

U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

**NUCLEAR WASTE TECHNICAL REVIEW BOARD
EBS PANEL MEETING**

SUBJECT: THERMOGRAVEMETRIC STUDIES

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Atmospheric Corrosion Studies

Atmospheric corrosion studies have determined that thin water layers on metal surfaces can be severely corrosive.

Atmospheric corrosion tests of Cu(99.98)

| | Corrosion rate ($\mu\text{m}/\text{yr}$) | |
|---|--|---------------------|
| | <u>10 yr</u> | <u>20 yr</u> |
| Altoona, PA Industrial | 1.3 | 1.4 |
| New York, NY Industrial marine | 1.2 | 1.3 |
| Sandy Hook, NJ Northern marine | 0.6 | |
| La Jolla, CA Severe marine | 1.4 | 1.2 |
| Key West, FL Tropical marine | 0.5 | 0.6 |
| Phoenix, AZ Rural dry | 0.05 - 0.2 | |
| State College, PA Northern rural | 0.56 | 0.43 |

A.W. Tracy, "Effect of Natural Atmospheres on Copper Alloys: 20-year Test," in Symposium on Atmospheric Corrosion of Non-Ferrous Metals, ASTM STP 175, 1956.

Effect of Relative Humidity and Sulfur Dioxide Concentration on the Corrosion of Copper

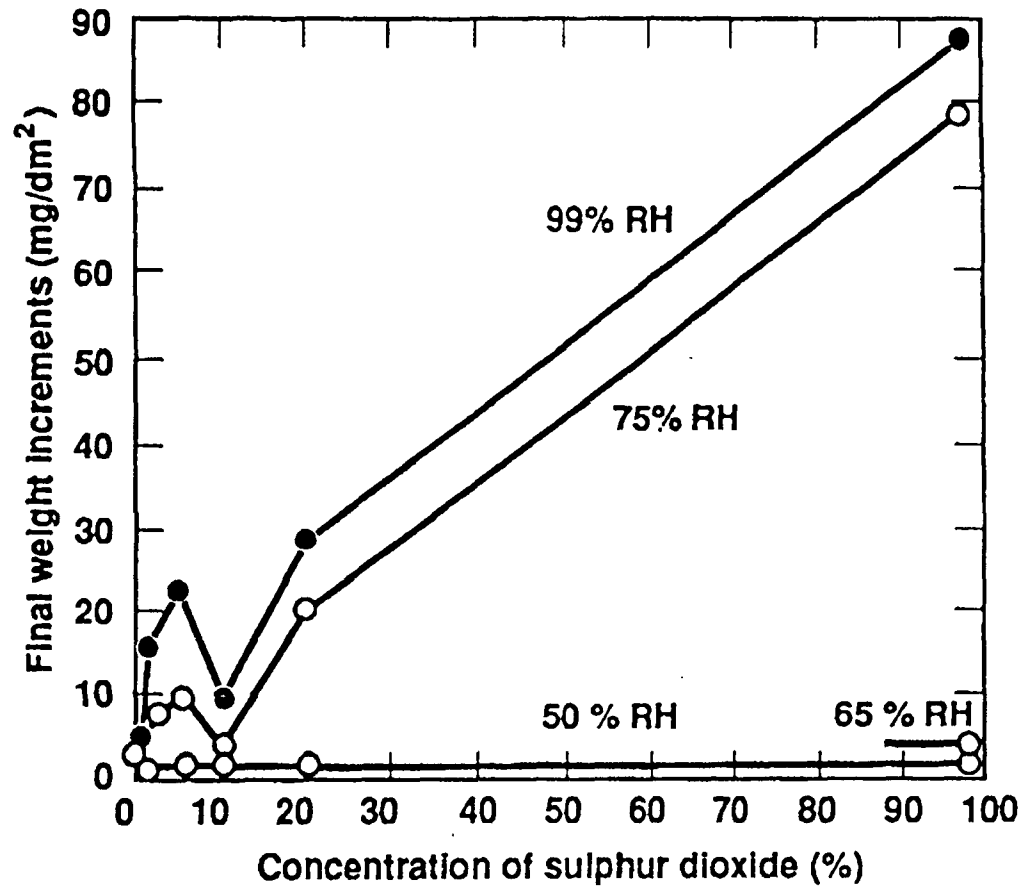


Figure 25. Relationship between corrosion and concentration of SO₂ in atmospheres of high relative humidity [87].

P.M. Aziz, H.P. Godard, "Mechanism by Which Non-Ferrous Metals Corrode in the Atmosphere," Corrosion Vol. 15, 1959, pp. 529t-541t.

Corrosion Rate as a Function of Relative Humidity for Various Metals.

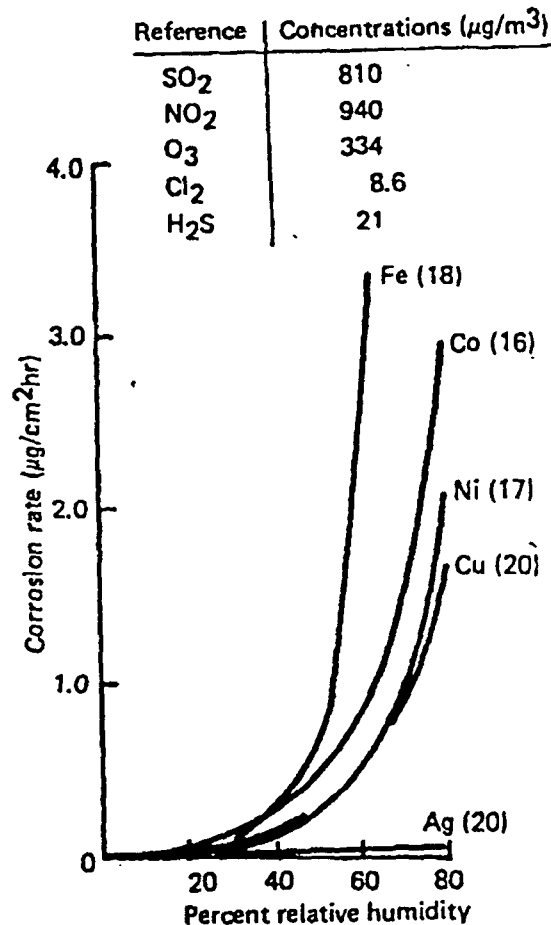


Figure 46.5. Corrosion rate versus relative humidity ($T = 25^\circ\text{C}$).

