

# Stainless Steels in Ammonia Production



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# INTRODUCTION

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Approximately 12 elements are essential to plant growth. Of these, nitrogen is the main nutrient and is required in much larger amounts than any other element. Ammonia is the principal source of fertilizer nitrogen, and most of the ammonia production in the world is applied directly to the soil or used in the manufacture of urea and other important nitrogen-base fertilizers. (1)\* Because of ammonia's importance to human needs, it is considered to be one of the most valuable and most widely produced chemicals in the world.

The ammonia production industry has grown by leaps and bounds since 1964, with U.S. production in 1977 an estimated 17 million to 18 million short tons per year, about four times that of 1960 (4.8 million short tons). (2)

Up until 1963, plant capacities ranged between 50 and 400 short tons per day, many using a multiplicity of parallel process systems, called multiple trains. In 1963, the first 600-short-tons-per-day single-train ammonia plant came on stream. This represented the beginning of large-capacity, single-train plants and was the first to use centrifugal compressors driven by steam turbines to compress synthesis gas to elevated pressures. (2)

Between 1965 and 1970, many single-train ammonia plants with capacities of 600 to 1000 short tons per day were built throughout the world. In recent years, larger plants have been commissioned, several with 1500 short tons per day capacity and one of 1700 short tons per day, ranked the largest in the world at present. (2)

With the advent of high-capacity

single-train plants came increasing demands on materials of construction. The process for making ammonia is considered to be only moderately corrosive, so considerable use is made of carbon and low-alloy steels for vessels and piping. However, numerous applications have been found for the AISI 300 and 400 Series stainless steels because of their superior performance under a wide variety of process conditions, not only for original fabrication but for replacement equipment and piping as well.

For example, stainless steels are used in

Catalytic steam reforming because of resistance to oxidation, carburization and nitriding at elevated temperatures;

Carbon dioxide removal systems where piping and vessels are subjected to hot, aqueous solutions containing carbon dioxide at moderate to high velocities;

Ammonia synthesis for superior performance in hot nitriding gases, resistance to hydrogen embrittlement and hydrogen attack, and excellent toughness at low temperatures;

Centrifugal turbomachinery where rotating and stationary components are subjected to erosion by high-velocity steam and corrosion by ammonium carbamate, CO and CO<sub>2</sub>;

Coolers and condensers for resistance to corrosion and fouling by natural waters.

The purpose of this booklet is to identify the many applications of stainless steels in a typical process for manufacturing anhydrous ammonia.

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\*Numbers in ( ) indicate reference.

# PROCESS DESCRIPTION

Anhydrous ammonia is manufactured by combining hydrogen and nitrogen in a molar ratio of 3:1, compressing the gas and then cooling it to about  $-27^{\circ}\text{F}$  ( $-33^{\circ}\text{C}$ ).

Nitrogen is obtained from air. Hydrogen is produced from a feedstock by one of the following processes;

Catalytic steam reforming of natural gas or naphtha;

Partial oxidation of heavy hydrocarbons (oils, distillates);

Cryogenic recovery from petroleum refinery gases or other cracking operations;

Gasification of coal or coke.

Currently, a high percentage of world ammonia production (an estimated 70 to 80%) uses hydrogen produced by catalytic steam reforming operations, with natural gas (methane) as the primary feedstock. As a result, the following process description is limited to ammonia production by catalytic steam reforming of natural gas, using six basic

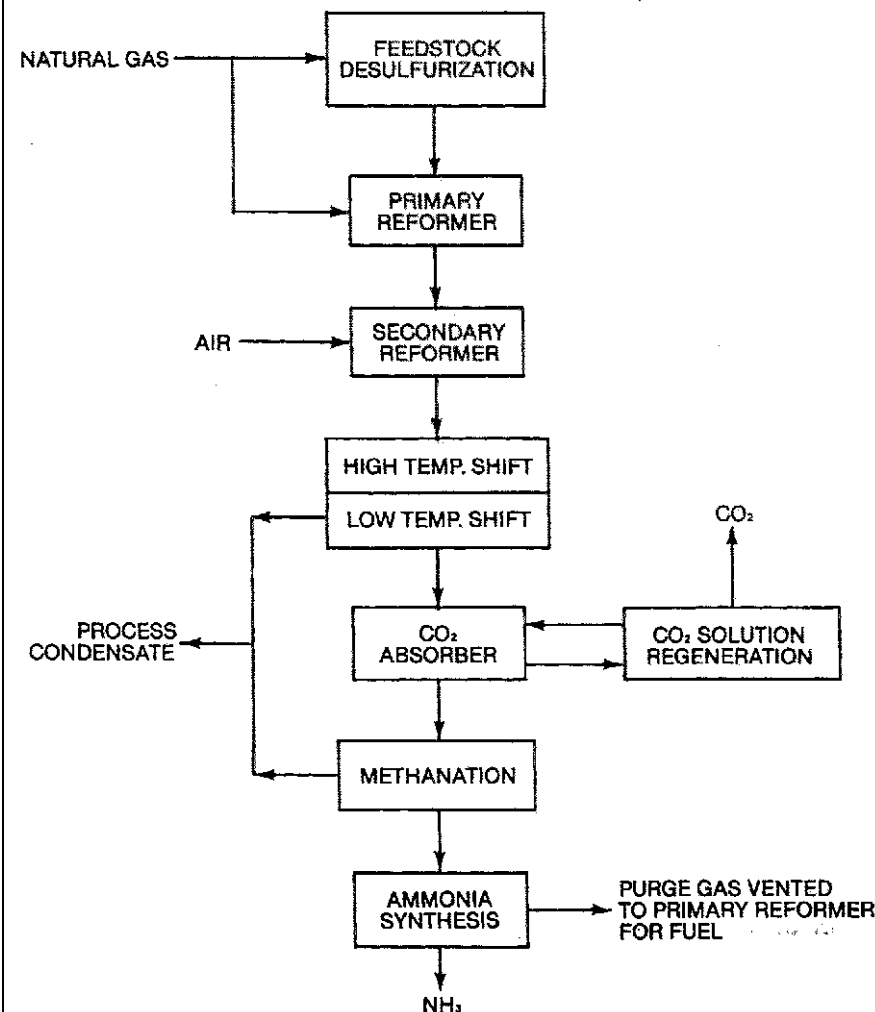
1. Desulfurization of natural gas
2. Catalytic steam reforming of natural gas
3. Carbon monoxide shift
4. Removal of carbon dioxide
5. Methanation
6. Synthesis of ammonia.

The first, third, fourth and fifth steps are designed to remove impurities such as sulfur, carbon monoxide, carbon dioxide and water from the feed, hydrogen and synthesis gas streams. In the second step, hydrogen is manufactured and nitrogen is introduced into the process. The sixth step produces anhydrous ammonia from synthesis gas. All ammonia plants use this basic process, although process conditions such as temperatures, pressures and flow rates vary from plant to plant.

Approximately 65 to 75% of the natural gas is used as feedstock for the primary reformer; and 25 to 35% is used as fuel for the reformer radiant section and for steam production. As natural gas reserves continue to dwindle, feedstocks based on heavier hydrocarbons and coal gasification processes (3) will undoubtedly be used increasingly in ammonia plants in years to come.

A process flow schematic of a typical ammonia plant which uses catalytic steam reforming of natural gas is shown in Figure 1. The six process steps are described in detail in the following sections.

**Figure 1**  
**Process Flow Schematic of a Typical Ammonia Plant**



## CORROSIVES FOUND IN MANY AMMONIA PROCESSES

Sulfur—present in natural gas feedstock, it causes high-temperature sulfidation of metals,

and it combines with other elements to form aggressive compounds, such as hydrogen sulfide, sulfur dioxide, and carbonyl sulfide.

**Chlorides**—may be present, either by entrainment in natural gas, as carryover from boiler feedwater, or in cooling waters. They may cause localized attack of some stainless steels.

**Carbon Dioxide**—occurs in steam reforming of natural gas. It combines with moisture to form carbonic acid.

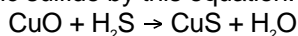
**Ammonia**—at high temperature has high potential for nitriding metals. At high pressure, corrosive ammonium carbamate may be formed. Condensed ammonia is a corrodent, and in anhydrous state it can cause stress-corrosion cracking of stressed carbon steels or high-strength, low-alloy steels.

**Hydrogen**—in itself not corrosive but can lead to blistering and embrittlement of steel. Also, it readily combines with other elements to produce corrosive compounds.

**Oxygen**—in high-temperature environments can cause oxidation scaling of metal surfaces of under-alloyed material.

poisoning the nickel catalyst in the primary reformer and depositing carbon on the catalyst. Sulfur can be present as hydrogen sulfide, mercaptans, carbonyl sulfide and organic sulfur compounds. Carbon beds are usually used when the sulfur content is less than 10 grains/per standard cubic foot (SCF), whereas hot iron oxide or zinc oxide (4) beds are used for gas with higher sulfur content. Most modern ammonia plants use activated carbon for feedstock desulfurization.

Natural gas at several hundred psig and ambient temperature is passed through the activated carbon bed. Sulfur compounds are absorbed on the carbon or reacted with the metallic oxide in the carbon to form a metallic sulfide by this equation:



When the carbon bed becomes loaded with sulfur, it is regenerated with steam or a mixture of steam and air at 300 to 555°F (149 to 290°C) for several hours. The free oxygen reacts with the metal sulfide to form the corresponding metal oxide and free sulfur, which remains trapped in the carbon bed pores. Much of the sulfur is vented to the atmosphere along with the steam.

#### Nature of Corrosion

Corrosion in the natural gas desulfurization step of the ammonia process is a function of purity of the natural gas feedstock and steam used for regenerating the activated carbon beds. Small quantities of sulfur are present at all times, either as H<sub>2</sub>S, SO<sub>2</sub> or carbonyl sulfide. Traces of chlorides may also be present, either by entrainment in the natural gas or as carryover from boiler feedwater used for steam manufacture. Thus, condensates highly corrosive to steel may be formed at the beginning of a carbon bed regeneration cycle. However, serious corrosion is avoided by addition of a small amount of ammonia to the steam to keep the condensate at a neutral or slightly alkaline pH.

#### Applications for Stainless Steels

The system for removing sulfur from the feedstock natural gas consists of two pressure vessels, each containing activated carbon for removal of mercaptan sulfur and hydrogen sulfide. Each vessel is designed to handle all the sulfur expected in the feed gas. As soon as the activated carbon in the first vessel becomes saturated with sulfur, the feed gas stream is diverted to the second vessel to allow steam regeneration of the carbon bed in the first vessel.

