



# **CORROSION SOLUTIONS**

For Chemical Pumps



## A WORLD LEADER IN MATERIAL TECHNOLOGY

# LaBour and Taber specialized pumps are available in a diverse range of materials to combat the arduous nature of the pumped liquids.

The materials are tailored to the particular industrial environment for which they are specifically designed.

The material options include metals as standard as stainless steel and as exotic as Titanium and Zirconium. The economical construction and optimum reliable performance of centrifugal pumps, or for that matter any other chemical equipment, is predicated upon selecting the right alloy.

Utilizing laboratory data, while admittedly produced under stringently controlled conditions, which quite often do not represent real life situations in industry, nonetheless provides a useful guide toward alloy selection. Thus the final selection also takes into consideration other factors such as presence of contaminants, resistance of welded joints, galvanic attack, non-uniformity of solutions and differences in operating conditions.

While every effort has been made to ensure that the information given in this booklet is technically correct, LaBour does not warrant its accuracy.

## A QUALITY COMPANY

Total quality procedures throughout the LaBour organization ensure that every pump package installed in the field has been manufactured, tested and supported to the highest standards attainable within the industry.



## INTRODUCTION

The annual cost of corrosion and of protection against corrosion in the world is staggering. A plant may spend considerable amounts of money each year in painting steel to prevent rusting. Corrosion in auto radiators, and exhaust systems adds up to more than a million dollars daily, while approximately four million water heaters are replaced each year. The Chemical Industry spends 1.7Billion annually on direct corrosion costs, which is eight percent of capital expenditures (excluding costs related to operation and maintenance).

The world's economy would be entirely different if it were not for corrosion. Even though corrosion is here to stay, its cost can be considerably reduced in industry through proper selection of materials, correct design of products, and preventative maintenance. Corrosion contributes to the depletion of our natural resources and the concern over this is becoming increasingly influential in inducing people to be "corrosion-cost" conscious.

In an effort to apply corrosion principles (from fluid flow to underground soil and atmospheric) to contained chemical systems, and in particular to centrifugal pumps, the following schematic diagrams have been used (Page 4). These indicate the different forms of corrosion that may take place in a pump. The diagrams depict an impeller in a casing. The seals, bearing brackets, etc. are to be imagined.

To view corrosion engineering in its proper perspective, it is necessary to remember that the choice of material depends on several factors:

- a. Cost
- b. Corrosion resistance
- c. Availability
- d. Strength
- e. Fabrication
- f. Appearance

In dealing with pump systems, some other factors need to be considered:

- a. Suction and operation conditions
- b. Continuous/intermittent service
- c. Are there several pumps involved? In series? Or parallel?
- d. Type of seal
- e. Flushing fluid
- f. Temperature change
- g. pH balancing chemicals

The above factors influence the corrosion rates of any given material, and each is dealt with in detail when considering a pump's hydraulics, but the choice of a proper material depends on how accurately these factors have been calculated. Additionally, any changes subsequently made in operation or processing are critical and may make re-evaluation of the sizing and choice of material necessary.

One other phenomenon that is difficult to specifically identify is defective casting corrosion. Identification requires an intimate knowledge of the material used, as well as the manufacturing techniques employed to make it into the particular casting in question. Most generally, these defects are located at specific points that bear a relation to gates, risers and design peculiarities.

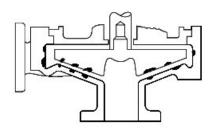
These defects do not show up during the manufacturer's pressure tests. They appear when corrosive liquid either eats out the foreign material, or starts local electrolytic action between the metal and an inclusion or segregation. Shrinking cavities in L, X or T sections will lower the strength of the material and could cause breakage at specific points. This type of occurrence is attributed to processing reasons rather than to corrosion.

Further, failure of a pump due to entry of foreign matter is more likely due to mechanical reasons rather than corrosion.

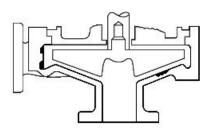


EIGHT FORMS OF CORROSION (Mechanics of Attack)

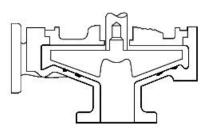
FIG. 1A



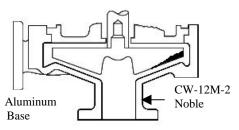
**General Corrosion** 



## **Localized Corrosion**

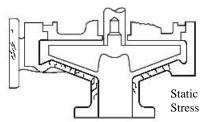


## Pitting

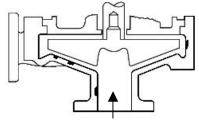


Galvanic

## Fig. 1B CRACKING PHENOMENA

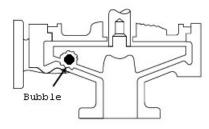


## **Stress Corrosion Cracking**

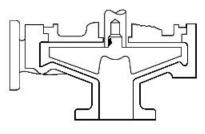


Erosion

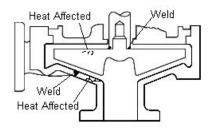




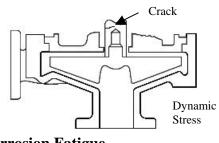
Cavitation



## **Crevice/Deposit Corrosion**



## Intergranular Corrosion

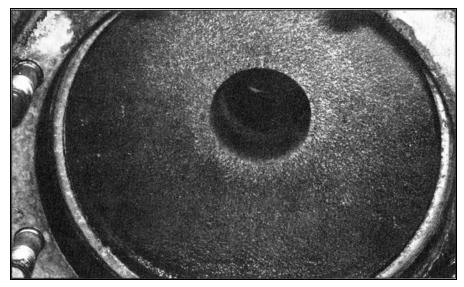


## **Corrosion Fatigue**

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## **GENERAL CORROSION**



General corrosion leads to relatively uniform thinning. For round bars and wires, corrosion proceeds radially inward at an essentially uniform rate around the entire circumference. Castings suffer corrosion starting at the wall exposed to the fluid (for example, the impeller face of the casting) and proceeding gradually and uniformly to the outer wall. In many instances it is complicated by the velocity, pressure, and nature of the pumped fluid. Methods of reducing or eliminating general corrosion are the use of coatings, the selection of a more corrosionresistant material (a general rule is to select an alloy with a higher chrome and/or nickel content), the use of inhibitors, or cathodic protection.

### General corrosion proceeds by many different means:

A. The corrosion reaction product is protective; it forms a passivating barrier that stifles further corrosion. In this case, the material is not inert, but continues to corrode at a low rate, and to continually repair the passive film. Most corrosionresistant austenitic materials, such as stainless steels, show this type of passivating behavior with the help of a surface film of oxides. This type of protection is very sensitive to solids in the pumped fluids. These solids may continually scour away the protective film that would otherwise form, thus leading to erosion-corrosion.

