Corrosion Handbook
For more than 75 years, APV has provided customers worldwide with the latest advancements in heat exchanger technology. Today, we continue to lead the industry with our world renowned state-of-the-art technology, unsurpassed process knowledge, and an unwavering commitment to our customers.

APV has evolved and grown over the years to better meet the changing needs of our customers and their industries. The first commercially successful plate-and-frame heat exchanger was introduced in 1923 by the Aluminum Plant and Vessel Company Ltd., which became known as APV. The first Paraflow Plate Heat Exchanger, constructed of cast gunmetal plates and enclosed within a crude frame, set the standard for today’s computer-designed thin metal plate.

Our vision for the future is rooted in a long standing tradition of excellence and commitment to progress. We strive to offer customers the highest quality products and services today, tomorrow and beyond.

APV founder: Dr. Richard Seligman

The cover photo depicts galvanically induced corrosion of 316 stainless steel caused by the deposition of active carbon used as a decolorizing agent for the sugar solution in contact with the metal.
The APV Corrosion Handbook is an essential tool in helping you minimize the impact of corrosion within your heat transfer applications. The handbook provides a detailed look at the various types of corrosion, the effects of the most common corrosive agents with respect to a variety of materials and an overview of how to cost effectively select the materials of construction most suited for your particular application.

**Materials Science and Corrosion Prevention**

<table>
<thead>
<tr>
<th>Section</th>
<th>Contents</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Materials of Construction</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>Selecting Materials of Construction</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>Types of Corrosion</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Corrosion of Specific Environments</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>Corrosion by Insulating Materials</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>Corrosion of Rubbers</td>
<td>37</td>
</tr>
</tbody>
</table>

For additional information specific to your needs, please contact APV at (919) 735-4570 or (800) 207-2708.
1. MATERIALS OF CONSTRUCTION
1.1 The “stainless steels”
Many people refer to this range of alloys as austenitic stainless steels, 18-8s, 18-10s, etc. without a full appreciation of what is meant by the terminology. It is worth devoting a few paragraphs to explain the basic metallurgy of stainless steels.

In 1913 Harry Brearly discovered that the addition of 11% chromium to carbon steel would impart a good level of corrosion and oxidation resistance. By 1914, these corrosion resisting steels had become commercially available. Brearly pioneered the first commercial use of these steels for cutlery, and also coined the name “stainless steels.”

For metallurgical reasons, which are outside the scope of this paper, these were known as “ferritic steels” due to their crystallographic structure. Unfortunately, they lacked the ductility to undergo extensive fabrication, and they could not be welded.

Numerous workers tried to overcome these deficiencies by the addition of other alloying elements, to produce a material where the ferrite was transformed to austenite (another metallurgical phrase) — that was stable at room temperature. Soft stainless steels that were ductile both before and after welding were developed in Sheffield, England (then the heart of the British steel industry) — exploiting scientific work undertaken in Germany. This new group of steels was based on 18% chromium steel, to which nickel was added as a second alloying element. These were termed the “austenitic stainless steels.” The general relationship between chromium and nickel necessary to maintain a fully austenitic structure is shown in Figure 1. The optimum combination is 18% chromium, 8% nickel — hence the terminology 18/8s.

Probably the next major advance in the development of stainless steels was the discovery that relatively small additions of molybdenum had a pronounced effect on their corrosion resistance, greatly enhancing their ability to withstand the effects of mineral acids and other corrodents such as chloride solutions. Needless to say, from these early developments, there has been tremendous growth in the production facilities and the number of grades of stainless steel available. Table 1 lists some of the more commonly available grades while Figure 2 illustrates how the basic 18/8 composition is modified to enhance specific physical or chemical properties.

Figure 1: Graph showing the various combinations of chromium and nickel that form austenitic stainless steels (Ref. 1).
Table 1: Composition of some of the more commonly used austenitic stainless steels. Unless indicated otherwise, all values are maximum.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>UNS NO.</th>
<th>CARBON</th>
<th>MANGANESE</th>
<th>SILICON</th>
<th>CHROMIUM %</th>
<th>NICKEL</th>
<th>MOLYBDENUM</th>
<th>OTHERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>302</td>
<td>S30200</td>
<td>0.15</td>
<td>2.00</td>
<td>1.00</td>
<td>16.0 — 18.0</td>
<td>6.0 — 8.0</td>
<td>—</td>
<td>Sulfur 0.030, Phosphorus 0.045</td>
</tr>
<tr>
<td>304</td>
<td>S30400</td>
<td>0.08</td>
<td>2.00</td>
<td>1.00</td>
<td>18.0 — 20.0</td>
<td>8.0 — 10.5</td>
<td>—</td>
<td>Sulfur 0.030, Phosphorus 0.045</td>
</tr>
<tr>
<td>304L</td>
<td>S30403</td>
<td>0.03</td>
<td>2.00</td>
<td>1.00</td>
<td>18.0 — 20.0</td>
<td>8.0 — 12.0</td>
<td>—</td>
<td>Sulfur 0.030, Phosphorus 0.045</td>
</tr>
<tr>
<td>316</td>
<td>S31600</td>
<td>0.08</td>
<td>2.00</td>
<td>1.00</td>
<td>16.0 — 18.0</td>
<td>10.0 — 14.0</td>
<td>2.0 — 3.0</td>
<td>Sulfur 0.030, Phosphorus 0.045</td>
</tr>
<tr>
<td>316L</td>
<td>S31603</td>
<td>0.03</td>
<td>2.00</td>
<td>1.00</td>
<td>16.0 — 18.0</td>
<td>10.0 — 14.0</td>
<td>2.0 — 3.0</td>
<td>Sulfur 0.030, Phosphorus 0.045</td>
</tr>
<tr>
<td>317</td>
<td>S31700</td>
<td>0.08</td>
<td>2.00</td>
<td>1.00</td>
<td>18.0 — 20.0</td>
<td>11.0 — 15.0</td>
<td>3.0 — 4.0</td>
<td>Sulfur 0.030, Phosphorus 0.045</td>
</tr>
<tr>
<td>317L</td>
<td>S31703</td>
<td>0.03</td>
<td>2.00</td>
<td>1.00</td>
<td>18.0 — 20.0</td>
<td>11.0 — 15.0</td>
<td>3.0 — 4.0</td>
<td>Sulfur 0.030, Phosphorus 0.045</td>
</tr>
<tr>
<td>321</td>
<td>S32100</td>
<td>0.08</td>
<td>2.00</td>
<td>1.00</td>
<td>17.0 — 19.0</td>
<td>9.0 — 12.0</td>
<td>—</td>
<td>Sulfur 0.030, Ti&lt;5×Carbon</td>
</tr>
<tr>
<td>347</td>
<td>S34700</td>
<td>0.08</td>
<td>2.00</td>
<td>1.00</td>
<td>17.0 — 19.0</td>
<td>9.0 — 13.0</td>
<td>—</td>
<td>Sulfur 0.030, Cb+Ta&lt;10×Carbon</td>
</tr>
</tbody>
</table>

Fig. 2: Outline of some compositional modifications of 18/8 austenitic stainless steel to produce special properties (Ref. 2).
In spite of the plethora of stainless steels available, grades 304 and 316 have, and continue to be, the workhorses for fabrication of dairy and food processing equipment. Although 316 stainless steel offers excellent resistance to a wide range of chemical and non-chemical environments, it does not offer immunity to all. In the case of the food industry, these are notably anything containing salt, especially low pH products. There was, therefore, a demand by industry to develop more corrosion resistant materials, and these are finding an increased use in the food industry for certain specific processing operations.

1.2 Super stainless steels and nickel alloys
The super stainless steels are a group of alloys which have enhanced levels of chromium, nickel, and molybdenum, compared to the conventional 18/8s. The major constituent is still iron, hence the classification under the “steel” title. Still, further increases in the three aforementioned alloying elements result in the nickel alloys. (The classification of an alloy is generally under the heading of the major constituent.) There are a large number of these alloys, but those of primary interest to the food industry are shown in Table 2, together with their compositions. In general terms, it will be noted that the increase in nickel content is accompanied by an increase in chromium and molybdenum. As previously stated, this element is particularly effective in promoting corrosion resistance.

Just like insurance, you only get what you pay for – and generally speaking, the higher the corrosion resistance, the more expensive the material. In fact, the differential between type 304 stainless steel and a high nickel alloy may be as much as 20 times, depending on the market prices for the various alloying elements – which fluctuate widely with the supply and demand position.

1.3 Aluminum
High purity grades of aluminum (±99.5%) and its alloys still are preferred for some food and pharmaceutical applications due to the reasonable corrosion resistance of the metal. This resistance is attributable to the easy and rapid formation of a thin, continuous, adherent oxide film on exposed surfaces. This oxide film, in turn, exhibits a

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>UNS. NO.</th>
<th>CARBON</th>
<th>MANGANESE</th>
<th>SILICON</th>
<th>COMPOSITION % CHROMIUM</th>
<th>NICKEL</th>
<th>MOLYBDENUM</th>
<th>OTHERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>904L</td>
<td>N08904</td>
<td>0.02</td>
<td>2.0</td>
<td>0.70</td>
<td>19.0−21.0</td>
<td>24.0−26.0</td>
<td>4.2−4.7</td>
<td>Cu 1.2−1.7</td>
</tr>
<tr>
<td>Avesta 254 SMO</td>
<td>S31254</td>
<td>0.02</td>
<td>2.0</td>
<td>0.80</td>
<td>19.5−20.5</td>
<td>17.5−18.5</td>
<td>6.0−6.5</td>
<td>Cu 0.5−1.0, N 0.18−0.22</td>
</tr>
<tr>
<td>Incoloy 825</td>
<td>N08825</td>
<td>0.05</td>
<td>1.0</td>
<td>0.50</td>
<td>19.5−23.5</td>
<td>38.0−46.0</td>
<td>2.5−3.5</td>
<td>Al 0.2, Ti 0.6−1.2</td>
</tr>
<tr>
<td>Hastelloy G-30</td>
<td>N06030</td>
<td>0.03</td>
<td>1.5</td>
<td>0.80</td>
<td>28.0−31.5</td>
<td>Bal.</td>
<td>4.0−6.0</td>
<td>Co 5.09, Cu 1.0−2.4, Cb+Ta 0.3−1.5, Fe 13.0−17.0</td>
</tr>
<tr>
<td>Inconel C-276</td>
<td>N10276</td>
<td>0.02</td>
<td>1.0</td>
<td>0.08</td>
<td>14.5−16.5</td>
<td>Bal.</td>
<td>8.0−10.0</td>
<td>Co 1.0, Fe 5.0, Al 0.4, Ti 0.4</td>
</tr>
</tbody>
</table>

Table 2: Composition of some of the more commonly used wrought super stainless steels and nickel alloys. Unless indicated otherwise, all values are maximum.
good corrosion resistance to many foodstuffs; and it is reported that fats, oils, sugar, and some colloids have an inhibitory or sealing effect on these films (Ref. 3). As aluminum salts formed by corrosion are colorless, tasteless, and claimed to be non-toxic – the metal is easy to clean, inexpensive, light, and has a high thermal conductivity. It still is used quite extensively in certain areas of food manufacture and distribution. However, in recent years, the claim of non-toxicity is being questioned as a high dietary incidence has been implicated in Alzheimer’s disease (senile dementia) with compounds of aluminum (aluminosilicates) being found in the brain tissue of sufferers (Ref. 4). However, the case is far from proven, and it is not clear if the increased levels of aluminosilicates are due to a high intake of aluminum per se or other factors such as dietary deficiency of calcium.

