressor Discharge		0	0	0	0	0	0	0	0	0	0	0
5	1st Stage Cooler	26.0	0	0	0	0	0	0	0	0	0	0	0
6	2nd Stage Compressor Scrubber		0	0	0	0	0	4.5	4.7	1.3	1.7	1.0	0
7	2nd Stage Compressor Discharge	15.0	1.7	0	0	0	2.0	0	0	0	1.8	0.9	0
8	2nd Stage Cooler Discharge		1.3	0	0	2.3	27.0	(A)	(B)	(B)	3.4	7.9	0
9	3rd Stage Compressor Discharge		0	0	0	0	0	0	0	0	0	0	0
10	3rd Stage Cooler	0	0	0	0	0	0	0	0	0	0	0	0
	Palo Alto Meter Station	0	0	0	0	0	0	0	0	0	0	0	0
	Sierra Vista Crossover	0	0	0	0	0	0	0	0	0	0	0	0

Notes:

A.

4-11-80 to 4-22-80	Probe Depleted	
4-22-80 to 4-28-80	(New Probe)	55.8 MPY
4-28-80 to 5- 4-80		84.5 MPY
5- 4-80 to 5- 7-80		121.9 MPY
5- 8-80	Probe Depleted	

B. Probe Not Relaced Until 7-19-80

* Inhibitor Pump Installed in Suction Line, 12-14-79

** Inhibitor Pump moved to 1st Stage Compressor Discharge, and Second Inhibitor Pump Installed at 2nd Stage Compressor Discharge, 7-18-80

TABLE 3

The monitoring of corrosion rates in the area upstream of the first stage of the compressor will continue and should an unacceptable corrosion rate be indicated, a third injection pump will be considered.

METHODS

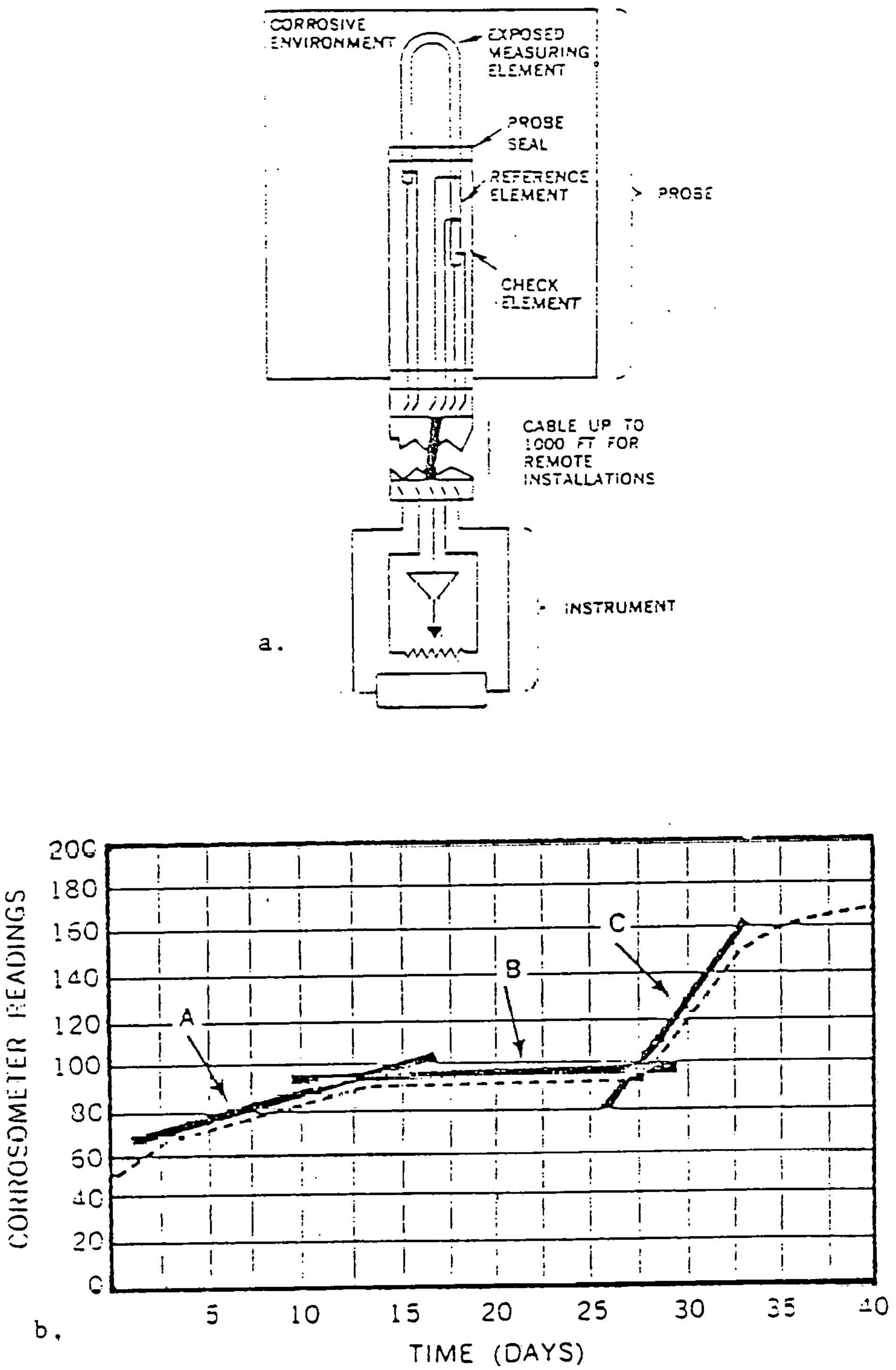
DESCRIPTION OF INSTRUMENTATION, INHIBITOR, AND INJECTION SYSTEM

Instrumentation

A corrosometer probe functions as a sensor that accumulates the corrosion history of a specific metal in an environment. The corrosometer operates on the fundamental principal that electrical resistance of a metal increases as the cross-sectional area of a conductor decreases due to corrosion attack . A second sensing element is encased in the body of the probe to establish a stable reference check (Figure 6).

When corrosion of the sensing element occurs, its electrical resistance changes. The electrical resistance is read on an indicating instrument or by a strip chart recorder. Changes in electrical resistance along with time of exposure are used to calculate corrosion rate.

Corrosometer probes are installed inside pipes where internal corrosion is suspected. Thus, corrosion rate can be monitored externally while the piping system is actually operating. The probes may also be used to evaluate the effectiveness of chemical inhibitors.



c. $\text{Corrosion Rate(MPY)} = \dfrac{\text{(reading)}}{\text{(time)}} \times 365 \times \text{probe multipuler}$

$$= \frac{86 - 75}{10 - 5} \times 365 \times 0.01 = 7.3 \text{ MP}$$

$$= \frac{97 - 96}{20 - 15} \times 365 \times 0.01 = 1.5 \text{ MP}$$

$$= \frac{130 - 100}{30 - 27.5} \times 365 \times 0.01 = 43.8 \text{ MP}$$

FIGURE 6 a. Schematic of a typical corrosometer probe
b. Typical data from a corrosometer probe
c. Determining the corrosion rates from the data shown in b.

The corrosion monitoring activity was also used to evaluate other available probes. Series 2171 (flush element) and Series 2550 (high sensitivity) probes were installed at several locations. All probes used were effective in monitoring periodic changes in corrosion rates.

Probe data was monitored at first with a portable Rohrback Magna model CK-3 corrosometer. This instrument is accurate and reliable, but is manually operated and requires almost full-time use to monitor the rapidly changing conditions.

Later an Automatics corrosometer model 4800 and corrosometer programmer model 4900 were installed. These instruments were used to provide continuous monitoring of the ten probes on a programmed sequence. This instrumentation is more useful in determining the effectiveness of inhibitor injection and detecting when operating upsets occur.

Inhibitor

During the test periods described above, only one brand of corrosion inhibitor was used (NALCO Visco 970). The inhibitor was recommended by a chemical company (NALCO) who has provided inhibitors to PGandE for the control of corrosion in a variety of environments.

