

# Corrosion at Elevated Temperatures

A comprehensive and thorough review of one of the chemical processing industry's most pervasive failure problems, corrosive attacks at temperatures generally above 1,000° F.

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High temperatures accelerate corrosion reactions, and normally innocuous gases, liquids and solids—air, for example—can become aggressive to metals and cause serious wastage. Generally speaking, such corrosion occurs at temperatures above 1000°F, but there are one or two cases included in this article where a high-temperature form of attack persists below the 1000°F breakpoint.

Corrosive agents at elevated temperatures may be divided for convenience into two groups, gaseous and liquid. The liquids in turn may be subdivided into two further groups, liquid metals and molten salts. Their corrosive effects will be discussed under these several headings.

## Almost all gases are corrosive at high temperatures

With the exception of the inert gases such as helium and argon, all permanent gases, including elements and compounds, can be corrosive to most metals if the temperature is high enough. For example, carbon steel is attacked by H<sub>2</sub>S above 500°F, by oxygen (or air) above 1000°F, and by nitrogen above 1800°F.

The reactions important in petroleum and petrochemical operations are with: oxygen (oxidation and decarburization); nitrogen (nitriding); gases containing carbon (carburization); hydrogen (hydrogen attack); and gases containing sulfur (H<sub>2</sub>S attack, sulfidation). Other gases such as fluorine and chlorine may be even more corrosive, but they are much less commonly encountered and will not be considered here.

**Oxidation.** For high temperature services, the first criterion is that the material be resistant to oxidation, or that oxidation will not occur at a rate which will cause failure. The oxidation potential of atmospheres varies with the composition of the gases contacting the metal and temperature. As temperatures go higher, more alloy is needed to resist oxidation. The temperatures shown in Table 1 have been defined as the "maximum temperatures without excessive scaling" (1, 2) in oxidizing atmospheres for the indicated alloys.

These temperatures would normally be limiting in air, steam, and carbon dioxide. Chlorine or sulfur compounds and other impurities can lower the resistance to oxidation. Oxidation resistance is directly related to the chromium content and depends on the formation and maintenance of

a chromium containing oxide surface layer. Impurities in the atmosphere can interfere with the continuity of the protective layer.

At lower temperatures and with few thermal cycles, the rate of growth of the oxide layer is parabolic; that is to say, it varies with the square root of time, and eventually it may cease to grow any thicker. At higher temperatures (above the limits shown in Table 1), the oxide layer ceases to be protective in this way.

The volume of oxide formed is greater than the volume of metal from which it forms. The growth of higher volume oxides leaves them in compression on the surface. The compressive stress can be enough to cause fracture of the oxide film and thus allow fresh metal to be exposed and oxidized. Thermal cycling, similarly, can cause local fractures of the oxide film, allowing faster oxidation. In addition, the film becomes detached from the metal surface, so that the rate of oxidation becomes linear, and the attack is no longer self-limiting.

**Catastrophic oxidation and burning.** The term "catastrophic oxidation" is used for the very rapid corrosion of molybdenum-bearing alloys in stagnant atmospheres. This

Table 1. Temperature limits for oxidation

Nominal Alloy Composition	Type	Maximum Temp. °F
1 Cr — 1/2 Mo . . . . .	—	1050 . . . . .
2-1/4 Cr — 1 Mo . . . . .	—	1075 . . . . .
3 Cr — 1 Mo . . . . .	—	1100 . . . . .
5 Cr — 1/2 Mo . . . . .	502	1150 . . . . .
9 Cr . . . . .	—	1200 . . . . .
12 Cr — Al . . . . .	405	1500 . . . . .
12 Cr . . . . .	410	1300 . . . . .
17 Cr . . . . .	440	1400 . . . . .
17 Cr . . . . .	430	1550 . . . . .
27 Cr . . . . .	446	2000 . . . . .
18 Cr — 8 Ni . . . . .	302	1650 . . . . .
18 Cr — 8 Ni . . . . .	303	1600 . . . . .
18 Cr — 8 Ni . . . . .	304	1650 . . . . .
25 Cr — 12 Ni . . . . .	309	1900 . . . . .
25 Cr — 20 Ni . . . . .	310	2000 . . . . .
18 Cr — 12 Ni + Mo . . . . .	316	1650 . . . . .
18 Cr — 8 Ni + Ti . . . . .	321	1650 . . . . .
18 Cr — 8 Ni + Cb . . . . .	347	1650 . . . . .

type of attack is, however, associated with melting of the oxide film. It is therefore discussed later under *Molten salt corrosion*.

In pure oxygen at elevated pressure, cast iron and steel will burn if heated to a sufficiently high temperature. This is a problem with oxygen compressors, where oil cannot be used as a lubricant and where friction sometimes raises the temperature locally to the ignition point. The resulting fire is to some degree self-sustaining and can cause severe damage.

Oxidation failures are generally a result of overheating. The criterion for failure is the loss of wall thickness to the point where the sound metal remaining is not enough to carry the load. The thickness of scale is many times greater than the thickness of metal loss. The sound metal thickness is measured by ultrasonic test to determine metal loss and rate of oxidation. In many cases, the extent of scaling and its appearance are an indication of the location of maximum temperature.

Metal loss by oxidation can be minimized by controlling temperature and burner adjustments to the recommended conditions. Avoid temperature cycling, which can cause the scale to crack and spall.

*Decarburization* is the reverse of carburization. An oxidizing gas removes carbon from the steel at the surface. More carbon diffuses outward as the surface carbon is removed. The rate of diffusion and carbon removal increase with temperature. The carbon is removed by combining with oxygen, carbon dioxide, or water vapor. The loss of carbon from the steel will improve corrosion resistance, ductility, and impact strength in the decarburized material providing fissures and voids are not formed. Most steel mill

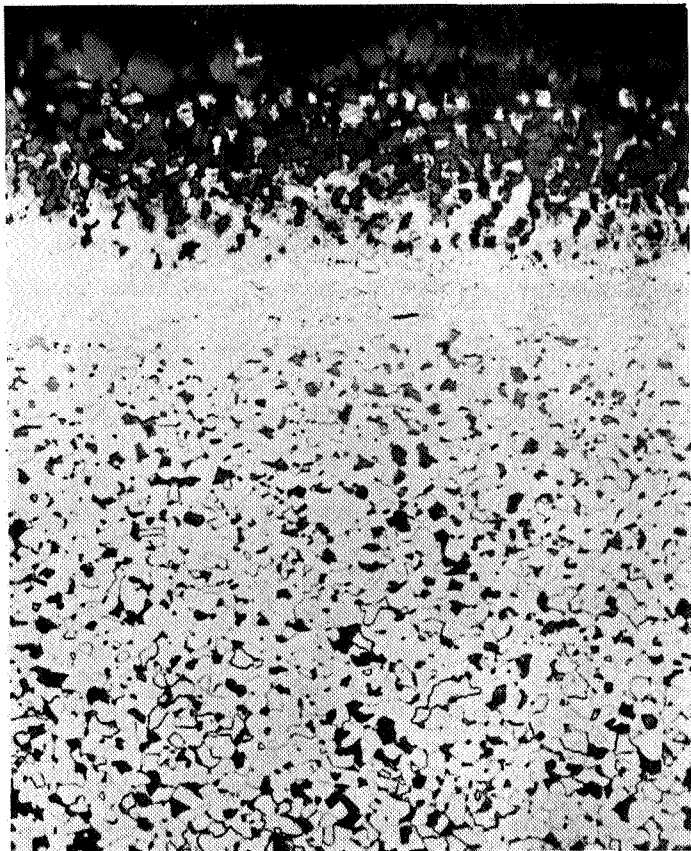


Figure 1. Decarburization and oxidation. Carbon — 1/2 molybdenum (100X).