For many years, aluminum was extensively used for containment vessels in the dairy and brewing industry. It was Richard Seligman who founded the then Aluminum Plant and Vessel Company (now APV, An SPX Brand) to exploit the technique of welding this material for the fabrication of fermenting vessels in the brewing industry (Ref. 5). Many of these original vessels are still in use in some of the smaller, privately owned breweries in the United Kingdom.

Although large fermenting vessels and storage tanks now tend to be fabricated from stainless steels, there is still widespread use of aluminum for beer kegs, beer cans, and a miscellany of small-scale equipment where the resistance of aluminum is such that it imparts no charge or modification of flavor, even after prolonged storage. While still used for holding vessels and some equipment when processing cider, wines, and perry, prolonged contact is inadvisable due to the acidity of the sulphites employed as preservatives for these products – inadvisable, that is, unless the surface of the metal has been modified by anodizing or has been protected with a lacquer.

In the manufacture of preservatives, aluminum is still employed for boiling pans, with the presence of sugar appearing to inhibit any corrosion. In the field of apiculture, it has even been used for making prefabricated honeycombs which the bees readily accepted.

Extensive use is made of aluminum and the alloys in the baking industry for baking tins, kneading troughs, handling equipment, etc.

In other areas of food manufacture and preparation, the use of aluminum virtually extends over the whole field of activity – butter, margarine, table oils and edible fats, meat and meat products, fish and shellfish, certain sorts of vinegar, mustards, spices; the list is almost endless.

No mention has so far been made of the application of this metal in the dairy industry. It still has limited application mostly in the field of packaging, e.g., bottle caps, wrapping for cheese, butter, carton caps for yogurt, cream, etc.

The uses of aluminum in the food industry so far mentioned have tended to be for equipment used in batch operation, hand utensils, and packaging. There are probably three major factors which have mitigated against its more widespread use, not only in the dairy industry but in brewing and many other branches of food processing.

1. Modern, highly automated plants operating on a continuous or semi-continuous basis employ a wide variety of materials of construction. Because of the position in the
electrochemical series (to be discussed later), aluminum and its alloys are susceptible to galvanic corrosion when coupled with other metals.

2. The commercial availability of stainless steels, their ease of fabrication, strength, ease of maintenance, appearance, and proven track record of reliability.

3. Since modern plants operate on a semi-continuous basis with much higher levels of fouling, cleaning regimes require strongly alkaline detergents to which aluminum has virtually zero corrosion resistance.

1.4 Copper and tinned copper
Copper and tinned copper were extensively used in former times due to their excellent thermal conductivity (eight times that of stainless steel), their ductility, ease of fabrication, and reasonable level of corrosion resistance. However, the demise of copper as a material of construction is largely attributable to the toxic nature of the metal and its catalytic activity in the development of oxidative rancidity in fats and oils. Even at the sub-part per million level, copper in vegetable oils and animal fats rapidly causes the development of off-flavors. In equipment where high levels of liquid turbulence are encountered, e.g., plate heat exchanger or high velocity pipe lines, copper is subject to erosion. Nevertheless, there is an area of the beverage industry where copper is still the only accepted material of construction, i.e., pot stills for scotch and Irish whiskey production. It is also used in the distillation of spirits such as rum and brandy. A lot of old copper brewing equipment, such as fermenting vessels and wort boilers, is still in use throughout the world. An interesting observation is that even though wort boilers in modern breweries are fabricated from stainless steel, they are still known as “coppers,” and U.K. craftsmen fabricating stainless steel are still known as “coppersmiths.”

1.5 Titanium
There are certain areas of the food industry, especially in equipment involving heat transfer, where stainless steels are just not capable of withstanding the corrosive effects of salty, low pH environments. More and more, food processors are accepting the use of titanium as an alternative, in the full knowledge that it offers corrosion immunity to the more aggressive foodstuffs and provides a long term solution to what was an on-going problem with stainless steels. Although relatively expensive (six to seven times the cost of stainless steel), being a low density material offsets this price differential for the raw material by almost half. It is ductile and fabricable using normal techniques, although welding it does require a high degree of expertise.

1.6 Other metals
Tin, in the form of tin plate, is extensively used in the canning industry where its long term corrosion resistance to a wide range of food acids makes it a material “par excellence” for this purpose.
Cadmium, used as a protective coating for carbon steel nuts and bolts, was favored at one time. However, the high toxicity of cadmium compounds has come under increased scrutiny from many health regulatory bodies, and now cadmium plated bolting is not permitted in food factories. Denmark and Sweden have totally banned the import of cadmium plated components into their countries and many other countries are likely to follow suit.
Lead and lead-containing products are generally not acceptable for food contact surfaces, although some codes of practice permit the use of lead-containing solder for capillary pipeline joints on water supplies and service lines.

2. SELECTING MATERIALS OF CONSTRUCTION (Ref. 6)

Designing equipment is a multi-discipline exercise involving mechanical engineers, materials/corrosion engineers, stressing experts, draftsmen, etc. The corrosion engineer has an important role in this team effort insofar as it is his/her job to ensure the materials specified will offer a corrosion resistance which is adequate for all the environmental conditions likely to be encountered during normal operation of the equipment. A piece of equipment which prematurely fails by corrosion is as badly designed as one in which the materials have been over-specified. Unfortunately, all too often the functional requirements for a piece of equipment are analyzed in a somewhat arbitrary manner. And the basic cost of the material often tends to outweigh other equally important considerations. Figure 3 shows the primary criteria which must be considered in the initial selection process.

- **Corrosion resistance**
  For any processing operation, there will be a range of materials which will offer a corrosion resistance which is adequate (or more than adequate) for a particular job. When considering corrosion resistance, the operational environment is the obvious one. But, the other point must be whether the material will also offer corrosion resistance to the chemicals used for cleaning and sanitizing.

- **Cost**
  Many of the materials originally considered will be eliminated on the grounds of their high cost. For example, there is no point in considering a high nickel alloy when a standard 300 series stainless steel, at a lower cost, will be perfectly satisfactory.

- **Availability**
  Availability is a less obvious feature of the material selection process. Many steel producers will require a minimum order of, say, three tons for a non-standard material. Clearly, the equipment manufacturer is not going to buy this large quantity when the job that is to be done may only require the use of one ton of material.

- **Strength**
  Strength is a factor which is taken into account at the design stage, but as with all the others, cannot be considered in isolation. For example, many of the new stronger stainless steels, although more expensive on a ton-for-ton basis than conventional stainless steels, are less expensive when considered on a strength/cost ratio.

- **Fabricability**
  There is little point in considering materials which are either unweldable (or unfabricable) or can only be welded under conditions more akin to a surgical operating theater than a general engineering fabrication shop.
• Appearance
Appearance may or may not be an important requirement. Equipment located outside must be resistant to environmental weathering, and therefore, may require the application of protective sheathing – which could double the basic material cost.

• Maintenance
Is the equipment to be essentially maintenance-free or is some maintenance, such as periodic repainting, tolerable? How long will the equipment operate without the need for major servicing?

When all these interrelated criteria have been considered, the long list of possible starters will have been reduced to maybe one or two. Also, through the selection process some of those materials initially rejected due to their high cost, for example, may have to be reconsidered because of other factors.

3. TYPES OF CORROSION

3.1 Defining corrosion
Before embarking on a discussion of the various forms of corrosion, it is worthwhile to consider the exact meaning of corrosion. There are several definitions of corrosion. For example, Fontana (Ref. 7) defines it as extractive metallurgy in reverse using the diagram, shown in Figure 4, to illustrate the point.

A more general and descriptive definition is “it is the deterioration or destruction of a material through interaction with its environment.” This covers all materials of construction including rubber, plastics and metal. However, the primary object of this paper is to deal with corrosion of metals, in particular stainless steels, and how this corrosion can be classified.

There are two basic forms of corrosion – wet and dry. Dry corrosion is concerned with the oxidation of metals at high temperatures and is outside the scope of this text. Wet corrosion occurs in aqueous solutions, or in the presence of electrolytes, and is an electrochemical process. It should be noted that the “aqueous” component of the system may be present in only trace quantities, e.g., present as moisture; the classical example being the corrosion of steel by chlorine gas. In fact, steel is not corroded by chlorine since steel is the material used for storing liquid chlorine. However, in the presence of even trace quantities of moisture, chlorine rapidly attacks steel – and for that matter, most metals.

The corrosion of metals involves a whole range of factors. These may be chemical, electrochemical, biological, metallurgical, or mechanical – acting singly or conjointly. Nevertheless, the main parameter governing corrosion of metals is related to electrochemistry. Electrochemical principles, therefore, are the basis for a theoretical understanding of the subject. In fact, electrochemical techniques are now the standard
method for investigating corrosion, although the “weight loss” approach still provides invaluable data. It is not proposed to discuss, in depth, the electrochemical nature of corrosion – but should further information be required, several excellent texts are available (Ref. 7, 8).

3.2 Forms of corrosion
Wet Corrosion can be classified under any of eight headings:
- Galvanic or bimetallic corrosion
- Uniform or general attack
- Crevice corrosion
- Pitting corrosion
- Intergranular corrosion
- Stress corrosion cracking
- Corrosion fatigue
- Selective corrosion (castings and free machining stainless steels)

3.2.1 Galvanic corrosion
When two dissimilar metals (or alloys) are immersed in a corrosive or conductive solution, an electrical potential or potential difference usually exists between them. If the two metals are electrically connected, then, because of this potential difference, a flow of current occurs. As the corrosion process is an electrochemical phenomenon and dissolution of a metal involves electron flow, the corrosion rates for the two metals are affected. Generally, the corrosion rate for the least corrosion resistant is enhanced while that of the more corrosion resistant is diminished. In simple electrochemical terms, the least resistant metal has become anodic and the more resistant cathodic. This, then, is galvanic or dissimilar metal corrosion.

The magnitude of the changes in corrosion rates depends on the so-called electrode potentials of the two metals; the greater the difference, the greater the enhancement or diminution of the corrosion rates. It is possible to draw up a table of some commercial alloys which ranks them in order of their electrochemical potential. Such a table is known as the galvanic series. A typical one, as shown in Table 3, is at the Harbor Island, NC, test facility. This galvanic series relates to tests in unpolluted sea water, although different environments could produce different results and rankings. When coupled, individual metals and alloys from the same group are unlikely to show galvanic effects which will cause any change in their corrosion rates.

