SUMMARY OF CORROSION TOPICS

(Discussed by Mr. Schillmoller,
International Nickel Co., Los Angeles, on 21 February 1960)

On Monday, February 21, Mr. C. M. Schillmoller of the International Nickel Co., gave a talk on corrosion problems--many points of which are of specific interest to SLAC. Some of these items are presented here.

After pointing out some of the economic aspects of corrosion control (corrosion damage amounts to over $8 billion per year in the United States alone), Mr. Schillmoller summarized the methods used on controlling corrosion. These are (1) coatings, inhibitors and other films (metallic and non-metallic) separating corroding medium from metal; (2) cathodic protection; (3) change of conditions; and (4) alloy selection.

1. Coatings

Briefly discussed were the uses of organic coatings, paints, and metallic coatings such as aluminum, cadmium, zinc (sacrificial) and tin and nickel.

2. Cathodic Protection

The use of direct current to neutralize emf in galvanic corrosion cells was discussed. The direct current is achieved either by using sacrificial anodes, like magnesium, zinc, and aluminum, or by impressed current from a battery attached to an underground piping system. The use of sacrificial anodes, batteries, and rectified A.C. on shipboard was also mentioned.

3. Change of Conditions

Some of the more important process conditions that affect corrosion rates were discussed.

a. Velocity

Since a greater velocity of fluid within a pipe provides more corrodatant per unit time, the velocity control limits for various materials were covered. In fresh water, fluid velocities of about 5 fps are tolerable for mild steel. Stainless steel can tolerate velocities in the order of 100 fps and velocities to over 50 fps can be tolerated for high-nickel alloys. However, practical limitations of pump sizes start to be exceeded around this range. The stainless steels and nickel-base alloys are less affected than other alloys since high velocity provides a surface cleaning action which removes deposits which
may act as corrosion sites. Indeed, slow velocities may prove damaging to these "stainless" alloys.

Also included was the effect of fluid impingement which acts as a mechanical force to remove an otherwise protective film.

Some typical limiting velocities of fresh and sea water on several materials were given for the following materials in the form of piping or heat exchanger tubes:

<table>
<thead>
<tr>
<th>Material</th>
<th>Limiting Velocity (fps) for:</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh Water</td>
<td>Sea Water</td>
<td></td>
</tr>
<tr>
<td>Steel</td>
<td>7</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>7</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Brass (admiralty)</td>
<td>7</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Brass (aluminum)</td>
<td>10</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>90-10 Cu, Ni</td>
<td>12</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>70-30 Cu, Ni</td>
<td>20</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Monel</td>
<td>50</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

b. Temperature

Whereas it is axiomatic that an increase of 10°C (18°F) will double chemical reaction rates, 20°C (36°F) is required for corrosion rates to double in a fresh water piping system; however, even this rule has many exceptions. In the home, a lower limit of 170°F is desirable so the "hardness" (CaCO₃) particles will remain in solution. Above 176°F, the solubility of oxygen in water decreases and the corrosion rate decreases. Temperature control must also be thought of in terms of the solubility of corrosion products, e.g., PbCl₂. If protective corrosion products are constantly dissolved from the pipe surface, accelerated corrosion will result.

Mr. Schillmoller uses an arbitrary maximum corrosion rate of 3 mils per year (mpy) for heat exchanger tubes and 20 mpy for vessels and piping to economically choose materials. A curve of corrosion rate versus temperature would look like Fig. 1 for sea water corrosion of mild steel piping systems.
From this figure it can be seen that, at a given temperature, corrosion rates will be greater for mild steel piping systems carrying sea water containing oxygen. This figure is applicable to sea water conversion units.

d. Oxygen Content

Many of the points discussed by Mr. Schillmoiler could not be separated from other variables and much of the information relating to oxygen is covered above. However, as a general rule, oxygen accelerates corrosion in all piping systems except those composed of chromium-containing alloys (stainless steels), aluminum and titanium. Several examples of oxidizing solutions are nitric acid, oxalic acid, bleaches, chromates, peroxides and two powerful "accelerators", ferric chloride, and copper sulfate. This concept is utilized for deaeration systems such as:
(1) seawater conversion units, (2) steam systems with sodium sulfite, hydrazine and other oxygen scavengers.

d. PH

For practical purposes, most water systems are considered to be neutral when the PH is controlled between 6 and 8. However, localized pockets can concentrate solute material and the attendant PH can vary considerably. In general, high PH is good for all metals except aluminum. Low PH, below 4.5, accelerates corrosion on steel, copper alloys and nickel alloys.

4. Alloy Selection

A number of considerations were discussed under this topic. They include:
(a) Availability of materials in sizes and shapes required.
(b) Physical and mechanical properties of various alloys related to the service conditions must be considered.