hot-rolled products have decarburized surfaces. Decarburization by itself has not caused failures. It is of more interest when combined with carburization or when gaseous atmospheres cycle from oxidizing to reducing, which causes cycles of carburization and decarburization. See Figure 1.

Steel may also be decarburized by hydrogen attack (to be discussed later). In this instance, the carbon is converted to methane ( $\text{CH}_4$ ), and the attack is not necessarily confined to the surface.

*Nitriding* is a process in which atomic, or dissociated, nitrogen combines with components of the alloy to form intermetallic compounds called nitrides. The source of atomic nitrogen can be dissociated nitrogen from the air, nitrogen from dissociated ammonia, or as a component of the feed, either as a gas or an ammonia containing compound.

Nitriding occurs at temperatures from 800°F up to the melting point. Alloys which contain chromium, molybdenum, aluminum, and vanadium are most easily nitrided. High nickel alloys, such as Inconel, are more resistant to nitriding since nickel nitride does not form. Carbon steels, low-alloy steels, stainless steels, and heat resistant alloys such as HK 40 are all susceptible to nitriding.

The rate of nitriding will be less from exposure to nitrogen in the atmosphere than it will be for exposure to dissociating ammonia or other nitrogen containing compounds. For most materials nitriding from the nitrogen in the atmosphere does not occur below 1800°F, because the rate of dissociation is low. The nitrided structure is hard and brittle. In austenitic stainless steel its presence can be detected by a magnet. Nitrided stainless steel has a dull grey color and, because the nitrogen has combined with the chromium, nitrided stainless steel will rust in the atmosphere.

The nitrided layer will have increased in volume and will be in compression. For example, austenitic stainless steel tubes, 0.368 in. O.D. x 0.034 in. wall, nitrided to a depth of 0.0125 in. on the inside surface and to a depth of 0.0021 in. on the outside surface. The compressive stress from the greater thickness on the inner wall and the volume change causes a diameter growth of 0.003 in. See Figure 2.

The depth and rate of nitriding is significant for thin parts such as wire mesh where the nitride layer can penetrate all the way through, making it extremely brittle. Completely nitrided stainless steel behaves like a ceramic and cannot resist mechanical or thermal stresses.

Most of the information about nitriding has been developed in connection with the processes in which nitriding is applied to steels intentionally to produce a hard, wear-resistant surface. It is advantageous for parts such as gear teeth where the compressive stress at the nitrided surface gives added fatigue resistance as well as the wear resistance of nitrides. These heat-treating processes are intended to produce a hard, wear-resistant case in as short a time as possible. Nitriding temperature is between 925° and 1050°F. Higher temperatures produce shallower depths of nitrided case.

In ammonia converter service, the amount of nitriding found is spotty, depending on the temperature and location in the converter. Austenitic stainless steel ammonia con-

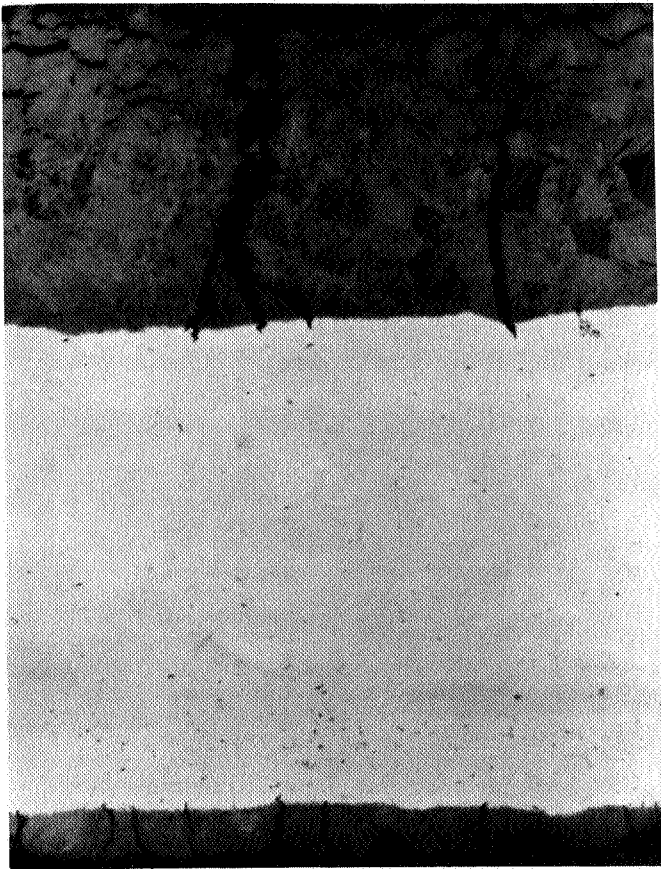


Figure 2. Nitriding. Type 304 stainless steel (100X).

verter baskets operating at 800°-900°F have shown the following thickness of nitrided layer: 2 yr., 0.001-0.007 in.; 2 yr., 0.00375 in.; and 3 yr., 0.005 in.

Austenitic stainless steel internals from the same baskets were nitrided to a depth of 0.020 to 0.025 in. The nitrided case is very brittle and can cause difficulties in welding if it is not removed by grinding, but the depths in the case reported would have no significant effect on the basket integrity. There is some indication that the rate of penetration of nitriding of austenitic stainless steels slows down after the initial penetration, as would be expected in a diffusion-controlled process. Van Grieken (3) reported that the rate of nitriding at 1022°F slowed down after the first year and that 25-20 alloy nitrided at a much lesser rate than 18-8.

Nitriding has also been found on the outside surface of centrifugally cast 25 Cr-20 Ni, furnace tubes which operate at 1700°-2000°F. These are isolated nitride needles with no significant depth. The nitrogen from the furnace products of combustion can form stable nitrides on exposed surfaces at high temperatures, but at a very slow rate. Fractured surfaces, which exhibit a high surface activity will show nitriding as isolated needles of nitrides where adjacent "as-cast" surfaces will not. Where carbides are exposed to the nitrogen-containing atmosphere, nitrogen can replace part of the carbon, forming carbo-nitrides.

