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**ELECTROPOTENTIAL MEASUREMENTS OF PASSIVATION
AND CORROSION OF STEEL COUPONS**

G. S. Petit
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MASTER

FEBRUARY 1977

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**OAK RIDGE GASEOUS DIFFUSION PLANT
OAK RIDGE, TENNESSEE**

prepared for the **U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION**
under **U.S. GOVERNMENT Contract W-7405 eng 26**

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AND CORROSION OF STEEL COUPONS

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Oak Ridge Gaseous Diffusion Plant
Union Carbide Corporation
Oak Ridge, Tennessee

Prepared for the U.S. Energy Research and Development Administration
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ABSTRACT

There is considerable interest at the Oak Ridge Gaseous Diffusion Plant (ORGDP) in the preparation of mild steel to resist corrosion (passivation) both in moist air and uranium hexafluoride (UF_6) environments. Steel prepared by the usual procedures to prevent rusting, such as oiling, plastic coating, painting, or phosphating, cannot be used in the presence of UF_6 .

Tests have shown that a chromate treatment or an ammoniacal citrate treatment for passivation are effective. The electropotential behavior of these two passivation treatments is described in this report. The initial electropotential measurement, when compared to that of an unpassivated coupon, gives the electropotential degree in volts of passivation. Continual exposure in the test, when compared to the unpassivated coupon, gives a profile of the durability of the passivation film.

The chromate passivation treatment was slightly superior to the citrate passivation.

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ELECTROPOTENTIAL MEASUREMENTS OF PASSIVATION AND CORROSION OF STEEL COUPONS

INTRODUCTION

There is considerable interest at the Oak Ridge Gaseous Diffusion Plant (ORGDP) in the preparation of mild steel to resist corrosion (passivation) both in moist air and uranium hexafluoride (UF_6) environments. Steel prepared by the usual procedures to prevent rusting, such as oiling, plastic coating, painting, or phosphating cannot be used in the presence of UF_6 .

Steel coupons treated with different passivation techniques were exposed to humid air and observed for rusting to determine which methods were the best for inhibiting steel corrosion. Of the methods evaluated, two showed the best passivation during the exposure test. The two methods are known as (1) the chromate treatment and (2) the citrate treatment.

It was desirable to obtain some quantitative data on the degree of passivation and the stability of this passivation to moist air ($\sim 95\%$ RH at 23°C). A system was designed to compare electropotential measurements of steel coupons (those passivated by the two methods and control or reference coupons cleaned but not passivated) versus a saturated calomel electrode in aerated distilled water. The difference in potential (voltage) at the outset of measurement was a direct measurement of the degree of passivation. Electropotential measurements over several hours gave profiles of the rate of oxidation of the various coupons.

SUMMARY

Electropotential measurement of steel coupons has been used to determine the amount of passivation obtained by chemical passivation using either a sodium chromate-sodium hydroxide solution or an ammoniacal citrate solution as the passivating agent. The coupons were tested in distilled water saturated with air, and a saturated calomel electrode was used as the reference electrode. Measurements were made using a multipoint *Speedomax G** recorder, with dual range of 0-100 mV and 0-1 V.

The initial potential measurement, when compared to the reference coupon (unpassivated), gives the extent of passivation achieved by the passivation treatment. A plot of the potential versus test time (h) gives an excellent profile of the durability of the passivation film and the rate of oxidation when the film is destroyed.

The stability of the passivation film upon exposure to 95% RH at 23°C for periods up to 45 days was also evaluated.

*Reference to a company or product name does not imply approval or recommendation of the product by Union Carbide Corporation or the U.S. Energy Research and Development Administration to the exclusion of others that may meet specifications.

EXPERIMENTAL

TEST APPARATUS

Speedomax G: Multipoint recorder, dual range 0-100 mV and 0-1 V.

Test Chamber: Battery jar filled with distilled water, saturated with air to supply oxygen.

Humidity Chamber: 240-liter volume Lucite chamber with a 15 liters/min flow of air saturated with moisture.

Reference Electrode: Saturated calomel electrode.

Coupons: Type A 106 mild steel, all with 8 in.² total surface area.