For the most part, operation takes place above the dew point and carbon steel is a satisfactory material of construction for the vessels and related piping. However, AISI Types 304, 321, or 316 stainless steels are specified for the wire mesh screens and grating which support the activated carbon beds in the desulfurizers. For this application, corrosion rates must be virtually nil, otherwise a corroded screen could result in carbon breakthrough and carryover into the primary reformer with potentially severe effect on reforming catalyst and radiant tubes.

Types 304 and 316 are also used in other applications where freedom from corrosion and corrosion products is essential, such as on-stream instrumentation and valve trim.

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## CONSIDERATIONS FOR SELECTING STAINLESS STEELS

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### Desulfurization of Natural Gas

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#### Process Description

The sulfur content of the natural gas feedstock must be reduced to as low a level as possible to prevent

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## Catalytic Steam Reforming of Natural Gas

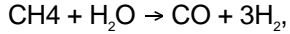
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#### Process Description

In this step (Figure 2), sweetened natural gas which leaves the desulfurizers at ambient temperature is preheated and mixed with steam and further preheated to 930 to 1020°F (500 to 550°C) in a waste heat recovery coil usually located in the primary reformer convection sections. The steam-to-gas ratio is maintained in

the range of 3 to 4 moles of steam per mole of gas.

The preheated steam/gas mixture enters the primary reformer tubes which are filled with a nickel-base catalyst. The reaction,



is endothermic. Heat is supplied from external burners which use natural gas or oil as fuel.

About 70% of the methane is converted to hydrogen in the primary reformer. The partially reformed gas leaves the primary reformer at 1345 to 1510°F (730 to 820°C) and enters the secondary reformer where it is mixed with air to produce a synthesis gas with a hydrogen-to-nitrogen ratio of 3:1. Heat required to complete the reforming reaction is obtained by combustion of the air/gas mixture over a bed of nickel-base catalyst similar to primary reformer catalyst.

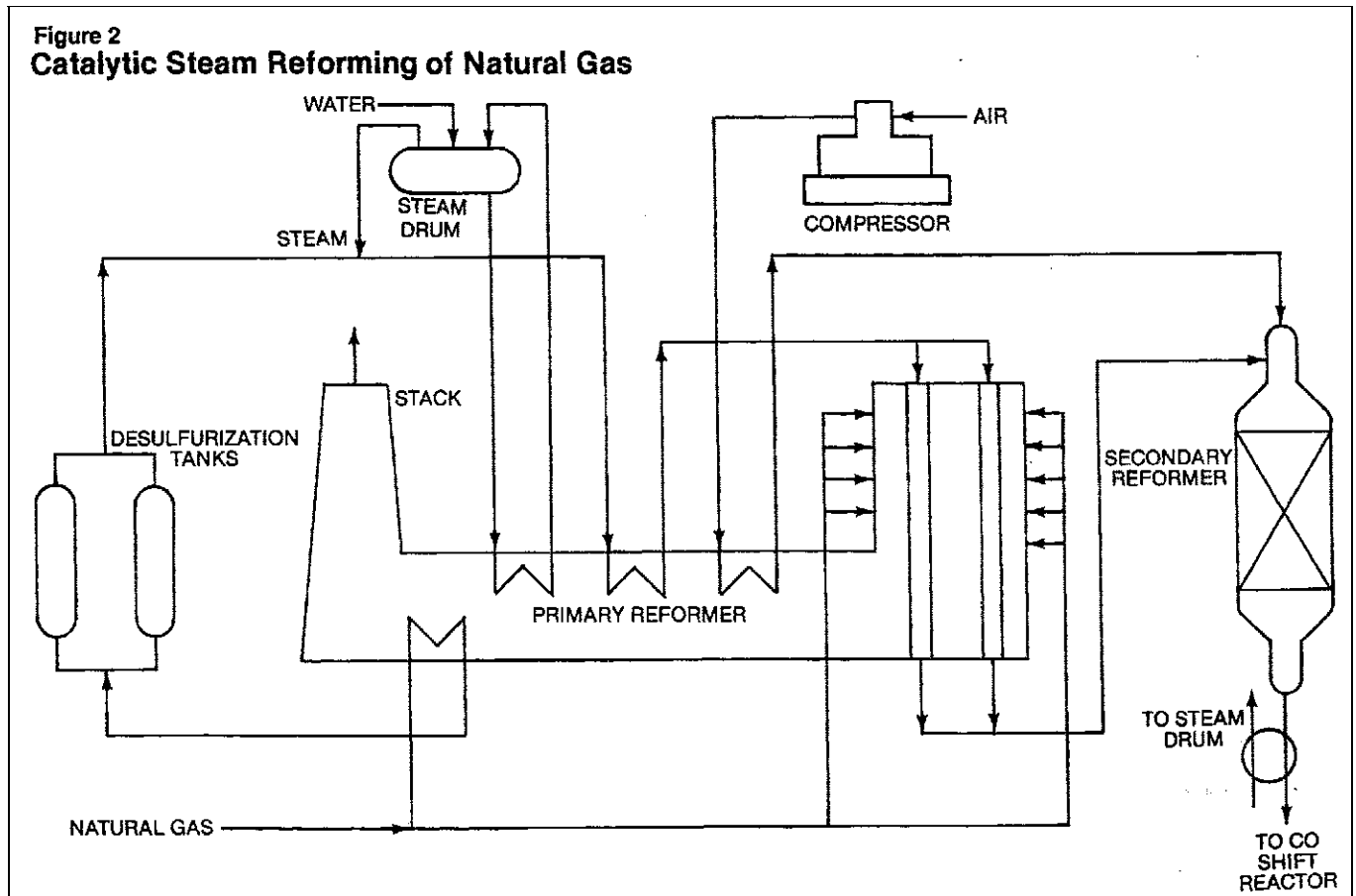
The virtually completely reformed synthesis gas leaves the secondary reformer at 1740 to 1830°F (950 to 1000°C) and is cooled in a waste heat boiler to about 680°F (360°C). The boiler produces steam at approximately 1500 psig (10.3 MPa) which is used to drive turbomachinery.

Heat in the flue gas which leaves the primary reformer radiant section at about 1760°F (960°C) is recovered in several preheat coils in the convection section. The flue gas exits through the reformer stack at 390 to 480°F (200 to 250°C).

### Nature of Corrosion

Catalytic steam reforming of natural gas occurs at elevated temperatures – 1290 to 1830°F (700 to 1000°C) – so materials of construction may be subjected to a number of high-temperature metal wastage

phenomena in addition to simple oxidation. Sulfur entrainment and boiler feedwater salts carryover in the natural gas/steam reformer feed can cause sulfidation and molten salt attack respectively of reformer catalyst tubes, outlet manifolds and transfer lines. Methane and higher hydrocarbons in feedstocks will carburize most metals rapidly at these temperatures if the proper steam-to-methane ratio is not maintained. Fluctuations in steam/methane ratios subject alloys to a highly destructive cyclic carburization/oxidation phenomenon similar to metal dusting. Trace amounts of impurities such as lead in reformer tube alloys will promote catastrophic oxidation of these alloys. Bunter fuels are also a source of high-temperature corrosives. For example, fuel oil ash deposits (on outer tube surfaces) which contain



sodium, vanadium and sulfur compounds can cause severe molten salt attack of reformer alloys.

### Applications for Stainless Steels

Virtually all ammonia plants use centrifugally cast high-alloy tubes to contain the nickel-base catalyst in the primary reformer furnace. The most commonly used tube alloy is similar in composition to Type 310 – nominally 25% chromium and 20% nickel, balance iron – but with a carbon content in the range 0.35 to 0.45% for improved high-temperature creep and stress rupture strength. The Alloy Casting Institute has designated this alloy as Grade HK-40.

Linings of castable and fired brick refractories are used for thermal protection of piping and equipment because of the high temperatures – 1290 to 1830°F (700 to 1000°C) – encountered throughout this system. Included are the process effluent transfer line from the primary to the secondary reformer; and secondary reformer; crossover lines between the secondary reformer and primary waste heat boilers; and the primary waste heat boilers themselves. To prevent refractory erosion by the hot, high-velocity gas streams, refractory surfaces are frequently lined with metal shrouds (1/16 to 1/4 inch thick) (1.58 to 6.35 mm) of Types 304, 321 or 310. Types 304 and 321 have demonstrated satisfactory oxidation resistance in piping and equipment operating at 1290 to 1650°F (700 to 900°C) (e.g. transfer lines), whereas Type 310 has provided good protection at temperatures between 1650 and 1830°F (900 and 1000°C).

Oxidation resistance is not the only criterion for using austenitic stainless steel shrouds in this system. The process gas stream has high potential for nitriding and, on occasion, carburizing metals and alloys. The austenitics provide reasonable life at low cost when compared with the more resistant and more expensive high-nickel alloys in this service.

Other satisfactory experience with stainless steels in steam/natural gas reforming includes Types 304, 321 and 310 inside the primary reformer firebox for heat shields around riser welds; jacketing around outlet manifold insulation; thermocouple sheaths; thermal/mechanical protection tubes around thermowells; manifold drain and sample nozzles; and flue gas sample tubing.

Types 304 and 321 are used for tie rods and tube supports on the process gas side of primary waste heat boiler tube bundles.

Virtually all piping and equipment throughout this system requires external thermal insulation to conserve heat. Sheet metal jacketing of Types 430 or 304 provide outstanding protection against weather and mechanical damage for all types of insulation – preformed, blanket or block.

High-pressure steam, which is generated in the primary waste heat boilers and, where utilized, auxiliary power boilers, requires boiler feedwater of exceptional purity to avoid fouling of heat transfer surfaces and turbine components by boiler salts. Most large, modern ammonia plants have facilities for demineralizing water with ion exchange resins. Water quality of *less than 5 parts per billion total impurities* is common. To maintain this purity and for good, all-around corrosion resistance in this aggressive medium, Type 304 is frequently specified for demineralized water storage tanks and piping, and trim in valves and pumps. Type 316 finds applications in the ion exchange resin system because of good resistance to *cold, dilute* caustic and sulfuric acid solutions which are used for regenerating the resin beds.

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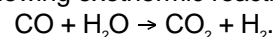
## Carbon Monoxide Shift

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### Process Description

The cooled synthesis gas from the

reforming steps contains about 12% CO and 8% CO<sub>2</sub> which are unwanted products of reforming. The gas is passed over a bed of chromium oxide-promoted iron oxide catalyst in the high-temperature shift converter (Figure 3) which operates at 625 to 1020°F (330 to 550°C). CO is converted to CO<sub>2</sub> and more hydrogen by the following exothermic reaction;



Gas leaving the high-temperature shifter at 800°F (425°C) is cooled to about 390°F (200°C) in a heat exchanger and is then passed over a bed of copper oxide/zinc oxide catalyst in the low-temperature shift converter. This step reduces the CO content of the synthesis gas to about 0.4%. The gas is cooled to 195 to 250°F (90 to 120°C) and enters the carbon dioxide removal system. Unreacted steam is condensed and separated from the synthesis gas in a knockout drum. This steam condensate may be reused in the process or discarded.

