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)

<table>
<thead>
<tr>
<th>Location</th>
<th>10 yr</th>
<th>20 yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altoona, PA Industrial</td>
<td>1.3</td>
<td>1.4</td>
</tr>
<tr>
<td>New York, NY Industrial marine</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Sandy Hook, NJ Northern marine</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>La Jolla, CA Severe marine</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Key West, FL Tropical marine</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Phoenix, AZ Rural dry</td>
<td>0.05 - 0.2</td>
<td></td>
</tr>
<tr>
<td>State College, PA Northern rural</td>
<td>0.56</td>
<td>0.43</td>
</tr>
</tbody>
</table>

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].

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

<table>
<thead>
<tr>
<th>Reference</th>
<th>Concentrations (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>810</td>
</tr>
<tr>
<td>NO₂</td>
<td>940</td>
</tr>
<tr>
<td>O₃</td>
<td>334</td>
</tr>
<tr>
<td>Cl₂</td>
<td>8.6</td>
</tr>
<tr>
<td>H₂S</td>
<td>21</td>
</tr>
</tbody>
</table>

Figure 46.5. Corrosion rate versus relative humidity (T = 25°C).

Corrosion Rate Dependence on Temperature and Water Partial Pressure

Figure 46.6. Corrosion rates of (a) cobalt versus $P_{H_2O}$ at various temperatures in the reference test environment and, (b) cobalt versus relative humidity ($P_{H_2O}/P^0_{H_2O}$) in the reference test environment.

Dependence of Copper Oxidation on H2S and Water Vapor

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

- A - Air Oxidized Cu - 0% RH
- B - Bare Cu - 0% RH
- C - Air Oxidized Cu - 80% RH
- D - Bare Cu - 80% RH
- E - Oxidized Cu - 80% RH

Air Oxidized Cu - 125°C, 18 hr ~225 Å Cu₂O
O₂ Oxidized Cu - 150°C, 1 hr ~300 Å Cu₂O

In the Linear Region

- B T = 79.8t
- C T = 247.5t
- D T = 330t
- E T = 156.7t

Where
T = Thickness in Å
r = Time in Hrs

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

Water Vapor Pressure (mm Hg)

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

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

- Rate Increases due to Increased Diffusion of O₂ to Surface
- Rate Decreases due to Decreased Solubility of O₂ in Water

Corrosion Rate (mm/yr)

Temperature (°C)

50° 80° 100°
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.

Effect of Water Vapor on the Oxidation of Low Carbon Steel


Fig. 1—Ferrous Iron in Scale Versus Temperature.
Thermogravimetric Analysis

Personal Computer
Data Acq/Control

Output Weight
Temperature
Time

Input Control
Variables

CAHN TG-131

Balance

Vent

RH Sensor

MFC 3
He Purge

MFC 2

MFC

Saturation Water Vapor

H₂O Level Switch

Dry Air

Air

Flow Controller
CDA 102 at 250 C

Dry Air

Water Vapor

Time (hr)
H$_2$O VAPOR  DRY AIR

DA102

40  34
Aqueous Adsorption Transition Temperatures

Increasing water partial pressure

Weight change

Temperature
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