

## THE ROLE OF CORROSION TESTING IN THE COAL-CHEMICAL PLANT

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### Introduction

It is a well-known fact that corrosion of plant equipment is costing the chemical producers millions of dollars annually. In the coal-chemical industry, as in any other industry today, it is imperative to minimize maintenance and replacement costs and to insure uninterrupted production to remain competitive. Although the high cost of corrosion cannot be entirely eliminated, it can be greatly reduced by the proper selection of constructional materials, by modifications in equipment design and operating procedure, and by the proper selection and application of protective coatings and inhibitors. However, the answer to a corrosion problem, whether it lies in replacement of the present materials of construction or in a modification in design, is usually not simple and cannot be readily ascertained without firsthand knowledge of the problem. This data can best be developed by conducting a well-planned corrosion-testing program.

Such a program can best be defined as one that will provide the most reliable data and the most convincing data from a given set of conditions. In planning a corrosion-testing program, both laboratory and plant tests should be considered. The laboratory test provides the closest control of the important variables and permits individual study of each variable. However, it is extremely difficult to duplicate in the laboratory the combination of effects, such as solution concentration, temperature, velocity, viscosity, that takes place under actual operating conditions in a chemical plant. The limited quantity of solution used in the laboratory test restricts the number and size of the materials in test. Further, unless the test solution is continuously renewed, it is difficult or impossible to maintain a constant concentration of known corrosive constituents in the solution, and thus the results may be erroneous. In a plant test, however, all the above variables are present. As a result, data obtained from plant tests with operating equipment are considered more reliable and are more convincing than laboratory data where plant conditions can only be approximated.

These remarks are not meant to suggest that laboratory data are misleading and have no place in a well-planned corrosion-testing program. On the contrary, laboratory tests can be used to screen a series of materials or inhibitors prior to being plant-tested, to provide data for comparison purposes, or to supplement plant data. In the development of new processes where previous corrosion experience is lacking or in plant corrosion problems where the equipment is inaccessible for corrosion testing, the corrosion engineer must often turn to laboratory data for guidance in selecting suitable constructional materials. When a new process is being developed and a pilot plant is to be constructed, corrosion tests should also be conducted in these facilities. Inasmuch as pilot facilities are often small, arrangements should be made early in the design stage to include adequate corrosion-testing locations. However, the data obtained from either laboratory or laboratory and pilot-plant studies should be used judiciously in selecting construction materials for a full-size piece of equipment.

### Plant Corrosion-Testing Methods

In plant corrosion testing, various methods are utilized depending upon the objective. The tests most frequently used are those described below:

#### Corrosion-Specimen Test

The corrosion-specimen test is probably the best known and most widely used method in the coal-chemical industry. The test consists of obtaining cleaned and weighed specimens of various materials, including the materials in the piece of equipment to be tested, and exposing them in the liquid and vapor space of the operating unit for a given period of time. The test specimens are normally welded to obtain information on the effect of welding on the corrosion performance of the material, which is an important factor in choosing materials of construction for equipment. Moreover, in certain environments, it is often desirable to expose stressed specimens in the equipment to develop information on the susceptibility of the various construction materials to stress-corrosion cracking.

Although the specimens can be individually suspended in the unit, they are normally placed in a specimen holder and separated with insulating material to prevent direct contact except when galvanic effects are being studied. Figure 1 shows a typical corrosion-test rack and its various components. (Special types of rack may have to be designed for units difficult in accessibility.) Although it is usually necessary to shut down the operating unit to install or remove a test rack, retractable holders can be constructed to permit testing during normal operations. However, this method limits the number of materials that can be tested at one time. If the unit is inaccessible, the specimens can usually be installed in the related piping, though the data will not be as representative as data obtained from the actual operating unit. In testing in a pipeline, the specimens are mounted on a pipe plug and placed in a tee in the line. However, care must be taken to install the specimens parallel with the flow so as not to cause a restriction in the line. Figure 2 shows a mounted pipe-plug specimen and method of installation. In special cases, the materials to be evaluated can be obtained in pipe form, and short sections of each can be installed in the line. Much like the test specimens, these sections should be cleaned and weighed prior to exposure and should be insulated from each other.