The inhibitor is defined by the supplier as a reaction product of amide amine alcohol, epichlorohydrin amine adduct with diethylamine. This product has been partially effective in controlling corrosion at Mountain View at various locations in the system.

As described above, it is apparent that an inhibitor must be injected at several locations in the system. Two such locations are now being utilized and one additional location may be required.

One problem associated with this inhibitor which was not anticipated, was that of gummy deposits on corrosometer probes, valves, cylinder heads and piston heads. When the volatile components of the inhibitor evaporated at high temperature, a residue (stemming very likely from polymerization reactions) of dark, viscous, organic amines was deposited and adhered to hot surfaces of metals in the compression stage.

Another inhibitor is currently being evaluated to determine whether it may be better suited for this application.

Injection System

Figure 7 shows the layout of the inhibitor injection system. The corrosion inhibitor is pumped at a predetermined rate into the process piping. Inhibitor is currently injected downstream of the first and second stages of the compressor.

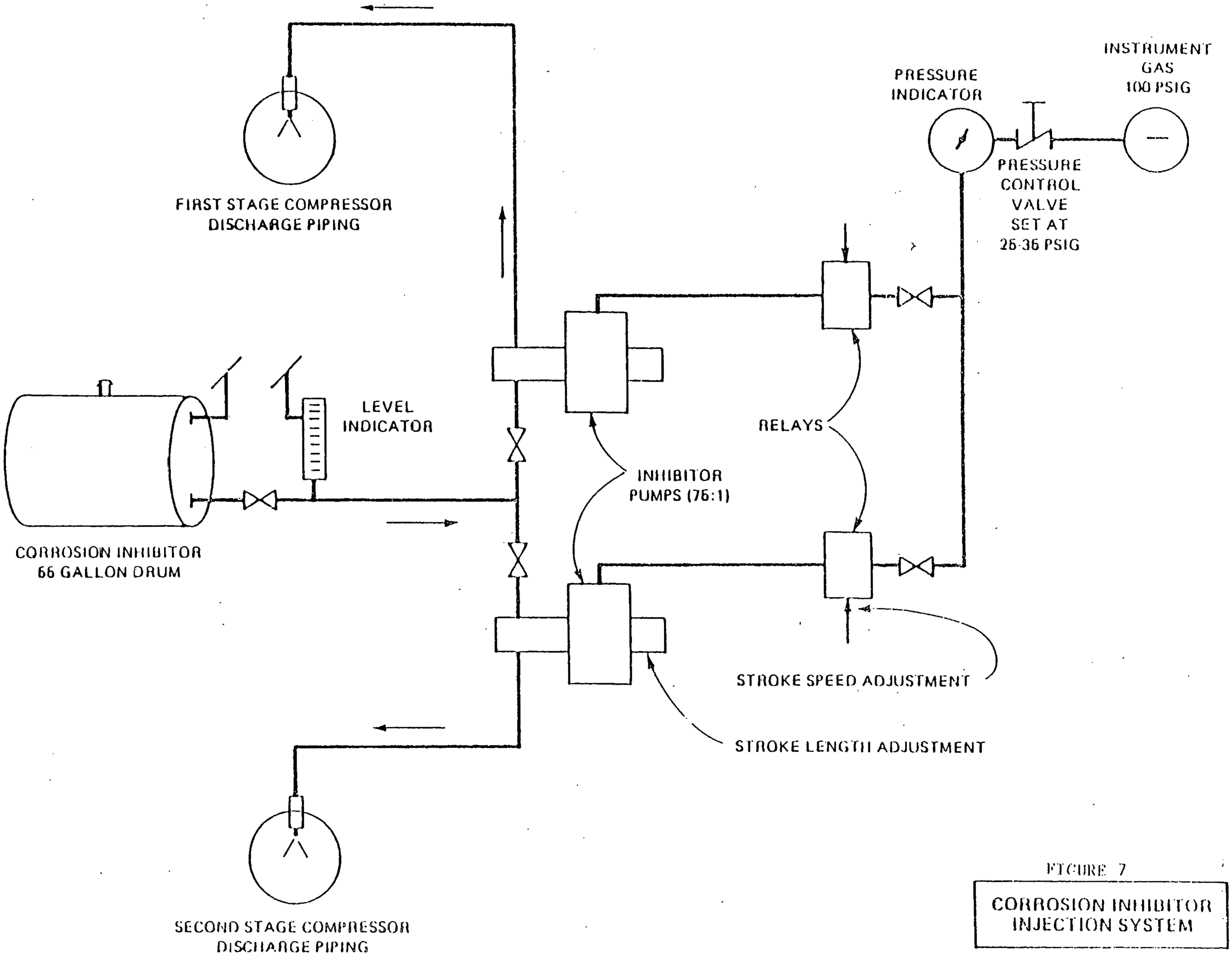


FIGURE 7

CORROSION INHIBITOR INJECTION SYSTEM

Figure 6 shows typical data from a corrosometer probe along with calculations of corrosion rate.

Specific probe types have different probe multipliers. Probes may be selected to measure corrosion rates in the ranges of 2, 4, 10 or 20 mils per year (MPY). The selection is based on the expected corrosion rate, and desired sensitively of readings.

Location of Probes

The corrosometer probe downstream of the plastic/steel pipe transition (probe #1, Figure 3) has indicated a varying corrosion rate throughout the monitoring period. Rates from 1.0 to 32.0 mils per year have been recorded.

An inhibitor injector was placed at this location in mid 1979. It was hoped that there would be a reduction of the corrosion at the suction valve of the first stage of the compressor. The injector was a gravity feed system, which did not work satisfactorily. In late 1979 a positive displacement pump was put in the place of the drip feed system. While corrosion at the first stage of the gas cooler continued, it was noticed that the inhibitor formed a solid deposit on the exhaust valves of the first stage of the compressor and the entrance to the first stage of the gas chiller. The deposits were attributed to the contact of the inhibitor with the hot surfaces in the compressor cylinder, and perhaps too high a rate of inhibitor injection. The injector was then moved to a point just downstream of the first stage of the compressor, in July 1980. Gummy deposits in the heat exchanger have continued to be a problem. Some cooling tubes have collected sufficient inhibitor condensate to block the flow of gas.

Consideration is being given to the possibility of using stainless steel components, another inhibitor, and an inhibitor injector with a better control of injection rate.

Downstream of the first stage of the cooler, corrosion on the corrosometer probe has been eliminated with the inhibitor. Cooling tube failures in the first stage may have been enhanced by vibration of accelerator rods within the tubes; this could have broken the inhibitor film and induced an erosion/corrosion type of failure. Appearance of the tubes on visual inspection gives no indication that this actually is occurring. Tubes in the second stage cooler do not have accelerator rods, however, and failures in this stage cannot be explained in this fashion.

The corrosometer probe in the liquid separator downstream of the first stage cooler indicated no corrosion until March of 1980. The relocation of the inhibitor injector upstream of the cooler reduced the corrosion rate in this liquid separator.

The seat of the second stage compressor suction valve has corroded and the gummy residue of the inhibitor has been collecting at the suction and discharge valves.

Corrosion probe #7, upstream of the second stage cooler, was one of the original four probes. Initially, a corrosion rate of 15 mpy was indicated, but the rate was reduced substantially when the first inhibitor pump was installed in December 1979.

Several tubes in the second stage of the heat exchanger have failed due to corrosion. Visual inspection revealed pitting in these tubes. Deposits of inhibitor residue were also found.

The corrosion rate indicated by the probe downstream of the second stage cooler rose dramatically in March 1980. A second inhibitor injection pump was placed upstream of the second stage cooler in July 1980, and the corrosion rate there has been reduced to less than 1 MPY.

The corrosion probes downstream of the third stage of the compressor and third stage cooler have never shown any evidence of corrosion. Furthermore, no gummy deposits have collected at these locations.

Corrosometer probes in the transmission line downstream from the plant have not indicated any corrosion during the monitoring period.