So far, no difficulties with nitrided HK-40 tubes have been reported, either from external or internal nitriding. In one instance, a tube which had been in service with a high-nitrogen (9% N<sub>2</sub>) natural gas feedstock was examined

after two years service. Carburization oxidation attack to a depth of 0.080-0.120 in. was found, but there was no nitriding either at or near the inside surface.

*Carburization* is the diffusion of carbon into a metal and the formation of metallic carbides within the structure of the metal. Carburization can occur at temperatures as low as 950°F over a long period of time, and it accelerates with higher temperatures. All the carbon, low-alloy, and austenitic steels can be carburized. The source of carbon can be products of combustion, the feed through the system, or contamination of the metal surfaces by oils or other carbonaceous materials.

A carburized case, like nitriding, is purposely formed on gears, shafts and other wearing parts. The carburized case in these "case hardened" parts is hard and wear-resistant, and if it is not properly heat-treated it is brittle. The commercial processes for carburizing use carbon monoxide and methane from cracked gases and oils, molten cyanide salts, where a combination of carburized and nitrided cases is produced, or solid carbonaceous pack carburizing material which generates carbon monoxide. These processes take place between 1500°F and 2000°F. In pack carburizing, the carbon monoxide reacts on the surface of the steel to form carbon dioxide and nascent carbon which diffuses into the steel. The carbon dioxide reacts with the carbonaceous pack carburizing compound to form carbon monoxide and the process continues.

Molten salts will accelerate carburization in an otherwise inert system by removing the protective oxide film. Methane, carbon monoxide, and coke all are common to petroleum refinery and chemical plant operations, and therefore parts operating at high temperature are quite often subject to carburization. Contamination of new parts by oil or preservatives can cause carburization as the parts are heated.

For refinery and petrochemical services the following effects of carburization are important:

1. The carburized area will be hard and brittle at ambient temperatures.
2. The additional carbon will provide higher strength.
3. The carburized zone will increase in volume.
4. The co-efficient of thermal expansion of carburized material will be less than that of the base material.
5. Carburized material will be less corrosion resistant, because the carbon will combine with the protective chromium. (See Figure 3.) The protective value of the chromium will be lost and the chromium carbides will be more easily oxidized.

Where the attack occurs at lower temperatures the carburized case is adherent and the outward appearance of the material is unchanged.

Carburizing can be detected by metallographic examination or by chemical analysis. In carbon and low-alloy steels, carburization can be found by hardness testing, and in austenitic stainless steels it may also be detected by a magnet. Brinell testing can be misleading because the depth of the Brinell impression is usually greater than the depth of carburization. Diamond indenters at two different loads can detect carburization. If the shallow impression shows a **much higher** hardness than the deep one and if it is above

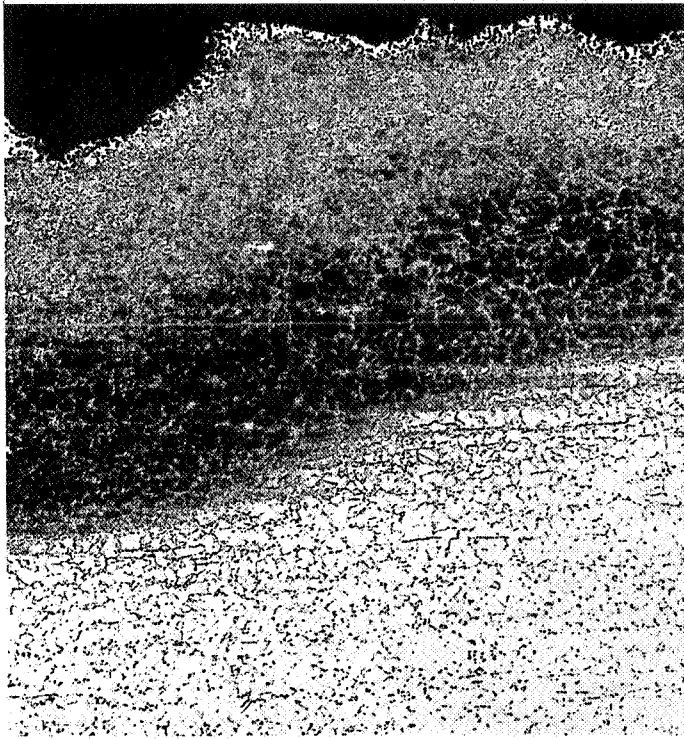


Figure 3. Carburization. Type 304 stainless steel (100X). 1100 to 1200° F. for 19,000 hr.

the equivalent of 300 Brinell, carburization can be present.

In austenitic stainless steels, unexpected atmospheric corrosion can be an indicator of carburization. If carburization has proceeded far enough to combine with sufficient chromium, the steel is no longer austenitic and carburization can be detected by the presence of magnetism.

Carburization can cause failures if the hard brittle layer is stressed in bending or tension. It can be responsible for accelerated oxidation or sulfur attack, because it combines with the protective chromium. The chromium carbides can be more easily attacked by sulfur or oxygen at elevated temperatures. The chromium depleted matrix also has less resistance to oxidation and sulfidation. If it proceeds far enough, the difference in volume and thermal expansion and the consequent residual and cyclic stress can cause spalling or fracture.

Ethylene pyrolysis tubes are subject to carburizing fluids internally at elevated temperatures, both in operation and during decoking. Tube failures occur because of the brittleness of the carburized material. In time, carburization proceeds all the way through the wall thickness and stresses accompanying the decoking operation cause brittle failures. The carburization is spotty and the internal surfaces can spall and pit as the brittle carburized layer flakes off.

Centrifugally cast tubes are now frequently used in ethylene furnaces, and the alloy composition has some effect on the rate of carburization. Mueller (4) quotes results of a 200-hr. test in ethylene furnace conditions (see Table 2).

The nature of the "special additions" is not disclosed, but it is known that columbium and tungsten improve carburization resistance. Proprietary alloys with such additions are available. Internal machining or honing of centrifugally cast tubes improves the resistance to the initial attack by carbon.