(c) Fabrication characteristics—the ability of the selected material to be rolled, forged, cast, welded, etc., has much to do with its physical and mechanical properties. The last two categories are not easily separated for most systems but must still be considered.

(d) The inherent corrosion resistance of the selected alloy that has been fabricated must also be considered.

(e) Cost is a factor in every material consideration—otherwise platinum and gold would be used for everything. The cost estimate should not only include "first cost" and "cost over life," but also the effect of replacement costs and, when applicable, tax write-offs.

Following this general discussion of corrosion considerations, questions were asked and are summarized below:

1. Mr. Schillmoller stated the general conditions required for stress corrosion cracking (SCC) for various materials:

   (a) Oxygen, when present in a chloride containing system, enhances stress corrosion cracking. Temperatures above 130°F are generally required for SCC to occur as is a chloride content of about 30 ppm. (Although the literature mentions SCC related to systems containing 1 to 5 ppm chlorine, failures in these systems are relatively rare unless pressures (stresses) are high and/or chlorides have a chance to concentrate in pockets.) Time of expected service and stress level are also important considerations. No standard rule can be made relating each of these variables.

   One technique which prevents SCC to occur in an iron-base system is to either remove the nickel, or increase it to over 42%. The occurrence of SCC (in boiling MgCl₂, a standard accelerated corrosion test) as related to the nickel content of stainless steels shows that the maximum incidence of cracking occurs at about 8% nickel, which is close to the nickel content of the 300 series of austenitic stainless steels. See Fig. 2, which summarizes corrosion rates as a function of nickel content.
A general graph showing time for stress corrosion cracking to occur versus stress level is shown for several alloys in Fig. 3.

From this it can be seen that SCC can be controlled either by alloy selection or by reducing the anticipated stress level.
2. The present philosophy of passivating stainless steel piping systems prior to use was discussed. Mr. Schillmoller feels, as do others, that the existing oxide film on as-received stainless steels is an adequate protection film and there is no need to passivate. Passivation is sometimes used as a cleaning procedure to remove foreign products. Frequently, when pickling is specified, a treatment consisting of a HNO₃/HF acid dip is used to remove the existing oxide film on stainless steels (as well as any other film and residues) and the film is reformed by an oxidizing treatment in nitric acid. It is desirable to clean the pipe in nitric acid to remove iron usually deposited from forming and cutting operations. If not removed, the iron may react,

\[ \text{Fe}^{++} \text{Plus} \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{FeO} \text{Plus} \quad \text{2H}^+ \]

to form pits in the stainless steel. These pits of "active" or unoxidized stainless steel are very anodic to the bulk of the "passive" or oxidized stainless. Galvanic corrosion can then proceed quickly at these sites and would result in perforation if the medium is a good electrolyte such as sea water.

The brown and blue oxide films due to welding are very tenacious and stable formations which will not detract from the general good corrosion resistance of stainless steel.

3. The aspects of corrosion of welded stainless steel were discussed. Mr. Schillmoller stated that more corrosion problems occur with welded stainless steels than with any other system. During welding, there is sufficient time for the chromium and carbon from the stainless steel to combine and precipitate at the grain boundaries which subsequently become less corrosion resistant and corrode preferentially to the other areas. Attempts to remove enough carbon (to form to the ELC grades of stainless steels typified by 304L and 316L) to minimize the problem have resulted in higher material costs. The general carbon content (0.08%) can be decreased to a practical lower limit (0.03%), but usually a 15 to 25% increase in cost is the result. Stabilized grades containing Cr (type 347) and Ti (type 321) are also more expensive than the standard grades. Intergranular corrosion can be caused by many inorganic acids and most warm organic acids.
Mr. Schillmoller stated that the use of "selected stock" containing 0.05% carbon would permit a greater time in the sensitizing range of 800 to 1600°F and still minimize corrosion problems due to chromium carbide precipitation (sensitization).

Nitric-hydrofluoric acid passivation treatments also attack these sensitized areas more drastically than does the normal nitric acid cleaning. Therefore, cases have occurred where pickling is more damaging than useful.

4. An interesting example of material selection was given by Mr. Schillmoller. Stress corrosion cracking caused unexpected failure of several 17-4 PH control rod drives in a GE reactor. A suggested alternate by the International Nickel Co. was to use Inconel "X" rods which would not fail by stress corrosion cracking, but GE instead developed a heat treatment which "solved" the problem. The heat treatment resulted in "overaging" the 17-4PH which in turn became slightly weaker than had been previously desired. Therefore, the control rod drives had to be increased in cross section to provide the additional strength which was lost due to the overaging treatment. GE changed conditions by reducing the stress level in the control rod. To change materials would be to admit that the wrong alloy selection has been made originally.

In many high strength alloys used in systems susceptible to SCC, it pays to overage and/or use the alloy at a low stress level.