D.W. Rice, R.J. Cappell, P.B.P. Phipps, P. Peterson, "Indoor Atmospheric Corrosion of Copper, Silver, Nickel, Cobalt, and Iron," in Atmospheric Corrosion, W.H. Ailor, ed., The Electrochemical Society, 1980, pp. 651-666.

Corrosion Rate Dependence on Temperature and Water Partial Pressure

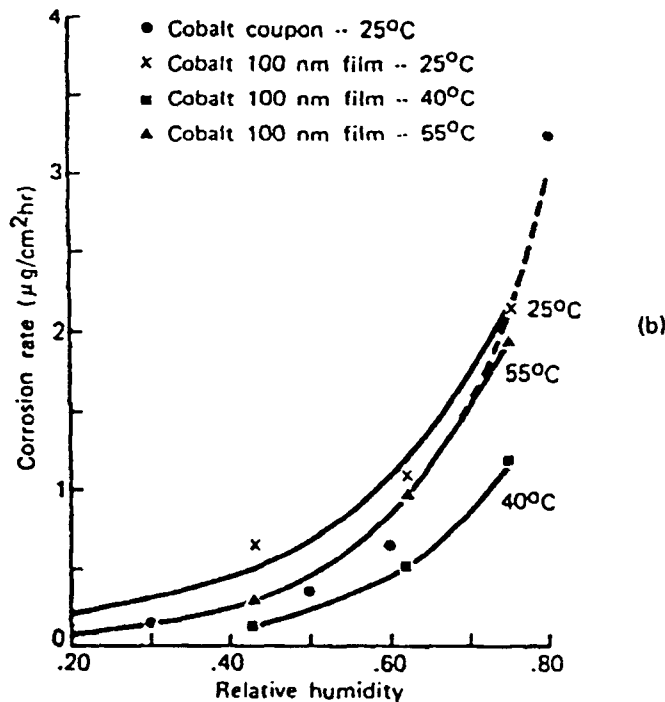
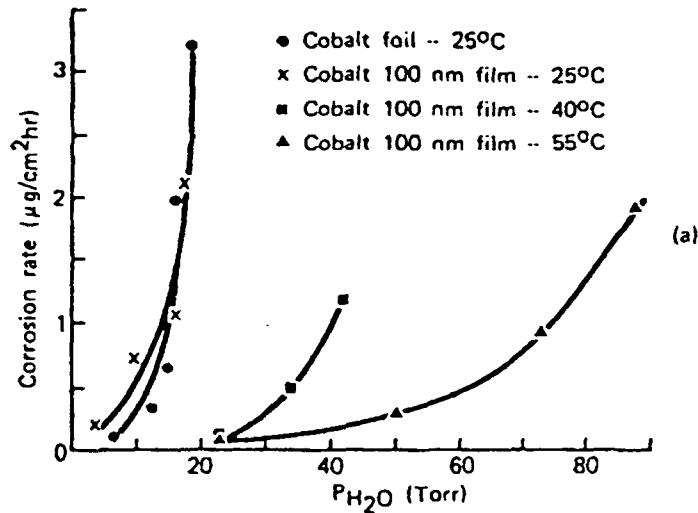


Figure 46.6. Corrosion rates of (a) cobalt versus $P_{\text{H}_2\text{O}}$ at various temperatures in the reference test environment and, (b) cobalt versus relative humidity ($P_{\text{H}_2\text{O}}/P_{\text{H}_2\text{O}}^0$) in the reference test environment.

D.W. Rice, R.J. Cappell, P.B.P. Phipps, P. Peterson, "Indoor Atmospheric Corrosion of Copper, Silver, Nickel, Cobalt, and Iron," in Atmospheric Corrosion, W.H. Ailor, ed., The Electrochemical Society, 1980, pp. 651-666.

Dependence of Copper Oxidation on H₂S and Water Vapor

Kinetic Growth Rate for Cu and Cu₂O Samples (5 ppm H₂S)