After exposure, the test specimens are carefully cleaned and reweighed, and their corrosion rates calculated from the weight losses. Care should be taken to examine the specimens for local effects, such as pitting, grooving, and cracking. The data obtained from this test method will provide information on the expected service life of the unit, type of corrosion occurring, and suitable replacement materials.

#### The Electrical-Resistance Method

The electrical-resistance method is a direct means of measuring corrosion continuously and is used in the chemical industry to follow the progress of corrosion in operating equipment.<sup>1</sup>\* A special probe and meter are utilized in conducting these measurements. Figure 3 shows an electrical-resistance probe, and Figure 4 shows a portable meter and a typical installation. Several of these corrosion-monitoring devices are commercially available. In making measurements, the probe containing an element of the material to be tested is placed in the system under study and is then electrically connected to the meter. The meter measures the change in electrical resistance of the probe element as the cross-sectional area of the element is reduced by corrosion. The amount of corrosion can then be read directly from the meter in microinches penetration of the probe element.

\* See References.

With the electrical-resistance method, corrosion data can be obtained in a few hours, whereas with weight-loss measurements data sometimes cannot be obtained for months because the removal of specimens is governed by plant operations. Unlike the use of corrosion-test racks, the electrical-resistance method does not require shutting down the operating unit to remove or change probe elements. The measurements are not affected by the accumulation of most corrosion products or sludge. However, the measurements are affected by corrosion products that carry current, such as sulfides. Like any test, this method also has its undesirable features in that it is limited to measuring a uniform type of corrosion and it is necessary to visually examine the probes to determine the presence of local forms of corrosion, such as pitting.

Probably the most widespread use of the electrical-resistance method is in the evaluation of corrosion-preventive measures, such as inhibitors. In addition, this method is especially useful for correlating corrosion with changes in operations.

#### Service Test

The service test is the most satisfactory method of corrosion testing. In this test, sections of the equipment to be tested are replaced with full-size experimental parts. Probably the most frequent use of this method is with heat exchangers and pumps, both of which are normally inaccessible for corrosion-rack testing. For example, in evaluating materials for replacing heat-exchanger tubes, full-size tubes constructed of various materials are placed in the tube bundle for testing. After a sufficient operating period (six months to one year), the tubes are removed from the exchanger and examined. In a test of this type, where large pieces of equipment are often handled, the examination of the equipment usually consists of a visual inspection. However, for some equipment—tubes, for instance—the thickness of the parts can be measured with a micrometer prior to and after exposure to determine change in dimensions as a result of corrosion.

Unlike the other methods previously mentioned, this method will readily detect local points of corrosion. Unfortunately, this method is often impractical and expensive.

#### Visual-Inspection Method

Visual inspection is probably the most common method of evaluating the performance of a piece of equipment. However, it usually requires a complete shut-down and clean-out of the unit. The data obtained from visual inspection plus ultrasonic measurements of wall thickness provide convincing information on the service life of a unit. As a result, this method is widely used by insurance and state inspectors in examining pressure-coded equipment and by maintenance personnel in conducting preventive corrosion programs.

#### Nondestructive Testing Method

In nondestructive testing, two of the more widely used pieces of equipment are the ultrasonic thickness gauge and the magnetic-particle inspection equipment for detecting surface discontinuities, such as cracks. The ultrasonic thickness gauge is an instrument for the nondestructive measurement of an unknown wall thickness from one side. This instrument utilizes the principle of ultrasonic resonance in measuring thickness. Several portable, battery-operated gauges are commercially available. Figure 5 shows the ultrasonic thickness gauge and method of application. This method is especially useful in determining the wall thickness of inaccessible equipment where visual inspection cannot be made. The magnetic-particle inspection method has been very useful on occasion in determining the integrity of high-pressure equipment.