Except for ethylene pyrolysis service, it is rare that

Table 2. Results of 200-hr. test in ethylene furnace conditions

Alloy	Oxidation		Carburization	
	mm.	in.	mm.	in.
25 Cr - 20 Ni . . . .	0.20 . . .	0.008 . . . . .	0.80 . . .	0.032
25 Cr - 35 Ni . . . .	0.20 . . .	0.008 . . . . .	0.75 . . .	0.030
30 Cr - 30 Ni . . . .	0.10 . . .	0.004 . . . . .	0.65 . . .	0.026

(with special additions)

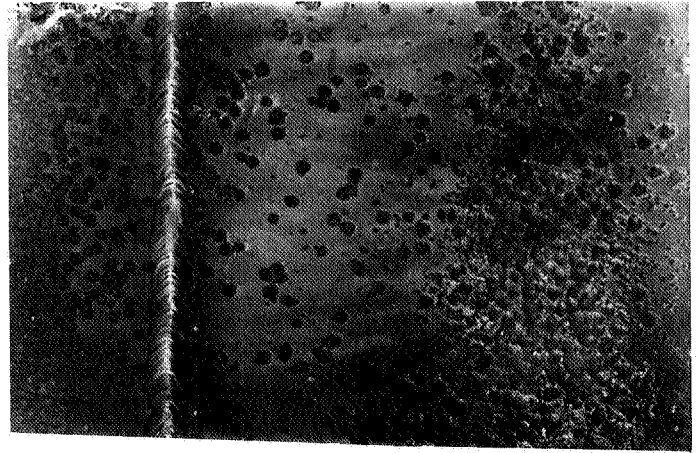


Figure 4. Metal dusting. Type 310 stainless steel.

carburization by itself will cause failures. Many items of equipment which have been carburized in service are in successful use today.

*Accelerated carburization: "metal dusting".* Metal dusting is a form of high-temperature deterioration in which the metal is penetrated rapidly over isolated areas in the form of pits, generally with an eroded or washed appearance. The pits contain a dust of loose powdery corrosion product of graphite, metal carbides and oxides. The dust is magnetic. Metal dusting occurs in atmospheres containing carbon monoxide, and generally hydrogen, at temperatures in the range of 800°F-1800°F.

The pits are severely carburized, and carburization appears to be the active reaction in producing dusting. The attack is more pronounced in high chromium alloys and

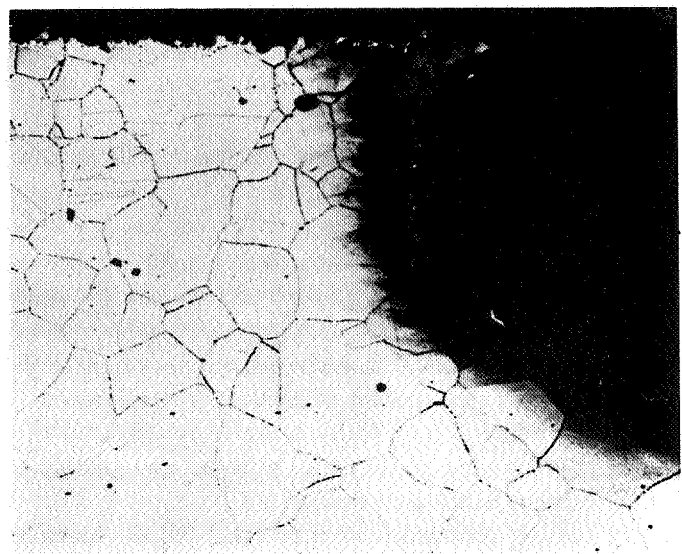


Figure 5. Metal dusting. Type 310 stainless steel (250X).

austenitic stainless steel, because the pits are usually isolated and unconnected, while the low alloy steels are more uniformly attacked. (See Figures 4 and 5.)

Trace amounts of sulfur and/or the addition of steam will inhibit the attack by metal dusting (5). The reaction is temperature and composition sensitive. Changes in process which cause only slight changes in gas composition can start or stop metal dusting. Changing metal temperature likewise can start or stop metal dusting in border-line conditions. Cold work, alloy and impurity content will also affect susceptibility, so that a change in alloy may prevent metal dusting in border-line conditions. Usually (but not in all cases) higher nickel alloys are more susceptible to metal dusting, so that if a lower nickel alloy will withstand the process conditions it may be worth trying; 27% Cr steel is resistant to this type of attack, but has other deficiencies such as embrittlement by sigma phase formation.

Happily, the occurrence of metal dusting is rare. Where it does occur, a review of operating history and metal temperatures may indicate the cause and the probable cure.

*Carburization/oxidation attack: "green rot"*. This is a description of the appearance rather than the mechanism by which corrosion occurs. It was noted first in nickel-chromium alloys, such as Nichrome, which are used for electric resistance-heating elements and heat-treating furnace fixtures. It occurs in atmospheres which are oxidizing to chromium and reducing to nickel. The green chromium oxide is found on the fracture surface and the unoxidized nickel or nickel-iron alloy which remains is magnetic. It can occur between 1200°F and 2100°F, but is normally encountered between 1650°F and 1800°F. Because it is sensitive to gas ratios in the environment, slight changes in process or firing conditions can cause it or can cure it. Green rot can occur in hydrogen if the dewpoint is not low enough.

Generally more oxidizing atmospheres will prevent and more reducing atmosphere will cause a borderline atmosphere to selectively oxidize chromium and reduce nickel. The presence of sulfur in the atmosphere reduces the rate of attack.

A different alloy composition or one higher in iron content can also prevent this type of oxidation. Metallographic examination is usually necessary to verify that green rot has occurred, because other green corrosion products of high alloy materials may be similar.

Carburization-oxidation is found in the bore of HK 40 steam/methane reformer tubes after service. Normally this proceeds to a shallow depth and then stops or slows down. In some cases, however, it proceeds at an accelerated rate due possibly to a film breakdown mechanism. This type of attack will be discussed later.

*Hydrogen attack*. The best documented and most predictable type of high temperature corrosion is hydrogen attack. The Nelson Chart, now published as API Publication 941 (6), contains in chart form the failures and some of the successes in hydrogen service at elevated temperatures. To review, atomic hydrogen will diffuse into steel and combine with the carbon to form methane. The methane molecule will occupy a large volume causing fissures and bursts within the steel. The rate of diffusion and of hydrogen

attack is proportional to the temperature and to the partial pressure of hydrogen.

Resistance to hydrogen attack depends upon the presence of alloying elements which form stable carbides, such as chromium, molybdenum, tungsten, columbium, titanium, or vanadium. These carbides resist reduction by hydrogen. The higher the pressure and temperature, the more alloy is required, but if sufficient alloying element is present, as in the austenitic chromium-nickel steels, the metal is resistant to hydrogen attack for any useable combination of temperature and pressure. The Nelson Chart defines the temperature and pressure at which attack of carbon and alloy steels will occur.

Hydrogen attack will be evident as decarburization and as cracks and fissures which can be detected by magnetic particle testing, ultrasonic testing, or in the early stages by microscopic examination. (See Figure 6.)

There is no time dimension on the Nelson Chart, but supplements to it in the API Publication show the time necessary for attack to begin for several materials. The means to avoid hydrogen attack are straightforward. Define the temperature and hydrogen partial pressure and select a material according to the Nelson Chart. Cladding a carbon steel will not protect it against hydrogen attack. Hydrogen will diffuse through the alloy cladding and attack the base material, if the base material is not resistant to hydrogen attack.