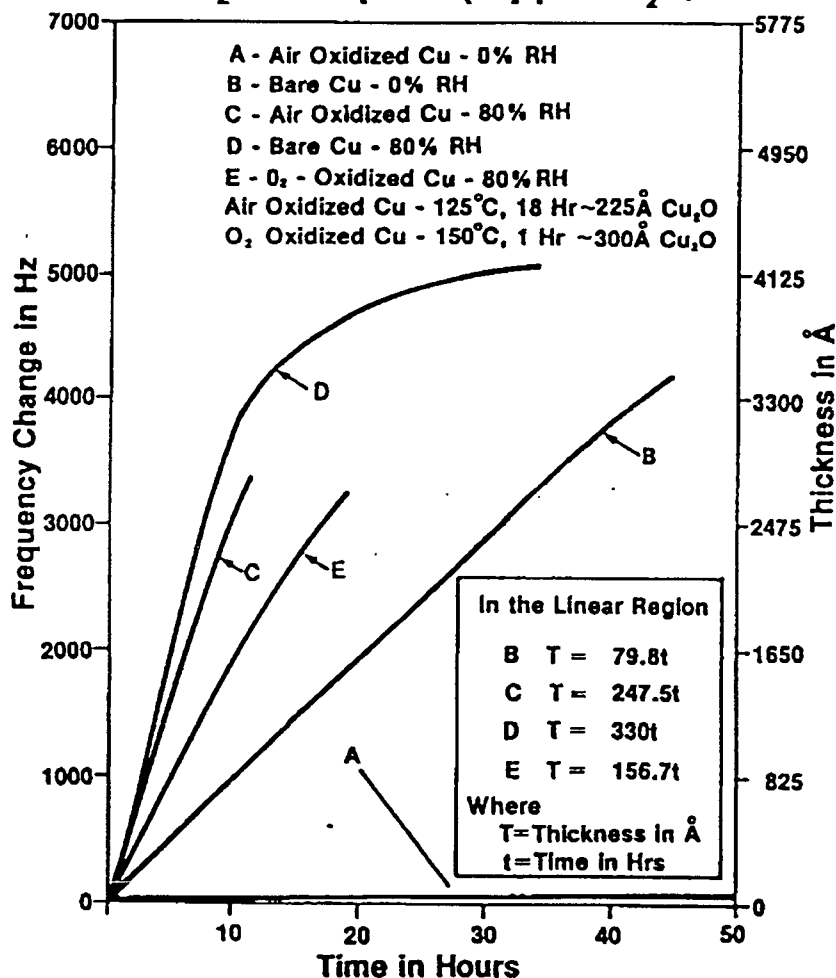
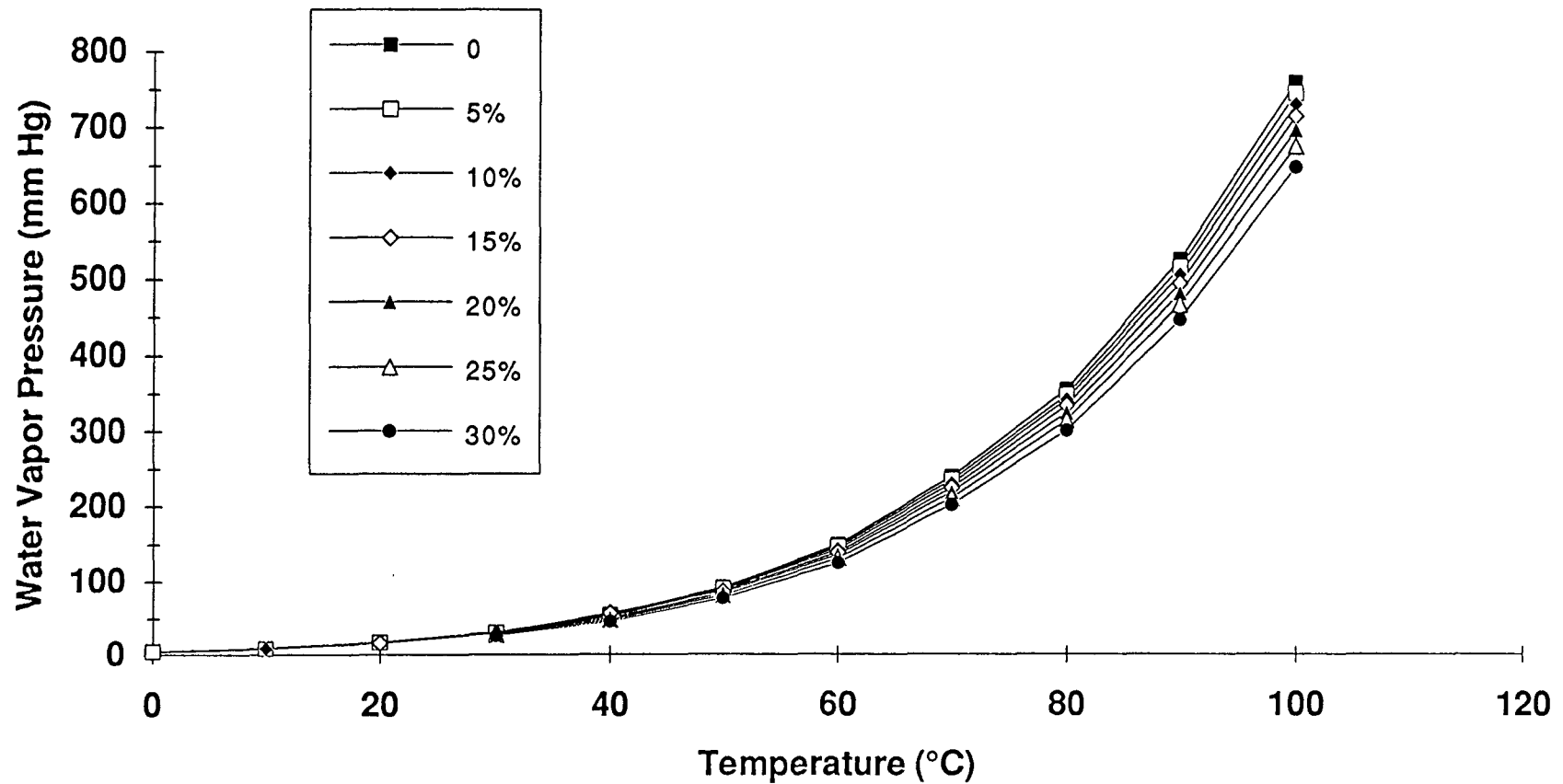


Fig. 7. Kinetic growth rate data obtained from quartz crystal microbalance is shown for various samples.