B. The corrosion product may be soluble in the pumped fluid at a rate determined by the electrode potential of the metal. This is illustrated very well when steel is used in oxygenated water.

C. A special case of an artificially controlled uniform dissolution process may be attempted by controlling the pH or current density of a given solution. This principle is utilized in chemical machining and electropolishing of stainless steels to improve either the corrosion resistance or frictional characteristics.

In pumps, the recognition of general corrosion is compounded by velocity and pressure variations. The surface casing may show whorls and pockets where velocity variations have influenced the rate of corrosion. These variations may appear to be caused by solids or erosive products in the fluid. However, close examination will always reveal the fact that corrosion has left an etched appearance on the surface.



### CASE HISTORY ILLUSTRATING **GENERAL ATTACK**

#### Alloy: Y-30 (N-7M)

### Environment:

30% hydrochloric acid with minor impurities. Temperature 150°F.

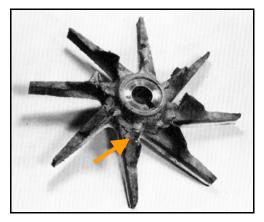
#### **Description:**

Notice the attack is all over the impeller surface without an exaggerated affect on the outer periphery. This pump was in service for two vears.

### Remedy:

Review cost and evaluate possibility of using higher-grade alloy, such as Zirconium, which is resistant up to 37% HCI to 158 °F.

CASE HISTORY **ILLUSTRATING SEVERE** GENERAL ATTACK



Alloy: CF-8M (316 S.S.)Environment:

70% Sulfuric Acid; Temperature 140°F.

### **Description:**

A CF-8M impeller was substituted for an R-55 impeller.

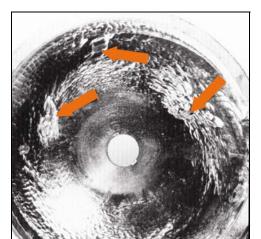
### Remedy:

Do not interchange castings without checking suitability of application.

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Erosion consists of two types of damage modes:

**A.** Mechanical-Chemical or Erosion-Corrosion:

In the erosion-corrosion mode, the flowing liquid may be free of abrasive particles. However, the velocity of the liquid may cause flow aberrations and turbulence due to surface discontinuities. The surface discontinuity may be a weld bead, or flashing in the volute of a casing. The liquid velocity, making the damage look erosive, removes this loosely adhered particle. There is a

defined "breakaway velocity" at which erosion-corrosion begins and is characteristic of a given alloy/pumped-fluid system.

If this mode is identified and there is no particle impingement, then reducing the flow rate will help reduce the erosion-corrosion. In contrast, the removal of the discontinuity may produce the same result. Impingement of abrasive particles carried by a fluid can affect the surface of the casing, impeller, etc. by causing mechanical damage. The particles are now capable of destroying the protective oxide film continually by fluid shear, thereby increasing the rate of damage. In this case, reducing the flow rate will not help. It is the angle of incidence of the abrasive particle that is of prime importance. Filtration of these particles wherever possible may be the best solution.

A good example of discontinuity, such as a scratch or a small pit, causing damage is often seen in mechanical seals. In this case, high-pressure fluid in the constricted scratch zone causes the development of a channel. A number of closely-knit channels cause the material to "wire-draw".

This usually reveals itself in a characteristic ripple pattern. The impingement of hard particles causes multiple cratering. Herein the surface undergoes deformation and eventually extrusion. It is the angle of impingement, velocity, hardness and angularity of the particles that affect this type of erosion. It is extremely sensitive to the flow paths and thus may appear to be localized.

### CASE HISTORY ILLUSTRATING EROSION FOR (A) AND (B)

### Alloy: CF-8M (316 S.S).

### Environment:

Sodium nitrate with other solids SP. GR. 1.24.

### Description:

Very little damage around shaft opening. Outer periphery shows damage increasing due to velocity and pressure. By-pass throat area shows severe damage. Erosion marks indicate direction of liquid flow.

### Remedy:

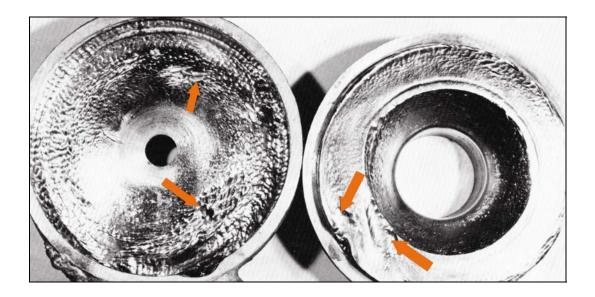
a) Check rotation on impeller and b) substitute with LaBour Alloy 48 (CD4Mcu) or other more abrasion resistant material. This will often correct the situation.



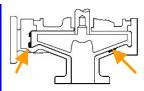
### **B.** Purely mechanical or Particle Erosion:

In the case of mechanical erosion, the action is limited to the outer periphery of the casing. It is here that the velocity and pressure of the liquid are the greatest. The central portion around the shaft opening is generally untouched.

Methods of preventing or reducing erosion-corrosion can be accomplished by use of one or more of the following methods. Use materials with improved corrosion resistance to provide a stronger protective oxide film. Improve the design of the system to reduce turbulence; alteration of the environment such as filtering to remove solids or reducing the temperature. Use coatings, such as hard facing, if the coating has the required corrosion resistance as well as hardness. Cathodic protection has been found to reduce erosion-corrosion in some applications.



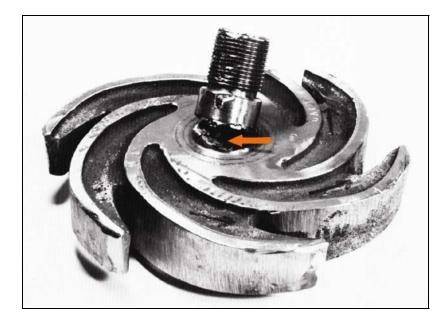




## Localized Corrosion

This form is used very loosely to describe corrosive attack in a specific small area. It is not to be confused with pitting and crevice corrosion. In castings, this form of attack is usually caused by mechanical faults such as inclusion, gas holes, segregation, or cold shuts. The corrosive liquid will eat out the foreign material, or set up local cells between the metal and the inclusion or segregation.

This form is very difficult to identify without complete knowledge of the foundry practices employed in making the casting. These bad spots in the casting will occur in certain, very localized areas and without regard to, or in connection with, any other type of corrosion. This form of corrosion in the pump industry may be referred to as defective casting corrosion.