The problem of dissimilar metal corrosion (being relatively well understood and appreciated by engineers) is usually avoided in plant construction, and in the author's experience, few cases have been encountered. Probably the most common form of unintentional galvanic corrosion is on service lines where brass fittings are used on steel pipelines – the steel suffering an increase in corrosion rate at the bimetallic junction.
One of the worst bimetallic combinations is aluminum and copper. An example of this is in relation to aluminum milk churns used to transport whey from Gruyere (a cheese manufacturer in Switzerland), where copper is used for the cheese-making vats and the whey picks up traces of this metal. The effect on the aluminum churns, which are internally protected with lacquer that gets worn away through mechanical damage, is pretty catastrophic.

<table>
<thead>
<tr>
<th>Noble or Cathodic</th>
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</thead>
<tbody>
<tr>
<td>Platinum</td>
</tr>
<tr>
<td>Gold</td>
</tr>
<tr>
<td>Graphite</td>
</tr>
<tr>
<td>Titanium</td>
</tr>
<tr>
<td>Silver</td>
</tr>
<tr>
<td>Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)</td>
</tr>
<tr>
<td>Hastelloy C (62 Ni, 17 Cr, 15 Mo)</td>
</tr>
<tr>
<td>18-8 Mo stainless steel (passive)</td>
</tr>
<tr>
<td>18-8 stainless steel (passive)</td>
</tr>
<tr>
<td>Chromium stainless steel 11-30% Cr (passive)</td>
</tr>
<tr>
<td>Inconel (passive) (80 Ni, 13 Cr, 7 Fe)</td>
</tr>
<tr>
<td>Nickel (passive)</td>
</tr>
<tr>
<td>Silver solder</td>
</tr>
<tr>
<td>Monel (70 Ni, 30 Cu)</td>
</tr>
<tr>
<td>Cupronickels (60-90 Cu, 40-10 Ni)</td>
</tr>
<tr>
<td>Bronzes (Cu-Sn)</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>Brasses (Cu-Zn)</td>
</tr>
<tr>
<td>Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)</td>
</tr>
<tr>
<td>Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)</td>
</tr>
<tr>
<td>Inconel (active)</td>
</tr>
<tr>
<td>Nickel (active)</td>
</tr>
<tr>
<td>Tin</td>
</tr>
<tr>
<td>Lead</td>
</tr>
<tr>
<td>Lead-tin solders</td>
</tr>
<tr>
<td>18-8 Mo stainless steel (active)</td>
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<tr>
<td>18-8 stainless steel (active)</td>
</tr>
<tr>
<td>Ni-Resist (high Ni cast iron)</td>
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<tr>
<td>Chromium stainless steel, 13% Cr (active)</td>
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<td>Active or Anodic</td>
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<td>2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)</td>
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<td>Cadmium</td>
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<td>Commercially pure aluminum (1100)</td>
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<tr>
<td>Zinc</td>
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<td>Magnesium and magnesium alloys</td>
</tr>
</tbody>
</table>

Table 3: The galvanic series of some commercial metals and alloys in clean sea water.
Another somewhat unique example of galvanic corrosion is related to a weld repair on a 304 stainless steel storage vessel. Welding consumables containing molybdenum had been employed to effect the repair. Although it is unusual for the steels to be sufficient to initiate galvanic corrosion, the environmental factors in this particular case were obviously such that corrosion was initiated (Figure 5). As stated, this is somewhat unique and it is not uncommon for 316 welding consumables to be used for welding 304 stainless steel with no adverse effects. As a practice, however, it is to be deprecated and the correct welding consumables should always be employed. Not all galvanic corrosion is bad; galvanic corrosion is used extensively to protect metal and structures by the use of a sacrificial metal coating. A classic example is the galvanizing of sheet steel and fittings, the zinc coating being applied not so much because it doesn’t corrode, but because it does. When the galvanizing film is damaged, the zinc galvanically protects the exposed steel and inhibits rusting. Similarly, sacrificial anodes are fitted to domestic hot water storage tanks to protect the tank.

3.2.2 Uniform or general attack
As the name implies, this form of corrosion occurs more or less uniformly over the whole surface of the metal exposed to the corrosive environment. It is the most common form of corrosion encountered with the majority of metals, a classic example being the rusting of carbon steel. Insofar as the corrosion occurs uniformly, corrosion rates are predictable and the necessary corrosion allowances are built into any equipment. In the case of stainless steels, this form of corrosion is rarely encountered. Corrodents likely to produce general attack of stainless steel are certain mineral acids, some organic acids and high strength caustic soda at concentrations and temperatures well in excess of those ever likely to be found in the food industry. The same remark applies to cleaning acids such as nitric, phosphoric and citric acids – but not for sulfuric or hydrochloric acids – both of which can cause rapid, general corrosion of stainless steels. Hence, they are not recommended for use, especially where corrosion would result in a deterioration of the surface finish of process equipment.

The behavior of both 304 and 316 stainless steels when subjected to some of the more common acids that are encountered in the food industry is graphically illustrated by Figure 6. These iso-corrosion graphs, i.e., lines which define the conditions of temperature and acid concentration which will produce a constant corrosion rate expressed in mils (0.001") or mm loss of metal thickness per year, are extensively used by corrosion engineers in the material selection process when the form of corrosion is general attack. They are of no value when the corrosion mode is one of the other forms which will be defined, such as pitting or crevice corrosion.
Fig. 6: Corrosion resistance of 304 and 316 stainless steels to mineral acids (reproduced by permission of British Steel Plc).
3.2.3 Crevice corrosion

This form of corrosion is an intense local attack within crevices or shielded areas on metal surfaces exposed to corrosive solutions. It is characteristically encountered with metals and alloys which rely on a surface oxide film for corrosion protection, e.g., stainless steels, titanium, aluminum, etc.

The crevices can be inherent in the design of the equipment (e.g., plate heat exchangers) or inadvertently created by a bad design. Crevice corrosion can be initiated at metal to non-metallic sealing faces. Any non-metallic material which is porous and used as a gasket, for example, is particularly good (or bad!) for initiating this form of attack. Fibrous materials which have a strong wicking action are notorious in their ability to initiate crevice attack. Similarly, materials which have poor stress relaxation characteristics, i.e., have little or no ability to recover their original shape after being deformed, are also crevice creators – as are materials which tend to creep under the influence of applied loads and/or at elevated temperatures. Although used for gasketing, P.T.F.E. suffers both these deficiencies. On the other hand, elastomeric materials are particularly good insofar as they exhibit elastic recovery and have the ability to form a crevice-free seal. However, at elevated temperatures, may rubbers harden. In this condition, they suffer the deficiencies of non-elastomeric gasketing materials.

Artificial crevices can also be created by the deposition of scale from one of the process streams to which the metal is exposed. It is necessary, therefore, to maintain food processing equipment in a scale-free condition – especially on surfaces exposed to service fluids such as hot/cold water, cooling brines, etc. – which tend to be overlooked during plant cleaning operations.

Much research has been done on the geometry of crevices and the influence of this on the propensity for the initiation of crevice corrosion (Ref. 9). However, in practical terms, crevice corrosion usually occurs in openings a few tenths of a millimeter or less, and rarely is encountered where the crevice is greater than 2 mm (0.08”).

Until the 1950s, crevice corrosion was thought to be due to differences in metal ion or oxygen concentration within the crevice and its surroundings. While these are factors in the initiation and propagation of crevice corrosion, they are not the primary cause.

Current theory supports the view that through a series of electrochemical reactions and the geometrically restricted access into the crevice migration of cations – chloride ions in particular – occurs. This alters the environment within, with a large reduction on pH and an increase in the cations by a factor as much as ten. The pH value can fall from a value of, say, seven in the surrounding solution to as low as two within the crevice. As corrosion is initiated, it proceeds in an autocatalytic manner with all the damage and metal dissolution occurring within the crevice. Corrosion results in significant loss of metal under the surface of site of initiation. As a result, deep and severe cutting of the metal occurs (see Figure 8). The time scale for initiation of crevice corrosion can vary from a few hours to several months, and once initiated, can very rapidly progress. Stopping the corrosion process can be extremely difficult as it is necessary to remove...
all the trapped reactants and completely modify the occluded environment. The difficulty of attaining this will be appreciated by reference to Figure 8, where the entrance to the crevice is only 0.5 mm (0.020”).

While methods for combating the onset of crevice corrosion can be deduced from the foregoing text, a reiteration of some of the more important precautions is as follows:

- Good quality, crevice free, welded joints are always preferable to bolted joints.
- Good equipment design (well designed, gasket-sealing faces) which avoids unintentional crevices and does not permit the development of stagnant regions.
- Frequent inspection of equipment and removal of surface deposits.
- Use of good quality, rubber gaskets rather than absorbent packings.
- Good gasket maintenance; replacement when hardened or damaged.

However, certain pieces of equipment are by virtue of their design highly creviced. In such cases, it is necessary to recognize the potential corrosion risk and select the materials of construction which will resist the initiation of crevice corrosion by the environment. Similarly, cleaning and sanitizing regimes must be developed to avoid the onset of attack.

In the case of stainless steels, although there are several ionic species which will initiate the attack, by far the most common are solutions containing chloride. The presence of salt in virtually all foodstuffs highlights the problem. Low pH values also enhance the propensity for initiation of attack.

Other environmental factors, such as temperature and the oxygen or dissolved air content of the process stream, all play a role in the corrosion process. Because the presence of oxygen is a prerequisite for the onset of crevice corrosion (and many other forms of attack), in theoretical terms complete removal of oxygen from a process stream will inhibit corrosion. In practice, however, this is difficult to achieve. Only in equipment where complete and effective deaeration occurs, such as a multiple effect evaporator operating under reduced pressure, will the beneficial effect of oxygen removal be achieved.

Stainless steels containing molybdenum (316, 317) have a much higher resistance to crevice corrosion than alloys without this element (304, 321, 347). The higher the molybdenum content, the greater the corrosion resistance. For particularly aggressive process streams, titanium is often the only economically viable material to offer adequate corrosion resistance.
3.2.4 Pitting corrosion

As the name implies, pitting is a form of corrosion which leads to the development of pits on a metal surface. It is a form of extremely localized but intense attack, insidious insofar as the actual loss of metal is negligible in relation to the total mass of metal which may be affected. Nevertheless, equipment failure by perforation is the usual outcome of pitting corrosion. The pits can be small and sporadically distributed over the metal surface (Figure 9) or extremely close together, close enough in fact to give the appearance of the metal having suffered from a general attack. In the case of stainless steels, environments which will initiate crevice corrosion will also induce pitting. As far as the food industry is concerned, it is almost exclusively caused by chloride containing media, particularly at low pH values.