Water Partial Pressure Over Aqueous Solutions of Sodium Carbonate



Oxygen Solubility in Water

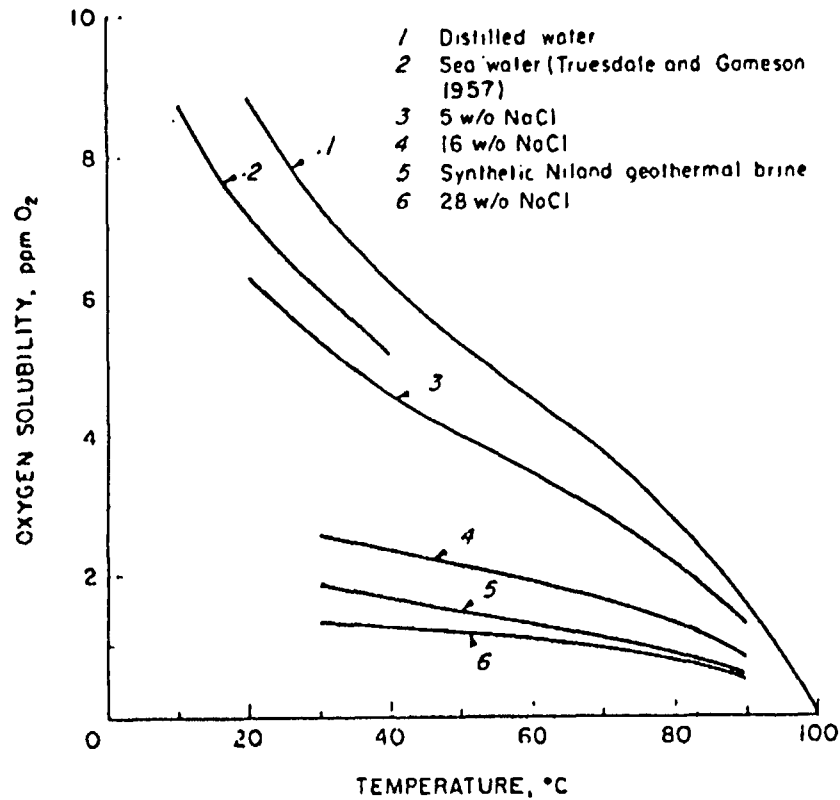
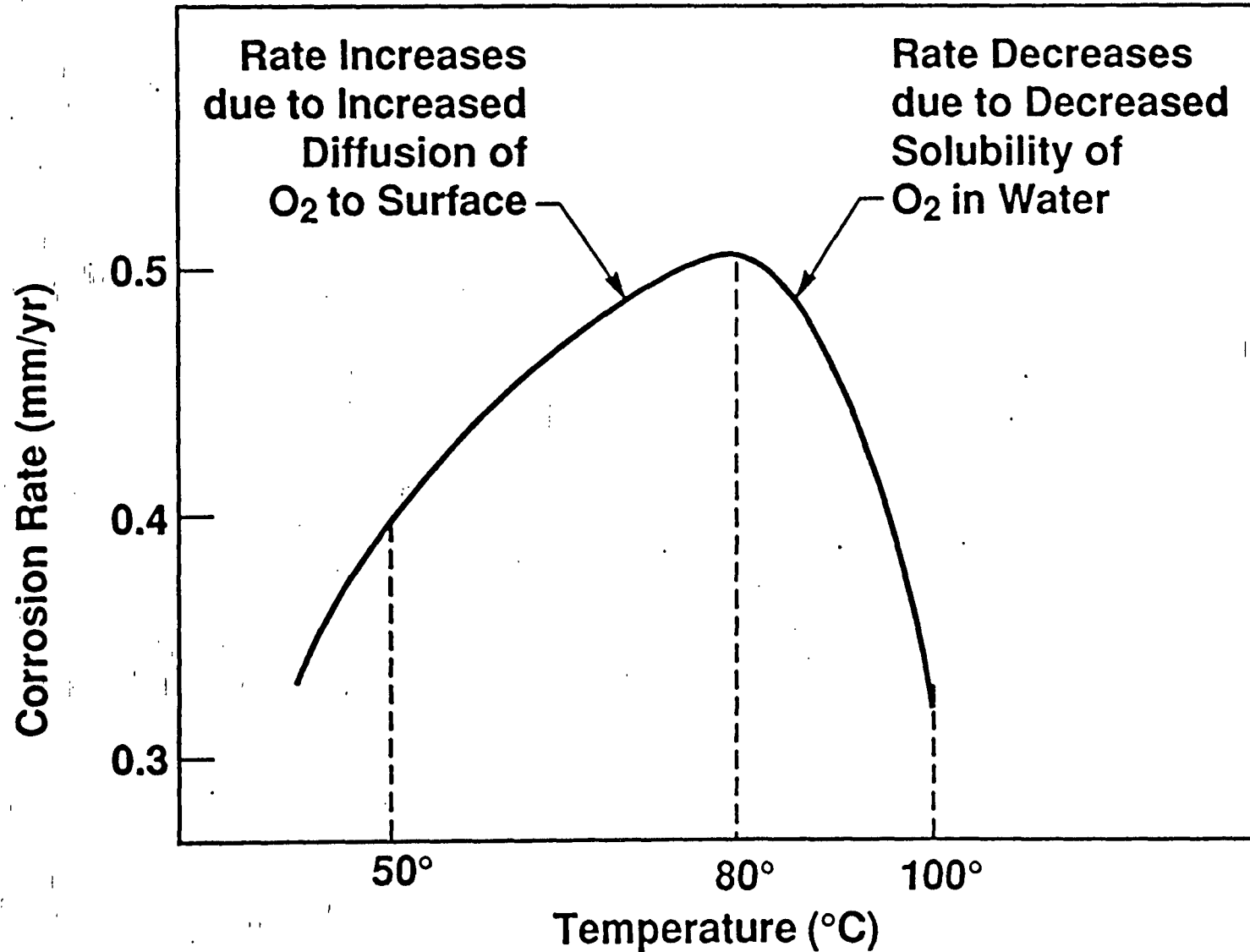


FIGURE 5. - Solubility of oxygen in water and brines from air saturated with water vapor at a total pressure of 760 mmHg

S.D. Cramer, "The Solubility of oxygen in Geothermal Brines," in Corrosion Problems in Energy Conversion and Generation, C.S. Tedmon, ed., The Electrochemical Society, 1974, pp. 251-262.