### Corrosion-Testing Applications

The corrosion-detection methods discussed above are the major plant tools which the corrosion engineer has to work with in his endeavor to control corrosion. Examples of how some of these methods have been used in solving specific corrosion problems in U. S. Steel's coal-chemical plants are given below. For each of the examples, a brief description of the process as it concerns certain pieces of plant equipment is given. Several additional examples of how corrosion testing has solved specific corrosion problems in coal-chemical plants have been presented by Larrabee and Mathay.<sup>2)</sup>

#### Corrosion-Rack Tests in Tar-Distillation Equipment

One area in the coal-chemical plant that has caused operators considerable corrosion trouble is the tar-distillation plant. In this operation, the tar removed from the coke-oven gas in the collecting mains is placed in decanters to permit separation of the flushing liquor and finely divided carbon that are carried along with the tar from the collecting mains. After decantation, the tar is washed and centrifuged to reduce the moisture and inorganic salt content of the tar. The tar leaving the centrifuge is then placed in storage tanks until further processing. Upon demand, the tar is pumped into a dehydrating flash drum, where it is further dehydrated and preheated to a high temperature. The tar leaving the flash drum enters the tar still (carbon-steel shell lined with AISI Type 316 stainless steel, with Type 316 internal parts), where it is fractionated into tar acid oils and pitch. The acid oil is further treated by distillation for the recovery of naphthalene and solvents.

Corrosion of the tar-distillation facilities is essentially controlled by the decantation, washing, and centrifuging operations. The agents in coal tar that are believed to be responsible for corrosion are the inorganic salts, ammonium chloride and ammonium thiocyanate.<sup>3)</sup> The tar-handling operations minimize the concentration of these contaminants. Of the two corrosion constituents, ammonium chloride is the most aggressive. The individual effect of thiocyanate and chloride compounds in acid oil on the corrosion of carbon steel was studied in laboratory tests. The results of these tests, Table I, show that operating problems with the tar-handling facilities can lead to serious corrosion problems as a result of large quantities of these corrosive constituents entering the tar-distillation equipment.

Recently, at one of the coal-chemical plants where serious operating problems were encountered in the tar-handling system, extensive corrosion of distillation equipment occurred. Interior inspection of the primary naphthalene fractionator revealed that the carbon-steel shell and AISI Type 410 stainless-steel internals of the fractionator were corroding. (The function of the primary naphthalene fractionator is to concentrate the crude naphthalene in the acid oil received from the tar still.) The corrosion attack was most severe at the top of the column where ammonium thiocyanate and ammonium chloride were found to concentrate. Following the inspection, the top of the column was lined with cement. At the same time, corrosion-test racks containing various metals were placed in the unit to determine suitable replacement materials, and the unit was again placed into operation. The types and chemical composition of the test materials contained in the racks are shown in Table II. After six months of operation, the fractionator was shut down and the test racks were removed. The results of these tests, Table III, show that AISI Types 304 and 316 stainless steels and USS TENELON stainless steel were practically unattacked.

Visual inspection of the unit revealed that the corrosion of the shell and internals had progressed to the point where replacement was necessary. On the basis of the above results, the corroded unit was recently replaced with a new AISI Type 316L stainless-steel fractionator. The low-carbon-grade Type 316L stainless steel was used in the construction to obtain maximum corrosion resistance at the weld areas.

Reducing the carbon content of the low-carbon stainless steels to the solubility limit of about 0.02 per cent minimizes or prevents carbide precipitation in the heat-affected zone of the metal during welding. As a result, the low-carbon stainless steels are less susceptible to intergranular corrosion at the weld areas.

#### Service Test in Wash-Oil System

In another coal-chemical plant, 150 million gallons of river water are used daily for cooling purposes. Although the water is treated with lime to raise the pH from about 3.8 to about 4.5 (further treatment being uneconomical because the water is not recirculated), the carbon-steel condenser tubes in the wash-oil regenerating system of the plant are corroded seriously and fail after about four months of service. (Wash oil is used to absorb from the coke-oven gas those constituents having boiling points below 200 C, such as benzol, toluene, and xylol.) The wash-oil condenser receives wash-oil vapors from a Dowtherm heat exchanger, which partially condenses the oil vapors coming from the wash-oil still. As shown in Figure 6, the hot oil flows through the shell side of the wash-oil condenser and is cooled by river water flowing through the tubes. The temperature of the oil is about 350 F. The cooling water enters the condenser at about 80 F and leaves at about 180 F.