RESULTS

Effect of Inhibitor

Since pressure equipment is involved, it is essential that corrosion be under complete control. The plant experience has shown that the inhibitor selected was not completely effective. This stemmed probably from the difficulty of inhibiting the severely corrosive combination of oxygen, carbon dioxide, and water and partly because of the problem of transporting inhibitor to all steel surfaces in a complex system such as this. There is also the difficult problem of monitoring the corrosion inhibition other than by direct inspection of the process equipment. This latter approach is impractical because of the long response time.

Prior to shutdown of the plant for corrosion inspection there were indications that corrosion had become severe: (1) corrosion of certain suction valves in the compressor, (2) failure by leakage of a number of cooler tubes in both the first and second stages, (3) indications by ultrasonic measurements of corrosion of the plant inlet piping, and (4) indications of significant corrosion of a few corrosometer probes located in various plant streams. A chronological listing of various items of corrosion experience together with pertinent plant operating factors is given in Table 2. A partial inspection of the plant following shutdown the week of March 16, 1981, revealed corrosion of piping downstream of both the first and second compression stages.

A description of the major examples of corrosion experienced in the plant follows.

Compressor valve corrosion. Suction valve seats on the second stage compressor corroded badly, and required replacement. A typical example of a corroded seat is shown in Figure 8. No corrosion failures of the valve plates have been reported. These were said to be of a stainless steel alloy, not further identified. Examination of the compressor on March 20 revealed no corrosion of the suction valve seats, which were replaced in January 1981. The valve corrosion problem has been mainly limited to the two lower suction valves of the second stage compressor with no major corrosion problems with the two upper suction valves or the four discharge valves. Examination of the cages of the various valves confirmed this experience, since only the cages from the two lower suction valves showed the same severe localized corrosion as experienced on the seats (Figure 9). In the case of both the seats and the valve cages, corrosion appeared to be associated with high velocity. There was no corrosion product (such as rust) present in the corroded area. In the one case where orientation of the cages was known, the severe corrosion was located on the side away from the center of the entry manifold. The other corroded valve cage showed corrosion to be also localized on one side, but in this case the orientation of the cage relative to the manifold was not known. In all cases the corrosion damage was severe, the depth of attack being as great as 0.2 inch.

Figure 8: Corroded suction valve seat from second-stage compressor

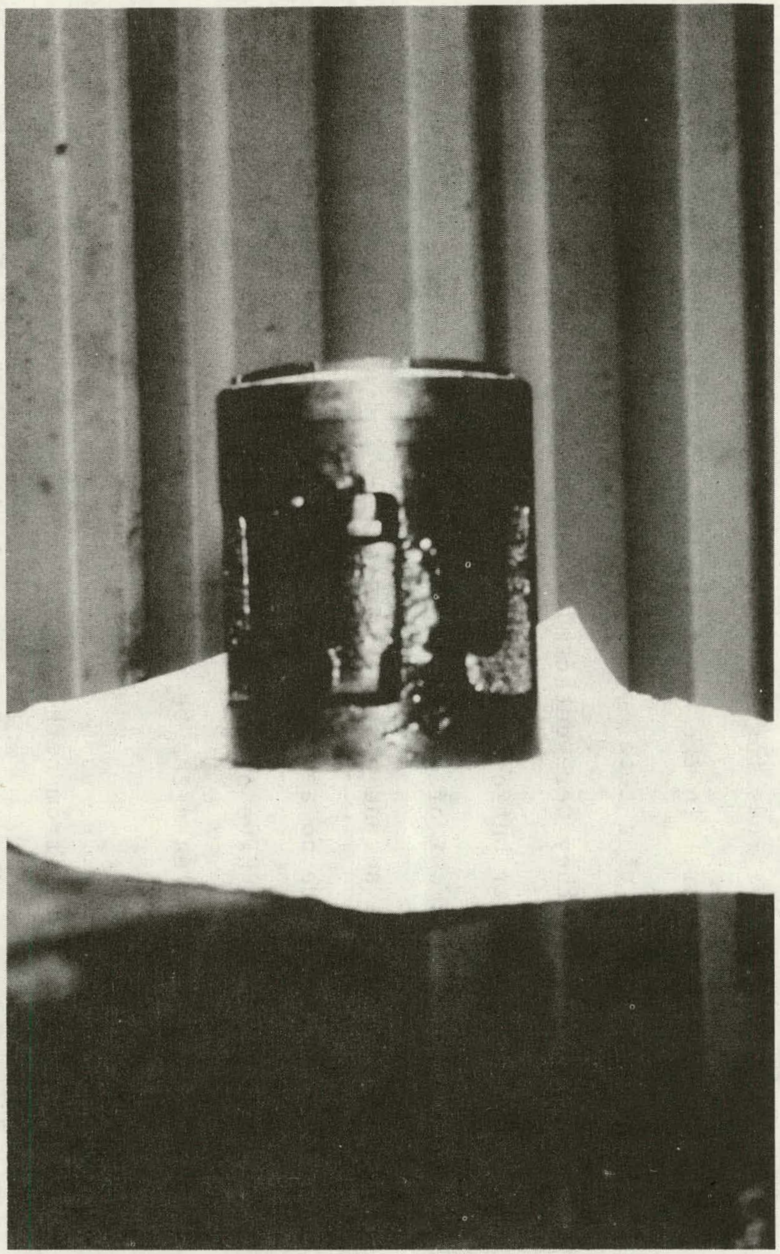


Figure 9: Corroded suction valve cage from second-stage compressor

The piston and cylinder of the second stage compressor showed no signs of corrosion damage. Some scoring had occurred, but it appeared to be of mechanical origin.

Gas cooler tube corrosion. Failures by leakage have occurred on a number of gas cooler tubes. The cooler tubes are of 16 gauge, 5/8 inch diameter carbon steel with aluminum fins, and are 11 feet long. The tubes in the first stage cooler have 1/4 inch diameter steel accelerator rods inside the tubes to increase gas velocity and heat transfer. In the first stage cooler there have been 23 failures out of a total of 70 tubes, the failed tubes being plugged off as they were detected. There was no obvious pattern to the failure distribution. In the second stage cooler there have been 7 failures out of a total of 58 tubes. Six of the failures occurred in the second pass of this stage, and one in the third pass. There were no accelerator rods in this stage. No failures due to corrosion have occurred in the third stage cooler. The distribution of leaks can be seen in Figure 10.

A number of tubes from both the first and second stage coolers were removed for examination. Photographs of typical examples are given in Figures 11, 12, 13, 14 and 15. The internal surfaces of the tubes were covered with a red-brown rust-type coating. Removal of the coating by light sand blasting revealed the presence of extensive corrosion of an irregular pitting type. The pits had rounded edges and were of various sizes and shapes.