Many theories have been developed to explain the cause of the initiation of pitting corrosion (Ref. 10), and the one feature they have in common is that there is a breakdown in the passive oxide film. This results in ionic migration and the development of an electrochemical cell. There is, however, no unified theory which explains the reason for the film breakdown. Evans (Ref. 11), for example, suggests that metal dissolution at the onset of pitting may be due to a surface scratch, an emerging dislocation or other defects, or random variations in solution composition. However, propagation of the pit proceeds by a mechanism similar to that occurring with crevice corrosion. Like crevice corrosion, the pits are often undercut and on vertical surfaces may assume an elongated morphology due to gravitational effects (Figure 10).

The onset of pitting corrosion can occur in a matter of days but frequently requires several months for the development of recognizable pits. This makes the assessment of the pitting propensity of a particular environment very difficult to determine, and there are no short-cut laboratory testing techniques available. Methods and tests solutions are available to rank alloys, the best known and most frequently quoted being ASTM Standard G48 (Ref. 12), which employs 6% ferric chloride solution. Another chemical method involving ferric chloride determines the temperature at which the solution will cause pitting within a 24-hour period, the results being expressed as the critical pitting temperature or CPT (Ref. 13). However, as stated, both of these methods are used...
to rank the susceptibility of a range of alloys rather than define the performance of a material in a service environment. Electrochemical methods have also been used. As with crevice corrosion, alloy composition has a profound effect on the resistance of a material to a pitting attack. Greene and Fontana (Ref. 14) summarized the effect of various elements as shown in Table 4.

### 3.2.5 Intergranular corrosion

A fact not often appreciated is that metals and alloys have a crystalline structure. However, unlike crystalline solids such as sugar or salt, metallic crystals can be deformed or bent without fracturing; in other words, they are ductile. In the molten state, the atoms in a metal are randomly distributed but on cooling and solidification, they become arranged in crystalline form. Because crystallization occurs at many points in the solidification process, these crystals or grains are randomly orientated and the region where they meet are grain boundaries. In thermodynamic terms, the grain boundaries are more susceptible to corrosion attack because of their higher free energy. Although, in practice the free energy of the grain boundary and the main crystals or grains in a homogeneous alloy are too small to make a significant difference. However, when the metal or alloy has a heterogeneous structure, preferential attack at or adjacent to the grain boundaries can occur. This is intergranular corrosion as shown in Figure 11.

When austenitic stainless steels are heated to and held in the temperature range of 600-900°C (1110-1650°F), the material becomes sensitized and susceptible to grain boundary corrosion. It is generally agreed that this is due to chromium combining with carbon to form chromium carbide, which is precipitated at the grain boundaries. The net effect is that the metal immediately adjacent to the grain boundaries is denuded of chromium and instead of having a composition of, say 18% chromium and 8% nickel, it may assume an alloy

![Fig. 11: Scanning electron micrograph of the surface of sensitized stainless steel showing preferential attack along the grain boundaries.](image-url)
composition where the chromium content is reduced to 9% or even lower. As such, this zone depleted in chromium bears little similarity to the main metal matrix and has lost one of the major alloying elements on which it relied for its original corrosion resistance. The lowering of corrosion resistance in this zone is so great that sensitized materials are subject to attack by even mildly corrosive environments.

As supplied from the steel mills, stainless steels are in the so-called solution annealed condition, i.e., the carbon is in solution and does not exist as grain boundary chromium carbide precipitates. During fabrication where welding is involved, the metal adjacent to the weld is subjected to temperatures in the critical range (600-900°C/1110-1650°F) where sensitization can occur. Therefore, this zone may be susceptible to the development of intergranular carbide precipitates. Because the formation of chromium carbides is a function of time, the longer the dwell time in the critical temperature zone, the greater the propensity for carbide formation. Hence, the problem is greatest with thicker metal sections due to the thermal mass and slow cooling rate.

By heating a sensitized stainless steel to a temperature of 1050°C (1950°F), the carbide precipitates are taken into solution. By rapidly cooling or quenching the steel from this temperature, the original homogeneous structure is re-established and the original corrosion resistance is restored.

The first stainless steels were produced with carbon contents of up to 0.2%, and as such, were extremely susceptible to sensitization and in-service failure after welding. In consequence, the carbon levels were reduced to 0.08% which represented the lower limit attainable with steel-making technology then available. Although this move alleviated the problem, it was not wholly successful, particularly when welding thicker sections of the metal. Solution annealing of the fabricated items was rarely a practical proposition and there was a need for a long term solution. It was shown that titanium or niobium (comumbium) had a much greater affinity for the carbon than chromium, and by additions of either of these elements, the problem was largely overcome. The titanium or niobium carbides which are formed remain dispersed throughout the metal structure rather than accumulating at the grain boundaries.

Grade 321 is a type 304 (18Cr, 8Ni) with titanium added as a stabilizing element, while grade 347 contains niobium. By far, the most commonly used is 321, grade 347 being specified for certain chemical applications.

Modern steel-making techniques such as AOD (air-oxygen decarburization) were developed to reach even lower levels of carbon, typically less than 0.03%, to produce the “L” grades of stainless steel. These are commercially available and routinely specified where no sensitization can be permitted. With these advances in steel-making technology, even the standard grades of stainless steels have typical carbon levels of 0.04/0.05%, and generally speaking, are weldable without risk of chromium carbide precipitates at metal thicknesses up to 6 mm (1/4”). Above this figure or where multipass welding is to be employed, the use of a stabilized or “L” grade is always advisable.
3.2.6 Stress corrosion cracking

One of the most insidious forms of corrosion encountered with the austenitic stainless steels is stress corrosion cracking (SCC). The morphology of this type of failure is invariably a fine filamentous crack which propagates through the metal in transgranular mode. Frequently, the crack is highly branched as shown in Figure 12, although sometimes it can assume a single crack form. Factors such as metal structure, environment, and stress level have an effect on crack morphology. The disturbing feature of SCC is that there is virtually no loss of metal, and frequently it is not visible by casual inspection and is only apparent after perforation occurs. Some claim that as much as 50% of the failures of stainless steel are attributable to this cause.

Another characteristic of SCC in stainless steels is that once detected, repair by welding is extremely difficult. Crack propagation frequently occurs below the surface of the metal and any attempt to weld repair results in the crack opening up and running ahead of the welding torch. The only practical method of achieving a satisfactory repair is to completely remove the affected area with a 15-25 cm (six to nine inches) allowance all around the area of visible damage and replace the section. Even then, there is no guarantee that the damaged zone has been entirely removed.

In most cases, there are three prerequisites for the initiation of SCC.

- **Tensile stress**
  This may be either residual stress from fabricating operations or applied through the normal operating conditions of the equipment. Furthermore, it has been observed that a corrosion pit can act as a stress raiser and a nucleation site for SCC.

- **Corrosive species**
  Although there are a number of ionic compounds which will act as the corrodent, in the food industry this invariably is the chloride ion. High strength caustic soda at elevated temperatures will also induce SCC, but the concentrations and temperatures required are well in excess of those ever likely to be encountered. Furthermore, the crack morphology is intergranular rather than transgranular. PH also plays a role, and generally speaking, the lower the pH the greater the propensity for SCC.

- **Temperature**
  It generally is regarded by many that a temperature in excess of 60°C (140°F) is required for this type of failure, although the author has seen examples occurring at 50°C (122°F) in liquid glucose storage vessels.

![Fig. 12: Photomicrograph of a typical stress corrosion crack showing its highly branched morphology and transgranular propagation.](image-url)
In the absence of any one of these prerequisites, the initiation of SCC is eliminated. Therefore, it is worth considering the practical approach to its elimination from equipment.

Figure 13 is a diagram representing the effect of stress on “time-to-failure.” As will be seen, by reducing the stress level below a certain critical point, the “time-to-failure” can be increased by several orders of magnitude. On small pieces of equipment, residual stress from manufacturing operations can be removed by stress relief annealing. For large pieces of equipment such as storage vessels, this approach is clearly impractical. Applied stress is very much a function of the operational conditions of the equipment and only by reducing the stress level, by increasing the thickness of the metal, can this be reduced. However, this is a somewhat impractical and uneconomic approach. Some (Ref. 15) claim that by placing the surface of the metal under compressive, rather than tensile stress, and by shot peening with glass beads, the problem of SCC can be minimized or eliminated. This, too, is not a practical proposition for many items of food processing equipment.

As for the matter of corrosive species, it is questionable if anything can be done about elimination. With foodstuffs, for example, this invariably will be the chloride ion, a naturally occurring or essential additive.

Similarly, little can be done in respect to the temperature as this is essential to the processing operation. As shown by Copson (Ref. 16), the tendency for iron-chromium-nickel alloys to fail by SCC in a specific test medium (boiling 42% magnesium chloride solution) is related to the nickel content of the alloy. Figure 14 shows this effect and it is unfortunate that stainless steels with a normal 10% nickel have the highest susceptibility to failure. Increasing the nickel content
of the alloy results in a significant increase in the time-to-failure. But of course, this approach incurs not only the increased cost of the nickel but also the added penalty of having to increase the chromium to maintain a balanced metallurgical structure. The more effective approach is by reducing the nickel content of the alloy. A group of stainless steels have been developed which exploit this feature, and although their composition varies from producer to producer, they have a nominal composition of 20/22% chromium and 5% nickel. Molybdenum may or may not be present, depending on the environment for which the alloy has been designed. These alloys differ from the austenitic stainless steels insofar as they contain approximately 50% ferrite, hence their designation, austenitic-ferritic, or more commonly, duplex stainless steels. It is only with the advent of modern steel-making technology, particularly in relation to the lower carbon levels that can be achieved, that these alloys have become a commercially viable proposition. Because of their low carbon content, typically 0.01-0.02%, the original problems associated with welding ferritic stainless steels and chromium carbide precipitation have been overcome. The alloys are almost twice as strong as the austenitic stainless steels, and are ductile and weldable. From a general corrosion standpoint, they are comparable with, or marginally superior to, their 300 series equivalent; but from an SCC standpoint in test work and from field experience, they offer a resistance order of a magnitude better. Also now available are fully ferritic stainless steels such as grade 444 which contains 18% chromium and 2% molybdenum. This alloy contains carbon at the 0.001% level, and therefore, does not suffer from problems of welding which were encountered with the original ferritic steels. Furthermore, stabilizing elements such as titanium and niobium are also alloying additions which minimize the tendency for intergranular chromium carbide formation. The big disadvantage of these materials is their susceptibility to grain growth during welding (Figure 15) which makes them extremely sensitive to fracture, even at room temperature. Welding sections thicker than 3 mm (1/8") are not regarded as a practical proposition, and therefore, their use tends to be limited to tubing.