In an effort to reduce the high maintenance and replacement costs caused by the rapid failure of carbon-steel condenser tubes, a service test was initiated to determine the suitability of stainless-steel tubes in the wash-oil condenser.<sup>4)</sup> Four AISI Type 304 stainless-steel tubes and four carbon-steel tubes were installed in the tube bundle of the condenser at the same time. After four months of exposure, the carbon-steel tubes failed because of severe pitting by the cooling water. After six months of exposure, two of the Type 304 tubes removed from the condenser were practically unattacked. Figure 7 shows a section cut from the center of each type of tube after the service test. (The marks on the interior surface of the Type 304 tube are fabrication marks.) The remaining two Type 304 tubes were removed after one year of exposure and were also found to be in excellent condition. Because of the excellent resistance of the Type 304 tubes to corrosion by the low pH river water, Type 304 tubes will be installed in the entire condenser. The use of Type 304 tubes should result in a substantial yearly savings through decreased maintenance costs.

#### Corrosion Monitoring of Foul-Gas Line

In the utilization of coke-oven gas as a fuel for the open hearth, soaking pits, and reheating furnaces, it is desirable to remove the sulfur from the gas as it constitutes an unwanted contaminant in steel. At one of the coal-chemical plants, a portion of the coke-oven gas is processed for the removal of sulfur and other contaminants prior to sending the gas to the open-hearth melting furnace. In this process, the coke-oven gas leaving the gas line enters an absorption tower, where the gas is scrubbed counter-currently with a sodium carbonate solution to remove hydrogen sulfide, hydrogen cyanide, carbon dioxide, and other contaminants. The desulfurized coke-oven gas leaves the top of the tower and is sent to the open-hearth furnace. The foul solution is removed from the bottom of the tower and pumped into a stripping column, where it is regenerated by steam distillation and recycled to the absorber. The foul gas leaving the top of the column is sent to the open-hearth shop, where it is used as fuel for the boilers. The service life of the carbon-steel line carrying the foul gas to the open-hearth boilers is usually about two years. A corroded portion of the pipe after two years of service is shown in Figure 8.

An electrical-resistance probe with a carbon-steel element was installed in the foul-gas line to ascertain the effect of operating variables on the rate of corrosion of the line. Corrosion readings with the resistance meter were taken over

a period of 15 days during which time the progress of corrosion was determined when (1) steam was being fed to the steam tracers, (2) steam was not being fed to the steam tracers and, (3) the line was being steamed out. A graph of penetration (microinches) of the probe element versus time, Figure 9, shows that an increase in corrosion takes place only during steam-out periods. The corrosion attack is believed to be the result of hydrogen sulfide, hydrogen cyanide, and thiocyanate attack in the presence of water. The corrosion rate of carbon steel based on the resistance readings for the first steam-out period was 964 mils per year and that for the second steam-out period was 526 mils per year. This investigation also showed that the use of steam tracers for maintaining temperatures higher than about 150.F (normal gas temperature) on the line seemed to have no effect on the corrosion rate of the line. As a result of the investigation, the number of steam-outs was reduced.

#### Summary

The examples cited above represent only a few of the corrosion studies conducted in the Corporation's coal-chemical plants to determine suitable materials of construction for withstanding the extremely corrosive environments normally encountered. To give some idea of the extent of corrosion testing within the Corporation's plants since 1954, over 3500 corrosion specimens have been exposed in about 150 process units. In this same period of time, detailed corrosion inspections have been conducted on 110 process units.

As a result of these corrosion studies, suitable materials have been determined for the replacement of 21 major operating units and 39 smaller units. In addition, the corrosion data have enabled the Corporation to assist customers in selecting materials for the construction of new chemical plants.