Corrosion of Carbon Steel in Neutral-pH Water Shows a Maximum



Atmospheric Corrosion Studies

- High corrosion rates are dependent on the presence of a thin aqueous film on the metal surface
 - thickness: 0.001 to 1.0 μm
- High corrosion rates are dependent on the presence of absorbed species in the aqueous film
- Temperature range of studies: 20 to 30°C
 - Present study requires that higher temperatures be investigated (70 - 150°C)

High Temperature Oxidation

Need to understand the effect that gas phase water has on the kinetics and mechanism of oxidation in temperature region where there is no water condensation.

Effect of Water Vapor on the Oxidation of Vanadium

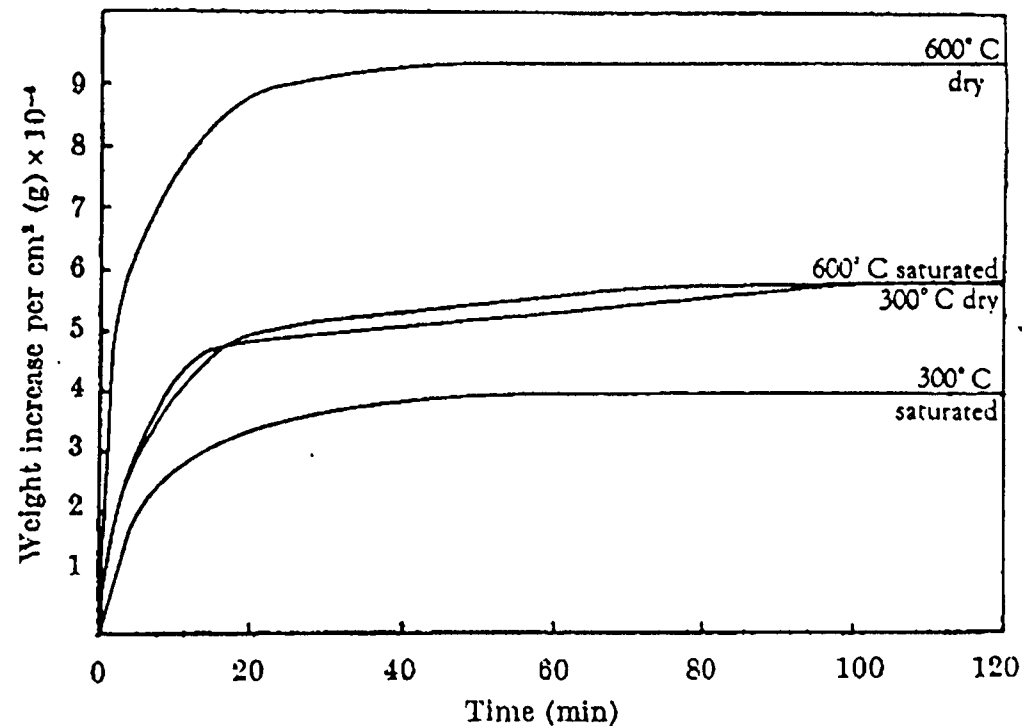


Fig. 3. Effect of humidity on the oxidation kinetics of vanadium at 300° and 600° C, at $P_{O_2} = 1.0$ atm., saturated at room temperature

J.R. Wilson, M.E. Lewis, "Oxidation of Vanadium in Dry and Moist Oxygen-Argon Mixtures," Nature, Vol. 206, 1965, pp. 1350-1351.