### CASE HISTORY ILLUSTRATING LOCALIZED CORROSION

### Alloy: CF-8M (316 S.S).

#### Environment:

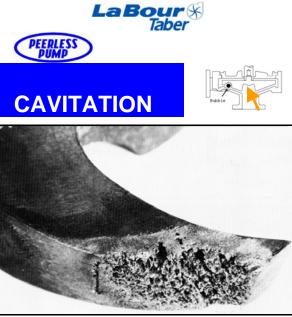
#### Unknown

### Description:

A shrinkage cavity was present at the junction of the stub to the impeller. The heavy cyclic loads during operation caused the initiation to rupture.

#### Remedy:

### Obtain a shrink free casting.



This form of erosion is

attributed to the following:

**A.** Formation of bubbles: At the eye of the impeller the pressure on the liquid is sufficiently reduced to cause the liquid to vaporize or form bubbles.

**B**. Collapse of bubbles: As the liquid is now pumped to the outer periphery of the impeller, the pressure is increased, causing the bubble to implode. Repetition of this process at high speed causes the bubbles to form and collapse rapidly.

These rapidly imploding bubbles may produce shock waves with pressure as high as 64,000 pounds per square inch. This is well beyond the yield strength of a number of materials. Such forces cause plastic deformation in metals,



which is indicated by the presence of slip lines on the impeller and casing.

An imploding bubble causes the metal to be roughened. This roughened area in turn acts as a nucleating site for a new bubble to form. The collapsing bubbles appear to cause closely spaced pitted areas and

considerable roughening of the surface. Some measures which can be taken to alleviate this problem are:

**A.** Change of the design to minimize the hydrodynamic pressure differences in the process fluid.

**B.** Use of a more corrosion-resistant material.

**C.** Smoothing of the finish on the impeller to reduce nucleating sites for the bubbles.

**D.** Use of a rubber or plastic coating that inherently possesses a strong metal-coating interface.

**E.** Cathodic protection: Hydrogen is evolved at the metal surface, cushioning the shock waves produced by the collapsing bubbles and thus preventing damage to the metal surface.

Cavitation damage is located anywhere between the inlet eye of the impeller and the tip of the blades. The closely spaced pits are usually seen on the lagging side of the blades. In certain violent instances, damage is noticed on the leading side of the blades. The extent and location of the damage is dependent on the fluid being handled, the temperature, partial pressures and the degree of recirculation flow inherent in the design.

### CASE HISTORY ILLUSTRATING CAVITATION TYPE DAMAGE

Alloy: Ni-Cr-Mo-Cu (LaBour AlloyR55)

### Environment:

Water with 50 ppm chloride at 110°F (44 C)

#### Description:

The imploding of bubbles during re-absorption on the pressure side of the blade causes damage in the form of closely spaced pits.

### Remedy:

a) Check the conditions under which the pump is operating and b) use a more cavitation resistant material.



## CASE HISTORY ILLUSTRATING CAVITATION TYPE DAMAGE- GAS CONCENTRATION CORROSION

Alloy: CF-8M (316 S.S.)

Environment:

Unknown.

### **Description:**

A restricted suction condition caused an insufficient amount of liquid to fill the discharge throat, yet a large amount of gas was present. This caused a vacuum on the low velocity side as shown.

### Remedy:

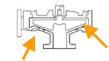
a) Review design of suction and b) determine if gas in liquid can be reduced.

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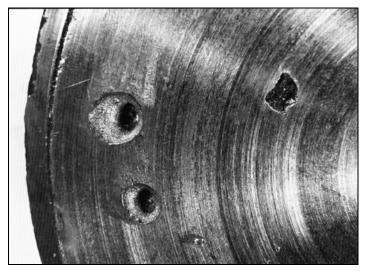
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This form of attack is extremely localized. It usually results in a cavity that has approximately the same dimensions in breadth and in depth. As the breadth increases, the depth increases, causing a hole through the wall of the casing. Pits have the following characteristics:



**A.** They are difficult to detect because they are often covered with corrosion products.

**B.** Pits usually grow in the direction of gravity. This is substantiated by the fact that they require a dense concentrated solution for continuing activity.

**C.** Pitting usually requires an extended initiation period before visible pits appear. This period ranges from months to years, depending on both the specific metal and the corrosive.

**D.** Pitting is autocatalytic. That is, the corrosion processes within a pit produce conditions which are both stimulating and necessary for the continuing activity of the pit.

**E.** Pitting is usually associated with stagnant conditions. For example, a type 304 SS pump would give good service handling sea water if run continuously, but would pit if shut down for extended periods of time.

**F.** Most pitting is associated with halide ions, such as chlorides, bromides, and hypochlorites. Fluorides and iodides have comparatively lesser pitting tendencies. Oxidizing metal ions, such as Cupric, Ferric, and Mercuric in combination with Chlorides are considered to be the most aggressive. Non-oxidizing metal ions such as Sodium Chlorides and Calcium Chlorides are much less aggressive. This type of corrosion differs from crevice corrosion in that it creates its own crevice. Materials that are susceptible to crevice corrosion do not necessarily become susceptible to pitting corrosion, whereas the reverse may be considered to be true.

### CASE HISTORY

ILLUSTRATING PITTING CORROSION

### Alloy: CF-3 (304L S.S.)

### Environment:

Hydrochloric and nitric acid mixtures. Temperature and concentration unknown.

### **Description:**

Several damage marks (caused during material handling) served as nucleating sites for an autocatalytic reaction to occur. This resulted in the pits shown.

#### Remedy:

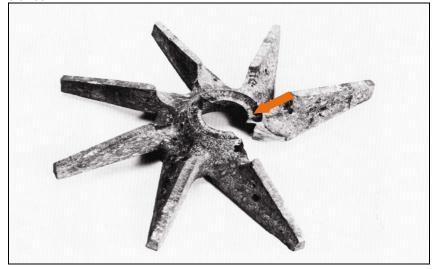
Use alloy with molybdenum such as CF3M (316L). Methods for combating Crevice Corrosion generally apply for pitting. The addition of Molybdenum of 2% or greater in stainless steels contribute greatly in increasing resistance to pitting.



## **CREVICE/DEPOSIT CORROSION**



This type of corrosion occurs in restricted areas, either metal to metal, (threaded drain plug), or metal to non-metal, (gasketed joints), where free access to the pumped fluid is restricted. It is aided by the presence of deposits such as sand, dirt, and carbonaceous material that shield and create a stagnant condition. In certain cases corrosion products will deposit and form a crevice.



As with pitting corrosion, an autocatalytic reaction fosters the growth of crevice corrosion. Thus, the initial driving force is often an oxygen or metal ion concentration cell, but continued growth by accumulation of acidic hydrolyzed salts within the crevice. The external surfaces are protected cathodically.