#### References

1. A. J. Freedman, E. S. Troscinski, and A. Dravnieks, "An Electrical Resistance Method of Corrosion Monitoring in Refinery Equipment," Corrosion, 14, No. 4, pp. 29-32 (April 1958).
2. C. P. Larrabee and W. L. Mathay, "Controlling Corrosion in Coal-Chemical Plants," Corrosion, 14, No. 4, pp. 37-40 (April 1958).
3. D. McNeill, "Causes and Prevention of Corrosion in Tar Stills," Corrosion Technology, November 1957, p. 385.
4. R. J. Schmitt, "Behavior of Carbon and Stainless Steels in Acid Waters," Corrosion, 14, No. 10, p. 15 (October 1958).

Table I  
Corrosion Rate of Carbon Steel Exposed to Samples  
of Tar Acid Oil at 220 C

Thiocyanate Concentration, grams per liter	Chloride Concentration, grams per liter	Corrosion Rate, mils per year	
		Vapor	Liquid
*	*	3	5
5	0	13	40
0	5	42	184

\* Present in residual amounts.

Table II  
Types and Composition of Test Materials  
Exposed in Primary Naphthalene Fractionator

Material	Per Cent									
	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	N
Carbon steel	0.18	0.50	0.930	0.03	0.043	0.05	0.03	0.02	*	*
AISI Type 410 stainless steel	0.06	0.48	0.022	0.005	0.55	*	0.32	12.2	0.03	*
AISI Type 201 stainless steel	0.10	6.0	0.038	0.015	0.40	*	5.4	16.7	*	0.15
AISI Type 304 stainless steel	0.08	1.2	0.022	0.014	0.51	*	9.0	18.5	*	*
AISI Type 316 stainless steel	0.06	1.5	0.03	0.014	0.46	0.23	13.4	17.8	2.3	*
USS TENELON stainless steel	0.08	14.2	0.024	0.008	0.79	*	0.29	16.6	*	0.32

\* Not determined; present in residual amounts.

Table III  
Corrosion-Rack Tests in Primary Naphthalene Fractionator

Material	Rack Location in Fractionator	Corrosion Rate, mils per year
Carbon Steel	Top	*
	Middle	106
AISI Type 410 stainless steel	Top	16
	Middle	1
AISI Type 304 stainless steel	Top	<0.1
	Middle	<0.1
AISI Type 316 stainless steel	Top	<0.1
	Middle	<0.1
USS TENELON stainless steel	Top	<0.1
	Middle	<0.1

\* Specimen completely disintegrated.

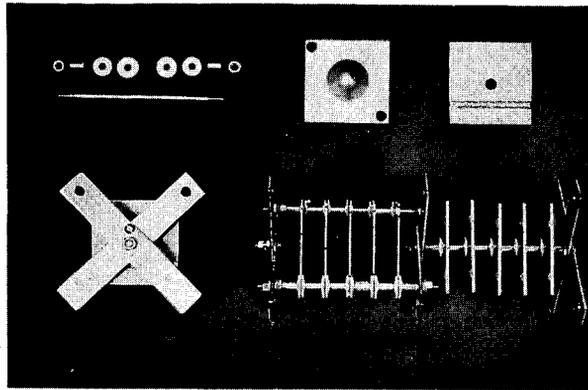


Figure 1. Corrosion-Test Rack and Component Parts.

Magnification: 0.125X

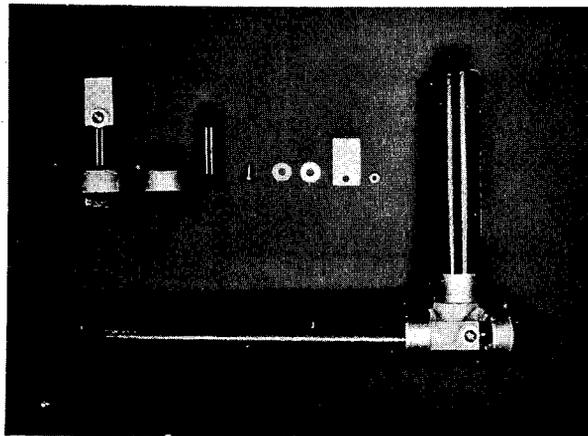


Figure 2. Mounted Pipe-Plug Specimen and Method of Installation.