*Sulfur attack*. The most common form of elevated temperature sulfidation in refinery operation occurs in catalytic desulfurizers. Above about 500°F a combination of hydrogen and hydrogen sulfide will attack carbon and chromium alloy steels at a relatively high rate. A loose, non-protective scale is formed which may contaminate catalyst beds or block downstream equipment. Charts are available showing the corrosion rate to be expected as a function of the mol% H<sub>2</sub>S in the gas and the temperature (7, 8) it will be seen that although the austenitic chromium-nickel steels have a good resistance to H<sub>2</sub>S, they may be attacked at a significant rate at higher temperatures.

Damage by H<sub>2</sub>S attack is avoided by selecting austenitic chromium-nickel steel where indicated by the charts, and by providing additional corrosion allowance if necessary; 12% or 17% Cr steels are sometimes used for H<sub>2</sub>S service (particularly if there is a fear of stress corrosion cracking by chlorides), but usually their resistance to H<sub>2</sub>S is only mar-

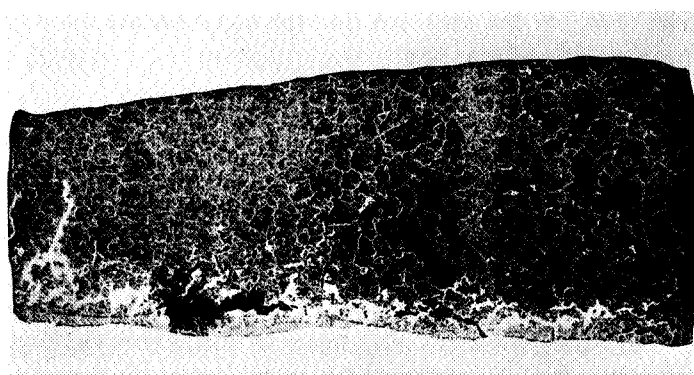


Figure 6. Hydrogen attack. A-105 carbon steel forging (10X).

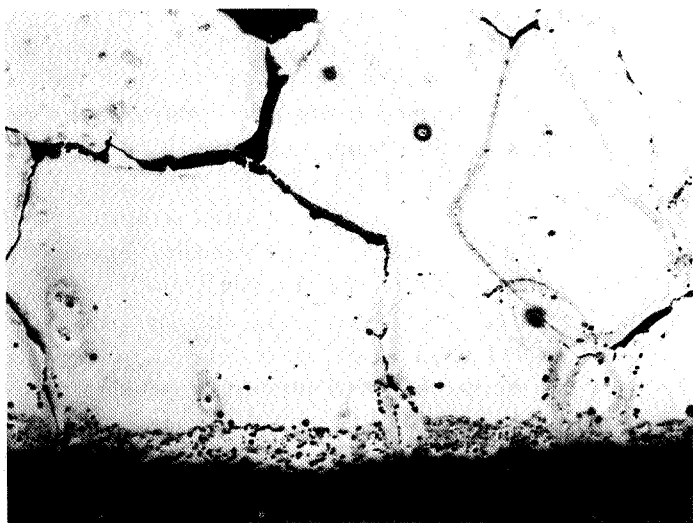


Figure 7. Sulfur attack. Pure nickel (100X).

ginally better than low alloy steel. Aluminized (aluminum-coated and diffused) steel is resistant to  $H_2S$  but has only been used on a limited scale because of concern about the integrity of the coating.

Attack by sulfur and sulfide compounds under oxidizing conditions, where  $SO_2$  is the corrodent, is similar to the attack by oxygen and steam. The same relative resistance as described under oxidation applies. The sulfide scale is not as adherent and protective as oxide scale and it will be more sensitive to cyclic service. Similar to oxidation resistance, the higher the chromium content the greater the sulfidation resistance.

The corroding sulfur, from fuel or feed or contaminants, will combine with chromium, iron, and nickel, and it can be detected by analyzing for sulfur in the scale and in the grain boundaries. (See Figure 7.)

Pure nickel and the high-nickel alloys such as Inconel 600 and the nickel alloy welding materials for Incoloy 800 are susceptible to attack by small quantities of sulfur in fuel or in feed. Sulfur as an impurity in paint or oil can also cause attack of nickel and high nickel alloys, if they are heated. In one case, welding slag left on a nickel alloy weld metal acted as a solvent and concentrator of sulfur in a furnace fuel. It absorbed and concentrated sulfur from products of combustion causing attack of the nickel alloy weld metal. (9)

Sulfur in fuels at concentrations as high as 2% has not caused attack as long as the atmosphere remained oxidizing. If there are other salts present, corrosive sulfur compounds can form, or the salts can flux the metal surface allowing accelerated sulfur attack.

#### Liquid corrosion results from several types

**Liquid metal attack.** Alloys used for handling liquid metals are subject to unique forms of mass transfer attack which are not considered here, because liquid metals are not normally handled in petroleum or petrochemical operations.

High alloy materials are subject to dissolution and intergranular attack by metals which are molten at the operating temperature. Aluminum, lead and zinc are common metals which should not be allowed near high temperature alloys.

One instance of attack of alloy steel furnace tubes has been reported as resulting from the inspiration of aluminum from aluminum spray painting near the furnace. Although it is not recommended, there have been many cases where aluminum paint on high temperature alloys has not caused attack at temperatures in the  $1000^\circ$  to  $1500^\circ F$  range. In these cases, the protective oxide on the high temperature alloy has not been penetrated by the aluminum which is held in the paint binder until the binder burns off.

Another potential source of low melting metal is the protective zinc-rich paint commonly used on structural steel. This paint should not be allowed on any high temperature material.

Liquid metal attack is usually intergranular and can be accompanied by increased oxidation if lead or zinc is present. Chemical analysis, metallographic and visual examination can detect the source of attack.

**Corrosion under molten salts.** Corrosion reactions such as oxidation or sulfidation may be accelerated if a molten salt or oxide is present on the metal surface. The salt or oxide reacts with and dissolves the normally protective solid oxide film. Oxygen, sulfur or other corrosive elements present in the molten salt may then attack the metal directly, and the product of the reaction is dissolved as fast as it is formed. If the metal becomes saturated with oxide or sulfide, the reaction will slow down, but if this does not occur the attack will proceed rapidly. In the case of oxidation, such rapid attack is sometimes termed "catastrophic oxidation."

**Catastrophic oxidation.** One of the earliest examples of catastrophic attack was that caused by ash from burning residual fuel oil. (10) Residual oil from Venezuelan and Mid-East crudes contains compounds of vanadium, sodium, and sulfur. When these oils are burned, the ash contains vanadium pentoxide, sodium salts, and sulfur compounds.