SAMPLE PREPARATION

The sample coupons were divided into three groups of four each. The coupons were of A 106 steel and of uniform size, 8 in.² surface area. All groups were degreased in methyl chloroform, dipped in hydrochloric acid (HCl), rinsed, polished in an ammonium acid fluoride (NH₄HF)-hydrogen peroxide (H₂O₂) solution (3 wt % NH₄HF - 6 vol % H₂O₂), rinsed, and air dried.

Group No. 1 - Treated as above (used as a control or reference).

Group No. 2 - Treated as Group No. 1, then dipped in a sodium dichromate (Na₂Cr₂O₇)-sodium hydroxide (NaOH) solution (5 wt % Na₂Cr₂O₇ - 5 wt % NaOH) at 65°C, rinsed in cold water, and air dried.

Group No. 3 - Treated as Group No. 1, then dipped in an ammoniacal citrate solution [5 wt % citric acid adjusted to pH 10 with ammonium hydroxide (NH₄OH)], rinsed in cold water, and air dried.

TEST CONDITIONS

A single coupon from each group was placed into the test chamber for electropotential measurements. The other three coupons from each group were placed into the humidity chamber. A coupon from each group was removed at 15-day intervals for electropotential measurements.

REVIEW OF ELECTROMOTIVE SERIES AND NERNST EQUATION

To acquaint the reader with the anticipated electropotential behavior of the various coupons during the testing, a brief review of the electromotive series of the metals and the Nernst equation will be helpful.

The electromotive series of the metals lists gold as the least reactive (noble) metal and lithium as the most reactive (base) metal. The electrode reactions and volts for gold, iron, lithium, and the saturated calomel cell (reference) are listed in Table 1.

Table 1

SINGLE ELECTRODE POTENTIALS AT 25°C

Electrode Reaction	E ₀ Oxidized, V
$\text{Li}^0 \rightarrow \text{Li}^+ + e$	+3.02
$\text{Fe}^0 \rightarrow \text{Fe}^{++} + 2e$	+0.44
$2 \text{Hg}^0 + 2 \text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2e$ (saturated calomel cell)	-0.244
$\text{Au}^0 \rightarrow \text{Au}^{+++} + 3e$	-1.42

Iron is 1.86 V more reactive (less noble) than gold, but 2.58 V more noble than lithium. The term *passivation of a metal* refers to making a metal less reactive, or shifting it to a more noble potential.

A measurement of the initial potential of the three test groups (just after preparation) versus the saturated calomel cell gives the degree of passivation as follows:

$$E_0 (\text{Group 1}) - E_0 (\text{Group 2 or 3}) = \text{Potential Shift}$$

If the value is positive, the Group 2 or 3 metal surface has been passivated, and the larger the positive difference, the greater the passivation.

According to the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln \left(\frac{\text{oxidized}}{\text{reduced}} \right) \quad \text{or} \quad (1)$$

$$E = E_0 + \frac{0.059}{N} \log \left(\frac{\text{oxidized}}{\text{reduced}} \right) , \text{ at } 25^\circ\text{C} \quad (2)$$

where:

R = gas constant = 8.314 joules-degree⁻¹-mole⁻¹,

T = temperature, °K,

N = electron transfer,

F = Faraday's number = 96,500 coulombs,

E₀ = original electrode potential measurement, V, and

E = final electrode potential measurement, V.

In the initial measurement, $E = E_0$ (reduced), the potential will change as the surface oxidizes in the oxygenated distilled water. When the entire surface has oxidized, no further potential change will occur, and the final measurement will be $E' = E_0$ (oxidized). The potential will change from E_0 (reduced) to E_0 (oxidized) during the test.

A plot of the potential versus time gives an excellent profile of the durability of the passivation when compared to the unpassivated (control) coupon.

RESULTS

The test results are presented graphically. The electropotential of each coupon (mV) is plotted versus time (h) in the test chamber. The electropotential behavior of freshly passivated coupons is presented in Figure 1. The results after 15, 30, and 45 days' exposure to the humidity chamber are presented in Figures 2, 3, and 4, respectively.

Freshly Passivated Coupons (Figure 1): The electropotential of the unpassivated coupon (Group 1) changed rapidly for the first 5 h (~250 mV), then gradually leveled off. This is the change anticipated according to the Nernst equation. The initial measurements for the passivated coupons (chromate - Group 2 and citrate - Group 3) were considerably lower than the unpassivated coupon, indicating passivation. The chromate-treated coupon was 180 mV lower than the unpassivated coupon, and the citrate-treated coupon was 140 mV lower than the unpassivated coupon.