3.2.7 Corrosion fatigue
Fatigue is not a form of corrosion because there is no loss of metal, but can be associated with other forms of localized attack. Because pure fatigue is an in vacuo phenomenon, a more correct term is corrosion fatigue or environmental cracking, which is the modern expression and takes into account cracking where the corrosive factor has played a major role on the crack morphology.

Fig. 15: Photomicrograph of a weld deposit on a ferritic stainless steel. Compare the size of grains in the weld with those in the parent material on the left.
The primary cause of corrosion fatigue is the application of fluctuating pressure loads to components which, while of adequate design to withstand normal operating pressures, eventually fail under the influence of cyclic loading. The components can be of extremely rigid construction, such as homogenizer block or of relatively light construction, such as pipework. There are many potential sources of the fluctuating pressure, the most common of which are positive displacement pumps (e.g., homogenizer or metering pumps), rapid acting on-off valves which will produce transient pressure peaks, frequent stop-start operations, dead-ending of equipment linked to a filling machine, etc.

Generally speaking, fatigue cracks are straight, without branching and without ductile metal distortion of the material adjacent to the crack. The one unique characteristic of fatigue cracks is that the crack face frequently has a series of conchoidal markings which represent the step-wise advance of the crack front – see Figure 16. Although, as stated, corrosion fatigue cracks are generally straight and unbranched – where fatiguing conditions are in a potentially corrosive environment – the influence of the corrosive component may be superimposed on the cracks. This can lead to branching of the cracks, and in the extreme case, the crack may assume a highly branched morphology which is almost indistinguishable from stress corrosion cracking. It is only when the crack face is examined under high-power magnification that it is possible to categorize the failure mode. An example of this is shown in Figure 17 which has all the features of stress corrosion cracking, but the scanning electron micrograph (Figure 18) clearly shows the step-wise progression of the crack.

The site for initiation of corrosion fatigue is frequently a discontinuity in the metal section of the component. This may be, for example, from a sharp change in diameter of a shaft where inadequate radiusing of the diametric change results in a high cyclic stress level through shaft rotation, and thus, an initiation point for fatigue.
A corrosion pit, which under cyclic loading will have a high stress level association, can also act as a nucleation site (epicenter) for fatigue failure. Because of the corrosive element, it is sometimes difficult to establish whether the pit and associated corrosion were the initiating mechanism for the cracking or the result of corrosion superimposed on a crack, the fracture force of which will be in an “active” state and therefore more susceptible to corrosion processes.

The whole subject of fatigue and corrosion fatigue is complex. However, as far as food processing equipment is concerned, avoidance of fatigue failure is best achieved by avoiding pulsing and pressure peaks. This requires the use of well engineered valving systems and avoiding the use of positive displacement pumps. Where this is impractical, provisions should be made to incorporate pulsation dampers which will smooth out the pressure peaks and minimize the risk of fatigue failures.

3.2.8 selective corrosion

3.2.8.1 corrosion of castings

There are a number of stainless steel components found in food process plants, such as pipeline fittings and pump impellers, which are produced as castings rather than fabricated from wrought material – notably, the cast equivalents of grade 304 (CF8) AND 316 (CF8M). Although the cast and wrought materials have similar, but not identical compositions with regard to their chromium and nickel contents, metallurgically they have different structures. Where the wrought materials are fully austenitic, castings will contain some ferrite or more terminologically correct, ¶ (delta) ferrite, in the basic austenitic matrix. The ferrite is necessary to permit welding to the castings, to avoid shrinkage cracking during cooling from the casting temperature. It also acts as nucleation sites for the precipitation of chromium carbides which will invariably be present, as it will not always be possible to solution anneal the cast components. The nominal ferrite level is usually 5% to 12%. Below 5%, cracking problems may be experienced. Above 12%, the ferrite tends to form a continuous network rather than remain as isolated pools.

Because the crystallographic structures of the ferrite and austenite differ (austenite being a face center cubic and the ferrite being a body center cubic), the ferrite has – thermodynamically speaking – a higher free energy which renders it more susceptible to attack, particularly in low pH chloride containing environments such as tomato ketchup and glucose syrups. Although the problem is not so severe when the ferrite occurs as isolated pools, when present as a continuous network, propagation of the corrosion occurs along the ferrite with the austenite phase being relatively unaffected – Figure 19. Because the products of corrosion are not leached out from the corrosion site and are more voluminous than the metal, corroded castings frequently assume a blistered or pockmarked appearance. The common environments...
encountered in the industry which produce preferential ferrite attack are the same as those causing stress corrosion cracking. Therefore, this form of damage is frequently also present – Figure 20. Depending on the method used to make the casting, the surface of the castings can be chemically modified, which reduces the corrosion resistance. Small components are usually cast by either the shell molding process or produced as investment castings. In the shell molding process, the sand forming the mold is bonded together with an organic resin which carbonizes when the hot metal is poured. This results in the metal adjacent to the mold having an enhanced carbon level with the formation of intergranular carbide precipitates. Hence, there is a susceptibility to intergranular attack and other forms such as crevice, pitting, and stress corrosion cracking. Methods of overcoming this include solution annealing or machining off the carburized skin of metal. With investment castings the mold is made of zircon sand (zirconium silicate), and fired at a high temperature to remove all traces of organic material and wax, which is used as a core in the mold making process. They do not, therefore, have this carburized layer and offer a much lower resistance to surface corrosion.

3.2.8.2 free machining stainless steels
Stainless steels are notoriously difficult to machine, especially turning, not so much because they are hard, but because the swarf tends to form as continuous lengths which clog the machine and weld to the tip of the machine tools. One method of overcoming this is to incorporate a small amount, typically 0.2%, of sulphur or selenium in the alloy. These elements react with the manganese to form manganese sulphide or selenide. These are insoluble in the steel and form as discreet pools in castings or as elongated, continuous stringers in, say, wrought bar. The effect of the sulphide inclusions is to cause the material to form chips, rather than long strings of swarf when
being machined. Both manganese sulphide and selenide have virtually zero corrosion resistance to dilute mineral acids or other corrosive media. Thus, the free cutting variants have a much lower corrosion resistance than their designation would imply. Indeed, some believe that the addition of sulphur to a type 316 material will offset the beneficial effect of the alloying addition of molybdenum. As stated, the sulphide inclusions will occur in castings as discrete pools. Therefore, there will not be a continuous corrosion path. However, one of the products of corrosion in acidic media will be hydrogen sulphide, which has a profound effect on the corrosivity of even dilute mineral acids, causing attack of the austenitic matrix.

In the case of wrought materials, in particular bar stock, the sulphide inclusions are present as semi-continuous stringers and can suffer so-called end-grain attack in mildly corrosive media.

Stainless steel nuts and bolts, which are produced on automatic thread cutting machines, are invariably made from free-cutting materials. Figure 21 illustrates the difference in corrosion resistance of a bolt made from this and a non-freeing machining 316. Both bolts were exposed to the same mildly acidic environment. When specifying materials of construction, this difference must be recognized. Any component turned from bar stock which is likely to come into contact with potentially corrosive environments should always be specified in 316 and not in the free machining, sulphur containing variant.

4. CORROSION OF SPECIFIC ENVIRONMENTS

From a corrosion standpoint, the environments likely to be encountered in the food industry which may cause premature equipment failure may be classified under main headings:

- Non-corrosive
- Mildly corrosive
- Highly corrosive
- Service fluids
- Alkaline detergents
- Acidic detergents
- Sanitizing agents

4.1 Non-corrosive foodstuffs

In general terms, natural foodstuffs such as milk, cream, natural fruit juice, and whole egg do not cause corrosion problems with 304 or 316 stainless steels. Prepared foodstuffs to which there is no added salt such as yogurt, beer, ice cream, wine, spirits, and coffee also fall within this classification. For general storage vessels,
pipelines, pumps, fittings or valves, grade 304 is perfectly satisfactory. However, for plate heat exchangers which are highly creviced and therefore prone to crevice corrosion, grade 316 is frequently employed. This offers a higher degree of protection against some of the more acidic products such as lemon juice which may contain small quantities of salt and also provides a higher level of integrity against corrosion by service liquids and sanitizing agents.

It is quite common to use sulphur dioxide or sodium bisulphate for the preservation of fruit juices and gelatin solutions. In such cases, storage vessels always should be constructed from 316. Although the sulphur dioxide is non-corrosive at ambient temperature in the liquid phase, as a gas contained in significant quantities within the head space in a storage tank, it tends to dissolve in water droplets on the tank wall.

In the presence of air, the sulphurous acid that forms is oxidized to sulfuric acid at a concentration high enough to cause corrosion of 304 but not of 316.

4.2 Mildly corrosive foodstuffs

This category of foodstuffs covers products containing relatively low levels of salt and where pH values are below seven. Examples include glucose/fructose syrups and gelatin, the production of which may involve the use of hydrochloric acid. For storage vessels, pipelines, fittings, and pumps, grade 316 has established a good track record. Boiling pans in this grade of steel are perfect for long and satisfactory service. The corrosion hazards increase in processing operations involving high temperatures and where the configuration of the equipment is such as to contain crevices, especially when the product contains dissolved oxygen. For example, multi-stage evaporators operating on glucose syrup will usually have the first stage, where temperatures may approach 100°C (212°F), constructed in a super stainless steel such as 904L. Subsequent effects where temperatures are lower and where the product has been deoxygenated may be fabricated in grade 316 stainless steel.

As previously indicated, it is common practice to use sulphur dioxide as a preservative in dilute gelatin solutions during storage prior to evaporation. In some cases, excess hydrogen peroxide will be added to neutralize the sulphur dioxide immediately before concentration. This can give a catastrophic effect on the 300 series stainless steels and on even more highly alloyed metals such as 904L, due to the combined effect of the chlorides present in combination with the excess hydrogen peroxide. Because of this, it is a more acceptable practice to make the peroxide addition after, rather than before, evaporation.

Gelatin for pharmaceutical end use is subject to UHT treatment to ensure sterility. This will involve heating the gelatin solutions to 135°C (285°F) and holding at that temperature for a short period of time. Plate heat exchangers are extensively used for this duty. Although plates made from 316 stainless steel give a reasonable life of typically two to three years, a corrosion-resistant alloy with an enhanced level of molybdenum is preferred.

4.3 Highly corrosive foodstuffs

The list of foodstuffs falling in this category is almost endless – gravies, ketchups, pickles, salad dressings, butter, margarine – anything to which salt has been added at
the 1-3% level or even higher. Also within this category must be included cheese salting brine and other brines used in the preservation of foodstuffs which undergo pasteurization to minimize bacterial growth on food residues remaining in the brine. Although these brines are usually too strong to support the growth of common organisms, salt resistant strains (halophiles) are the major problem.

Low pH products containing acetic acid are particularly aggressive from a corrosion standpoint, but selection of materials for handling these products very much depends on the duty involved.