FORCED AIR INTERSTAGE GAS COOLER , RIGHT SIDE HEADER

SHOWING THE THREE STAGES OF THE COOLER AND LOCATIONS OF FAILED TUBES

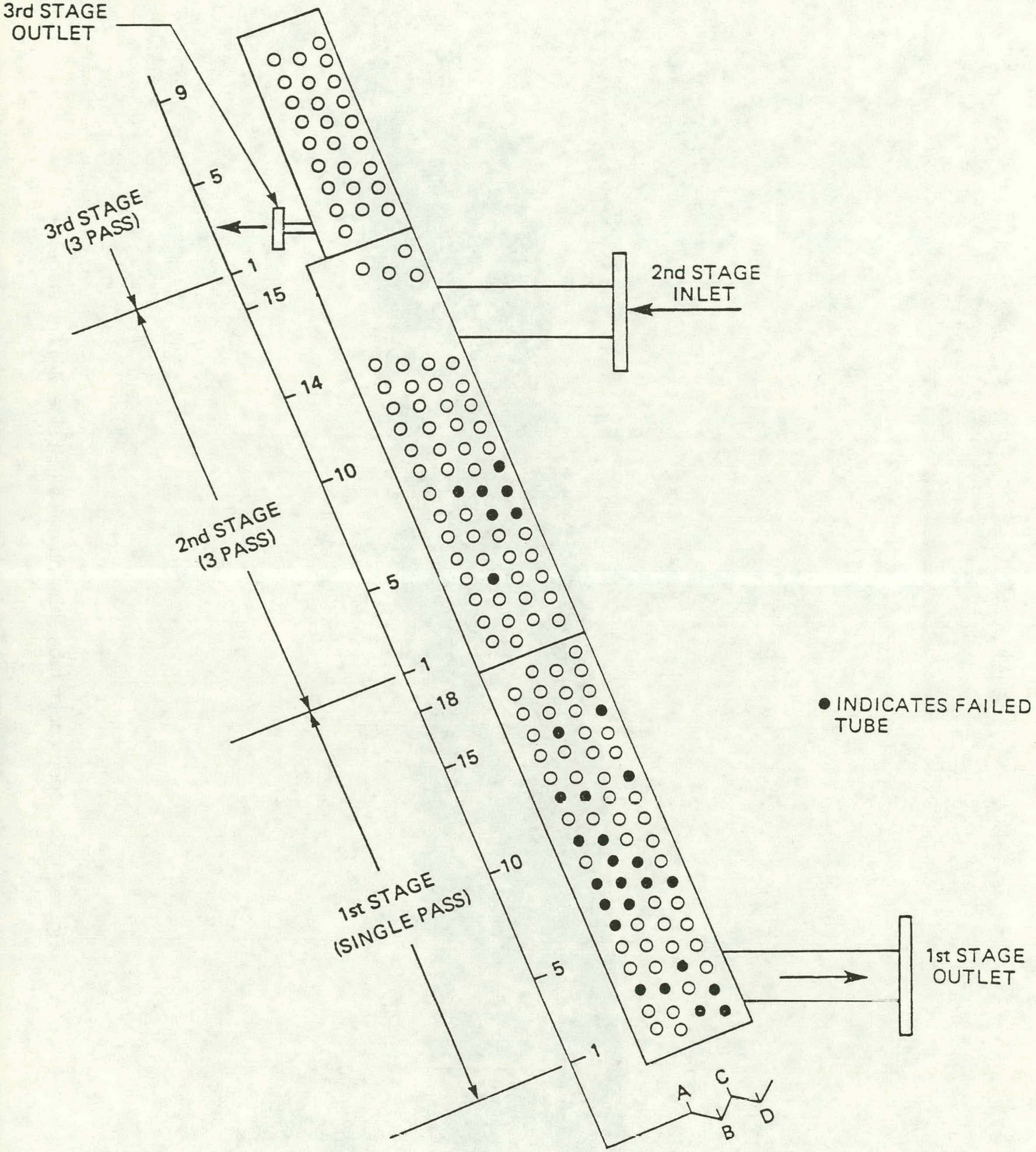


FIGURE 10

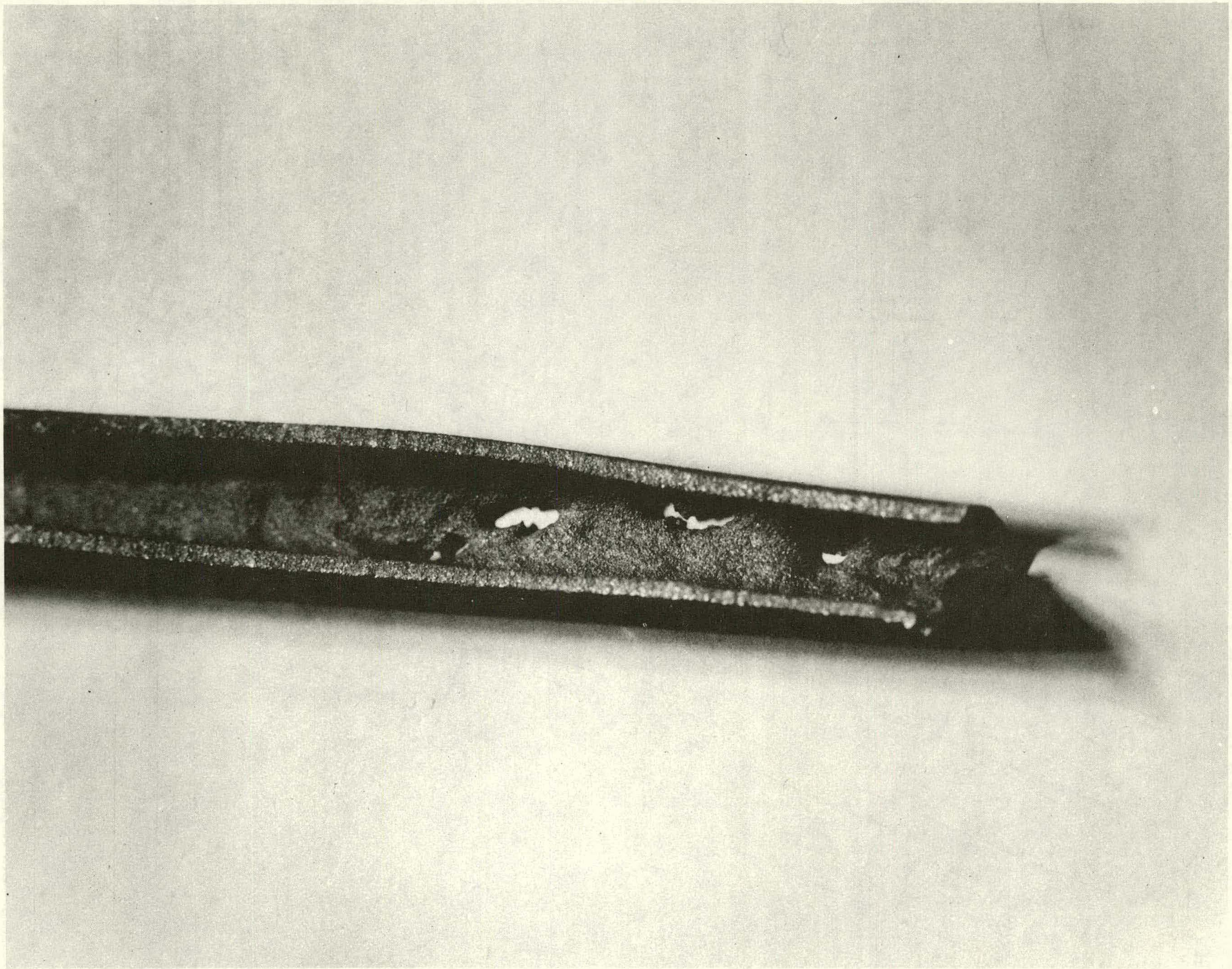


Figure 11: Corroded cooler tube showing holes (left side, 7A, first stage)