Effect of Water Vapor on the Oxidation of Low Carbon Steel

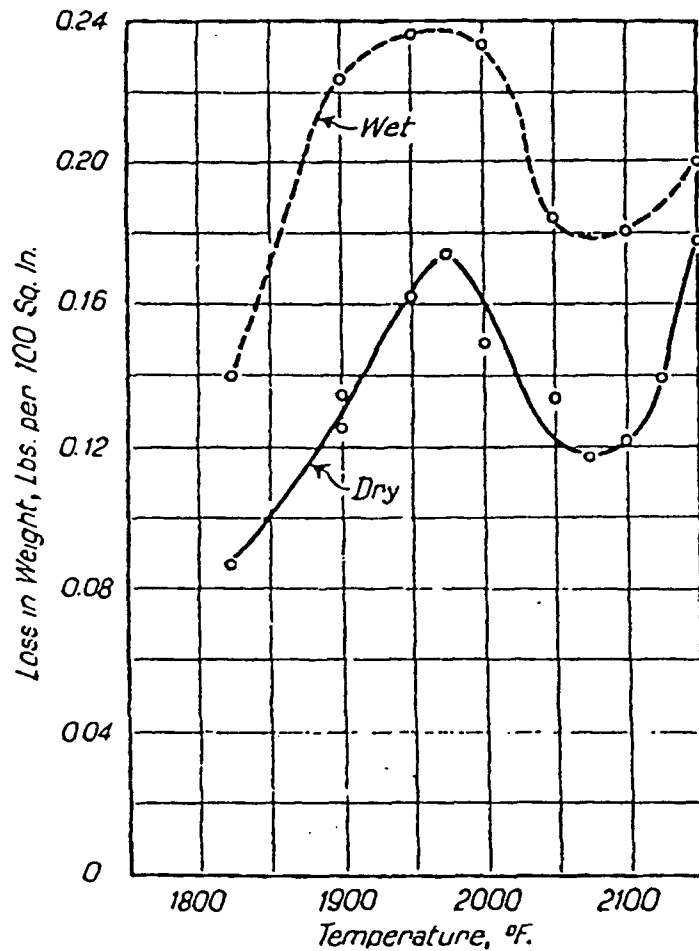
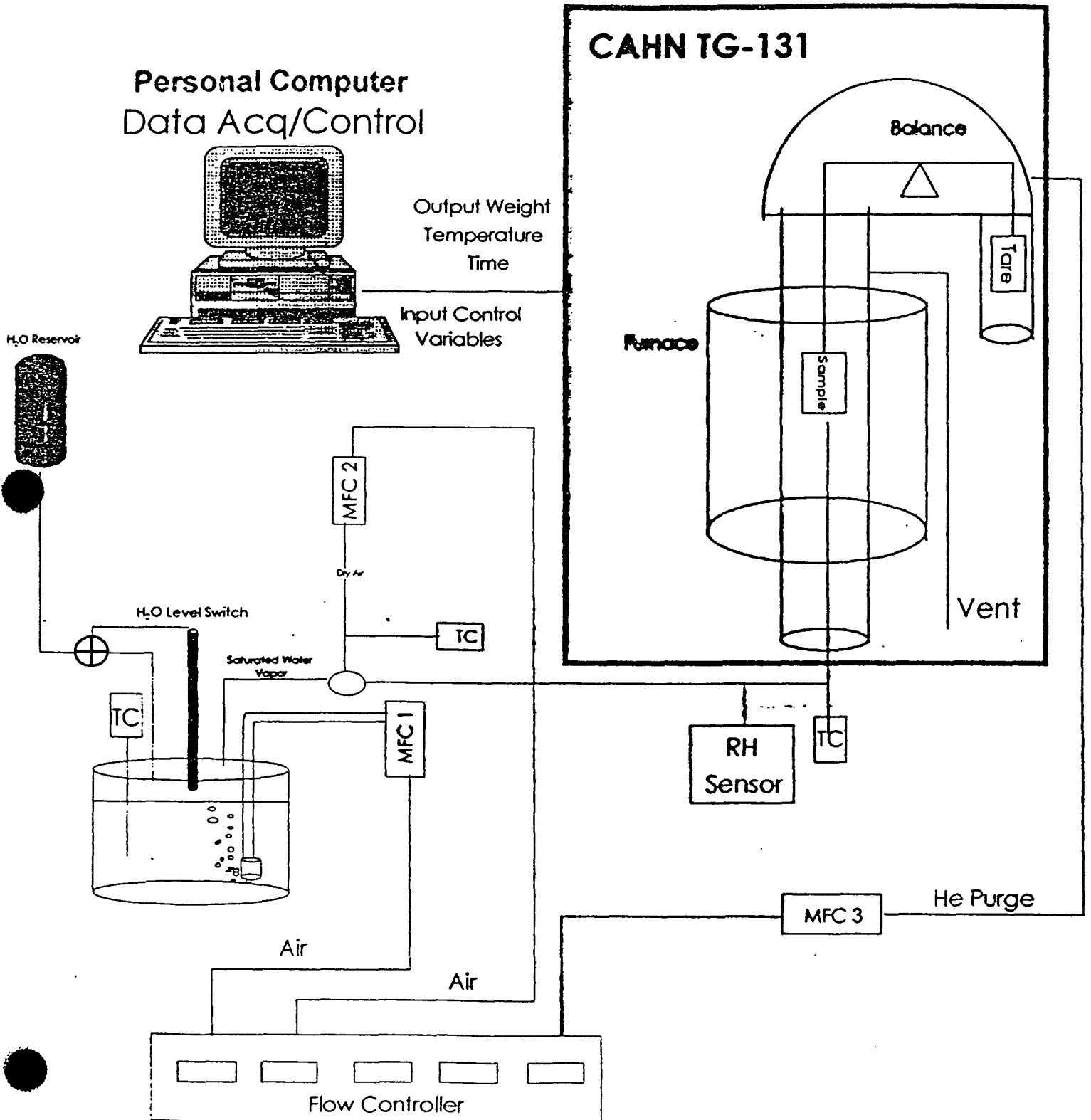