The oxide and salts settle out on horizontal surfaces in furnaces and boilers. They form low-melting point mixtures which flux away the protective oxides. Attack can occur at metal temperatures as low as  $1000^\circ F$ , and greatly accelerated attack takes place at  $1300^\circ F$  and higher temperatures. The protective oxide coatings of most commercial alloys are fluxed away, and a combination of oxidation, sulfur attack, and penetration occurs. Because the vanadium oxides and salts are not removed by the reactions and continue to be supplied by the fuel, attack continues (see

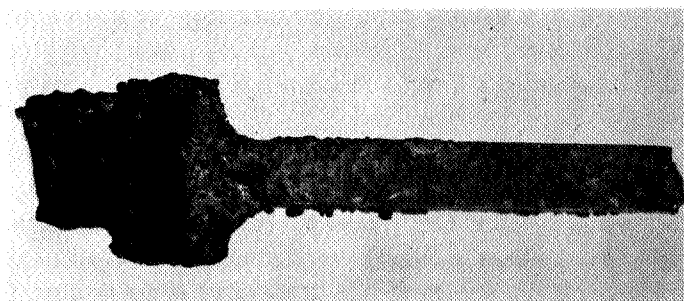
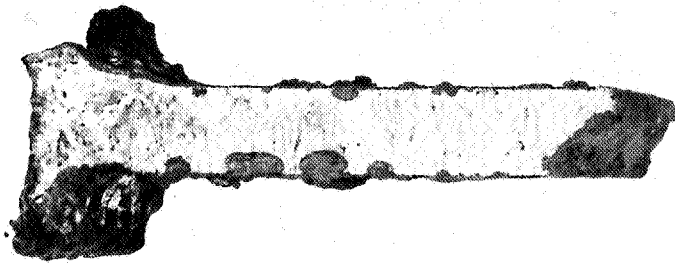


Figure 8. Vanadium pentoxide attack. HH (25 Cr - 12 Ni) casting.



**Figure 9. Vanadium pentoxide attack. Fractured surface of casting in Figure 8.**

Figures 8 and 9). Failure of furnace and boiler components can occur in a year or less.

One method of prevention of attack is to add minerals to the residual oil which prevent the residual salts and oxides from melting by forming higher melting point mixtures. Dolomite, and magnesium hydroxide or similar minerals are mixed with the residual fuel fired to the burners.

Protection is provided by the formation of higher melting point compounds which will not flux the protective oxide. Further protection is provided by the mineral coating which builds up on the surfaces; 20 ppm vanadium is considered low; while 200 ppm found in Mid-East crude residues is high and will cause attack. Even 20 ppm will accumulate in time and cause attack. When sodium plus vanadium are greater than 100 ppm, the ash can be expected to be corrosive.

Within the last five years, there has been successful experience with a 50 Cr - 50 Ni alloy which has better resistance to vanadium pentoxide and salt attack from residual fuel.

The next example is typical of catastrophic oxidation due to a component of the alloy. Alloys containing molybdenum, vanadium, or tungsten are susceptible to a unique form of catastrophic oxidation in which oxidation of the alloying element accelerates attack. Molybdenum oxide has a low melting point, 1463°F. When mixed with sodium oxides, the mixture can melt as low as 930°F.

Type 316 stainless steel (18% Cr, 12% Ni, 2.5% Mo) is susceptible to chloride stress corrosion cracking. To inhibit the possibility of chloride stress corrosion cracking under wet thermal insulation, insulation is treated with sodium silicate. After a short time at elevated temperatures the time varying inversely with the temperature, the molybdenum oxide-sodium oxide mixture forms, melts, and allows catastrophic oxidation of the 316 stainless steel. The attack proceeds rapidly, once started, and failure can occur in several hours time (see Figures 10 and 11).

Molybdenum oxide's low melting point, 1463°F, can allow catastrophic oxidation without the presence of other salts. As long as sufficient oxygen is present, a protective film is formed and molybdenum does not oxidize catastrophically. Laboratory tests in stagnant atmospheres have produced catastrophic oxidation of molybdenum containing alloys at high temperatures, 2000°F and higher. Molybdenum-containing alloys with over 30% nickel are considered immune to catastrophic oxidation. (11)



**Figure 10. Catastrophic oxidation. Type 316H stainless steel.**



**Figure 11. Catastrophic oxidation. Type 316H stainless steel.**

If 316 stainless steel is used at temperatures above 1200° insulation should be free of salts. Because Code-allowable stresses for Type 316 above 1300°F are no longer significantly better than those for Type 304 stainless steel, and at 1400° and 1500°F Type 304 has a higher allowable stress, Type 316 is now rarely used at high temperatures.

Accelerated internal oxidation of HK 40 reformer tubes has been reported. (12) The appearance was massive oxidation of localized areas of the internal surface of tubes. Carburization was found under the oxidation. The failure mechanism appeared to be selective oxidation of carburized areas. Carburization reduces the resistance to oxidation by combining carbon with the chromium. Carburization occurred because of the breakdown in the normally protective oxide film.

The substance which caused the breakdown of oxide

film was not found. Possible contaminants were sulfur or water-treating chemicals. Subsequent investigation showed that tubes which had been attacked contained over 200 ppm of lead. Since then, HK 40 tubes are ordered with 100 ppm maximum lead content, although it is not certain how the small amount of lead contributed to the attack of HK 40.

This type of catastrophic attack usually occurs suddenly, sometimes after a long period of operation with no attack. The long period of successful operation prior to attack can be a time of operation without contaminants, or it can be the time necessary for breakdown of protective oxide films. Prevention of catastrophic attack requires protection from all potentially harmful contaminants, and operation under specified conditions.

**Salt attack.** As discussed previously, salts can promote high temperature attack by the following mechanisms:

1. The molten salt will flux the protective oxide away allowing the exposed metal surface to be subject to accelerated oxidation or carburization.
2. Components of the salt, such as sulfur or chlorine, can attack the high temperature material.
3. The molten salt can dissolve and concentrate harmful components of the gases to which it is exposed, causing accelerated attack.
4. Salts can decompose or combine with water to form corrosive gases or solutions such as chlorine, acids, etc.

The normal salt attack proceeds as a fluxing action by a molten salt. Sodium sulfate is one of the most common aggressive agents in high temperature attack. Its melting point is 1623°F. Sodium sulfate is found in many natural and treated waters. It can also form by reaction of sodium chloride in salt air with the products of combustion of sulfur bearing fuels.

This reaction has been responsible for sodium sulfate high-temperature corrosion of jet engine parts in marine atmospheres. Sodium sulfate can form lower melting point eutectic mixtures with other salts and can form a mixed sulfate with iron which melts at 1148°F. Sodium, potassium, and other metal salts such as chlorides, sulfates, and carbonates are all potentially harmful. The elevated temperature will accelerate reactions with products of combustion or with the metallic surfaces.

Salts can also cause attack of refractories by forming low-melting point mixtures with components of the refractory.

The sources of salt can be unexpected. We have seen salt attack at the bottom manifold inside a reformer furnace caused by sodium sulfate in untreated water. The water had overflowed a cooling water jacket and fallen through the furnace onto the bottom manifold. The water evaporated, leaving salt on the high-alloy manifold. Attack proceeded quickly by carburization and oxidation.