This kind of attack occurs in many media, though it is very common in chloridecontaining environments. It is slow to start, but grows at an ever-increasing rate. There are a number of actions that can be taken to prevent crevice corrosion:

A. Use of welded joints instead of threaded joints.

**B.** Weld on both sides of a flange to pipe joint, thus avoiding penetration from either side.

**C**. Ensuring that the pump is completely drained.

D. Use of gaskets that are non-absorbent, such as Teflon®, wherever possible.

**E.** Use of flushing in seal areas to avoid stagnant conditions in the bore of the stuffing box cover.

### CASE HISTORY ILLUSTRATING CREVICE CORROSION

### Alloy: LaBour R-55 (Ni-Cr-Mo-CU)

### **Environment:**

Dilute sulfuric acid with small amounts of hydrochloric acid and sodium chloride. Temperature and concentration unknown.

### **Description:**

The gasketed shielded area has limited diffusion of oxidizing ions, thus creating an imbalance and the initiation of corrosion. Note the pitting that is usually associated with this type of corrosion.

### Remedy:

a) Review gasket material and b) consider welding the joint between impeller and shaft



TABLE 1 – GALVANIC SERIES IN PURE SEA WATER

Corroded End (anodic, or least noble) Magnesium Magnesium Alloys

↓ Galvanized Steel or Galvanized Wrought Iron

Aluminum (5052, 3004, 3003, 1100, 6053 in this order) ↓

Cadmium

↓ Aluminum (2117, 2017, 2024 in this order)

> Mild Steel Wrought Iron Cast Iron

> > NI-RESIST\*

Type 410, Stainless Steel (active)

50-50 Lead Tin Solder

Type 304, Stainless Steel (active) Type 316, Stainless Steel (active)

> Lead Tin  $\downarrow$ Muntz Metal Manganese Bronze Naval Brass Nickel 200 (active) **INCONEL alloy 600 (active)** Yellow Brass Admiralty Brass **Aluminum Bronze** Red Brass Copper Silicon Bronze 70-30 Copper Nickel Comp. G-Bronze Comp. M-Bronze

Vickel 200 (passive)\* INCONEL 600 (passive)\*

MONEL400\*

Type 304, Stainless Steel (passive) Type 316, Stainless Steel (passive) INCOLOY alloy 825\* ↓ INCONEL alloy 625\* HASTELLOY C\*\*

Titanium Protected End (cathodic, or most noble)



A potential difference exists between two dissimilar metals when they are immersed in a corrosive and conductive solution. If these metals are now connected electrically and conductive on the outside, an electron flow is produced. One of the two metals will corrode faster than the other metal. The metal, which is corroding at a faster rate, becomes anodic, while the other metal is cathodic.

The most commonly used series, based on potential measurements and galvanic corrosion tests in unpolluted seawater is shown alongside. (Table 1)

A similar series is needed for all of the various situations. The number of tests required would be almost infinite. Thus the series should be used only for predicting galvanic relationships. The separation between the two metals or alloys in the series is an indication of the probable magnitude of corrosive effects. Effects such as polarization (potential shifts as the alloys tend to approach each other), area, distance and geometry play a definite role in galvanic corrosion.

There are several ways in which to combat galvanic corrosion:

**A.** Material selection is extremely important. Substitution of impellers of different alloys in an existing system must be done carefully. Care should be taken to avoid wide separation in the relevant galvanic series.

**B.** The liquid pumped may be controlled by the use of a corrosion inhibitor.

**C.** Barrier coatings and electrical isolation by means of insulators to break the electrical continuity are sometimes employed.

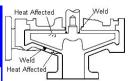
D. Cathodic protection by way of using sacrificial metals may be introduced.

**E.** Design changes involving the avoidance of the unfavorable area ratios, using bolts and other fasteners of a more noble metal than the material to be fastened, avoiding dissimilar metal crevices (as at threaded connections), and using replaceable sections with large corrosion allowances of the more active member.

<sup>\*</sup>International Nickel Company Trademark







## INTERGRANULAR CORROSION

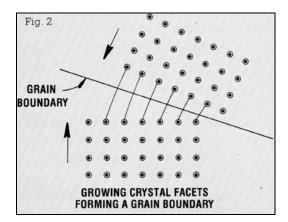
In a survey conducted by the *Material Technology Institute of the Chemical Process Industries*, it was shown that sensitization and resulting intergranular corrosion were the cause of over half of the reported incidents of unsatisfactory performance.

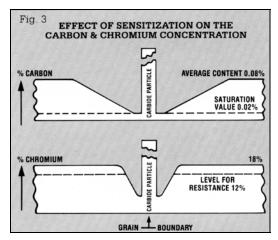
Metals and alloys consist of individually oriented crystals, which flow from the molten state (castings or weld metal). These crystals develop into specific atomic arrangements known as crystal structures (e.g. cubic, hexagonal etc.). These crystal structures can be manipulated by varying chemistry and heat treatment. Each type of atomic arrangement has specific physical and mechanical properties of its own. Two important arrangements in stainless steels are called "ferrite" and "austenite." During the solidification process, the development of facets indicative of their crystal structure is prevented when the growing crystals impinge on each other. Where the crystals come in contact with each other, their facets form a boundary that takes the form of a lattice. These boundaries have a much greater degree of structural imperfection than within the "grains." The resulting energy states at the boundaries can promote the concentration of alloying elements, and of metallic and non-metallic impurities, and of greatest importance - precipitates.

Sensitization may be referred to as carbide precipitation in the grain boundaries. The structure of low carbon austenitic stainless steels consists of three crystallographic phases: Ferrite, austenite and carbide under equilibrium condition. Rapid cooling of these steels will ensure the retention of austenite (a high temperature phase), but if they are heated to within a range of approximately 800°c to 1600°F for any appreciable length of time, the carbide will precipitate in the grain boundaries. The effect of sensitization on the chromium and carbon concentration is shown in Figure 3. The figure depicts a transient state only. Figure 2 shows the variation in carbon content in passing from one grain, through the grain boundary, to another grain. The chromium content varies in the manner shown in the lower portion of Figure 3. There is a narrow region at the grain boundary, which contains less than 12% chromium. This is below the 12% chromium minimum required for corrosion-resistance. *If there were no carbon present in the alloy, this condition would not be possible.* 

The sensitization of an austenitic alloy permits corrosive attack to start at the grain boundary, (lowest energy level), where there is a deficiency of *free chromium*. Since the grains (high energy level) are more resistant than the boundaries (low energy level), corrosion follows the boundaries, which is typical of intergranular corrosion.

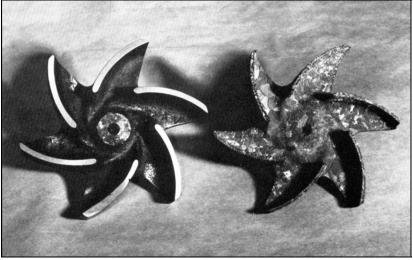
In translating this phenomenon to the macro-scale, the attack is first recognized as "ditching" along the grain boundaries, on the surface of the casting. As the attack progresses, it permeates the complete casting wall and results in leakage and possible grain dropping. It should be noted that cracking, however, does occur in austenitic alloys, and is mainly due to stress corrosion.