When trying to define the corrosion risk to a piece of equipment handling potential corroducts, several factors come into play. While temperature, oxygen content, chloride content, and pH are the obvious ones, less obvious and equally important is contact time. All three main forms of corrosion induced in stainless steels (crevice, pitting, and stress corrosion cracking) have an induction period before the onset of corrosion. This can vary from a few hours to several months, depending on the other operative factors. In a hypothetical situation where stainless steel is exposed to a potentially corrosive environment, removal of the steel and removal of the corroducts will stop the induction and the status quo is established. On repeating the exposure, the induction period is the same. In other words, the individual periods the steel spends in contact with the corroduct are not cumulative and each period must be taken in isolation.

When the contact period is short, temperatures are low and a rigorous cleaning regime is implemented at the end of each processing period – 316 stainless steel will give excellent service. However, where temperatures are high and contact periods are long, the corrosion process may be initiated. This is especially common in crevices such as the interplate contact points on a plate heat exchanger, where albeit at a microscopic level, corroducts and corrosion products are trapped in pits or cracks. Geometric factors may prevent the complete removal of this debris during cleaning. Under such circumstances, the corrosion process will be ongoing.

Due to the perishable nature of foodstuffs, storage is rarely for prolonged periods or at high temperatures and regular, thorough cleaning tends to be the norm. The one exception to this is buffer storage vessels for holding “self preserving” ketchup and sauces. For such duties, an alloy such a 904L, Avesta 254SMO, or even Inconel 625 may be required.

While all the foregoing applies to general equipment, the one exception is plate heat exchangers. Their highly creviced configuration and the high temperatures employed make them particularly susceptible. Plates made from grade 316 have a poor track record on these types of duties. Even the more highly alloyed materials do not offer complete immunity. The only reasonably priced material which is finding increased usage in certain areas of food processing is titanium.

The fact that butter and margarine have been included in this group of corroducts requires comment. Both these foodstuffs are emulsions containing typically 16% water and 2% salt. A fact not often appreciated is that the salt is dissolved in the water phase, being insoluble in the oil. From a corrosion standpoint, therefore, the margarine or butter may be regarded as a suspension of 12% salt solution, and as such, is very corrosive to 316 stainless steel at the higher processing temperatures. The only mitigating feature which partly offsets their corrosivity is the fact that the aqueous salty phase is dispersed in an oil rather than the reverse, and the oil does tend to
preferentially wet the steel surface and provide some degree of protection. However, the pasteurizing heat exchanger in margarine rework systems invariably has titanium plates as the life of 316 stainless steel is limited and has been known to be as little as six weeks.

4.4 Corrosion by service fluids

4.4.1 Steam
Being a vapor and free from dissolved salts, steam is not corrosive to stainless steels. Although sometimes contaminated with traces of rust from carbon steel steam lines, in the author's experience no case of corrosion due to industrial boiler steam ever has been encountered.

4.4.2 Water
The quality and dissolved solids content of water supplies varies tremendously with the aggressive ionic species, chloride ions, being present at levels varying between zero, as found in the lakeland area of England, to several hundred parts per million, as encountered in coastal regions of Holland. It is also normal practice to chlorinate potable water supplies to kill pathogenic bacteria with the amount added dependent on other factors such as the amount of organic matter present. However, most water supply authorities aim to provide water with a residual chlorine content of 0.2 ppm at the point of use. Well waters also vary in composition depending on the geographical location, especially in coastal regions where the chloride content can fluctuate with the rise and fall of the tide.

What constitutes a “good” water? From a general viewpoint, the important factor is hardness, either temporary hardness caused by calcium and magnesium bicarbonates which can be removed by boiling, or permanent hardness caused by calcium sulphate which can be removed by chemical treatment. While hardness is a factor, chloride content and pH probably are the most important from a corrosion standpoint. What can be classified as a non-corrosive water supply from a stainless steel equipment user? Unfortunately, there is no hard and fast rule which will determine whether or not corrosion of equipment will occur. As repeatedly stated throughout this article, many factors come into play. The type of equipment, temperatures, contact times, etc., all play a role in the overall corrosion process. Again, as stated before, the most critical items of equipment are those with inherent crevices – evaporators and plate heat exchangers, among others. Defining conditions of use for this type of equipment will be a regulatory factor. Even then, it is virtually impossible to define the composition of a “safe” water, but as a general guideline, water with less than 100 ppm chloride is unlikely to initiate crevice corrosion of type 316 stainless steel, while a maximum level of 50 ppm should be used with type 304.

Cooling tower water systems are frequently overlooked as a potential source of corrodenets. It must be appreciated that a cooling tower is an evaporator, and although the supply of makeup water may contain only 25 ppm chloride, over a period of operation this can increase by a factor of ten unless there is a routine bleed on the pond.
Water scale deposits formed on heat transfer surfaces should always be removed as part of the routine maintenance schedule. Water scale deposits can accumulate chloride and other soluble salts which tend to concentrate, producing higher levels in contact with the metal than indicated by the water composition. Furthermore, water scale formed on a stainless steel surface provides an ideal base for the onset of crevice corrosion.

As previously stated, potable water supplies usually have a residual free chlorine content of 0.2 ppm. Where installations have their own private wells, chlorination is undertaken on site. In general terms, the levels employed by the local water authorities should be followed and over-chlorination avoided. Levels in excess of 2 ppm could initiate crevice corrosion.

4.4.3 Cooling brines

Depending on the industry, these can be anything from glycol solutions, sodium nitrate/carbonate or calcium chloride. It is the latter which is used as a 25% solution. This can give rise to corrosion of stainless steel unless maintained in the ideal condition, especially when employed in the final chilling section of plate heat exchangers for milk and beer processing. However, by observing certain precautions, damage can be avoided.

The corrosion of stainless steels by brine can best be represented as shown in Figure 22. An exponential rise in corrosion rate with reducing pH occurs in the pH range of 6–4 and corresponds with the change in mode of attack, i.e., form pitting to general

![Fig. 22: The effect of pH and temperature on the pitting of stainless steel by brine.](image-url)
corrosion. It will be seen that, ideally, the pH of the solution should be maintained in the region 14-11. However, calcium chloride brine undergoes decomposition at pH values higher than 10.6:

\[
\text{CaCl}_2 + 2\text{NaOH} + 2\text{NaCl} \]

When scale deposition occurs heat transfer surfaces become fouled with calcium hydroxide scale. Furthermore, the scale which forms traps quantities of chloride salts which cannot be effectively removed and remain in contact with the equipment during shutdown periods. This is particularly important in equipment such as plate heat exchangers which are subjected to cleaning, and possibly hot water sterilization cycles at temperatures of 80°C (176°F) or higher.

The other aspect, non-aeration, is equally important. Air contains small quantities of carbon dioxide which form a slightly acidic solution when dissolved in water. This has the effect of neutralizing the buffering action of any alkaline component in the brine:

\[
\text{i.e., } 2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \\
\text{Na}_2\text{CO}_3 + \text{CaCl}_2 \rightarrow 2\text{NaCl} + \text{CaCO}_3 \\
\text{or } \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} 
\]

Therefore, the pH of the brine decreases and assumes a value of about pH 6.5, which is the region where pitting incidence is highest. Furthermore, scale deposits of calcium carbonate are laid down on heat transfer surfaces creating the problems referred to above.

The precautions to be observed when using brine circuits are:

- **Ensure correct pH control and maintain in the pH range of 9.5-10.**
- **Eliminate aeration.** In particular, make certain the brine return discharge line is below the surface in the storage tank during running and that the method of feeding brine from the tank does not cause vortexing with resultant air entrainment. Baudelot evaporators cause aeration of the chilling liquor and should never be used on brine circuits.
- **When cleaning and sterilizing the brine section of a pasteurizer,** flush out all brine residues until the rinse water is free of chloride. As an added precaution, it is advisable to form a closed circuit and circulate a 1/4% - 1/2% caustic soda or sodium metasilicate solution to ensure that any brine residue is rendered alkaline.
- **In plate heat exchangers and similar equipment,** make sure that stainless steel brine section components remain free of scale.
- **When shutting down the plant after a cleaning run,** it is advisable to leave the section full with a dilute (1/2%) caustic solution. Before startup, this should be drained and residues flushed out prior to re-introducing brine.

When operating conditions prevailing in a plant do not permit such a disciplined cleaning, operating, and shutdown procedure, only two materials can be considered for the brine section of a plate heat exchanger. These are Hastelloy C-276 or titanium. The corrosion resistance of both of these materials is such that cleaning and sanitizing of the product side of the heat exchanger can be carried out without removing the brine. Although both are more expensive than stainless steels, especially Hastelloy C-276, the flexibility of plant operation (which their use permits) could offset their premium prices.
4.5 Alkaline detergents
Supplied to food processing plants either as bulk shipments of separate chemicals or as carefully preformulated mixtures, the composition of alkaline detergent formulations can vary widely in accordance with individual preference or the cleaning job to be done. The detergents, however, generally include some or all of the following compounds:

- sodium hydroxide
- sodium polyphosphate
- sodium metasilicate
- sodium carbonate

Additionally, it is common to find that a selection of sequestering agents such as E.D.T.A. and any of the many available wetting agents also may be present in the formulations. None of these compounds are corrosive to stainless steels at the concentrations and temperatures used by the food industry for cleaning. 316 stainless steel is unaffected by concentrations of sodium hydroxide, as high as 20%, at temperatures up to 160°C (320°F). They can, therefore, be used with impunity at their usual maximum concentration of 5%, even in UHT operation where temperatures can rise to 140°C (284°F).

Companies have reported that some of these preformulated alkaline detergents cause discoloration of the equipment. The discoloration starts as a golden yellow, darkening to blue through mauve and eventually black. It has been established that this discoloration is caused by the E.D.T.A. sequestering agent which complexes with traces of iron in the water. It then decomposes under certain conditions of pH and temperature to form an extremely fine film of hydrated iron oxide, the coloration being interference colors which darken as the film thickness increases. Although the film is not aesthetically pleasing, it is in no way deleterious and removing it by conventional cleaning agents is virtually impossible.

Some alkaline detergents are compounded with chlorine release agents such as sodium hypochlorite, salts of di- or trichlorocyanuric acid which form a solution containing 200-300 ppm available chlorine at their usage strength. Although the high alkalinity reduces the corrosivity of these additives, generally speaking, they should not be employed on a regular basis at temperatures exceeding 70°C (160°F).

4.6 Acidic detergents
Alkaline detergents will not remove the inorganic salts such as milkstone and beerstone deposits frequently found in pasteurizers. For this, an acidic detergent is required and selection must be made with regard to their interaction with the metal. Sulfuric and hydrochloric acids will cause general corrosion of stainless steels. Although it could be argued that sulfuric acid can be employed under strictly controlled conditions because stainless steels, especially grade 316, have a very low corrosion rate, its use could result in a deterioration of surface finish. This, in corrosion terms, is an extremely low rate but from an aesthetic viewpoint, is undesirable.