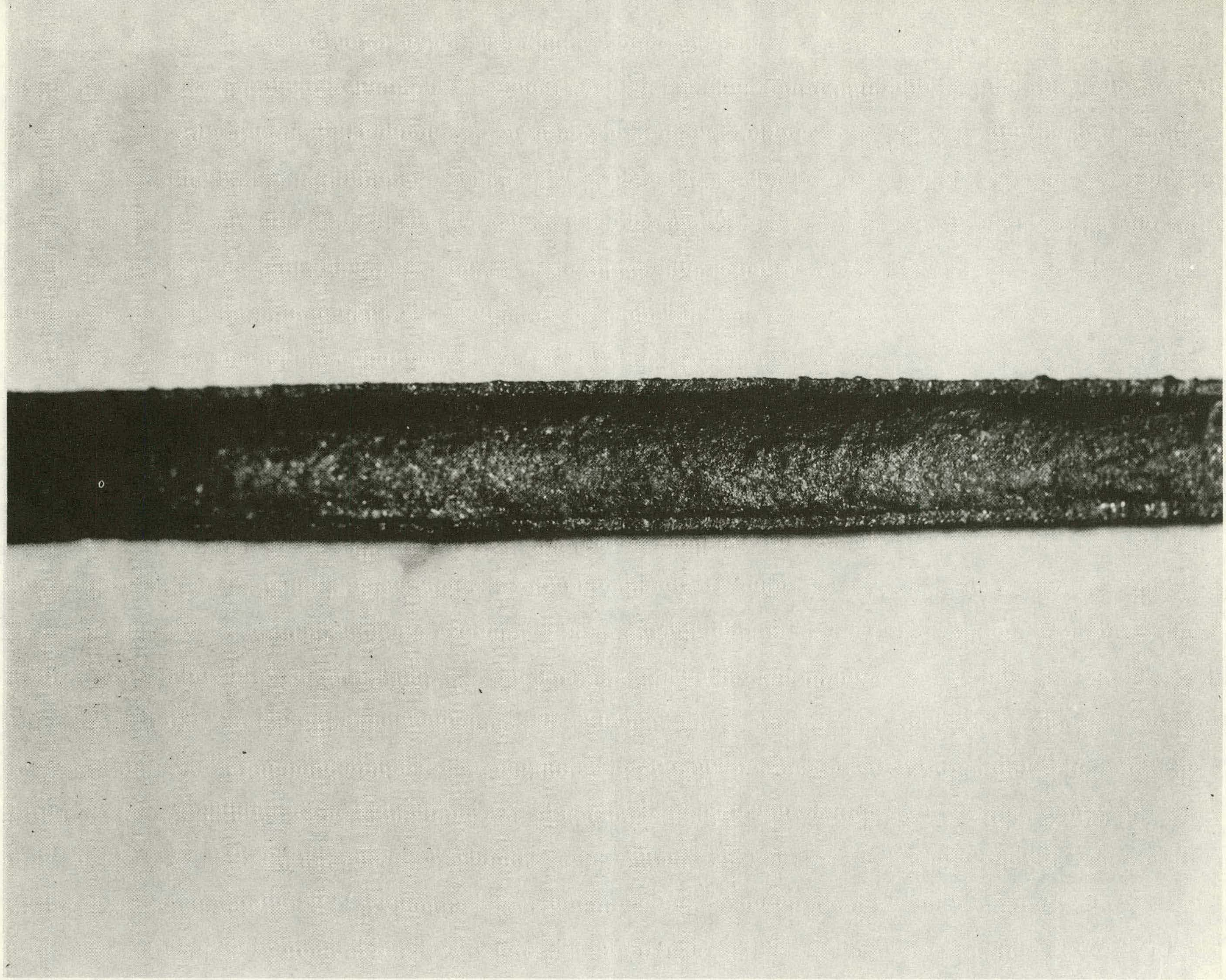


Figure 12: Corroded cooler tube showing erosion effect (left side, 7A, first stage)

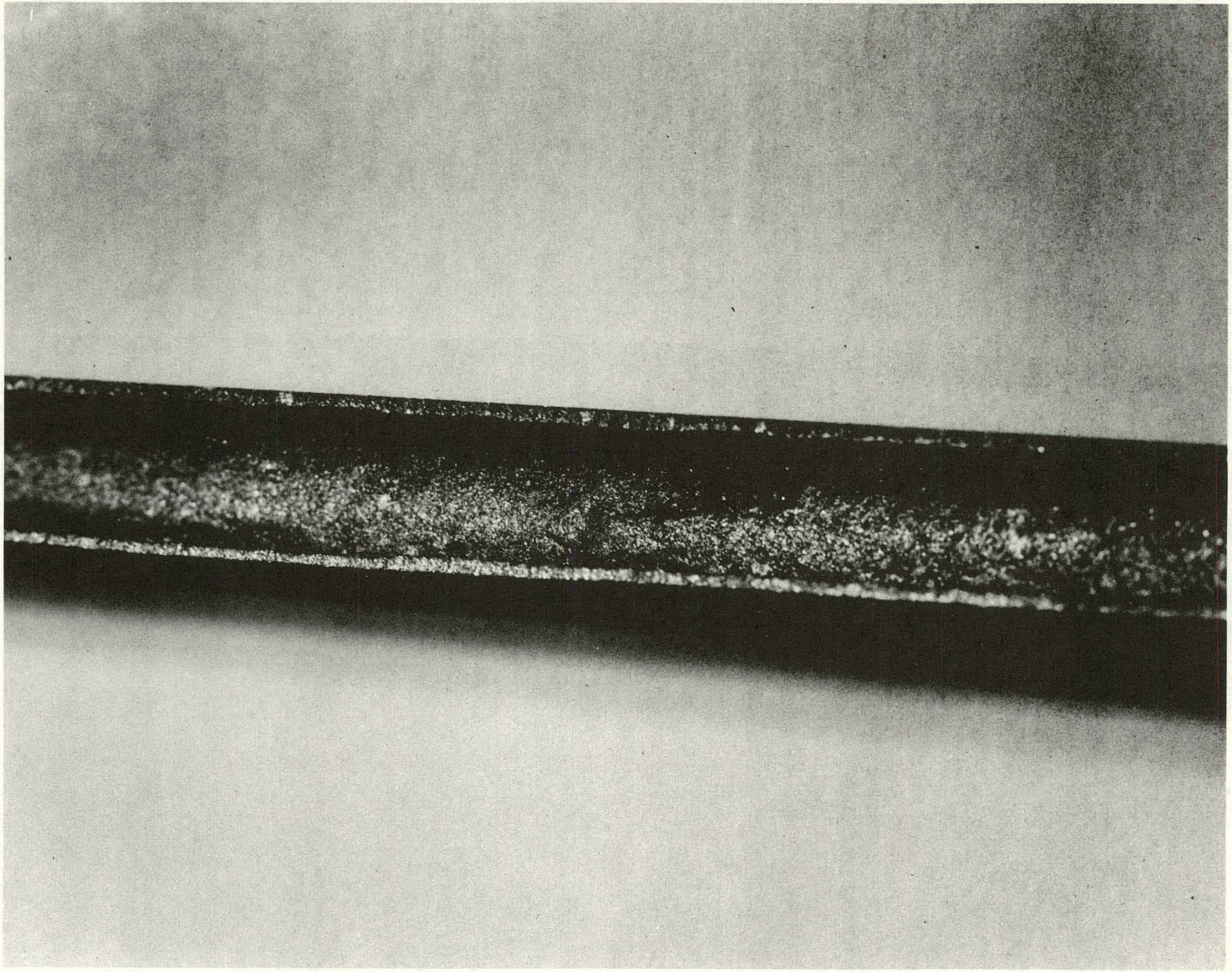


Figure 13: Corroded cooler tube (center, 2A, first stage)