### Nature of Corrosion

Principal corrodents in the carbon monoxide shift step are CO, CO<sub>2</sub>, H<sub>2</sub>, and steam condensate. CO<sub>2</sub> is not particularly corrosive as a hot, dry gas but forms corrosive carbonic acid when dissolved in steam condensate. However, ammonia additions to condensate are effective in keeping rates of attack at an acceptable level. Hydrogen is not corrosive as such, but can diffuse into carbon and low-alloy steels and cause embrittlement of hardened regions (e.g. weld heat-affected zones) at low to moderate temperatures and severe reductions in strength and ductility at elevated temperatures by chemical attack of the unalloyed iron carbides in steel to form methane.

### Applications for Stainless Steels

Major equipment in the carbon monoxide shift system (Figure 3) includes pressure vessels for the primary and secondary catalytic con-

version of CO to CO<sub>2</sub> in the synthesis gas, heat exchangers which cool the catalytic converter effluents and recover waste heat in the process, and a separator for removing steam condensate for reuse as process water. Generally, the carbon and low-alloy steels such as carbon-0.5% Mo and 1¼Cr-½Mo are specified for vessels and piping exposed to the hot CO-CO<sub>2</sub>-H<sub>2</sub> gas streams.

However, Types 304 and 410 are employed for the wire mesh screens and grating that support the catalyst beds in the primary and secondary shift converters, as well as for grid sections installed on top of the beds to keep the catalyst from shifting and for more uniform gas distribution through the beds. Thermocouple sheaths, thermowells and thermowell guide tubes are frequently of Type 304 be-

cause of excellent resistance to attack by CO, CO<sub>2</sub>, H<sub>2</sub> and steam.

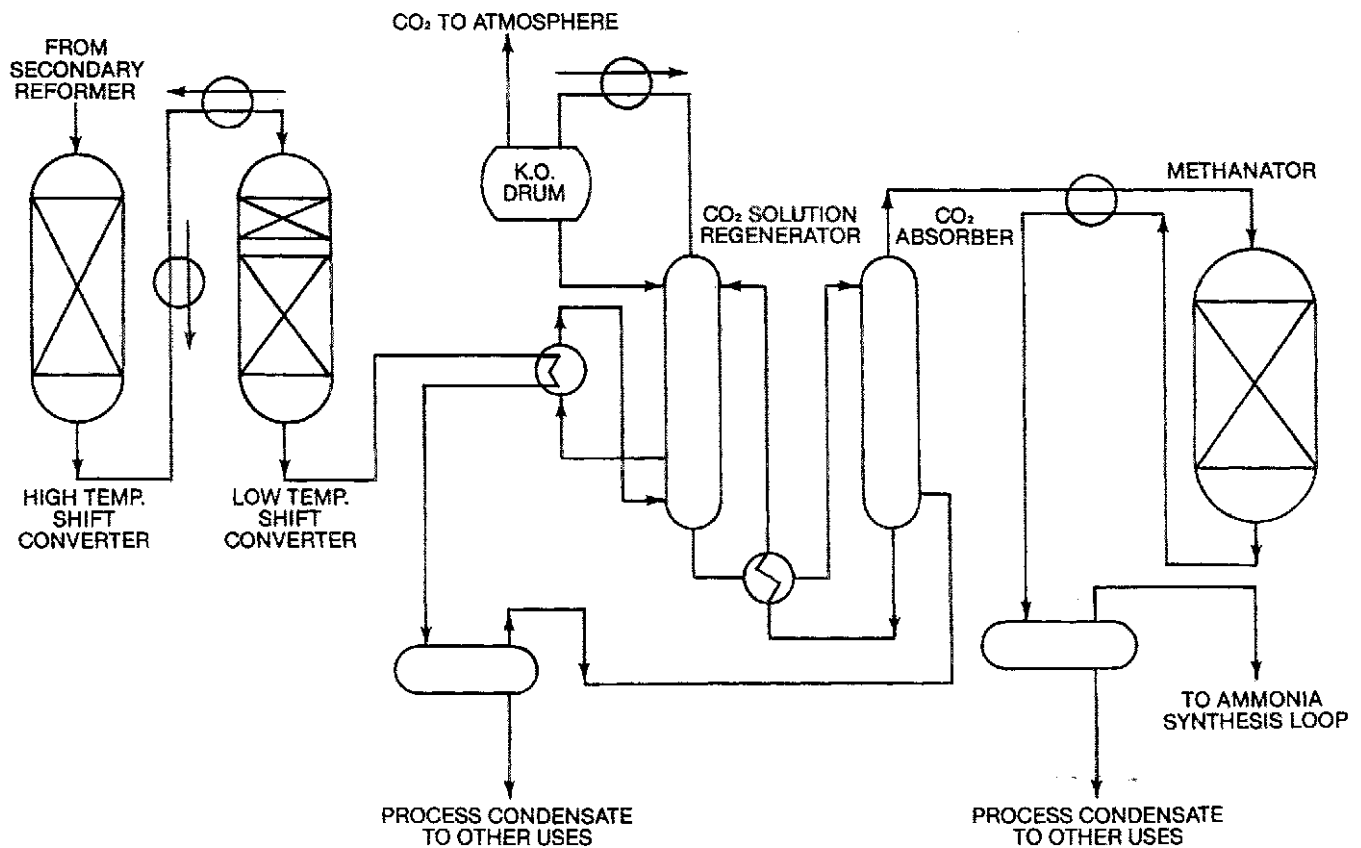
In some plants, the secondary shifter effluent is cooled to its dew point by direct contact with a fine spray of recycle process water (steam condensate) in a section of piping. The spray quench piping sections at and immediately downstream of the internal spray nozzle are specified as Type 304 for resistance to impingement erosion-corrosion by water droplets in the high-velocity gas stream.

After additional cooling of shifter effluent to 150 to 160°F (65 to 70°C) in a heat exchanger, most of the water vapor condenses and is removed in a separator or knock-out drum. Piping to the separator was frequently specified as all plain carbon steel, or carbon steel for

Type 304 for fittings such as tees and ells where impingement erosion-corrosion by the wet gas stream is cause for failure. After several years' service and especially with increased process throughput, many plants have replaced all original carbon steel sections with Type 304 stainless steel for greatly prolonged life.

The carbon steel separator is subjected to corrosion by CO<sub>2</sub> dissolved in water (carbonic acid) and thus has a finite life. Type 304 stainless steel linings are frequently installed after original corrosion allowances are used up, as an economical alternative to vessel replacement. One method consists of welding strips of stainless steel sheet to the steel shell. Another consists of surface preparation by grit blasting followed by flame spray metallizing with stainless steel pow-

**Figure 3**  
**Carbon Monoxide Shift, Synthesis Purification and Methanation Steps**





der or wire. This porous lining, usually 0006 to 0.010 inch (0.1524 to 0.254mm) thick, is then sealed with a catalyzed epoxy or epoxy-phenolic coating.

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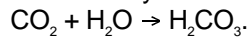
## Removal of Carbon Dioxide

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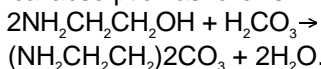
### Process Description

Following shift conversion, carbon dioxide must be removed from the mixture of hydrogen and nitrogen (Figure 3). About 1.2 metric tons of CO<sub>2</sub> are produced for every metric ton of ammonia manufactured. (5)

The removal of CO<sub>2</sub> depends on its acidic character. It tends to form carbonic acid in water by this reaction:



Carbonic acid undergoes reversible reactions in solutions of amines by chemical absorption as follows:



The carbonate thus formed decomposes on heating into CO<sub>2</sub> and the amine. This drives off the CO<sub>2</sub> and regenerates the absorption solution.

The classical method for removing CO<sub>2</sub> is absorption in monoethanolamine (MEA). Approximately 80% of all ammonia plants use this solution. The remaining plants use hot potassium carbonate or proprietary solutions based either on amines or carbonates.

In the MEA system, synthesis gas containing CO<sub>2</sub> is passed up through an absorption tower countercurrent to a 15-20% solution of MEA in water. The amine solution which is rich in CO<sub>2</sub> is preheated and then regenerated in a reactivating tower. CO<sub>2</sub> is first removed by steam stripping and then heating. CO<sub>2</sub> of about 98-99% purity is either vented to the atmosphere or used as feedstock for other processes such as methanol and urea.

The regenerated MEA is cooled in a heat exchanger and solution cooler and returned to the absorption tower. This process permits CO<sub>2</sub> removal at atmospheric pressure with consequent reduction in compression requirements.

### Nature of Corrosion

Process conditions in CO<sub>2</sub> removal systems can result in moderate to severe corrosion of materials of construction by contact with hot, aqueous solutions of CO<sub>2</sub> in the presence of MEA, potassium carbonate or other absorbants. Solution temperatures range from 105 to 300°F (40 to 150°C). Corrosion of steel is accelerated by increased process stream velocities which occur, for example, in pumps, pressure let-down valves, at piping tees and ells, etc. Heat transfer conditions which cause hot wall effects, as in reboilers and other heat exchangers, also accelerate corrosion. Other corrodents in these systems include products of degradation of MEA. However, accumulation of these complex organic compounds may be controlled by side-stream solution reclaiming operations. Also, corrosion inhibitors such as filming amines and certain proprietary additives (6) have been used effectively to reduce corrosion in process piping and equipment.

### Applications for Stainless Steel

For efficient conversion to ammonia, the hydrogen/nitrogen synthesis gas must contain no more than 10 parts per million CO<sub>2</sub> plus CO. Thus ammonia plants require heavy investment in equipment and piping specifically for the removal of CO<sub>2</sub> (Figure 3). Its acidic nature makes CO<sub>2</sub> the most corrosive constituent in the ammonia manufacturing process. However, effective and economical use is made of austenitic stainless steels, primarily Types 304 and 316, in both wrought and cast form, throughout this system because of demonstrated resistance to hot

aqueous solutions containing CO<sub>2</sub>.

Most of the equipment in CO<sub>2</sub> removal systems consists of large, vertical scrubbing and distillation-type vessels, and heat exchangers. The CO<sub>2</sub> absorber, where CO<sub>2</sub> in shifter effluent gas is absorbed in an aqueous solution of MEA, generally consists of a carbon steel shell with substantial corrosion allowance, filled with Type 304 ring packing or fitted with special Type 304 trays.