The dip (lower potential) of both types of passivated coupons for the first few hours indicates the formation of slightly better passivation film by possibly a monolayer-oxide formation or a slight change in the chemical composition of the initial passivation film.

The curves for both types of passivation treatment are practically identical for the first 30 h, after which the rate of potential change (oxidation) for the citrate-treated coupon is slightly greater than for the chromate-treated coupon. In spite of the increased corrosion rate of the citrate-treated coupon over the chromate-treated coupon, the citrate-treated coupon took 65 h before reaching the 500 mV potential that the unpassivated coupon reached after only 5 h.

Coupons After Exposure to the Humidity Chamber: In comparing the initial test with no humidity exposure (Figure 1) and the test results after the various exposures in the humidity chamber (Figures 2, 3, and 4), one must be sure to recognize the different time scale used for Figure 1. The test time scale for Figure 1 is 0-100 h, while for Figures 2, 3, and 4 it is only 0-20 h.

The humidity exposure altered the protective passivation film of both the chromate and citrate treatment even after only 15 days. An apparent anomaly exists in the data for the citrate-treated sample after 30 days of exposure, where the initial potential was much higher than for the 15- and 45-day exposures.

Figure 1
A 106 STEEL - NO EXPOSURE TO 95% RH AIR

Figure 2
A 106 STEEL AFTER 15 DAYS EXPOSURE TO 95% RH AIR

Figure 3
A 106 STEEL AFTER 30 DAYS EXPOSURE TO 95% RH AIR

Figure 4
A 106 STEEL AFTER 45 DAYS EXPOSURE TO 95% RH AIR

It is assumed that the 30-day exposure sample was not initially passivated to the extent of the other coupons treated by the citrate passivation step.

The initial electropotential measurement of all coupons exposed to the 95% RH in air shows a decrease in passivation compared to freshly passivated coupons. The dominating factor is the 15 days exposure to the moist air (~95% RH), and possibly less is equivalent to the first 25 h of test time for freshly passivated samples by either method, that remains the same even after 45 days of exposure. It is also noted that the corrosion rate of all passivated samples by either method exposed to the humid air (~95% RH) is about 5 times as fast as freshly prepared samples, but still considerably less than the unpassivated samples.

No appreciable difference was noted in the corrosion rate of the samples not passivated (control) either freshly prepared or after exposure to the humid air.

All test results show that passivation by either method inhibits corrosion of mild steel, but the chromate passivation film protects the steel for longer exposure time than does the citrate film. The test results also show that even limited exposures (15 days) to moist air reduce the passivation protection, but the passivation still offers considerable protection for longer periods of time than nonpassivated steel.

The additional amount of energy required to oxidize a mole of steel that has been passivated by the chromate or citrate method can be calculated by using the following equation:*

$$\Delta F = -nFE \quad (3)$$

where:

ΔF = free-energy change,

n = electron transfer,

F = Faraday's number = 96,500 coulombs or 23,060 calories, and

E = cell potential, V.

E will be the difference between the initial potential measurements of Group 1 and that of Groups 2 or 3. The difference for chromate passivation was 0.180 V, which yields a ΔF of 12,450 calories. The citrate difference was 0.140 V, or ΔF of 9,780 calories.

*Glasstone, Samuel, *Textbook of Physical Chemistry*, 2nd ed, 11th printing, 1956, c/1946, New York, D. Van Nostrand Company, Inc., pp 923-924.

DISCUSSIONS AND CONCLUSIONS

The electropotential technique described provides the ability to continually record the electropotential behavior during the test, thus permitting a detailed profile of the changes occurring at any time during the test. Graphic presentation of these data gives the electropotential shift due to passivation, comparative stability of passivation by different methods or by modification of a given method, and the rate of oxidation when the passivation is changed or destroyed.

These limited tests indicate that a two-phase process takes place when steel passivated by either the citrate or the chromate method is exposed to humidity. At first the passivation film greatly inhibits corrosion. However, the film is altered after continued exposure to high humidity, and corrosion does occur but at a slower rate than for nonpassivated steel.

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