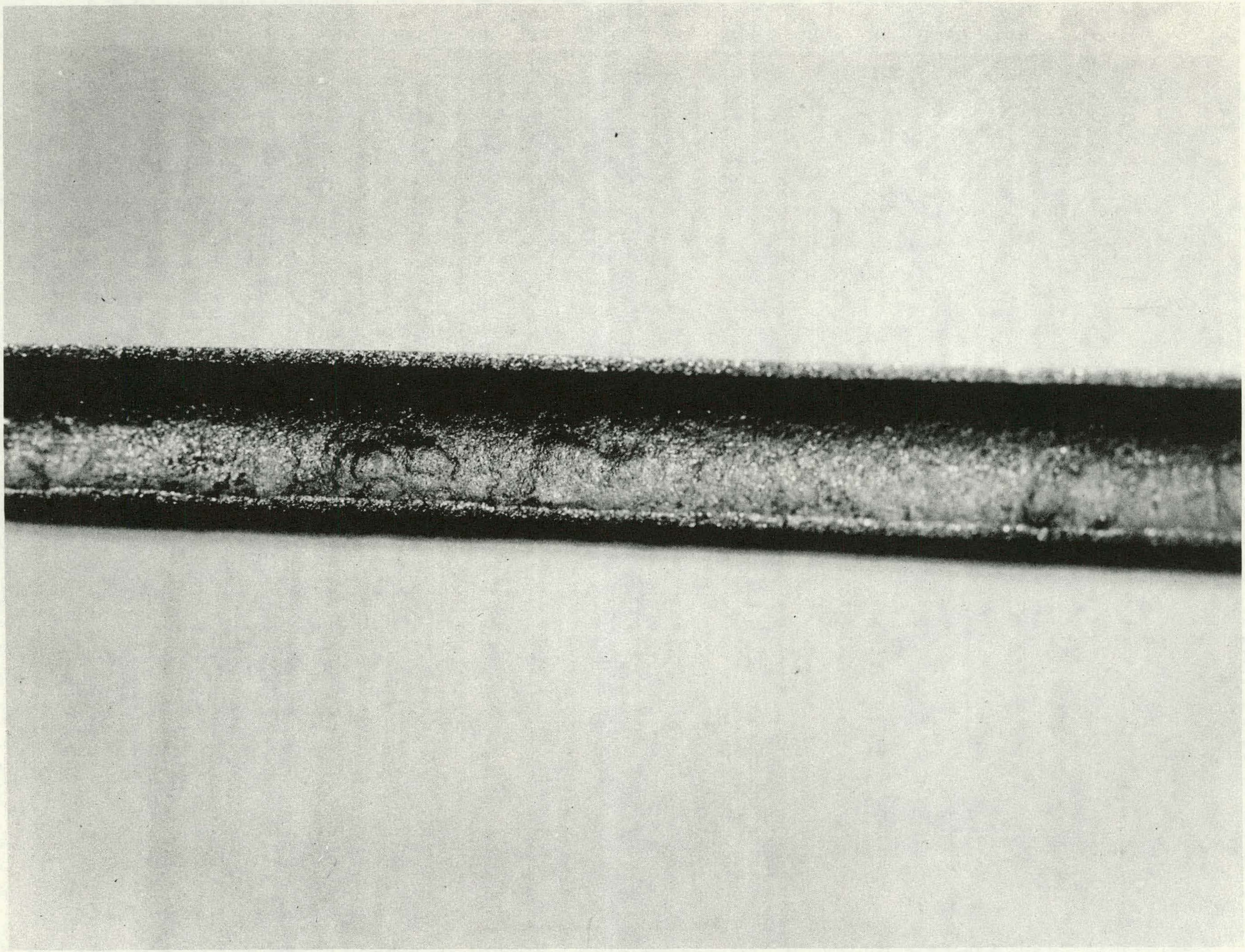


Figure 14: Corroded cooler tube (right, 7A, first stage)

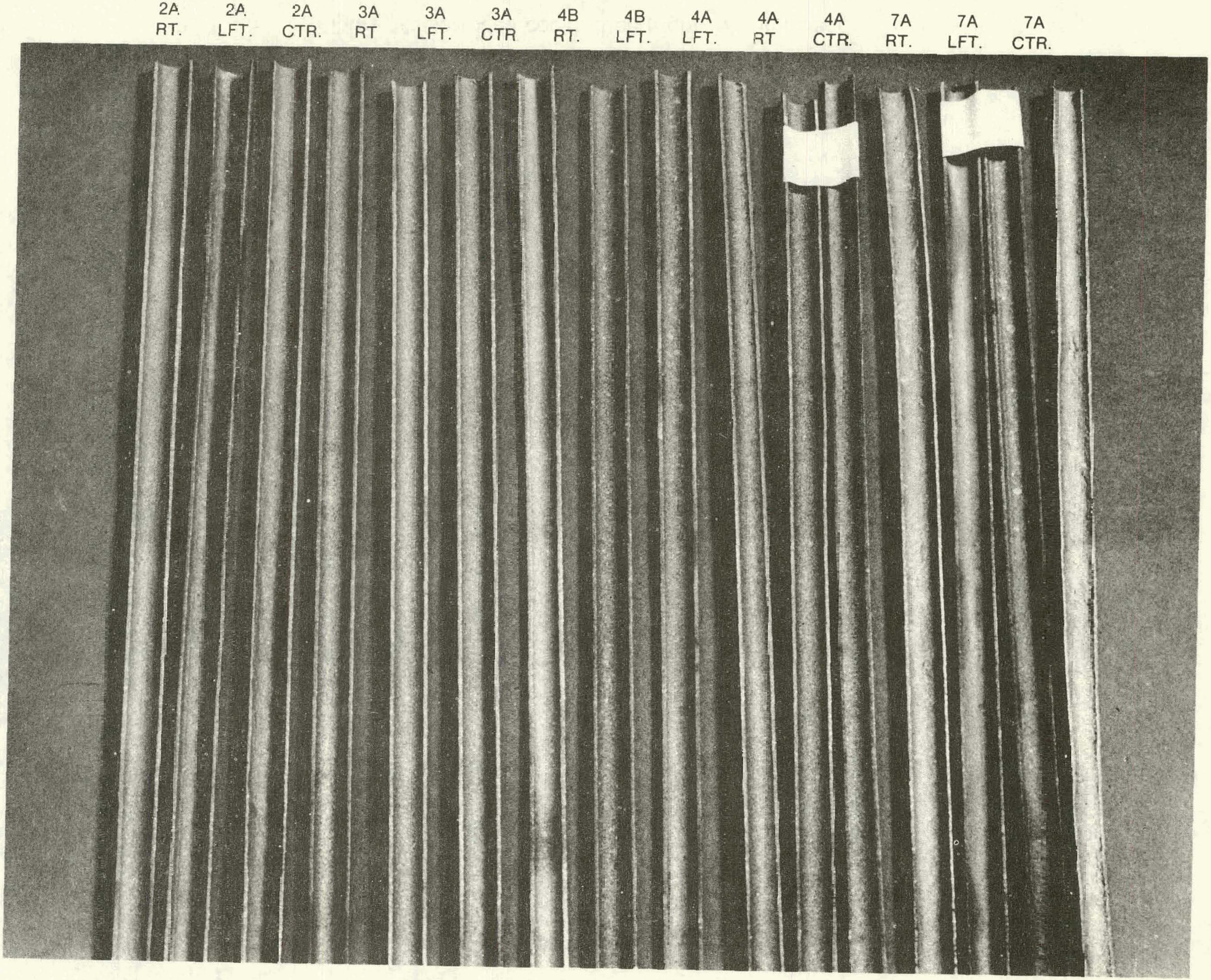


Figure 15: Corroded cooler tubes from first-stage (see Figure 10 for coordinate system)

The holes in the tubes were about 0.1 inch in diameter. There was no pattern of the corrosive attack relative to the circumference of the tubes. Variations in severity of attack occurred among different tubes and along the length of individual tubes. Table 4 describes the appearance of the tubes removed for examination. The two tubes from the first stage showed the most severe attack, corrosion being most severe in a zone beginning about one-fourth of the tube length from the inlet and extending along the remainder of the tube. The holes were in a zone 2 to 3-1/2 feet from the inlet end. The three tubes from the third pass of the second stage cooler (tubes 3A, 4A, and 4B) showed only mild corrosion with minor pitting.

Pipe and vessel inspection. This consisted of ultrasonic measurements of wall thickness, boroscopic examination of internal surfaces, and destructive inspection of piping suspected of being heavily corroded. A summary of the ultrasonic probe readings is given in Table 5. The readings indicated that the 8 inch line upstream of the first stage compressor had possible corrosion loss of wall thickness of up to 0.02 inch. This corresponds to values of up to 0.04 inch loss measured in April 1980 in this same general location. No significant thickness loss was measured on the 4 inch line downstream of the first stage liquid separator, except for the elbow near the inlet to the separator. This elbow was removed for examination (see below). No significant thickness loss was noted for the 3 inch line downstream of the second stage cooler except for an elbow at the inlet to the liquid separator, which indicated

Table 4 Appearance of Gas Cooler Tubes Removed March 1981

Location	Tube No. (Refer to Figure 10)	Appearance
1st stage	2A	Rust type coating over entire surface. Irregular localized corrosion - no definite pattern except less severe near inlet. One hole about 41 inches from inlet end.
1st stage	7A	Rust type coating over entire surface. Irregular localized corrosion - no definite pattern except less severe near inlet 9 holes (about 0.1 inch diameter) at 25 to 32 inches from inlet end.
2nd stage, 3rd pass	3A	Rust type coating over entire surface. Numerous small shallow pits - no definite pattern. This tube had not failed at the time of inspection.
2nd stage, 3rd pass	4A	(similar to 3A)
2nd stage, 3rd pass	4B	This tube had an appearance similar to 3A but had failed. No holes could be found however, and the hole may have been no larger than a pinhole.
3rd stage	-	Oil coating, No significant corrosion.

a possible loss of 0.03 inch. Because of the indicated high corrosometer readings in this location, a section of piping about 12 feet long was removed for visual examination (see below).