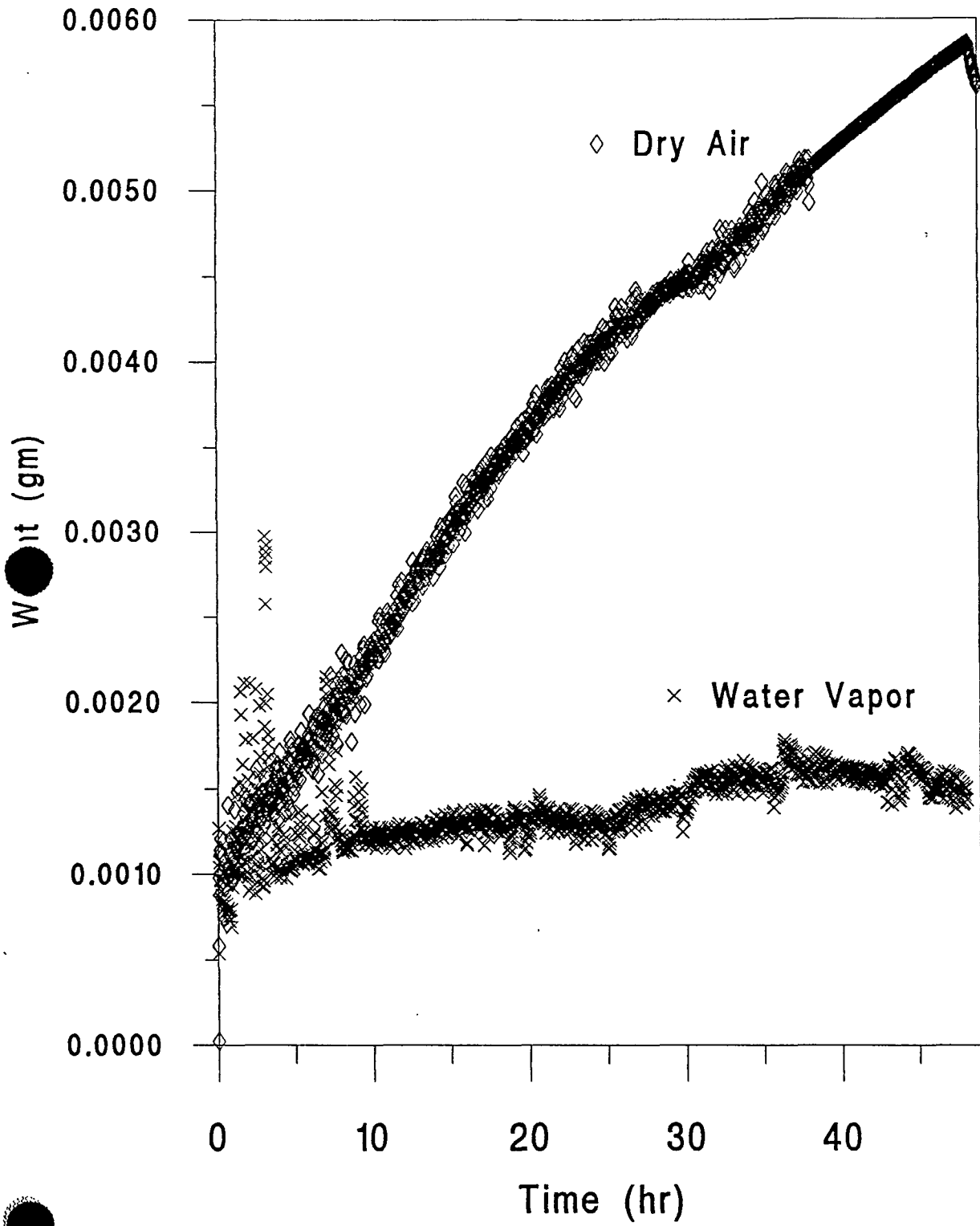
Fig. 1—Ferrous Iron in Scale Versus Temperature.

C.A. Siebert, H.G. Donnelly, "The Effect of Humidity of Air on the Oxidation of a Low Carbon Steel," Trans A.S.M., Vol. 28, 1940, pp. 372-379.