Figures 12, 13 and 14 show the form of a typical salt attack. The salt is not removed in the reaction although subsequent shutdown and cleaning operations can remove it.

Nothing can be done to protect metals against salt attack. The remedy lies in prevention of introduction of salts. Any change in fuel or feed should be examined to be sure

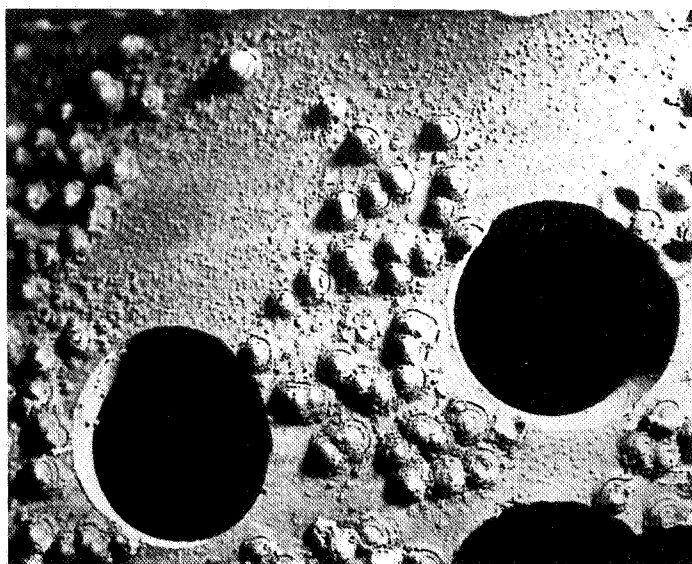


Figure 12. Salt attack. Type 310 stainless steel. Actual size.

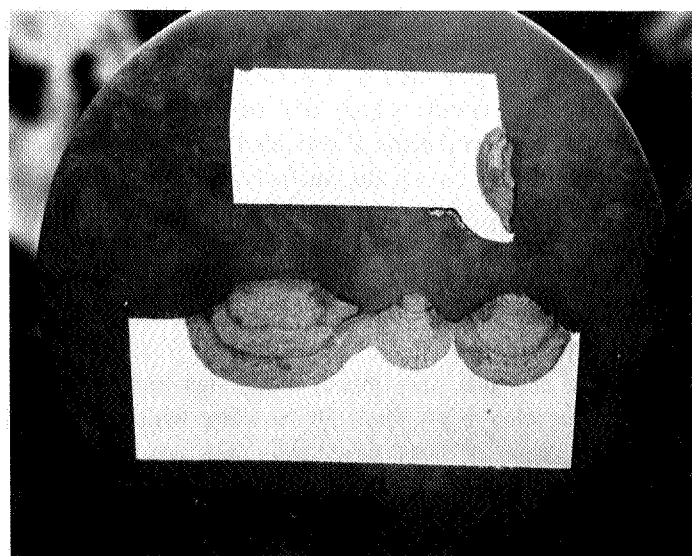


Figure 13. Salt attack. Type 310 stainless steel (3X).

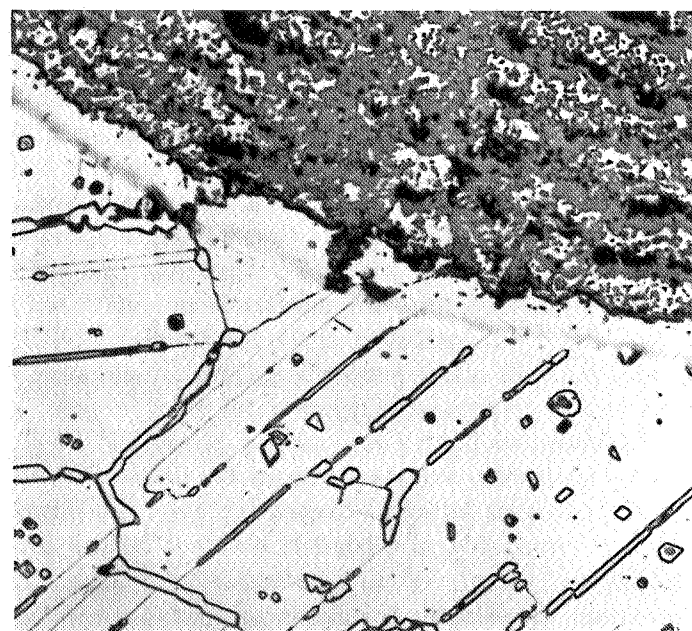


Figure 14. Salt attack. Type 310 stainless steel (100X).



that no increase in contaminants is added. Paints, cleaning agents, and spills should be examined to be sure that no salt residue remains on metals which will be exposed to high temperatures.

### How to diagnose the failures

The various types of elevated temperature corrosion just described fall into two types. First is the predictable reactions; such as oxidation, carburization, nitriding, H<sub>2</sub>S attack, and hydrogen attack, which proceed at rates dependent on temperature and concentration of the reacting gas. Generally speaking, such reactions are insensitive to minor changes in process conditions; and provided that the correct material of construction is used (as determined from the relevant corrosion chart), the operability of the plant will not be affected.

The second, and much more hazardous, type is that in which small amounts of surface contamination or small changes in gas composition can result in catastrophic rates of corrosion. For example, it appears that the risk of metal dusting is related to a gas composition which is carburizing to chromium and iron, oxidizing to chromium and iron, and reducing to nickel. However, this relationship has not been established with certainty. Nor is it easy to make the necessary calculations for a complex gas mixture. Further, experience indicates that even where the gas appears to be outside the metal dusting range of composition, attack can nevertheless take place in dead pockets—behind shrouds for example.

The determination of causes and cures will require an analysis of: 1) operating history; 2) visual examination; and 3) laboratory examination. Of these, the review of operating history is most important. Obviously, changes in operating temperature or thermocouple malfunctions can be directly associated with accelerated high temperature attack. Changes in product or in feed, although nominally identical to previous analyses, may introduce contaminants which accelerate corrosion.

Pipeline natural gas can be variable in sulfur content and higher hydrocarbons. An unannounced change in gas source or winter-time enrichment can upset the oxidizing-reducing balance of products of combustion or of process gases. The Btu value will stay within contract limits, but the chemical composition can vary and can cause a change in high temperature corrosion.

Crash shutdowns can interrupt normal flows and introduce sources of unexpected high-temperature corrosion. Normal start-up procedures will usually remove contaminants. Particular care should be taken to purge away all water, to be sure that no residual salts are left on parts which will be exposed to high temperatures.

Flooding, particularly with brackish water, can leave a residue of corrosive materials. Sodium chloride can, in combination with products of sulfur combustion, form aggressive salts which cause attack of high temperature materials.