The "rich" (With CO<sub>2</sub>) solution iron the bottom of the absorber is heated and then fed near the top of the CO<sub>2</sub> stripper where CO<sub>2</sub> is released from the solution, after which it is called "lean" because of low CO<sub>2</sub> content. Many plants require an upper shell section of Type 304, either solid or clad on carbon steel, and Type 304 sieve trays in the stripper. The stripper overhead piping, condenser and accumulator, which handle the wet CO<sub>2</sub> stripped from the MEA solution, are frequently Type 304 also.

The heat required to operate the CO<sub>2</sub> stripper is supplied by exchanging rich solution with steam or hot process gas (i.e. shifter effluent) in shell-and-tube reboilers. The corrosion accelerating effects of heated surfaces are maximized in these vessels. Here too, however, Type 304 has given good service for tubing and tube supports. On occasion, corrosion of Type 304 may be excessive e.g. operation at higher temperatures or with excessive amounts of MEA degradation products. Under these conditions, Type 316 generally provides somewhat better service.

Hot, lean solution from the bottom of the stripper is cooled by heat exchange with the cool, rich solution in the shell-and-tube solution exchangers. Both Types 304 and 316 have been specified for original vessels—tubes, tube supports and solid or clad tube sheets and shells—or for units which replaced original carbon steel equipment where the superior erosion-corrosion resistance justified the higher cost of stainless steel.

Type 304 has also found wide

spread application for both rich and lean solution piping, pumps, valves and on-stream instruments. Cast versions of this alloy, designated as Grade CF8 by the Alloy Casting Institute, are used for pump casings and impellers and valve bodies. Neither intergranular corrosion nor stress corrosion cracking by process streams appear to be problems with application of austenitic stainless steels throughout this system.

Many CO<sub>2</sub> removal systems require reclaimers which purge degradation products from rich solution. Austenitic stainless steels are nearly always specified for these vessels because of superior resistance to corrosive complex organic compounds.

Nearly all ammonia plant operators use corrosion inhibitors in their CO<sub>2</sub> removal systems to minimize corrosion of carbon steel portions of piping and equipment. One of the most effective appears to be a proprietary inhibitor labeled "Amine Guard" by its developer, Union Carbide. They report significant reductions in corrosion rates of both mild steel and Type 304 after addition of this inhibitor to MEA systems serving two ammonia plants. (6)

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## Methanation

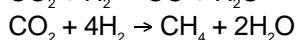
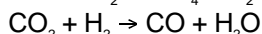
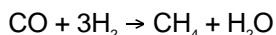
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### Process Description

All CO<sub>2</sub> absorption systems leave a small amount, i.e. less than 1%, of residual carbon oxides in the gas. Both CO<sub>2</sub> and residual carbon monoxide must be removed, otherwise they will poison most ammonia synthesis catalysts. Removal is accomplished by a catalytic methanation process (Figure 3). Heat of reaction is recovered from the methanator effluent by exchange with boiler feedwater.

The synthesis gas is passed over a nickel-containing catalyst (NiO on alumina) at 600 to 1110°F (316 to 600°C) and pressures up to 600

atmospheres according to these reactions:



This reaction is the reverse of that involved in steam reforming of methane. Reversal is accomplished through use of lower temperatures and absence of excess water, both of which favor the formation of methane.

The methanator exit gas is cooled to 100°F (38°C) and contains less than 20 ppm carbon oxides. Condensate is removed in a process condensate drum. The final synthesis gas at 100°F (38°C) and about 370 psig (2.55 MPa) contains hydrogen and nitrogen in a ratio of 3:1, and less than 1.5% methane.

### Nature of Corrosion

Corrodents in the methanation step are similar to those in the carbon monoxide shift—CO, CO<sub>2</sub>, H<sub>2</sub> and condensed water. Although methanation reaction pressures are lower and temperatures are somewhat higher, this process is no more aggressive to materials of construction than is the CO shift process.

### Applications for Stainless Steels

Applications of stainless steels – mostly Type 304—in the methanator are limited to wire mesh screens and grating, which support the catalyst bed in the methanator, thermocouple sheaths, thermowells and other on-stream instruments and valve trim. Otherwise, plain carbon and low alloy steels dominate the materials of construction in the methanation step.

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## Synthesis of Ammonia

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### Process Description

Many variations of the original

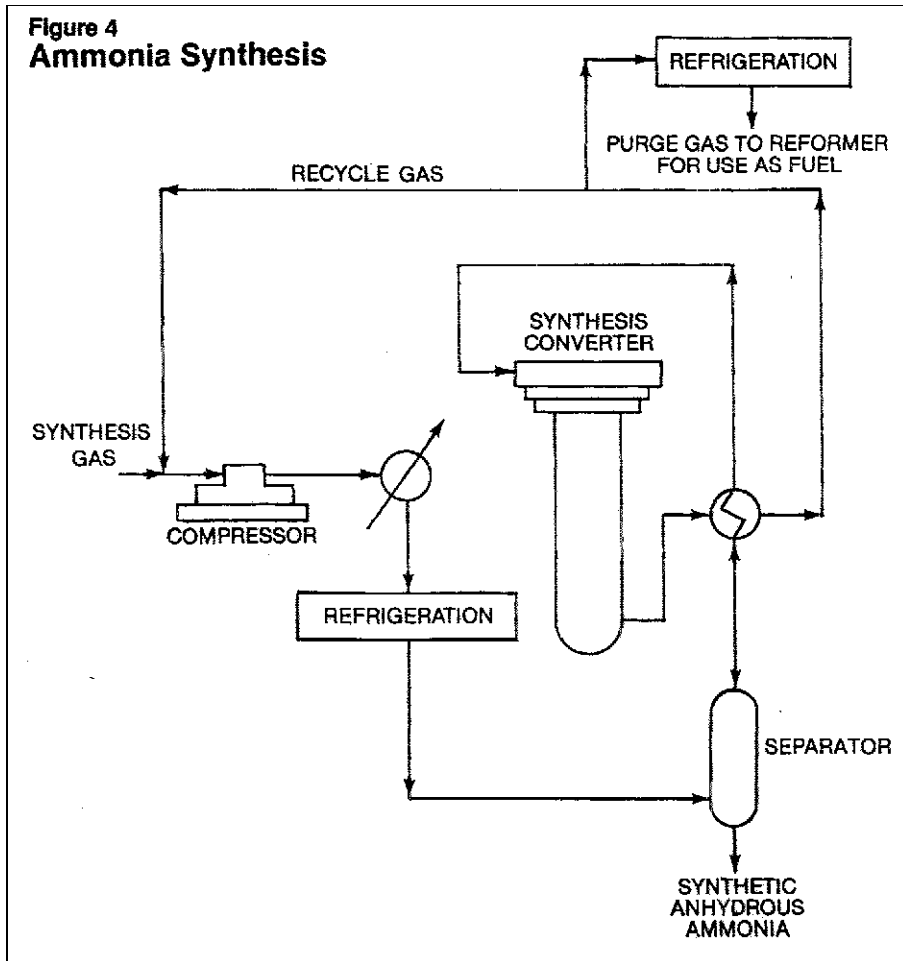
Haber process for the synthesis of ammonia are now used commercially. All are fundamentally the same, i.e. nitrogen is fixed with hydrogen as ammonia in the presence of a catalyst. However, they vary with regard to flow arrangement and construction of equipment, composition of catalysts, temperatures and pressures.

The first step in ammonia synthesis is compression of the synthesis gas from the methanator (Figure 4). Within the last 15 years, a revolution has occurred in the ammonia industry through the application of centrifugal compressors driven by steam turbines for handling synthesis gas at pressures between 2000 psig (13.8 MPa) and 10,000 psig (69 MPa). These machines require lower investment, maintenance and energy requirements per ton of ammonia than reciprocating machines.

Synthesis gas is compressed in several stages to 2000-5000 psig (13.8-34.5 MPa) and mixed with recycled synthesis gas from the reactors. The combined gas stream is cooled to -10 to 32°F (-23 to 0°C) in a refrigeration cooler. Condensed ammonia is separated from the unconverted gas in a liquid-vapor separator and a pressure let-down separator. The gas is preheated to about 360°F (180°C) before entering the converter. At this point, the synthesis gas contains hydrogen and nitrogen in the proper 3:1 ratio, along with 12-14% inerts and about 4% ammonia.

In the converter, synthesis gas is dispersed through a promoted iron oxide (Fe<sub>3</sub>O<sub>4</sub>) catalyst (an iron oxide catalyst whose activity is increased or promoted by the addition of oxides of aluminum or potassium). The gas which exits the catalyst beds in the converter is about 700°F (370°C) and contains approximately 15% ammonia and 14% inerts. This hot gas is used to preheat boiler feedwater for the steam system and is then interchanged with feed gas to the converter. The ammonia-rich gas is recycled through the synthesis compressor be-

**Figure 4**  
**Ammonia Synthesis**



fore being cooled to condense the ammonia. A small portion of the overhead gas is purged to prevent accumulation of inerts in the circulating gas system. The purge gas is cooled to 10°F (-23°C) to minimize loss of ammonia, and burned as fuel in the primary reformer. Some plants use a recently developed cryogenic system to recover hydrogen from the purge gas which is then used as feedstock to produce additional ammonia. (7)

Liquid ammonia from the primary, secondary and purge separators collects in the let-down separator where the ammonia is flashed to atmospheric pressure at -27F (-33C) to remove additional impurities such as argon. The flash vapors are condensed in a pressure let-down chiller. Anhydrous liquid ammonia of high purity is transferred from the let-down

separator to low-temperature atmospheric pressure storage.

### Nature of Corrosion

Ammonia is synthesized in the converter at temperatures between 840 and 930°F (450 and 500°C), and the synthesis gas has high potential for nitriding metals at these temperatures. Another requirement for ammonia synthesis is fairly high pressure (2000 to 5000 psig) (13.8 to 34.5 MPa). Corrosive ammonium carbamate may be formed during the several stages of compression of synthesis gas prior to introduction into the converter. Condensed ammonia is also a corrodent, and in the anhydrous state, can cause stress-corrosion cracking of stressed carbon steels and heat-treated, high-strength,

low-alloy steels. (8) Other process considerations for materials selection include hydrogen at elevated temperatures and pressures: steam at pressures up to 1500 psig (10.3 MPa) used for driving high-performance turbines; and maintenance of product purity.