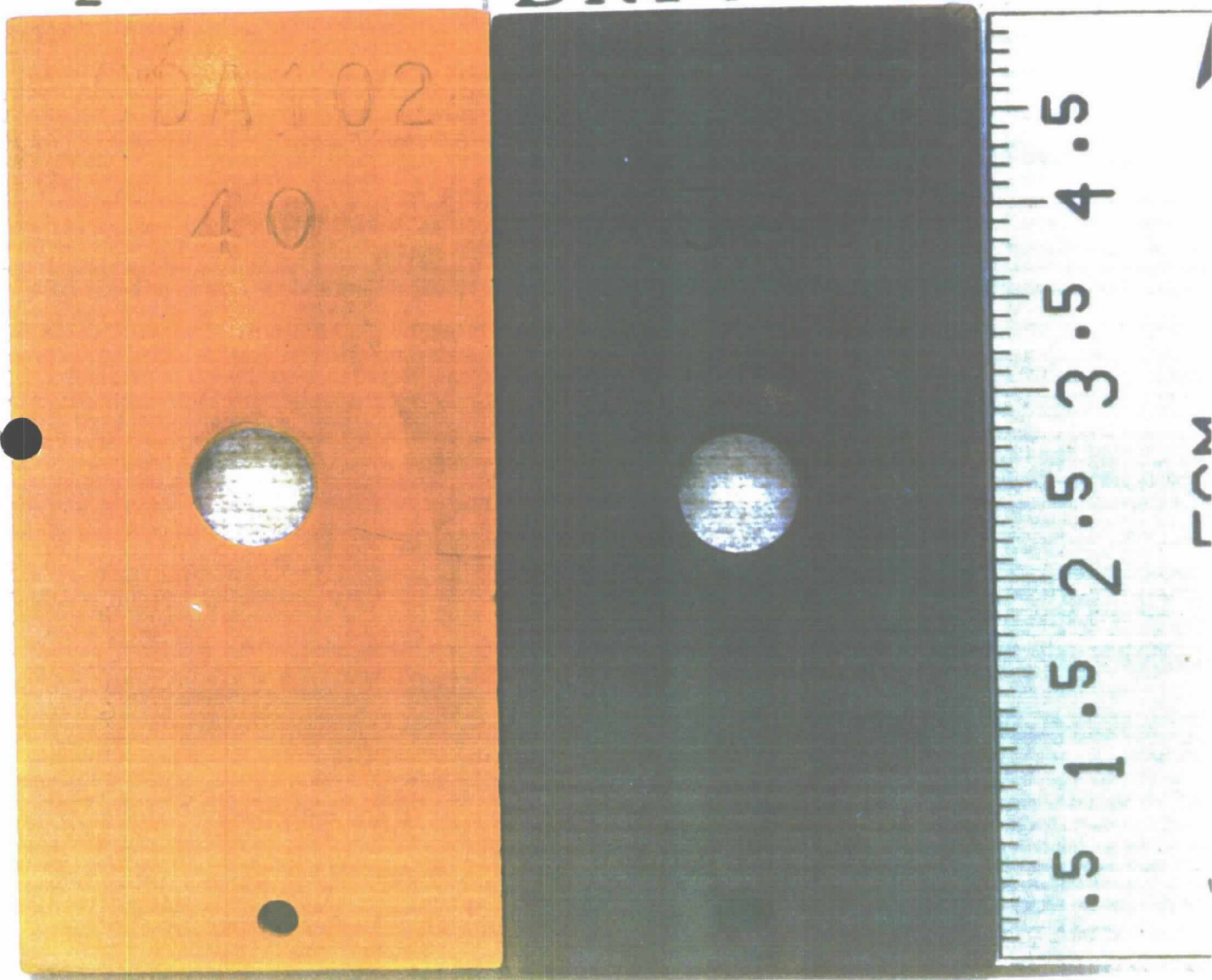
Thermogravimetric Analysis



CDA 102 at 250 C



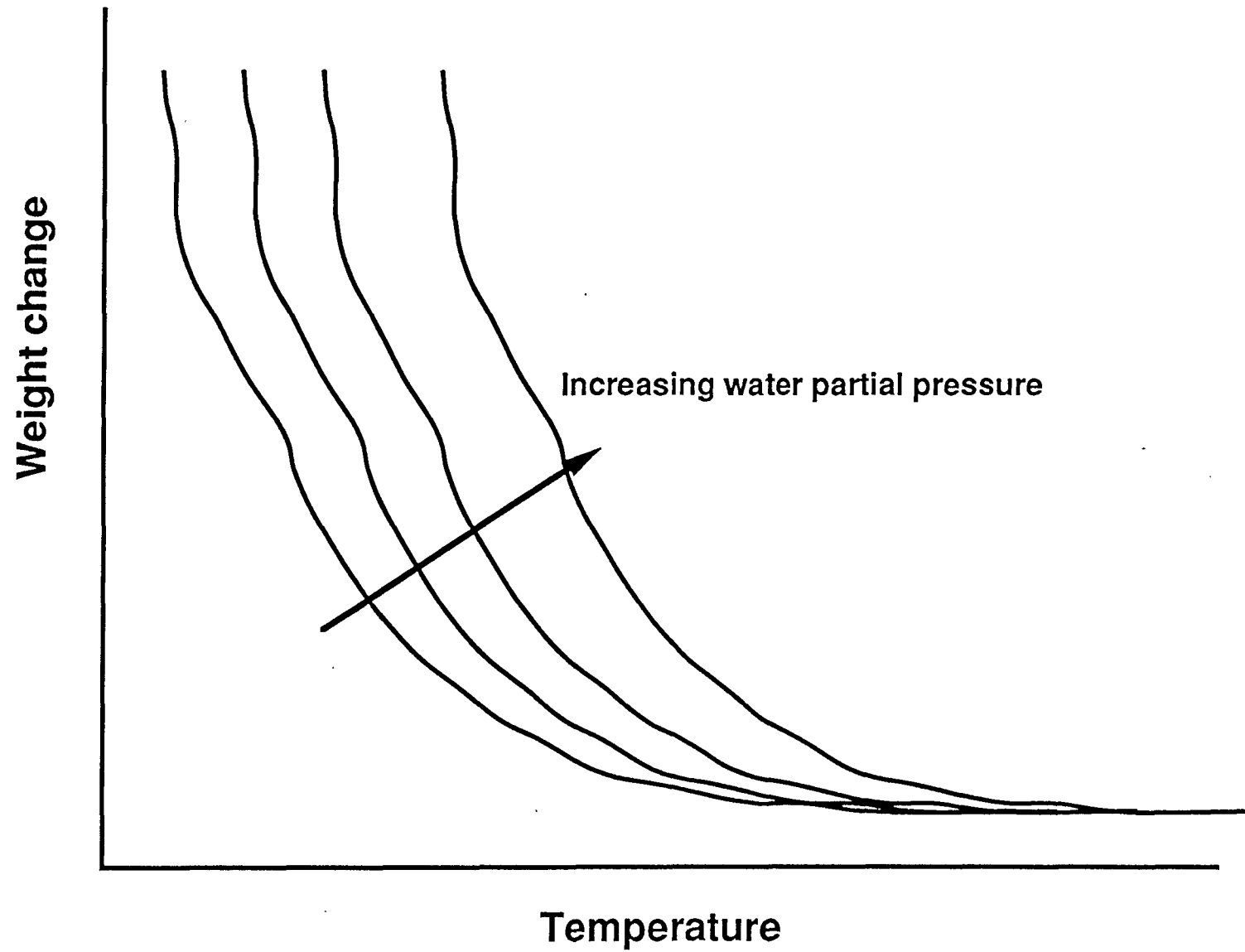
H₂O VAPOR DRY AIR



40

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Aqueous Adsorption Transition Temperatures



Focus of TGA Experimental Work

- Oxidation in air/water mixtures
 - 75 - 300°C
 - Various partial pressure of water

- Determine temperature and water vapor partial pressure regions where aqueous corrosion will occur
 - temperature
 - water partial pressure
 - metal
 - adsorbed species
 - gas-phase species