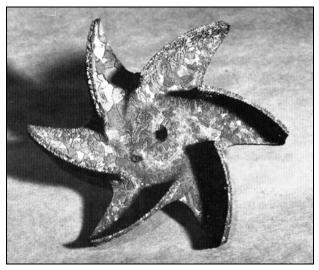




(a)



## (b)



In practice at the foundry level, it must be mentioned that sensitization will occur during slow cooling in the mold. Immediate cooling of castings from the mold has been tried. However, the hostility of this production step has limited its applicability. Quench cracks have been noted in stress concentration areas also. Sensitization is prevented by providing a solution anneal above the sensitizing range temperature.

# INTERGRANULAR CORROSION (a)

### Alloy: CW-12MW (LaBour Alloy Y-17)

CASE HISTORY ILLUSTRATING

### Environment:

25% Hydrochloric acid with 100 ppm Chlorine. Temperature: Ambient.

**a)** The impeller on the left was solution annealed and then put in service.

**b)** The impeller on the right is in the sensitized condition. This impeller has undergone severe corrosion with grain dropping occurring at the tip of the blades.

## CASE HISTORY ILLUSTRATING INTERGRANULAR CORROSION (b)

Alloy: CW-12MW (LaBour Alloy Y-17)

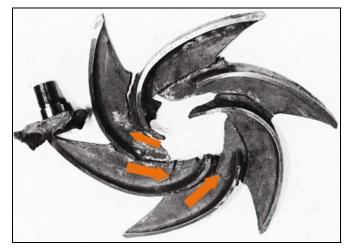
### Environment:

25% Hydrochloric acid with 100 ppm Chlorine. Temperature: Ambient. Close-up of the impeller on the right in **(a)** above.





## STRESS CORROSION CRACKING



Two characteristics are necessary for environment cracking to occur: a tensile stress and a corrosion reaction. There are several forms of environmental cracking such as stress corrosion cracking, hydrogen induced cracking, liquid metal cracking, and corrosion fatigue. Generally, cracks produced by this method are unexpected and sometimes are dangerous. They are often wrongly interpreted. For example, intergranular corrosion does not require a tensile stress, however, the morphology of the cracks may be very similar to stress corrosion cracking. Welding sometimes produces hot-short cracks which may be identified as stress corrosion cracking.

The stresses that exist in a given situation are usually very complex. The surface net stress in contact with the pumped fluid will be the controlling parameter. The cracks produced are perpendicular to the stress vector. These cracks may be single (as in corrosion fatigue), or multiple (as in stress corrosion cracking). They may be intergranular or transgranular.

Several of the parameters and the controlling methods used are discussed below:

A. Stress. For a given alloy and fluid, a threshold stress for cracking exists. In such instances, stresses below the threshold will not cause cracking, but as the stress is increased above the threshold, cracking is immediately evident. Lowering the residual and thermal stresses by heat treatment and shot peening is carried out to decrease the stress levels below the threshold. The latter generates compressive stresses in the material, which often offset the tensile stress necessary for cracking to occur. Compatibility of various materials in contact with respect to polarization of potentials along with geometrics that increase salt ion concentrations (like crevices) should be considered in detail.

B. Metallurgical: The list of specific environments that aid in stress corrosion cracking is different for each major alloy classification. For example, caustics being handled by a carbon steel, chlorides pumped by stainless steel pumps, and copper alloys in an ammonia environment. The most common method is to utilize another alloy that is not susceptible to this attack.

## CASE HISTORY ILLUSTRATING STRESS CORROSION CRACKING

Alloy: CF-3 (304L S.S.)

**Environment:** 

50% Caustic (sodium hydroxide) with trace amounts of sodium chlorides. Temperature 150°F

Description: A drastic brittle fracture in a ductile material in a period of four months.

Remedy: Use a different alloy type.

The importance of microstructure may be illustrated by placing:

1. A sensitized 316 SS material in a nitric acid solution. Stress corrosion cracking is noticed.

2. A solution-annealed 316 SS material in the same solution. This will not induce cracks.

C. The corrosive liquid in certain cases can be made less effective in causing stress corrosion cracking by the use of an inhibitor such as chromates in a caustic solution. Elimination of the critical chemicals from the liquid is probably the most desirable. A review of the entire system is usually necessary if this attack has been identified.

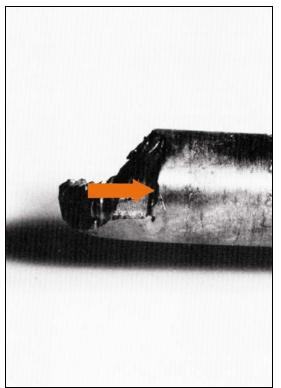
D. An increase in temperature generally has a detrimental effect, that is, it tends to induce stress corrosion cracking. If, however, the temperature is high enough to remove the critical chemicals, such as to cause total dehydration, then the tendency reduces.

E. Coatings and electro-chemical techniques are also used. The coatings normally act as a barrier between the metal and pumped fluid. Electro-chemical techniques are generally used to polarize an alloy to an oxidizing potential out of the range that will cause stress corrosion cracking.

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# CORROSION FATIGUE



This attack results from the cyclic tensile stress and corrosive fluid in contact. There is some mystery in this type of attack due to the fact that failure in this mode may occur in the absence of corrosive action. Most of the discussion in stress corrosion cracking is applicable to corrosion fatigue.

Pump shafts have often failed due to mechanical fatigue with no contribution by the corrosive. On the other hand, stress corrosion cracking under static tensile stress has also been known to occur. The phenomenon then covers a broad spectrum and is difficult to define clearly.

## CASE HISTORY ILLUSTRATING

### FATIGUE CORROSION

Alloy: AISI 316 S.S.

**Description:** A crack propagated at an inclusion present in the material after several months of operation.





The acids most generally used by industry are Sulfuric, Nitric, Phosphoric and Hydrochloric acids; and these cause some of the most severe corrosion problems. The widespread use of these acids places them in an important position with regard to costs and destruction by corrosion. In some cases, corrosion increases with the concentration of the acid, in others it decreases. Oxidizing and reducing mixtures of acids and salts also causes different reactions to different materials. Velocity and aeration are factors that must be taken into consideration. Finally, impurities in the system can cause severe problems.

## SULFURIC ACID

Selection of a metal for this service depends primarily on the reducing or oxidizing nature of the solutions. Below 85% at room temperature and about 65% up to 150°F the acid is reducing and is better handled by materials resistant to reducing conditions. In higher concentrations, the acid is oxidizing and materials resistant to oxidizing media are essential.