### Applications for Stainless Steels

Although carbon steel exhibits a low corrosion rate in this system, carbon steel tubes in the water-cooled exchangers have failed prematurely in service because of fouling and corrosion by aggressive natural waters used for cooling. Type 430 stainless steel replacement tubes have provided many years of leak-free service at some plants, especially in units where water is circulated through the tubes. This alloy is also immune to chloride stress-corrosion cracking by chloride-bearing waters. In some waters, pitting of Type 430 under deposits could be a problem, especially where the water is circulated on the shell side of the exchanger with more opportunity for accumulation of deposits at baffles and tube sheets. In these cases, the new ferritic stainless steels which contain 26% Cr and 1% Mo may find application because of superior pitting resistance as compared to Type 430 stainless steel and similar immunity to chloride cracking. Two grades are specified in ASTM A-268: Grade XM-27 (UNS S44625) which is furnished with very low carbon and nitrogen contents, and Grade XM-33 (UNS S44626): Both alloys are stabilized. Another grade of ferritic stainless steel that may be considered is ASTM A-268, Grade UNS S44400, which contains 18% chromium and 2% molybdenum and is stabilized with titanium and niobium.

Synthesis converters are pressure vessels consisting of heavy wall carbon or low alloy steel shells, which contain a removable cartridge filled with the promoted iron oxide catalyst required for conversion of synthesis gas to ammonia. The cartridge con-

tains an integral tubular heat exchanger that preheats fresh inlet gas with hot reacted gas from the last catalyst bed. The combination of both reacted and unreacted gases at 2000+ psig (13.8+ MPa) and temperatures approaching 930°F (500°C) can be quite destructive to carbon and low alloy steels and other metals with regard to hydrogen embrittlement and attack, and nitriding. Therefore, Type 304 is nearly always specified as the optimum material of construction for the catalyst cartridge and integral heat exchanger. In general, the austenitic stainless steels are resistant to nitriding and hydrogen embrittlement and immune to hydrogen attack. Over a period of several years' operation, shallow—up to about 0.005 inch (0.127mm)—nitriding will occur in the hottest regions, resulting in a hard, brittle skin on the stainless steel surface. However, this appears to have little or no effect on the structural integrity of this equipment.

In the early 1960's, investigators from the International Nickel Company, Inc. published results of about 3 years exposure of corrosion coupons of austenitic and ferritic stainless steel and nickel-base alloys in Haber-Bosch (9) and Casale process (10) ammonia converters. The operating conditions were as follows:

Haber-Bosch—915 to 1020°F (490 to 550°C); 5200 psig (35.9 MPa)

Casale—Nominal 1005°F (540°C); 11,000 psig (75.8 MPa)

The following conclusions were drawn from these tests;

1. Nickel and nickel-base alloys exhibited the best nitriding resistance in both exposures.
2. Depth of nitriding is a function of operating pressure; coupons exposed in the higher pressure Casale converter were penetrated to greater depths than those exposed in the Haber-Bosch converter.

3. The austenitic stainless steels showed good resistance.

4. Increased nickel contents resulted in increased resistance to nitriding.

Thus, it follows that the newer modified Haber process converters which operate at lower temperatures and pressures are affected to a lesser extent by the process stream.

Much of the piping and equipment, e.g. heat exchangers, around the converter are fabricated from low alloy steels such as carbon-½% Mo and 1¼%Cr-½% Mo for resistance to hydrogen attack. At certain combinations of temperature and hydrogen partial pressure, nascent hydrogen will diffuse into plain carbon steels and combine with carbon to form methane. The results are loss of strength by decarburization plus loss of ductility by microfissuring. Hydrogen attack has caused catastrophic failures of piping and vessels. The American Petroleum Institute Publication 941, "Steels For Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants", Second Edition (June 1977), is an update of a compilation of data from plant experience and laboratory tests which G.A. Nelson of the Shell Development Corporation initiated in the 1940's. Curves showing safe limits for plain carbon and low alloy steels are plotted vs. temperature and hydrogen partial pressure.

Curves for the austenitic stainless steels are not included because these materials are virtually immune to this phenomenon under all combinations of temperature and hydrogen partial pressure. Thus, critical on-stream instruments, control valves and valve trim in the converter loop are frequently specified in austenitic stainless steels, primarily Types 304 and 316. Where higher mechanical strengths are required, such as for valve stems subjected to heavy cyclic loads, the precipitation hardening stainless steel A-286 (15Cr-26Ni-1 ¼Mo-2.15Ti), designated

as Grade 688 in ASTM-A-638, has given excellent service. For comparison, the precipitation hardening S17400 stainless steel in Condition H950 has failed prematurely by hydrogen embrittlement under identical conditions.

The ammonia synthesis system contains a large investment in refrigeration facilities and equipment for handling process streams at low temperatures. These facilities are required for ammonia condensation in the synthesis loop, recovery of ammonia from vented gases, synthesis gas compressor inter-stage chilling, plus refrigeration and storage of the anhydrous liquid ammonia product.

Plain carbon steels have satisfactory corrosion resistance in the process streams. However, all equipment components—vessel plates, forgings, tubing, pipe, etc.—generally require Charpy V-notch impact testing or drop weight testing to insure good fracture toughness at temperatures between 32 and -27°F (0 and -33°C). Procurement of certified components is not much of a problem for large, new investments in facilities, but could pose a problem when components are required on short notice, i.e., during major shutdowns for modifications or repairs. Under these circumstances, plants frequently substitute austenitic stainless steel components because of availability from stock and excellent fracture toughness down to -328°F (-200°C) and beyond, generally without an impact test requirement. Welds are readily made between the stainless steel components, usually Types 304 and 316, and the existing carbon steel parts, by gas tungsten arc and/or shielded metal arc processes with Type 309 or 310 weld filler metal.

In general, anhydrous liquid ammonia is considered to be noncorrosive to a variety of metals and alloys including carbon steel and all classes of stainless steels. Recent work (11) has shown many metals and alloys—including the aforementioned carbon steel and stainless

steels, along with titanium, zinc, Monel and aluminum alloys—exhibiting either very low weight losses or slight weight gains in anhydrous liquid ammonia after one to eight month's exposure at room temperature.

The intergranular stress-corrosion cracking, or "season" cracking as it is commonly known, of some copper alloys, most notably the brasses, by moist ammonia has been well documented. So has the more recent disclosure of stress-corrosion cracking of stressed carbon steels and high-strength low alloy steels by air-contaminated liquid anhydrous ammonia (8), and inhibition of this cracking by addition of a minimum of 0.2%

water to the ammonia. It is noteworthy that the austenitic stainless steels have shown no cracking tendencies in ammonia under any conditions.

## Turbine-Driven Centrifugal Compression Trains

Turbine-driven centrifugal compression trains are listed as a seventh heading, because there are four such trains in most modern-day ammonia

plants, with similarities in materials of construction. Plants require compression trains for the following services:

1. Compress natural gas feed to the primary reformer operating at pressures of 440 to 550 psig (3 to 3.8 MPa).
2. Provide air to the secondary reformer.
3. Compress synthesis gas to the converter operating at pressure: of 2000 to 5000 psig (13.8 to 34.5 MPa).
4. Provide refrigeration for several key steps in the synthesis of ammonia.

Virtually all of the 1500 psig (10.3 MPa) steam generated in waste heat

**TABLE 1**  
**Chemical Analysis, %**  
**(Maximum unless noted otherwise) (12)**

AISI Type (UNS)	C	Mn	P	S	Si	Cr	Ni	Mo	Other
405 (S40500)	0.08	1.00	0.040	0.030	1.00	11.50/14.50			Al 0.10/0.30
410 (S41000)	0.15	1.00	0.040	0.030	1.00	11.50/13.50			
422 (S42200)	0.20/0.25	1.00	0.025	0.025	0.75	11.00/13.00	0.50/100	0.75/1.25	V 0.15/0.30 W 0.75/1.25
430 (S43000)	0.12	1.00	0.040	0.030	1.00	16.00/18.00			
304 (S30400)	0.08	2.00	0.045	0.030	1.00	18.00/20.00	8.00/10.50		
304L (S30403)	0.030	2.00	0.045	0.030	1.00	18.00/20.00	8.00/12.00		
309 (S30900)	0.20	2.00	0.045	0.030	1.00	22.00/24.00	12.00/15.00		
309S (S30908)	0.08	2.00	0.045	0.030	1.00	22.00/24.00	12.00/15.00		
310 (S31000)	0.25	2.00	0.045	0.030	1.50	24.00/26.00	19.00/22.00		
310S (S31008)	0.08	2.00	0.045	0.030	1.50	24.00/26.00	19.00/22.00		
316 (S31600)	0.08	2.00	0.045	0.030	1.00	16.00/18.00	10.00/14.00	2.00/3.00	
316L (S31603)	0.030	2.00	0.045	0.030	1.00	16.00/18.00	10.00/14.00	2.00/3.00	
321 (S32100)	0.08	2.00	0.045	0.030	1.00	17.00/19.00	9.00/12.00		Ti 5 x C (Min.)

recovery and auxiliary boilers is used to drive the turbines in these trains. Each turbine is capable of generating thousands of horsepower at speeds between 6000 and 10,000 rpm. Type 403 is an industry standard for buckets and shrouds on rotors where stress levels are low-to-moderate. At higher stress levels, heat treated Type 422 has provided excellent service. Type 405 is frequently specified for stationary components such as diaphragms and nozzle blocks, especially where welding is required. Steam admission and throttle valve seats and plugs of Type 410 with a hard surface weld overlay on seating

surfaces for added wear resistance are also industry standards.

Austenitic stainless steels have been applied to some extent in shell-and-tube surface condensers that use cooling water to condense the large quantities of turbine exhaust steam for reuse as process condensate. However, steam temperature must not be excessive or chloride stress-corrosion cracking may occur in some chloride-bearing cooling waters. One major chemical company maintains the steam temperature at or below 140°F (60°C) to avoid stress-corrosion cracking problems. The ferritic stainless steels which contain a

nominal 26% Cr and 1 % Mo may find application in condensers that operate at higher steam temperatures or in more-aggressive cooling waters. Alternately, several highly alloyed austenitic stainless steels may be considered.

The multi-stage centrifugal compressors are heavy users of stainless steels also. Type 410 is in common use for rotor impellers because of good corrosion and erosion resistance, strength and fabricability. In cases where stress levels are high and particularly where impellers are fabricated by welding, Type 410 with addition of niobium in the range of 0.15 to 0.25% has been specified for improved fracture toughness in the heat treated condition and good weldability in the annealed condition. Stationary parts such as inlet guide vanes are frequently fabricated in austenitic or ferritic stainless steels.

Other applications in compression trains and related equipment include Type 304 for interstage separator demister pads, valve trim and on stream instrument components. The new ferritics may find application in interstage coolers of shell-and-tube design and cooled with natural waters.