1. Examination was made of the 4 inch pipe elbow in the line from the first stage cooler discharge to the liquid separator. The elbow was located at the end of a horizontal run just before the gas stream entered the liquid separator. Flow in the elbow was from horizontal to vertical upward. A photograph of the elbow is given in Figure 16. The inner surfaces were covered with a uniform rust-type coating. Severe corrosion was evident in an area of about four square inches on the outer bend at the downstream end of the bend, ending at the weld joining the elbow to the vertical piping. The maximum depth of attack was approximately 0.1 inch, and had the appearance of being velocity related. The pipe just above the elbow showed no sign of severe attack.

2. The 3 inch diameter horizontal piping downstream from the second stage cooler was examined. The length of the section examined was about 12 feet long. At the end nearest the cooler, the upper half of the pipe was covered with brown rust-type coating, and the bottom half had an oily film, possibly corrosion inhibitor. In the midsection of the pipe the oily film covered the entire inner surface of the pipe (Figure 17). At the end of the pipe the upper half was covered with the brown rust-type coating and the oily film was

Figure 16: Corroded 4″-diameter pipe elbow from first-stage piping

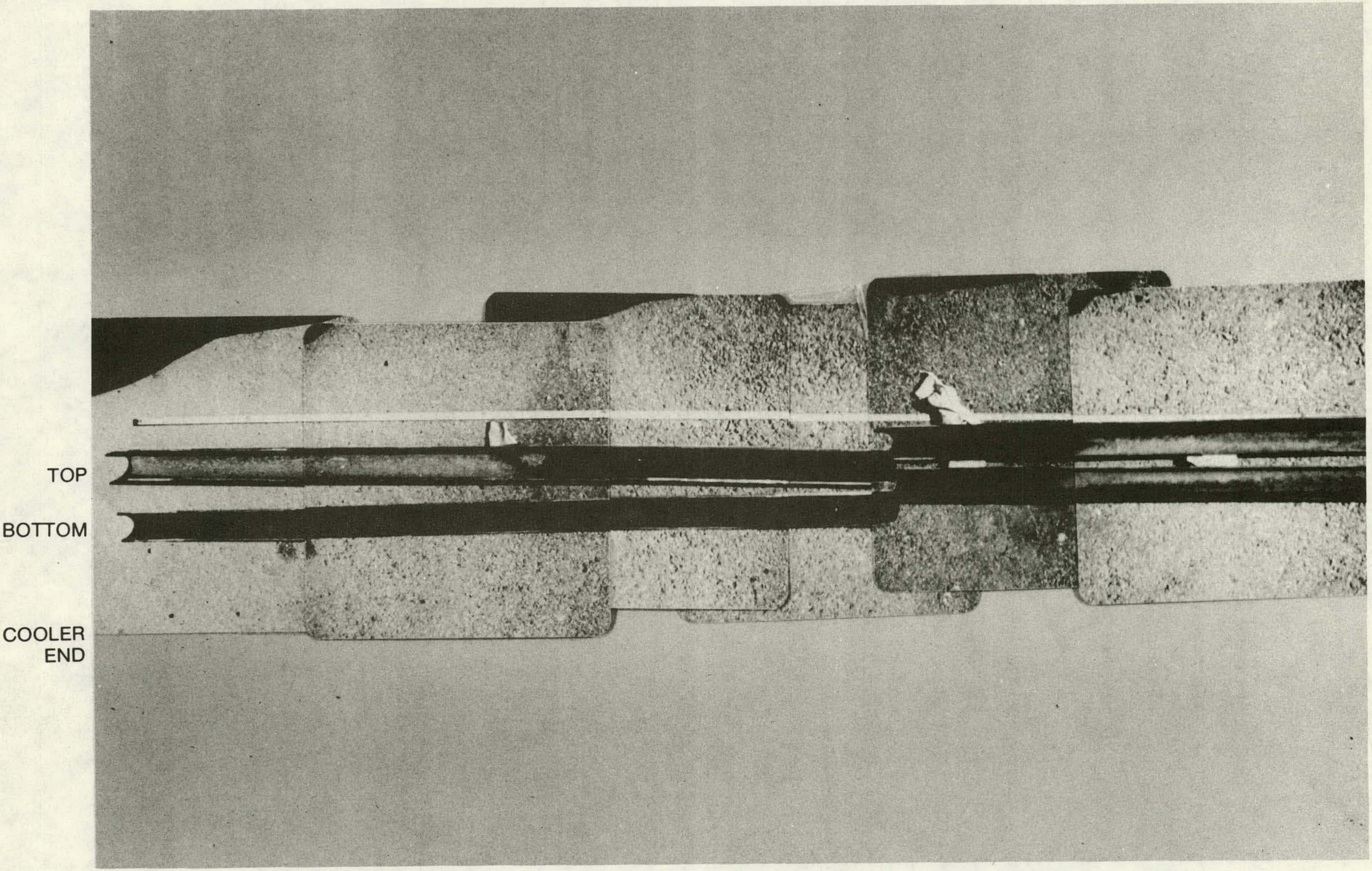


Figure 17: 3″-diameter second-stage piping downstream of cooler showing distribution of corrosion product and oily film

confined to a band along the bottom. Before cleaning the pipe there were no signs of significant corrosion damage. After cleaning by light sand blasting, the pipe was examined visually. Measurements indicated no significant general corrosion. Numerous small pits were found in a wide band along the bottom of the pipe. The maximum depth of the pits was about 0.02 inch.

TABLE 5

Mountain View Landfill
Ultrasonic Test Data

			Top of Pipe		Bottom of Pipe	
Location	Pipe Size, Inch	Nominal Wt, Inch ± 10%	2nd Reading w/Paint Inch ± 0.006"	2nd Reading w/out Paint Inch ± 0.006"	2nd Reading w/Paint Inch ± 0.006"	2nd Reading w/out Paint Inch ± 0.006"
1st Stage Compression - Suction	8	0.322 (.290-.354)	0.320 (.314-.326)	0.300 (.224-.306)	0.330 (.324-.336)	0.320 (.314-.326)
1st Stage Compression - Discharge	4	0.237 (.215-.260)	0.244 (.238-.250)	0.220 (.114-.226)	0.265 (.259-.271)	0.250 (.244-.256)
2nd Stage Compression - Suction	4	0.237 (.215-.260)	0.253 (.247-.259)	0.233 (.227-.239)	0.267 (.261-.273)	0.230 (.224-.236)
2nd Stage Compression - Discharge	3	0.216 (.194-.238)	0.240 (.234-.246)	0.226 (.220-.232)	0.236 (.230-.242)	0.220 (.214-.226)
3rd Stage Compression - Discharge	2	0.218 (.196-.240)	0.231 (.225-.237)	0.213 (.207-.219)	0.235 (.229-.241)	0.221 (.215-.227)

NOTE: The following must be taken into consideration while studying the above table.

1) The accuracy on the ultrasonic thickness gauge is ± 0.006".

2) The nominal wall thickness can vary up to ± 10.0%.

DISCUSSION AND CONCLUSIONS

Adequacy of probe data, testing program, and utility of corrosion inhibitor in controlling corrosion.

Due to the heterogeneous nature of the corrosive environment, i.e., a dispersed liquid phase in a predominant gas phase, corrosometer probes would not be expected to reflect all possible corrosive conditions. Those least detected are associated with local high velocity conditions or with local stagnant water phase conditions. Corrosometer probes and standard corrosion specimens would be expected to reflect only the general corrosion condition at the probe location, not localized effects elsewhere in the system. For a system such as this, the value of the probes is not in monitoring the severity of corrosion conditions in the various locations, but rather as means of determining when changes in the general corrosivity of the gas stream occur. They provide a means for correlating corrosion effects with some operating change, such as a change in inhibitor concentration, inhibitor type, or stream composition. The preferred way to monitor effectively the severity of corrosion is by inspection of the piping and vessels in those locations where experience has shown corrosion to be severe, or where there is a logical reason for anticipating a severe corrosion environment. An orifice type specimen can be used to evaluate the velocity effects observed in the compressor inlet and in the pipe bends. Such a specimen consists of a flat plate orifice inserted between flanges, the diameter of the orifice being selected to be slightly less (about 25 percent) than the I.D. of the pipe. Evaluation is by a combination of weight loss, diameter measurement, and general appearance after exposures of several weeks.