### **Cast Iron:**

Cast irons show good resistance in very strong sulfuric acids. In a number of instances, it is more economical to use cast irons, although the corrosion rates are higher. The resistance in these alloys is attributed to the graphite network interfering with the reaction between the acid and the metallic matrix. In oleum, however, the acid is known to penetrate the metal along the graphite flakes, and a little corrosion in these confined areas builds up enough pressure to split the iron. This wedging action is confined to cast irons and is not apparent in ductile iron, which may be satisfactory for oleum service.

### Types 304 and 316 Stainless Steels:

These stainless alloys are occasionally utilized for cold, very dilute sulfuric acid and under conditions that are not strongly reducing in nature.

### CN-7M (LaBour Elc. K):

This is a very widely used alloy for applications involving sulfuric acids. It provides resistance over the entire range of concentration, including oleum. The isocorrosion chart reveals the dip in the curve at around 60-80% concentration range at approximately 150°F. This will maintain the corrosion rate within 20 mils per year. If the pump, for example, is to be used intermittently, then the temperature limitations may be increased to 180°F. Ferric sulfate and copper sulfate in the acid act as inhibitors and

decrease attack. Ferric chloride and cupric chloride in appreciable concentrations are known to cause pitting.

### Ni-Cr-Mo-Cu (LaBour Alloy R55):

Ni-Cr-Mo-Cu is a nickel-chromium-molybdenum-copper alloy that shows outstanding resistance to sulfuric acid and many other media. It will withstand the corrosion of both oxidizing and reducing agents to moderately high temperatures (176°F). It is not recommended for halogen acids or halogen salt solutions in contact with the material. It costs more than CN-7M, but provides resistance over a wide range of oxidizing and reducing conditions. The 6% copper in the alloy is kept in solid solution, which is essential for sulfuric acid service. The Ni-Cr-Mo-Cu alloy has numerous advantages over CN-7M and is the most widely used LaBour alloy for sulfuric acid and most sulfur compounds, such as sulfur dioxide and hydrogen sulfide gases. The copper in these alloys does not discolor the product.

### CW-12MW & N-7M (LaBour Alloys Y-17 & Y-30):

Alloy CW-12MW is a nickel-chromium-molybdenum alloy that shows a great deal of thermal stability at high temperatures. It is useful over the entire concentration range and oxidizing conditions. The chromium content in the alloy provides excellent resistance to oxidizing conditions. This alloy is very suitable for chlorides, up to 220 ppm, at a maximum temperature of 156°F and over the entire concentration range.

Alloy N-7M on the other hand, is a nickelmolybdenum alloy. This alloy is also known to possess good corrosion resistance in the intermediate and strong concentration range of sulfuric acid. It is better suited to reducing conditions, and is particularly susceptible to oxidizing contaminants such as nitric acid, chlorine, cupric and ferric chlorides, ferric sulfates, and even aeration.

### NITRIC ACID

One of the most important ingredients for resistance to nitric acid is chromium. As the chromium content increases, the corrosion rate decreases. The minimum amount of chromium generally accepted is 18%. This makes the austenitic stainless



steels very well suited for practically all concentrations and temperatures. The addition of molybdenum to stainless steels, as in type 316, as opposed to 304, does not improve corrosion resistance to nitric acid.

### Types 304 and 316 Stainless Steels:

Type 304 stainless steel exhibits excellent resistance to nitric acid at room temperatures up to 86°F, and also to boiling acids up to 50% strength. The corrosion resistance decreases as the concentration and temperature are increased beyond 50% and 86°F. Type 304 does, however, show excellent resistance to red and white fuming nitric acids at room temperature.

Because of the susceptibility of sensitized type 304 (when exposed in the 800°F to 1600°F range) to intergranular attack in nitric acid, boiling 65% nitric acid (Huey test) is often used to detect the existence of this condition prior to fabrication. This is only an indicative test and is not a prediction of definite behavior.

Nitric acid, when mixed with sulfuric, phosphoric, or acetic acids, shows reduced corrosivity to stainless steels and CN-7M alloys. On the other hand, mixtures of nitric acid with hydrochloric or hydrofluoric acid are corrosive to stainless steels and their rates depend on concentration and temperatures.

### N-7M & CW-12MW (LaBour Alloys Y-30 & Y-17):

These alloys are not suited for nitric acid services as they are readily corroded.

### Ni-Cr-Mo-Cu (LaBour Alloy R55):

This alloy shows good resistance, but does not increase resistance sufficiently to justify the additional cost.

### CD4Mcu (LaBour Alloy 48):

This shows excellent resistance and is probably the only age-hardenable stainless type alloy that shows good resistance, even in the hardened condition.

### Titanium:

This alloy has outstanding resistance at all concentrations and at temperatures well above the atmospheric boiling points. It shows less than 5 mpy in 65% nitric acid at 350°F. It is an expensive material, but in some cases is the only material that will do the job. The presence of oxidizing ions in nitric acid tends to decrease the corrosion resistance of titanium - maybe its only drawback.

## PHOSPHORIC ACID

Phosphoric acid is obtained by the wet process, and used in the production of fertilizers. The acid obtained by the electric furnace process is purer in form and is used in the manufacture of soap, detergent, food, plasticisers and insecticides. Because of the impurities, such as sulfates, fluorides, and fluosilicates, present in acid made by the wet process, and the nearly pure acid from the electric furnace process, the corrosion behavior and alloy selection are based on the manufacturing process. Other variables include the concentration, temperature, aeration, etc.

In a number of studies, it has been found that the cupric and ferric ions in solution inhibit the corrosion of stainless steels in phosphoric acid. The cupric ion may be provided by the initial corrosion of an alloy such as CD4MCU or CN-7M. On the other hand, the addition of chloride or fluoride ions to the phosphoric acid, in effect, produces mixtures of phosphoric and hydrochloric or hydrofluoric acids, which increases the corrosion rates by breaking down the passive film.

There is some debate about stainless steels that have been affected by sensitizing processes: corroding intergranularly. Until there is more evidence, it would be prudent to use extra low carbon or stabilized alloys for severe services.

### CN-7M (LaBour Elc. K):

CN-7M is widely used in phosphoric acid service. Great care is taken to make sure that the castings are properly solution-annealed, especially after welding.

### Ni-Cr-Mo-Cu (LABour Alloy R55):

This is usefully resistant to all concentrations of phosphoric at temperatures up to 194°F.

### N-7M (LaBour Alloy Y-30):

This is excellent in hot concentrated pure phosphoric acid. However, copper ions (an impurity) behave somewhat differently in solution. Copper ions at first decrease the corrosion rate, but beyond about 10 ppm, they tend to increase the corrosion rate. If this alloy must be used, the copper content must be controlled to extremely low values.