## STAINLESS STEELS

There are a total of 57 separate and distinct compositions that are recognized by American Iron and Steel Institute as standard AISI-numbered stainless steels. Of these 57 types, nine are regularly used in ammonia production equipment. The chemical compositions of these types (plus their low-carbon counterparts)\* are shown in Table 1, and their mechanical properties are shown in Table 2.

\*Note: Intergranular corrosion does not appear to be a problem in ammonia production. However, the low-carbon grades are readily available for chemical plant construction so they are identified for the information of the reader.

**TABLE 2  
Nominal Mechanical Properties  
(Annealed sheet unless noted otherwise) (12)**

AISI Type (UNS)	Tensile Strength		Yield Strength (0.2% offset)		Elongation In 2" (50.80 mm) %	Hardness Rockwell
	ksi	MPa	ksi	MPa		
405 (S40500)	65	448	40	276	25	B75
410 (S41000)	70	483	45	310	25	B80
422* (S42200)	145	1000	125	862	18	320 (Brinell)
430 (S43000)	75	517	50	345	25	B85
304 (S30400)	84	579	42	290	55	B80
304L (S30403)	81	558	39	269	55	B79
309 (S30900)	90	621	45	310	45	B85
309S (S30908)	90	621	45	310	45	B85
310 (S31000)	95	655	45	310	45	B85
310S (S31008)	95	655	45	310	45	B85
316 (S31600)	84	579	42	290	50	B79
316L (S31603)	81	558	42	290	50	B79
321 (S32100)	90	621	35	241	45	B80

\*Hardened and Tempered Bar

# Metallurgical Structure

Stainless steels in the *Austenitic* group, containing chromium and nickel, are identified as AISI 300 Series types. (Those containing chromium, nickel, and manganese are identified as 200 Series types.)

Although the austenitic grades have different compositions, they have common characteristics. They can be hardened by cold working, but not by heat treatment. Annealed, all are nonmagnetic; however, some may become slightly magnetic on cold working. They have excellent corrosion resistance, mechanical properties (at ambient as well as low or elevated temperatures), and formability.

Type 304 (frequently referred to as 18-8) is the general-purpose stainless steel of the austenitic group with a nominal composition of 18% chromium and 8% nickel.

In the *Ferritic* group are the straight-chromium, 400 Series types that cannot be hardened by heat treatment, and are only moderately hardened by cold working. They are magnetic and have good ductility and resistance to corrosion and oxidation. Type 430, nominally 17% chromium, is the general-purpose stainless steel of the ferritic group.

In addition to the AISI types, some proprietary ferritic stainless steels are also candidate materials for ammonia production applications. Several of these are listed in Table 3. These stainless steels represent improvements in refining practices, particularly with respect to carbon and nitrogen removal, achieved commercially only in the last five years.

In the *Martensitic* group are the straight-chromium 400 Series types that can be hardened by heat treatment. They are magnetic. They resist corrosion in mild environments, have

fairly good ductility, and some can be heat treated to tensile strengths exceeding 200,000 psi (1379 MPa).

Type 410 with about 12% chromium is the general-purpose stainless steel of the martensitic group.

# High-Temperature Mechanical Properties

Stainless steels are used routinely up to temperatures of 1500°F (816°C) because they possess good high-temperature strength, ductility, and resistance to high-temperature oxidation and sulfidation. Types 309 and 310 are quite frequently used in oxidizing environments at temperatures as high as 1800°F (982°C).

Figure 5 shows the Allowable Design Stresses from the ASME Unfired Pressure Vessel Code, Section VIII Division 1 versus temperature for several austenitic stainless steels, ferritic stainless steels, chromium-molybdenum steels, and carbon steel. This graph portrays the value of chromium additions to steel for ele-

vated temperature applications and the added advantage of nickel plus chromium.

The stresses that will cause rupture of several austenitic stainless steels in 10,000 and 100,000 hours are shown in Figures 6 and 7 as a function of temperature. Stresses that will cause creep at the rates of 0.0001 and 0.00001 per cent per hour are shown in Figures 8 and 9. Interpolation to other rupture times, creep rates, and stresses can be made by using Figures 10 to 16, which show the effects of applied stresses on the rupture times and creep rates for the same stainless steels at different temperatures.

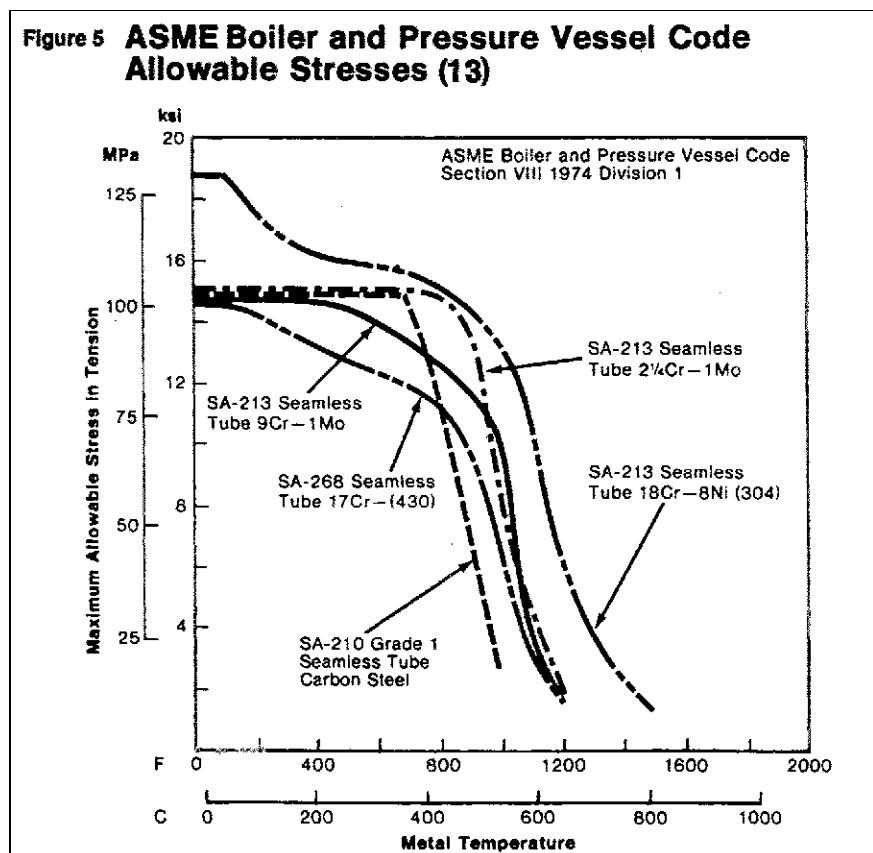
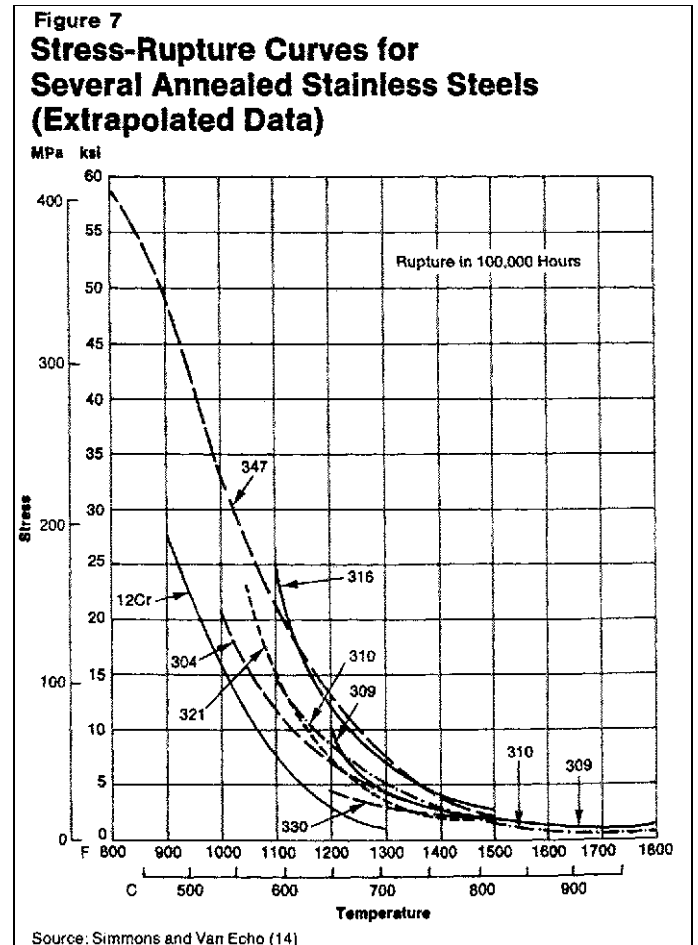
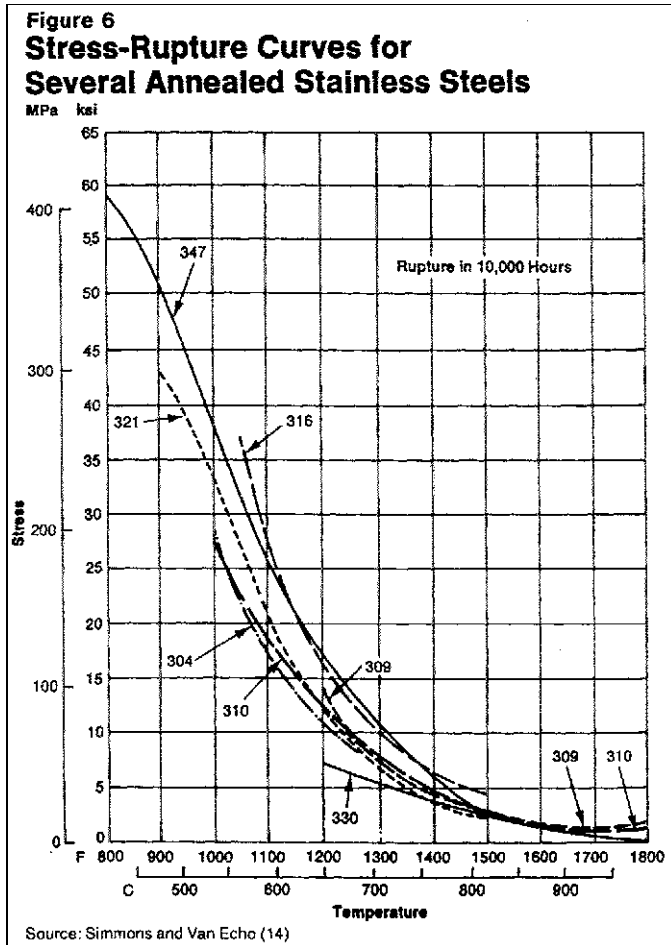