Acids such as phosphoric, nitric and citric, when used at any concentration likely to be employed in a plant cleaning operation, have no effect on stainless steels and can be used with impunity. Three cautionary notes are worthy of mention:

- It is always preferable to use alkaline cleaning before the acid cycle to minimize the
risk of interacting the acid with any chloride salt, and therefore, minimize the formation of hydrochloric acid.

- It is inadvisable to introduce an acid into a UHT sterilizing plant, when it is at full operating temperature (140°C/285°F), as part of a “clean-on-the-run” regime.
- Nitric acid, being a strong oxidizing agent, will attack certain types of rubber used as gaskets and seals. As a general guideline concentrations should not exceed 1% and a temperature of 65°C (150°F), although at lower concentrations the upper recommended temperature is 90°C (195°F).

Another acid which is finding an increased use in the food industry for removing water scale and other acid soluble scales is sulfamic acid. Freshly prepared solutions of up to 5% concentration are relatively innocuous to stainless steels, but problems may arise when CIP systems incorporating recovery of detergents and acids are employed. Sulfamic acid will undergo hydrolysis at elevated temperatures to produce ammonium hydrogen sulfate.

\[
\text{NH}_2\text{SO}_2\text{OH} + \text{H}_2\text{O} > \text{NH}_4\text{HSO}_4
\]

This behaves in much the same way as sulfuric acid. In situations where the use of this acid is contemplated, prolonged storage of dilute solutions at elevated temperatures is inadvisable, although at room temperature the hydrolysis is at a low rate.

4.7 Sanitizing agents

Terminology for the process of killing pathogenic bacteria varies from country to country. In Europe, disinfection is preferred; in America, sanitizing. Regardless, the term should not be confused with sterilization which is the process of rendering equipment free from all live food spoilage organisms including yeasts, mold, thermophilic bacteria, and most importantly, spores. Sterilization with chemicals is not considered to be feasible and the only recommended procedure involves the circulation of pressurized hot water at a temperature of not less than 140°C (285°F).

For sanitization, while hot water (or steam) is preferred, chemical sanitizers are extensively used. These include non-corrosive compounds such as quaternary ammonium salts, anionic compounds, aldehydes, anphoterics, and potentially corrosive groups of compounds which rely on the release of halogens for their efficacy. By far, the most popular sanitizer is sodium hypochlorite (chloros), and this is probably the one material that has caused more corrosion in food plants than any other cleaning agent. For a detailed explanation of the corrosion mechanism, refer to an article by Boulton and Sorenson (Ref. 17) which describes a study of the corrosion of 304 and 316 stainless steels by sodium hypochlorite solutions. It is important, if corrosion is to be avoided, that the conditions under which it is used are strictly controlled. For equipment manufactured from grade 316 stainless steel, the recommended conditions are:

- Maximum concentration – 150 ppm available chlorine.
- Maximum contact time – 20 minutes.
- Maximum temperature – room temperature, which is well in excess of the minimum conditions established by Tastayre and Holley, to kill pseudomonas aeruginosa (Ref. 18).

In addition, several other precautions must be observed:

- Before introducing hypochlorite, equipment should be thoroughly cleaned and free of
scale deposits. Organic residues reduce the bactericidal efficiency of the disinfectant and offer an artificial crevice in which stagnant pools of hypochlorite can accumulate.

- It is imperative that acidic residues be removed by adequate rinsing before introducing hyperchlorite solutions. Acid solutions will react with hypochlorite to release elementary chlorine, which is extremely corrosive to all stainless steels.

- The equipment must be cooled to room temperature before introducing hypochlorite. In detergent cleaning runs, equipment temperature is raised to 80/85°C (176/185°F) and unless it is cooled during the rinsing cycle, a substantial increase in temperature of the disinfectant can occur. An important point, frequently overlooked, is that a leaking steam valve can cause a rise in the temperature of equipment even though it is shut off.

- After sanitizing, the solution should be drained and the system flushed with water of an acceptable bacteriological standard. This normally is done by using a high rinse rate, preferably greater than that used in the processing run.

While these comments relate specifically to the sanitizing of plate heat exchangers, similar precautions must be taken with other creviced equipment. Examples include manually operated valves which should be slackened and the plug raised to permit flushing of the seating surface. Pipeline gaskets also should be frequently checked to make sure that they are in good condition and not excessively hardened. Otherwise, they will fail to form a crevice-free seal over their entire diameter. Where it is not possible to completely remove hypochlorite residues, such as in absorbent gland packing materials, hot water is preferred.

All the foregoing specifically relate to sodium hypochlorite solutions. Other sanitizing agents which rely on halogen release, such as di- and trichlorocyanuric acid, should also be used under strictly controlled conditions.

Iodohpors also are used for sanitizing equipment. These are solutions of iodine in non-ionic detergents and contain an acid, such as phosphoric, to adjust the pH into the range at which they exhibit bactericidal efficacy. This group of sanitizers is employed where hot cleaning is not necessary or on lightly soiled surfaces such as milk road tankers, farm tanks, etc. Extreme cautions should be exercised with this group. Although used at low concentrations (50 ppm), prolonged contact with stainless steel can cause pitting and crevice corrosion. Furthermore, in storage vessels which have been partially filled with iodophor solutions and allowed to stand overnight, pitting corrosion in the head space has been observed due to iodine vaporizing from the solution and condensing as pure crystals on the tank wall above the liquid line. Another factor is that iodine can be absorbed by some rubbers. During subsequent processing operations at elevated temperatures, the iodine is released in the form of organic iodine compounds, especially into fatty foods, which can cause an antiseptic taint. The author knows of one dairy which used an iodophor solution to sanitize a plate pasteurizer to kill an infection of a heat resistant spore-forming organism. The following day, there were over 2,000 complaints of tainted milk. CIP cleaning cycles did not remove the antiseptic smell from the rubber seals and complete replacement with new seals was the only method of resolving the problem.

Another sanitizing agent which is increasing in popularity, especially in the brewing industry due to its efficacy against yeasts, is peracetic acid. It will not cause corrosion of 304 and 316 stainless steels and the only precautionary measure to be taken is to
use a good-quality water containing less than 50 ppm of chloride ions for making up the solutions to their usage concentration. Due to the strongly oxidizing nature of some types of peracetic acid solutions, deterioration of some types of rubber may occur. A recent survey, undertaken by the IDF, of the use of peracetic acid in the dairy industry (Ref. 19) found few corrosion problems were reported. The general consensus was that it permitted greater flexibility in the conditions of use, compared with sodium hypochlorite, without running the risk of damage to equipment. For comprehensive information on the cleaning of food processing equipment, albeit primarily written for the dairy industry, refer to the British Standards Institute publication BS 5305 (Ref. 20).

5. CORROSION BY INSULATING MATERIALS
Energy conservation is now widely practiced by all branches of industry, the food industry being no exception. For example, in the brewing industry, wort from the wort boilers is cooled to fermentation, and the hot water generated in the process is stored in insulated vessels (hot liquor tanks) for making up the next batch of wort. An area of corrosion science which is receiving increased attention is the subject of corrosion initiated in stainless steels by insulating materials. At temperatures in excess of 60°C (140°F) these can act as a source of chlorides which will induce stress corrosion cracking and pitting corrosion of austenitic stainless steels. Among the insulating materials which have been used for tanks and pipework are:

- Foamed Plastics – polyurethane
- polyisocyanurate
- phenic resins, etc.
- Cellular and foamed glass
- Mineral fiber – glass wool, rock wool
- Calcium silicate
- Magnesia
- Cork

All insulating materials contain chlorides to a lesser (10 ppm) or greater (1.5%) extent. The mineral-based insulants, such as asbestos, may contain them as naturally occurring water soluble salts such as sodium or calcium chloride. The organic foams, on the other hand, may contain hydrosoluble organo-chlorine materials used as phosphates, or chlorine containing materials present as impurities. Insulation manufacturers are becoming increasingly aware of the potential risk of chlorides in contact with stainless steels and are making serious efforts to market a range of materials which are essentially chloride free.

Even though many of the insulating materials contain high levels of chloride, in isolation they are not corrosive. Corrosion, being an electrochemical process, involves ionic species. In the absence of a solvent (water) the chloride or salts present in the insulation cannot undergo ionization to give chloride ions. Therefore, they essentially are non-corrosive. Similarly, where organo-chlorine compounds are present, water is necessary for hydrolysis to occur with the formation of hydrochloric acid or other ionizable chloride compounds. The main problem, therefore, is not so much the insulant but the interaction of
the insulant with potential contaminants to release corrosive species. Under ideal conditions, if the insulating material could be maintained perfectly dry, then the chloride content would not be a critical factor in the material specification process. Unfortunately, it must be acknowledged that even in the perfectly regulated installation, this ideal is rarely (if ever) achieved. Therefore, thought must be given to recommended guidelines.

Any material which is capable of absorbing water must be regarded as a potential source of chloride. Although the chloride content of the insulant may be extremely low (25 ppm), under extractive conditions when the insulation becomes wet and concentration effects come into play, even this material may cause the initiation of stress corrosion cracking. The chloride content of the contaminating water cannot be ignored. Even a “good quality” water with a low chloride content (say 30 ppm), if being continuously absorbed by the insulant, forms a potential source of chlorides. Through evaporation, it can reach very significant levels and initiate the corrosion mechanism. The more absorptive the insulant, the greater the risk, and materials such as calcium silicate and certain types of foams must be regarded as least desirable. It is interesting to note that one of the least absorptive insulants from those listed is cork. In the experience of the author, there has been no reported case of this insulant causing problems with stress corrosion cracking of stainless steels. Of course, it could be argued that the bitumen used as an adhesive to stick the cork to the vessel walls has to be applied so thickly that the bitumen forms an impermeable barrier preventing contact of contaminated water with the stainless steel substrate. Irrespective of the protection mechanism, the net effect is that cork has an extremely good “track record.” Unfortunately, due to the cost, cork is now rarely used.

No hard and fast rule can be applied for specifying the acceptable, maximum, tolerable, chloride content of an insulating material. Any specification must take into account what is commercially available, as well as all the other factors such as price, flammability, ease of application, etc. To specify zero chloride is obviously impractical and even a figure of 10 ppm may be difficult to achieve in commercially available products. As a general compromise, a 25 ppm maximum is considered to be technically and commercially feasible while minimizing the potential source level of chloride corroden.