Magnification: 0.125X

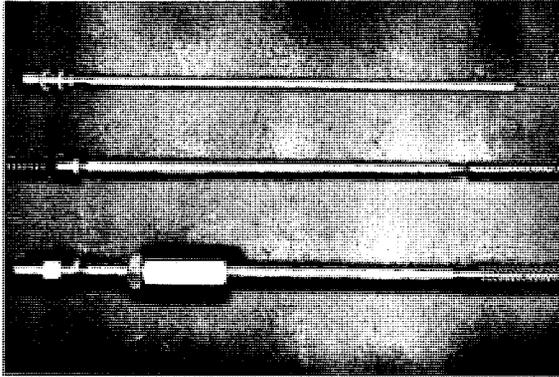


Figure 3. Electrical-Resistance Probe.

Magnification: 0.0625X



Figure 4. Portable Electrical-Resistance Meter and Typical Installation.

Magnification: 0.0625X

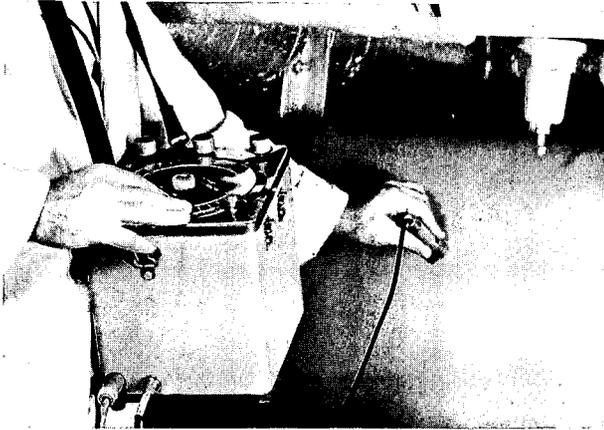


Figure 5. Ultrasonic Thickness Gauge and Method of Application.

Magnification: 0.125X

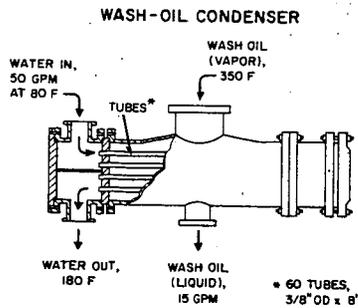


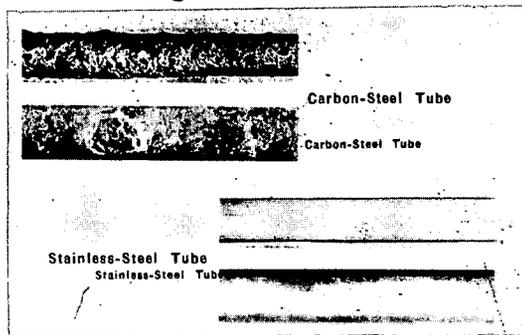
Figure 6.



FOUL-GAS LINE AFTER TWO YEARS OF SERVICE

Figure 7.

Magnification: 0.50X



TUBES AFTER EXPOSURE IN A WASH - OIL CONDENSER

Figure 8.

Magnification: 1X

CORROSION-PROBE MEASUREMENTS  
IN FOUL-GAS LINE

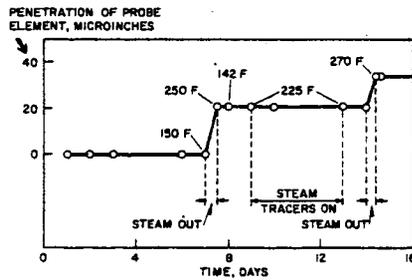


Figure 9.