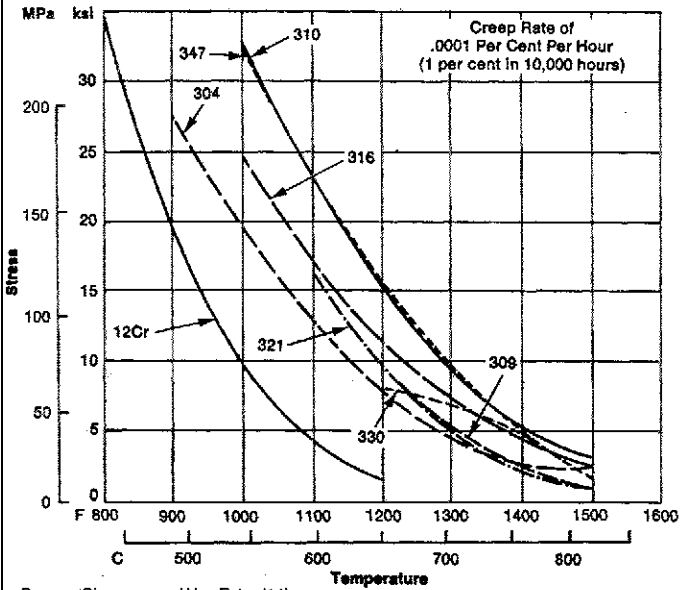
TABLE 3		
Alloy	ASTM	UNS
18Cr-Ti (Alloy 439)	XM-8	S43035
18Cr-2Mo-Ti/Nb (Alloy 444)	*	S44400
18Cr-2Mo-S	XM-34	S18200
26Cr-1 Mo (E-Brite 26-1)	XM-27	S44625
26Cr-1 Mo-Ti	XM-33	S44626

\*This steel is covered in ASTM Specifications, e.g. A 176 and A 268, but ASTM no longer gives "XM" designations, relying instead on the UNS (Unified Numbering System) designation.



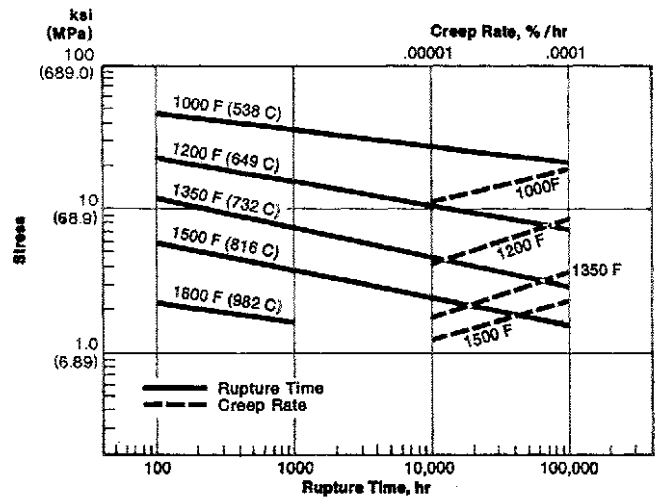


**Figure 8**  
**Creep-Rate Curves for**  
**Several Annealed Stainless Steels**



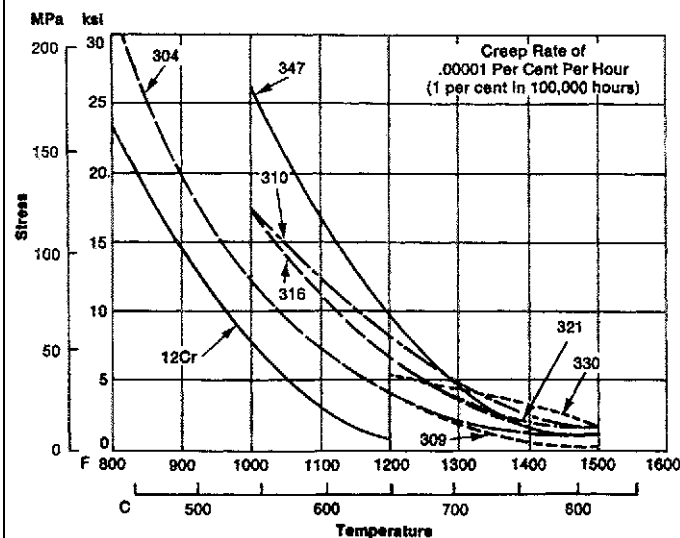
Source: Simmons and Van Echo (14)

**Figure 10**  
**Stress Versus Rupture-Time and**  
**Creep-Rate Curves for Annealed Type 304**  
**Stainless Steel Based on Average data**



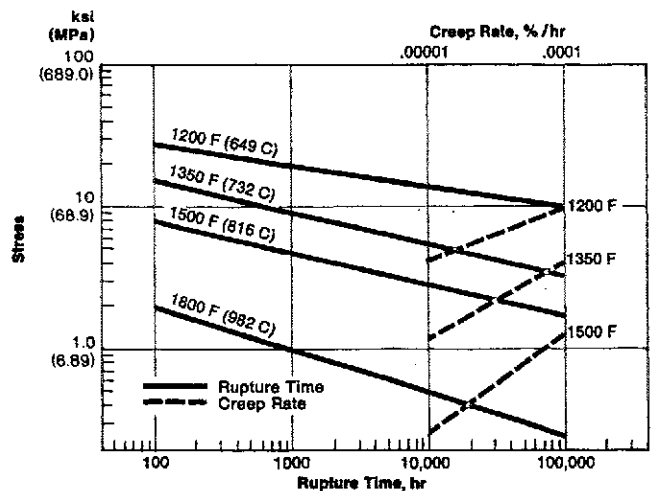
Source: Simmons and Van Echo (14)

**Figure 9**  
**Creep-Rate Curves for**  
**Several Annealed Stainless Steels**



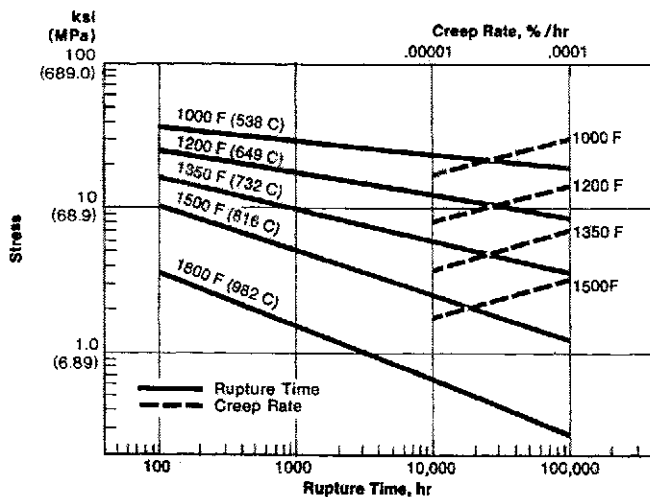
Source: Simmons and Van Echo (14)

**Figure 11**  
**Stress Versus Rupture-Time and**  
**Creep-Rate Curves for Annealed Type 309**  
**Stainless Steel Based on Average Data**



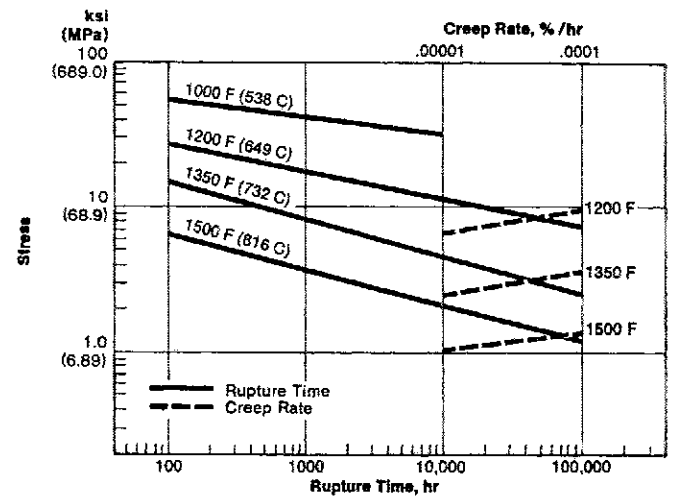
Source: Simmons and Van Echo (14)

**Figure 12**  
**Stress Versus Rupture-Time and**  
**Creep-Rate Curves for Annealed Type 310**  
**Stainless Steel Based on Average Data**



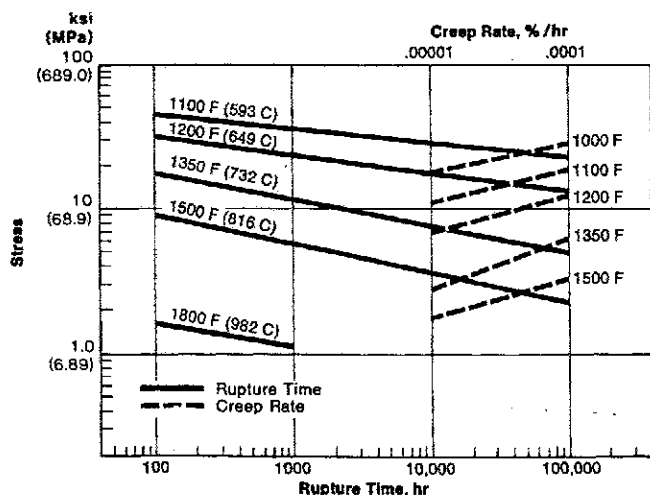
Source: Simmons and Van Echo (14)

**Figure 14**  
**Stress Versus Rupture-Time and**  
**Creep-Rate Curves for Annealed Type 321**  
**Stainless Steel Based on Average Data**



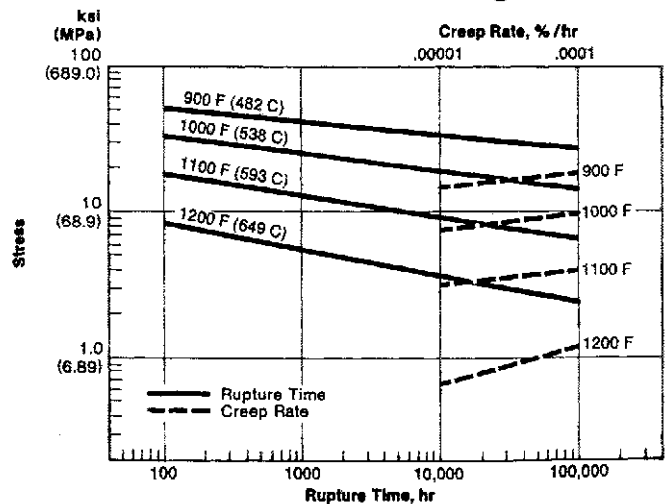
Source: Simmons and Van Echo (14)