The primary function of the insulant is to provide a thermal barrier between the outside of the vessel and the environment. It does not provide a vapor or moisture barrier and provision of such protection must be regarded as equally important in the insulating process. As previously mentioned, the use of bitumen as an adhesive for cork insulation must provide an extremely good water barrier, although there are a wide range of products marketed specifically for this purpose. These include specially developed paints of undefined composition and zinc free silicone alkyd paints, as well as silicone lacquer. These silicone-based products are particularly appropriate because of their inherent, low-water permeability and also their stability at elevated temperatures. Aluminum foil has also been successfully used as a water/vapor barrier between the stainless steel and the insulant. There is little doubt that the foil provides an extremely good barrier but at laps between the sheets of foil, ingress of water can occur unless sealing is complete, the achievement of which is most unlikely. Furthermore, it is likely that there will be tears in the foil, providing yet another ingressation path for water.
However, it is believed that aluminum foil has a role additional to that of a barrier. From an electrochemical aspect, being “anodic” to stainless steel, it will provide galvanic protection of the steel in areas where there is a “holiday” in the foil, thus inhibiting corrosion mechanisms. When insulation material becomes wet, the insulating efficiency shows a dramatic fall off. In fact, the thermal conductivity of wet insulation will approach that of the wetting medium. It is ironic that the thermal conductivity of water is among the highest known for liquids. It is imperative that from the standpoint of preventing moisture ingression to minimize corrosion risks and maintain insulation efficiency, the insulation is externally protected from rain and water. There is a variety of materials available for this such as aluminum sheeting, plastic coated mild steel, spray applied polyurethane coatings, etc. Much of the value of the protection will be lost unless particular attention is taken to maintaining a weather-tight seal at the overlaps in individual sheets of cladding. There are many semi-flexible caulking agents which can be employed for this. One which is particularly effective is the RTV silicone rubber which exhibits extremely good weather resistance and long-term reliability. Nevertheless, maintenance is required, especially around areas of discontinuity such as flanged connections, manway doors, etc. Operators are beginning to realize that routine maintenance work on insulation is as important as that on all other items of plant and equipment. Insulation of a vessel or pipeline is a composite activity with many interactive parameters. It is impossible to set specification rules, as each case must be viewed in the light of requirements. Therefore, these notes must be regarded as guidelines rather than dogma. For further information, an excellent publication by the American Society for Testing Materials (Ref. 21) is essential reading.

6. CORROSION OF RUBBERS
Many involved in the field of corrosion would not regard the deterioration of rubber as a corrosion process. The author’s opinion differs from this viewpoint as rubber undergoes deterioration by interaction with its environment.

6.1 General
Rubber and rubber components form an essential part of food processing equipment – joint rings on pipelines, and gaskets on heat exchangers and plate evaporators. Although natural rubber was the first material to be used for manufacturing these components, today they are made almost exclusively from one of the synthetic rubbers listed in Table 5. Unlike metals and alloys which have a strictly defined composition, the constituents used in the formulation of rubbers are rarely stipulated. More often, they will reflect the views and idiosyncrasies of the formulator on how to achieve the desired end product. The important constituents of a rubber are:

- **Basic polymer**
  Largely determines the general chemical properties of the finished product.
- **Reinforcing fillers**
  These are added to improve the mechanical properties and will invariably be one of the
grades of carbon black – or if a white rubber is required, mineral fillers such as clays or calcium silicate.

- **Vulcanizing agents**
  These cross link the basic polymer and impart rubber-like properties which are maintained at elevated temperatures.

- **Anti-oxidants**
  To stabilize the rubber against oxidative degradation, hardening or softening, after prolonged operating periods at elevated temperatures.

- **Processing aids**
  Which facilitate the molding of the rubber.

- **Plasticizers**
  To modify the mechanical properties.

A complicating factor which has to be considered when formulating rubber for food contact surfaces is the acceptability (or non-acceptability) of the compounding ingredients. Some countries, notably Germany and the U.S.A., have drawn up lists of permitted ingredients (Ref. 22, 23). Other countries regulate the amount of material which can be extracted from the finished article by various test media. Invoking these regulations may impose limits on the in-service performance of a rubber component which could be a compromise, exhibiting desirable properties inferior to those achievable if it were for a non-food application. For example, the resistance to high-pressure steam of some rubbers can be enhanced by using lead oxide as an ingredient. Obviously, such materials could not be contemplated for any food contact application.
6.2 Corrosion by rubber

The majority of rubbers and formulating ingredients have no effect on stainless steels even under conditions of high temperature and moisture. There are two notable exceptions, polychloroprene and chlorosulphonated polyethylene. Both of these contain chlorine, which under the influence of temperature and moisture, undergo hydrolysis to produce small quantities of hydrochloric acid. In contact with stainless steel, this represents a serious corrosion hazard causing the three main forms of attack.

When specifying a rubber component, it is easy to avoid these two polymers but many of the rubber adhesives are produced from one of these polymers. That is the reason why manufacturers of heat exchangers and other equipment which necessitates sticking the rubber onto metal, specify what type of adhesive should be used. Many DIY adhesives and contact adhesives are formulated from polychloroprene. It is common for a maintenance engineer to stick gaskets in a heat exchanger to get his/her supply of rubber cement from the local hardware shop. The results can be catastrophic as shown in Figure 23. Similarly, many self-adhesive tapes use a polychloroprene-based adhesive, and direct contact of these steels should be avoided.

Fig. 23: Catastrophic failure of the gasket groove of a heat exchanger plate by stress corrosion cracking caused by the use of a polychloroprene-based adhesive.
6.3 Corrosion of rubber by environments

From the standpoint of food processing, the environments likely to interact with rubber are classified under the following headings:

- Foodstuffs containing no fat or a low level of fat, e.g., milk.
- Fatty products: butter, cream, cooking oils, shortenings.
- Alkaline detergents.
- Acid detergents.
- Sanitizing agents.

Unlike the corrosion of metals which is associated with oxidation and loss of metal, rubber deterioration usually takes other forms. When a rubber is immersed in a liquid, it absorbs that liquid or substances present in it to a greater or lesser degree. The amount of absorption determines whether the rubber is compatible with the environment. The absorption will be accompanied by changes in mass, volume, hardness and tensile strength. For example, immersing an oil-resistant rubber in vegetable oil may produce a change in volume of only 2-3%, whereas a non-oil-resistant rubber may swell by 150% or more. Such a volumetric change will be accompanied by a large reduction in the tensile strength and a high degree of softening.

Table 6: Performance of rubbers in some environments found in the food and beverage industries.

<table>
<thead>
<tr>
<th>Products</th>
<th>SBR</th>
<th>Medium Nitrile</th>
<th>Natural Rubber</th>
<th>Poly-chloroprene</th>
<th>Butyl</th>
<th>EPDM</th>
<th>Silicon (7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole milk</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Beer, wines and spirits</td>
<td>G-F</td>
<td>E</td>
<td>F</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Fats, oils and cream</td>
<td>F</td>
<td>E</td>
<td>F</td>
<td>G</td>
<td>P</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>Sauces</td>
<td>E</td>
<td>E</td>
<td>F (8)</td>
<td>E</td>
<td>E (8)</td>
<td>E</td>
<td>E</td>
</tr>
<tr>
<td>Salad dressings</td>
<td>F</td>
<td>E</td>
<td>F</td>
<td>G</td>
<td>P</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>Fruit drinks and juices (9)</td>
<td>E</td>
<td>E</td>
<td>G</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
</tr>
</tbody>
</table>

Cleaning Agents

| Sodium hydroxide (1)                    | G   | E              | G              | G                | E     | E    | E           |
| Sodium carbonate (2)                   | E   | E              | E              | E                | E     | E    | E           |
| Sodium hypochlorite (3)                | G   | G              | G              | G                | E     | E    | E           |
| Nitric acid (4)                        | F   | F              | P              | F                | G     | G    | G           |
| Phosphoric acid (5)                    | E   | E              | E              | E                | E     | E    | E           |
| Quaternary ammonium compounds (6)      | E   | E              | E              | E                | G     | G    | G           |

Notes:

1. All strengths up to 5% at maximum operating temperatures of the rubber.
2. Sodium carbonate and other detergent/additives, e.g., sodium phosphate, silicate.
3. Sodium hypochlorite as used at normal sterilizing concentration – 150 mg/l.
4. Nitric acid as used at normal cleaning strength of 1/2 to 1%.
5. Up to 5% strength.
6. Used as an aqueous 1% solution.
7. Depending on the type of basic polymer.
8. Depending on the fat/oil content.
9. The performance of a rubber will be affected by the presence of essential oils.
Broadly speaking, a rubber should not exhibit a volumetric or weight change greater than 10%, nor a hardness change of more than ten degrees (International Rubber Hardness Degrees – IRHD or Shore A) to be classified as compatible. Data presented in Tables 6 and 7 indicate the compatibility of rubbers with some food industry environments. But for more information, refer to one of the national or international test procedures (Refs. 24, 25, 26).

<table>
<thead>
<tr>
<th>Peracetic Acid Concentration (active ingredient)</th>
<th>Temp. °C</th>
<th>Medium Nitrile</th>
<th>Butyl (resin cured)</th>
<th>EPDM</th>
<th>Silicon</th>
<th>Fluoro Elastomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05% (500 mg 1⁻¹)</td>
<td>20 60 85</td>
<td>R R (?)</td>
<td>R R R R R R</td>
<td>R R R</td>
<td>R R (%)</td>
<td></td>
</tr>
<tr>
<td>0.10% (1 mg 1⁻¹)</td>
<td>20 60 85</td>
<td>R N.R. (?)</td>
<td>R R N.R. R N.R. R</td>
<td>R R R</td>
<td>R N.R. R</td>
<td></td>
</tr>
<tr>
<td>0.25% (2.5 mg 1⁻¹)</td>
<td>20 60 85</td>
<td>R N.R. N.R. N.R.</td>
<td>R R N.R. N.R. N.R.</td>
<td>R R N.R.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5% (5 mg 1⁻¹)</td>
<td>20 60 85</td>
<td>— N.R. N.R. N.R.</td>
<td>R R N.R. N.R. N.R.</td>
<td>R R N.R.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R – Little effect on the rubber    (?) – Possibly some degradation
N.R. – Not recommended as significant degradation may occur

Table 7: Suggested limits of concentration and temperature for peracetic acid in contact with rubbers.

After a basic training in chemistry, author Dr. Colin Cowan undertook academic and industrial research into the use of clay minerals as absorbents. Dr. Cowan, who is currently retired after more than 30 years of service with APV, headed a British based multidiscipline laboratory dealing with all aspects of materials technology. He also operated a technical services laboratory in Tonawanda, NY with emphasis on the specification of metallic and non-metallic materials for processing equipment.
REFERENCES

3. The British Aluminum Co., Ltd., Aluminum in the Chemical and Food Industries, 1951
4. Ferry, G., New Scientist, 27 February 1986, 23
15. Woelful, M. and Mulhall, R., Metal Progress, 57-59, Sept. 1982
20. BS 5305 Code of practice for cleaning and disinfecting of plant and equipment used in the dairying industry. British Standards Institute, London
22. Sonderdruck aus Bundesgesundheitsblattm 22, 1, 79, W. Germany
23. USA Code of Federal Regulations, Title 21, Food and Drugs Section 177.2600, Rubber Articles Intended for Repeated Use