### CD4Mcu (LaBour Alloy 48):

This alloy works very well at the same temperatures and concentrations as CN-7M, is less expensive and has the added advantage of handling abrasives better than CN-7M. Wrought materials used in conjunction with CD4MCU castings, such as shafts and piping, are now available.

### HYDROCHLORIC ACID

This is the most difficult of acids to handle from a standpoint of corrosion. Hydrochloric is corrosive to most common metals and alloys. Oxidizing agents and minor impurities such as ferric chloride (or cupric chloride) and nitric acid present a very rugged corrosive condition. Great care and good judgment is required to obtain a balance between service life and cost of the equipment.



### CW-12MW (LaBour Alloy Y-17):

This alloy shows good resistance to all concentrations of hydrochloric acid at room temperature and has been used successfully up to 120°F. Due to its high chromium content, it provides better resistance to oxidizing environments. It must be kept in mind, however, that dissolved oxygen is not strong enough to passivate the material.

### N-7M (LaBour Alloy Y-30):

This alloy is widely used to handle hydrochloric acid at all concentrations and temperatures up to the boiling point. Due to the absence of chromium in this alloy, its resistance to aeration and oxidizing impurities such as nitric acid or ferric chloride (when present even in small quantities) is often destructive.

### CF-8M & CN-7M (316SS and LaBour Elc. K):

The austenitic stainless steels, including CN-7M, are to be used only at very low concentrations at room temperature. Increasing the temperature decreases the critical concentrations at which the stainless steels start to corrode. Rapid corrosion occurs at pH 4 or 5 or below. Pickling solutions which are sometimes handled by these materials require inhibitors if the pump is to be handling the liquid on a continuous basis.

### Nickel and Nickel Irons:

Aeration affects these alloys to a great extent. They are generally not considered to be suitable for hydrochloric acid service because they are susceptible to influences other than the acid itself and must be used, with caution, only when specific conditions are definitely known.

### Zirconium:

This alloy is recommended for all concentrations at room temperature. The cost of this material must be justified with service life. As the temperature is increased, the critical concentration decreases. Zirconium is good up to 35% concentration and boiling point temperatures. Upwards of 35%, the temperature limit is 160°F (70°C).

### ACETIC ACID

Acetic acid is an intermediate chemical used in the production of cellulose acetate for paints and acetic anhydride for artificial fibers. Various processes are used to produce the acids, which include:

**A.** Acetaldehyde Process: The most widely used process; it has specific problems with regard to material selection due to catalyst carry-overs, formation of peroxides and acetic anhydride.

**B.** Butane Oxidation: In selection of materials of construction you must consider formation of peroxides, formic acid and other solvents which are typical of this process. The effect of contaminants is twofold:

**1.** Contaminants such as sulfur dioxide and sulfur trioxide increase the corrosion rate. Formic acid also increases the corrosion rate. This increased corrosivity can normally be tolerated by type 316 stainless steel.

2. The presence of aldehydes, ketones and esters in the process stream have been known to greatly reduce the corrosion rate. Acetic anhydride usually will increase the corrosive attack, especially when the acetic acid is at 100% concentration. In this instance, CN-7M is wellutilized. Chlorides in the stream have been known to cause stress corrosion cracking of the austenitic stainless steels: CW-12MW is usually recommended if this is the case. If there is a possibility of temperature increase, the low carbon grades such as 316L and 304L should be evaluated to prevent excessive corrosion and contamination of the acid. The iron contamination is greatly increased as the temperature and time of exposure is increased, especially in the case of 304. Ferroxyl testing of pumps servicing a meticulous grade of acetic acid is often done before shipment. Practice "A" of ASTM A262 (Oxalic Acid Etch), is often recommended as a qualification test to determine the sensitivity of the alloy to attack by an acetic acid environment.

CW-12MW and N-7M both provide excellent resistance to acetic acid at all concentrations and temperatures. These alloys are more expensive than type 316 stainless steel and CN-7M, thus a service life-cost justification should be done before LaBour Alloy Y-30 (N-7M) and Y-17 (CW-12MW) are utilized.

## CORROSION BY ALKALIS

Of all the available alkaline materials, caustic soda (sodium hydroxide) is the most widely used. It is produced along with chlorine by the electrolysis of sodium chloride. The type of electrolytic cell used for production determines the purity that is obtainable. Mercuric cells produce 50% grade caustic, whereas the diaphragm cells produce 9% to 15% grade caustic, which is further purified before sale. The major users of caustic soda are the chemical, pulp and paper, and aluminum industries.

Iron and steel are widely used at low temperatures (if iron contamination is not detrimental), whereas nickel and nickel alloys are used at higher temperatures. This is because iron and steel are susceptible to caustic

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embrittlement and high corrosion rates at the higher In concentrations above 75%, and including molten caustic soda, cast nickel does an excellent job. When temperatures above 600°F (316°C) are to be considered, the cast nickel pump castings should be solution-annealed to minimize the possibility of graphite precipitation at grain boundaries and a resultant loss in ductility.

Velocity and aeration have little effect, except at high temperatures such as above 1000°F. The thermal decomposition at 500°F (260°C) of impurities such as chlorates (present in caustic soda produced by the diaphragm cell method) increases the corrosion rate of cast nickel. In such instances, caustic soda produced by other methods should be utilized, or reducing agents such as sucrose or dextrim may be added to minimize corrosion and product contamination.

Oxidizable sulfur compounds also tend to increase the corrosion rate of cast nickel at elevated temperatures.

### Types 304 and 316 Stainless Steels:

The cast versions of austenitic stainless steels such as types 304 and 316 are used up to 10% concentration and up to the boiling point of caustic soda. However, at concentrations above 10% the critical temperature decreases. Chlorides in the process stream have been known to contribute to stress corrosion cracking of these temperatures.

alloys and consideration must be given to the stress and temperature limitations of these alloys.

### CN-7M (LaBour Elc. K):

Pumps made of this material have been used for handling caustic soda up to 50% and 250°F (120°C). Galvanic effects must be considered if this alloy is to be used with nickel and nickel based alloys.

### Ni-Cr-Mo-Cu (LaBour AlloyR55):

This alloy is used in similar situations to CN-7M. It provides better stress corrosion cracking resistance than CN-7M.

### CW-12MW & N-7M (LaBour Alloys Y-17 & Y-30):

The data available for these alloys is not sufficient to make any indicative statements. They have been used up to 50% at the boiling point.

### Type 2 Nickel Cast Iron (Ni-Resist):

Type 2 nickel cast iron and spheroidal nickel iron are both used where minimum contamination of the product by copper is desired. These alloys may be used up to 70% caustic soda concentrations. Stress relief of these alloys may help minimize stress corrosion cracking of these allovs.