The probes indicated moderate corrosion rates prior to the start of the inhibition program, and in the line upstream from the first inhibitor injection point. The only location showing significant corrosion rates following inhibition was in Location 8 (Figure 3), downstream from the second stage cooler, and this during March-May 1980. One operating change made during this time was the installation of a bypass from downstream of the second stage separator to the inlet of the liquid separator upstream from the first stage compressor. The amount of gas bypassed varied from about 11 to 32 percent of the total flow during a period from March through December 1980. The question has been raised whether or not this bypass operation could be related in some way with the rise in corrosion rates of the probe at Location 8. One possibility that can be proposed is that the effect of the bypass operation would be to reduce the water content of the gas entering both the first stage and the second stage compressors. Assuming that water acts as a carrier for the inhibitor, this could lower the amount of inhibitor transported through the second stage cooler into the line where the probe was located. It is also possible that some minor change in position of the probe occurred which exposed it more effectively to a corrosive water phase, or there was a change in flow pattern. This is unlikely. Either explanation is difficult to prove without further experimentation.

Materials Selection

Corrosion resistant alloys. It is believed that the alloy most likely to be resistant to the severe corrosion experienced in the treatment plant would be Type 316 stainless steel (Type 316L stainless steel for welded items). The major uncertainty about the use of Type 316 stainless steel in this service is the possibility of stress corrosion cracking if the process stream contains significant chloride ion. Chloride ion can also cause crevice corrosion of stainless steels. At present there is insufficient information available as to the chloride contents of the various separated water streams to provide a basis for an estimation of the probability of a stress corrosion cracking problem existing. The one analysis available is for the water from the condensate holding tank and would consist of water from all the separator vessels. The analysis was made in 1978 by Nalco (Table 6). The chloride content was 158 ppm, a value sufficiently high to be of concern from the standpoint of chloride stress corrosion cracking of austenitic stainless steels.

TABLE 6 ANALYSIS OF WATER FROM
CONDENSATE HOLDING TANK
(ANALYSIS BY NALCO 10/78)

WATER ANALYSIS

DISSOLVED SOLIDS			RESULTS AS COMPOUNDS	
CATIONS	mg/1	meq/1		mg/1
Sodium, Na (calc.)	522.	22.7		
Calcium, Ca	55.2	2.8	as CaCO3	138.
Magnesium, Mg	21.3	1.8	as CaCO3	87.7
Barium, Ba			as BaSO4	
Sum of Cations	599.	27.2		
ANIONS				
Chloride, Cl	158.	4.4	as NaCl	260.
Sulfate, SO4	75.7	1.6	as Na2SO4	112.
Carbonate, CO3			as CACO3	
Bicarbonate, HCO3	1290.	21.2	as CaCO3	1060.
Sum of Anions	1530.	27.2		
TDS CALCULATED	2130.			
Total Iron, Fe	313.	16.8	as Fe	313.
Acid to Phen, CO2	2330.	53.0	as CaCO3	5300.

OTHER PROPERTIES		CaCO3 STABILITY (Index)		CaSO4 SOLUBILITY (meg/1)
pH (units)	5.5	-1.4	@ 70F	
Spec Gravity	.994	-.7	@120F	
Turbidity (jtu)	220.	-.5	@170F	

In the event that an alloy resistant to chloride stress corrosion cracking should be used, there are a number of possibilities. The selection is determined by cost and availability in the forms required for the equipment items being considered. These alloys include:

> Carpenter 20 Cb-3, Inconel 625, Hastelloy G, Incoloy 825, Ebrite 26-1, Sandvik 3RE60, Titanium (grade 12).

Evaluation of Type 316 stainless steel and alloys selected from the above list could be accomplished by exposure of test heat exchanger tubes in the gas cooler and by use of orifice type specimens previously described.

The possible presence of hydrogen sulfide in the untreated gas could cause sulfide stress cracking effects if high strength steel alloys are used in any of the equipment items handling this gas. If certain limits of hydrogen sulfide are exceeded in a specific process stream, materials selected for use with that stream should conform to National Association of Corrosion Engineers Standard MR-01-75, "Sulfide Stress Cracking Resistant Metallic Materials for Oil Field Equipment." The suggested limits for hydrogen sulfide contents are:

1st stage, 45 psig	80 ppm H_2S
2nd stage, 160 psig	30 ppm H_2S
3rd stage, 350 psig	15 ppm H_2S

Hydrogen sulfide is not usually observed in the landfill gas but one analysis showed 150 ppm H_2S in the raw gas.

Relative cost of corrosion control options

Options for corrosion control include: (1) metal part replacement (use of different alloys); (2) dehydration of the raw gas; and, (3) the use of a scrubber in front of the system. To replace all metal parts with corrosion resistant alloys would prove very expensive. Only where valves and pipes are subjected to severe corrosion can these materials be economically employed.

Dehydration of the gas would eliminate virtually all corrosion but is relatively expensive and difficult to achieve at low-pressure. Positive control of corrosion of carbon steel can be achieved if the gas stream can be dehydrated to such a low value that there is no possibility of a water phase forming on the steel surfaces. One possible criterion would be for all gas streams in contact with steel to have a dew point at least 10 - 20°F below the lowest possible temperature that the equipment is likely to experience. Monitoring of the dehydration system should include frequent water content measurements of all critical gas streams as well as corrosometer probe monitoring at all interstage cooler outlet lines. A water spray wash could be installed in front of the system to remove much of the entrained water. Although the gas would be saturated with water the wash water would remove much of the chlorides and fluorides which would allow alloy replacement downstream with less concern for stress corrosion cracking.

If oxygen could be removed from the gas stream, the corrosion problem would be less severe, but there would still be a problem. One advantage of removing oxygen would be to improve the probability of successful application of inhibition. Oxygen can be reduced by decreasing the air intrusion into the landfill. To do this would require improving the cover on the landfill or reducing the gas flowrate. Reducing the gas flowrate will increase the unit cost of the gas. Removing oxygen from the gas is difficult and expensive.

Effect of corrosion on other utilization methods

If other methods of utilization of landfill gas are to be employed, corrosion will still continue to be a serious problem. For example, in combustion of the gas to generate electricity corrosion agents will still exist in the gas. Steps must be taken to protect turbine blades, boiler tubes, or engine manifolds and valves. However the gas is to be utilized corrosive constituents in the gas will have to be considered where metal components come in contact with them.

RECOMMENDATIONS

Preventive measures for corrosion control are chemical inhibition, corrosion resistant alloys, dehydration, and inspection.

For the existing plant, periodic inspection of pressure equipment items and process piping will be made to detect any corrosion damage before mechanical integrity of the system is reduced. Inspections will include ultrasonic measurements, X-ray examination, visual examinations, and wall thickness measurements as appropriate for the particular equipment items involved.

In general, all items exposed to the gas stream at temperatures below the dew point will be inspected. Preliminary inspection revealed that bends and other locations where local turbulence could occur are subject to severe corrosion. Inspection will be made of areas where stagnant water layers can collect since these could be sites of differential aeration corrosion cells. Pitting in these locations could be quite localized. Included in this category would be the various liquid separators, carbon pretreatment vessels, and those portions of the adsorbers which are exposed to the gas stream at temperatures near or below the dew point.

Process considerations make it difficult to dehydrate the gas stream prior to the second compressor stage, and some other corrosion control measures will be required for those equipment items exposed to the wet gas up to the second stage. A combination of corrosion inhibition and corrosion resistant alloys will be employed to control corrosion prior to dehydration.

Future plants should be designed to either dehydrate the gas as soon as possible to eliminate corrosion or wash the gas prior to compression to remove chlorides and sulfides so that regular stainless alloys can be used without fear of stress corrosion cracking occurring. Corrosion inspections should still be a routine part of plant maintenance.

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