Any change in operating conditions should be considered as to its possible effect on high-temperature corrosion. Since, in most cases, whether corrosion occurs or not will

depend on the interaction of gases with each other and on contaminants, it is difficult to predict whether a particular change will cause corrosion. The record is much better for hindsight. After corrosion occurs, analysis of the operating history can show the possible causes, so that future corrosion can be avoided.

Visual examination can sometimes indicate the cause of high temperature attack. The scale and corrosion products are usually thick, grey-black, magnetic, and friable. The unusual color, salt deposit, or melted metal in or near the attack can be a clue as to the cause. The location and distribution of attack, whether it is spotty or uniform, whether it is at one elevation or at all elevations, the orientation, all the geography of attack may be connected with temperature profile or gas or solids distribution and can indicate the cause of attack.

Temperature is a most important variable, and since the temperature of furnace parts is usually measured by means of an optical pyrometer, which is subject to instrument and operator error, every effort should be made to check the accuracy of the temperature measurement.

The questions which can be answered by a chemical and metallurgical laboratory examination are:

1. How hot was the part?
2. Was the part of the specified analysis?
3. What is the composition of the scale?
4. Are there any salts in the scale?
5. Is the part carburized or decarburized?
6. Is there evidence of hydrogen attack, nitriding or intergranular attack?

After the review of operating history, visual examination, and laboratory examination results, there may well be more than one possible cause of high temperature corrosion. Assuming that there has been no previous corrosion, the source of attack is usually something that has changed. We cannot oppose change, but we should be aware of the possible effects of change on high temperature materials. #

### Literature cited

1. Tables of Data on Chemical Compositions, Physical and Mechanical Properties of Wrought Corrosion-Resisting and Heat-Resisting Chromium-Nickel Steels, American Society for Testing and Materials, December, 1942.
2. "Steels for Elevated Temperature Service," United States Steel Corp., June, 1972.
3. Van Grieken, C.A., comments to "Corrosion Mechanisms in Ammonia Synthesis Equipment," V. Cinal, First International Congress on Metallic Corrosion, 1961.
4. Mueller, K., "Die Aufkohlung bei Crackrohren fuer die Aethylenherstellung," *Nickel Berichte*, 26, No. 6, pp. 121-128 (1968).
5. Schueler, R.C., "Metal Dusting," *Hydrocarbon Proc.*, 51, 73 (Aug., 1972).
6. "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants," American Institute Petroleum Pub-

lication No. 941, July, 1970.

7. Couper, A.S., and Gorman, J.W., "New Computer Correlations to Estimate Corrosion of Steels by Refinery Streams Containing Hydrogen Sulphide," Paper No. 67, 26th annual conference, National Association of Corrosion Engineers, March, 1970.
8. McCoy, J.D., and Hamel, F.B., "Effect of Hydrosdesulfurizing Process Variables on Corrosion Rates," Preprint 44-70, 35th Midyear Meeting, American Petroleum Institute Division of Refining, May, 1970.
9. Fitzharris, J.J., and Bird, D.B., *Materials Protection*, 7, No. 9 (Sept., 1968).
10. Bonar, J.A., "Fuel Ash Corrosion," *Hydrocarbon Proc.*, 51, 76 (Aug., 1972).
11. "Catastrophic Oxidation of High Temperature Alloys," J.H. DeVan, ORNL-TM-S1, November, 1961.

12. Gackebach, R.E., and Shay, F.J., "A Study of Localized Massive Scaling on Interiors of Reformer Tubing," *Materials Protection and Performance*, p. 19, June, 1971.



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## DISCUSSION

**JIM SHERMAN**, DuPont Co.: It may be just worth noting that among the agents of corrosion by liquid metals you mentioned Zinc. A likely source is the galvanized coating on structural members such as subway grating, diamond plate and other things. And a likely agent in transporting this on to reformer tubes is to have a fire in the upper structure of your reformer.

**ZEIS**: That's possible.

**SHERMAN**: I have one question. Is cadmium also included among these agents?

**ZEIS**: Yes, It's aggressive but it's not normally found except in valve parts and trim. I think most users don't allow it.

**SHERMAN**: Would you recommend the removal of any metal of that type even if it were very, very small quantities or merely suspected?

**ZEIS**: Well, you'd have to look at it two ways. Certainly you would not want it on any high temperature part because as it's heated up it will either oxidize and disappear or would melt and cause attack. In a fire condition — if it's in a place where it could melt, and get on to the tubes, it could cause attack. It would be worthwhile eliminating low melting point metals if you want to prepare for a fire condition.

**J.M.A. VAN DER HORST**: I would like to say something about nitriding. Generally it is said that Inconel 600 is resistant to nitriding. However when it is exposed at high temperatures (~800° F) to pure ammonia a nitride layer is formed. At every temperature change of the Inconel, this nitride layer spalls off, exposing a fresh surface for nitriding. As a result metal thickness is reduced in a short time.

**ZEIS**: That's interesting and International Nickel hasn't said anything about it.

**VAN DER HORST**: No, they don't generally mention it. Only when you question them on the subject will they admit that Inconel doesn't stand up. Secondly, you mentioned that austenitic stainless forms a brittle nitride layer. However if you nitride e.g. 304 stainless steel at 1400° F or higher in pure ammonia, the nitride layer formed is coherent with the base metal, has low hardness and is not brittle.

**W.D. CLARK**, ICI England: I can confirm from our own experience two of the points made by Mr. Zeis. We had a small gas leak from a welded connection to a cast HT header. The gas fired, and caused the aluminum cladding on the insulation to melt and a small pool of aluminum formed on top of the header. In spite of the 'tough' oxide film on the header and on the aluminum, alloying took place and penetrated a quarter inch into the steel in quite a short time.

Secondly we have had bad results with Inconel on ammonia converter interchanger duty. It was not clear that it had nitrified, but it certainly became very brittle.

Can you summarise what is known on the practical results of firing reformers on oils which contain more vanadium than is desirable? You seemed to imply that 20 ppm was satisfactory.

**ZEIS**: This is all we could say on a theoretical basis, because as far as we know nobody has fired any vanadium containing fuel to a Kellogg reformer. We've had no reports of that. We did have an indication from Mr. Sawyer yesterday that Allied had some experience back in the '50's with attack of HK 40 tubes by vanadium. I'm not sure whether these were vertical or horizontal, but there has been no other practical experience that we know of.

Based on what's happened with firing these fuels in other furnaces, we know that the attack can take place as was shown on the slide.

**J.M. BLANKEN** — UKF — Holland: Do you think there is a risk of sudden failure of say a 200 mm thick 3% Cr steel shell nitrified to a certain depth? Would cracks in the nitrified layer propagate through sound material?

**ZEIS**: Yes, I'd say that's possible, if it were stressed, in tension. As you could see from that slide of the nitrified austenitic material, the cracks all stopped at the base metal, but that could very well be because base metal is a very ductile material. The cracks in the nitride layer may or may not propagate, depending on imposed stress. Normally there is a compressive stress from the nitride which will discourage crack propagation.