## **CORROSION BY LIQUID METALS**

Heat-transfer characteristics of low boiling point metals make them particularly attractive for use in the power plant industries, as operating at higher temperatures increases the efficiency of a power plant. Water and steam require high-pressure equipment, which, besides beina hazardous, is also expensive. The liquid metals and fused salts employed are usually high thermal conductors. Due to their low melting points, they save a great deal in initial heat-up during the start-up of a power plant. In addition, they require lower pumping power due to their lower density. For example, mercury requires very high pumping power, whereas sodium requires low pumping power.

Liquid metals cause different types of corrosive attack. The most salient feature is the lack of electrochemical reactions. In the simplest type of attack, the solid metal dissolves in the liquid metal, resulting in uniform thinning or preferential leaching of a selective constituent from the solid metal. This dissolution may result in the formation of brittle alloy phases.

This kind of uniform thinning also occurs when solid metal may dissolve at a hot zone of a pump and precipitate on the walls of a cool zone, where its solubility is less.

Contact of dissimilar metals with the same liquid metal can cause transfer of one solid metal through the liquid metal

to the other solid metal. This causes rapid dissolution without saturation, leading to destruction.

Finally, impurities such as dissolved gases can change the solubility limits, the wetting tendencies, and the activity of the solid metal ions.

The surface area to volume ratio is of utmost importance. The greater the ratio, the lower is the corrosion rate. This is because the greater the liquid volume, the greater is the amount of solid metal that can be held in solution.

### Types 304 and 316 Stainless Steels:

These alloys may be used to pump sodium and sodiumpotassium alloys. They have a temperature limitation of 1000°F. If used intermittently, care should be taken to prevent carburisation by carbonaceous material. Both of these alloys can handle lithium, thallium, mercury, bismuth and bismuth-lead alloys up to various temperatures.

Grey cast iron: is also good for some of these liquid metals, such as Cadmium and Bi-Pb-Sn alloys.

Cast nickel: possesses the greatest resistance to stress cracking in lead, bismuth, tin, and their alloys. They do not undergo as many rupture failures, as do the nickel chromium steels.

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## **ALLOY DESIGNATION & NOMINAL COMPOSITION**

METAL	DESIGNATIONS				MINIMUM/MAXIMUM CHEMICAL COMPOSITIONS									
	ASTM	ACI	AISI	UNS	Cr	Ni	Mo	Cu	Si	Mn	c	S	Р	Fe
A-48	A296/A351 (CD4 MCu)	CD4 MCu	None	None	24.5/26.5	4.75/6.0	1.75/2.25	2.75/3.25	1.0 (max)	1.0 (max)	0.04 (max)	0.04 (max)	0.04 (max)	(bal)
ELCOMET "K"	A296/A351 (CN-7M)	CN-7M	F/A 20	J9150	19.0/22.0	27.5/30.5	2.0/3.0	3.0/4.0	1.5 (max)	1.5 (max)	0.07 (max)	0.04 (max)	0.04 (max)	(bal)
304	A296/A351 (CF-8)	CF-8	304	J92600	18.0/21.0	8.0/11.0			2.0 (max)	1.5 (max)	0.08 (max)	0.04 (max)	0.04 (max)	(bal)
304 ELC	A296/A351 (CF-3)	CF-3	304L	J92500	17.0/21.0	8.0/12.0			2.0 (max)	1.5 (max)	0.03 (max)	0.04 (max)	0.04 (max)	(bal)
316	A296/A351 (CF-8M)	CF-8M	316	J92900	18.0/21.0	9.0/12.0	2.0/3.0		2.0 (max)	1.5 (max)	0.08 (max)	0.04 (max)	0.04 (max)	(bal)
316 ELC	A296/A351 (CF-3M)	CF-3M	316L	J92800	17.0/21.0	9.0/13.0	2.0/3.0		1.5 (max)	1.5 (max)	0.03 (max)	0.04 (max)	0.04 (max)	(bal)
CAST STEEL	A216-53T (WCB)	WCB	Carbon Steel	J03002	0.4 (max)	0.5 (max)	0.25 (max)	0.5 (max)	0.6 (max)	1.0 (max)	0.3 (max)	0.045 (max)	0.04 (max)	(bal)
R-55	None	None	None	None	21.0/24.0	50.0/55.0	5.5/6.5	5.5/6.5	3.5/4.5	0.6/0.9	0.15 (max)	0.04 (max)	0.04 (max)	5.0 (max)
NICKEL	A296 (CZ-100)	CZ-100	Nickel 200	None		(bal)	-	1.25 (max)	2.0 (max)	1.5 (max)	1.0 (max)	0.03 (max)	0.03 (max)	3.0 (max)
Y-30	A494 (N-12M-2)	N-12M	Hastelloy (B)	N10002	1.0 (max)	(bal)	30.0/33.0		1.0 (max)	1.0 (max)	0.07 (max)	0.03 (max)	0.04 (max)	3.0 (max)
Y-17	A494 (CW-12M-2)	CW-12M	Hastelloy (C)	N10001	17.0/20.0	(bal)	17.0/20.0		1.0 (max)	1.0 (max)	0.07 (max)	0.03 (max)	0.04 (max)	3.0 (max)
MONEL	A296 (M-35)	M-35	MONEL (K/400)	None		(bal)		26.0/33.0	2.0 (max)	1.5 (max)	0.35 (max)	.03 (max)	0.03 (max)	3.5 (max)
NI-#2	A436/720 (Type 2)	None	None	F41002	1.5/2.5	18.0/22.0		0.5 (max)	1.0/2.8	0.5/1.5	3.0 (max)	0.12 (max)	0.04 (max)	(bal)
CAST IRON	A278-75 (CLASS 40)	None	None	None	COMPOSITION BY MUTUAL AGREEMENT									
DUCTILE IRON	A395/A445	65-45-12	None	F33100	COMPOSITION BY MUTUAL AGREEMENT									
SILICON BRZ	B271-73/B584-73/B198-12A	None	None	C87200				(bal)	3.0/4.0	1.0/2.0				
TITANIUM	B367 (C-3)	C-3	Titanium	R50550	N 0.05 (max)/H 0.01 (max)/O 0.35 (max)/C 0.1 (max)/Fe 0.3 (max)									
TITANIUM/Pd	B367 (C-8A)	C-8A	Titanium/Pd	R52550	N 0.05 (max) H 0.01 (max)/O 0.35 (max)/C 0.1 (max)/Fe 0.3 (max)/Pd 0.12 (min)									

Notes:

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- 2. Registered trademark of International Nickel Company.
- 3. Registered trademark of Haynes International.
- 4. Registered trademark of Huntington Alloys.
- 5. Gases are present due to vacuum process required in the production of Titanium and Titanium Pb.

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P.O. Box 7026 Indianapolis, IN 46207-7026 Phone: (317) 924-7384 Fax: (317) 924-7388

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