**Figure 13**  
**Stress Versus Rupture-Time and**  
**Creep-Rate Curves for Annealed Type 316**  
**Stainless Steel Based on Average Data**



Source: Simmons and Van Echo (14)

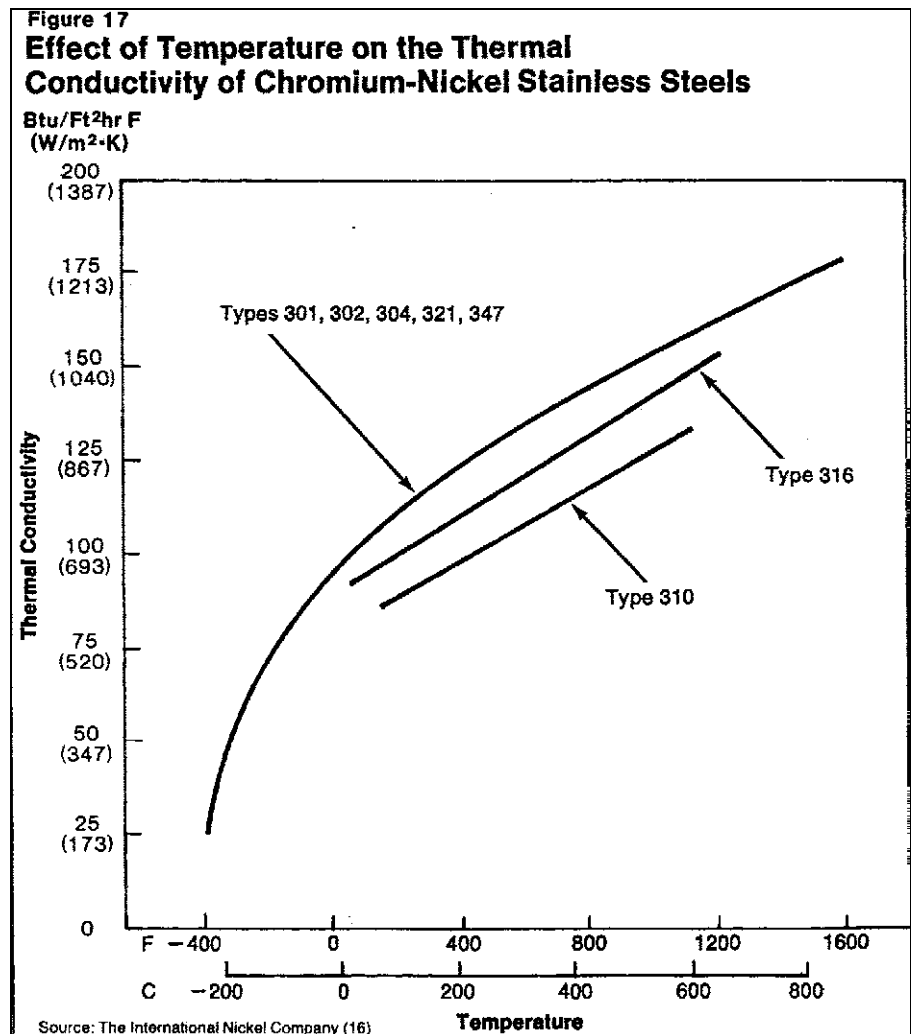
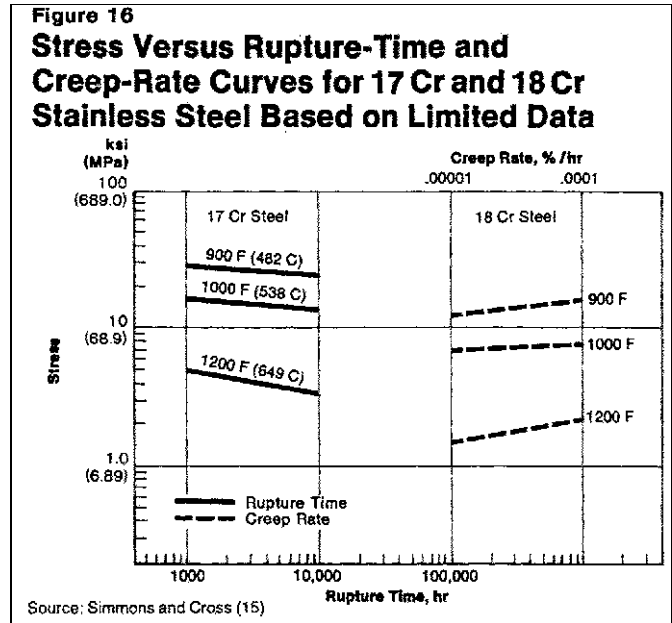
**Figure 15**  
**Stress Versus Rupture-Time and**  
**Creep-Rate Curves for Type 410**  
**Stainless Steel Based on Average Data**



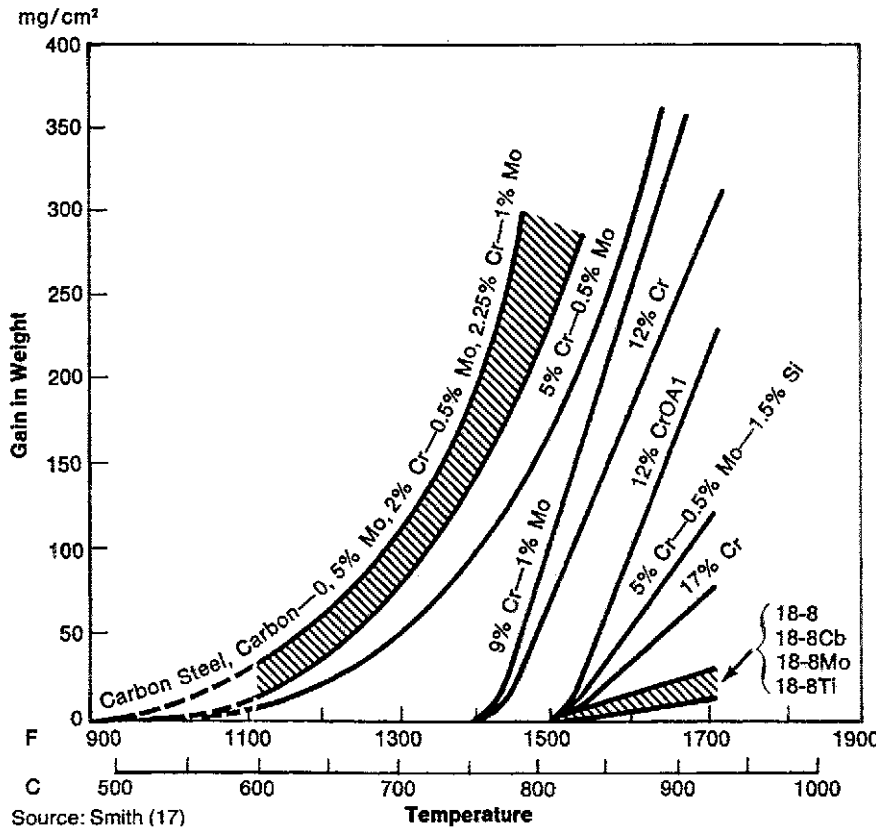
Source: Simmons and Cross (15)

# Thermal Conductivity

Curves showing the average effect of temperature on the thermal conductivity of seven austenitic stainless steels are shown in Figure 17. Heat transfer efficiency is a subject of increasing importance among plant engineers because of the need to achieve closer to optimum performance in heat exchangers and thus economize on heat investment and energy utilization. The thermal conductivity of the ferritic stainless steels is somewhat higher than that of the austenitics.



**Figure 18**  
**Comparative Scaling Behavior of Various Steels**  
**During 1000-Hr Exposures in Air at Temperatures**  
**from 1100 to 1700 F (595 to 925 C)**



**TABLE 4**  
**Maximum Service Temperatures for Satisfactory Use Under**  
**Oxidizing Conditions Without Excessive Scaling (18)\***

AISI Type*	Continuous Service		Intermittent Service	
	C	F	C	F
304	925	1700	870	1600
308	980	1800	925	1700
309	1095	2000	980	1800
310	1150	2100	1035	1900
316	925	1700	870	1600
317	925	1700	870	1600
321	925	1700	870	1600
330	1150	2100	1035	1900
347	925	1700	870	1600
405	705	1300	815	1500
410	705	1300	815	1500
430	815	1500	870	1600

\*The temperature limits shown may have to be revised downward in the presence of combustion products or gases high in sulfur compounds and if vanadium-containing ash is present.

## Oxidation Resistance

The most important alloying element for increasing scaling resistance above 1000°F (538°C) is chromium. This element appears to oxidize preferentially to iron. It forms a tightly adherent layer of chromium-rich oxide on the surface of the metal, retarding the inward diffusion of oxygen and inhibiting further oxidation. Other elements such as silicon and aluminum also increase scaling resistance, particularly when added to a steel containing chromium. Nickel imparts high temperature strength, it stabilizes the austenitic structure, and it adds a small measure of high-temperature corrosion resistance.

Figure 18 provides an indication of the relative scaling resistance of commonly used high-temperature alloy steels.

Stainless steels containing less than 18% chromium are limited to temperatures below 1500°F (816°C). Those containing 18-20% chromium are useful to temperatures of 1800°F (982°C), while adequate resistance to scaling at temperatures up to 2000°F (1093°C) requires a chromium content of at least 25%, such as Types 309 and 310. The maximum service temperature, based on an oxidation rate of 10 mg per sq cm in 1000 hours, is given for several stainless steels in Table 4. Steam will increase the oxidation rate.

For conditions in which temperatures vary, temperature limits also shown in Table 4 in the column "Intermittent Service."

Additions of silicon also increase resistance to oxidation, such as in Type 314, but silicon tends to decrease high-temperature strength.

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# Sulfidation Resistance

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Sulfur attack is second only to air oxidation in frequency of occurrence and is of even greater consequence because deterioration is likely to be more severe.

Like oxidation, sulfidation proceeds by converting metal to scale, which may be protective, except that sulfide scales are friable and tend to exfoliate, exposing bare metal to further sulfidation.

As with oxidation, resistance to sulfidation relates to chromium content. Unalloyed iron will be converted rather rapidly to iron sulfide scale, but when alloyed with chromium and nickel, sulfidation resistance is enhanced. Silicon also affords some protection to sulfidation.

In addition to the usual factors of time, temperature, and concentration, sulfidation depends upon the form in which the sulfur exists. An alloy possessing useful resistance to sulfur in one form may actually experience accelerated corrosion when the sulfur is present in another form.

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