METALS *and* ALLOYS *in the* CHEMICAL INDUSTRY

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I. INTRODUCTION AND THEORY

INTRODUCTION

THE development in the treatment, production, and transportation of chemicals during the past hundred years has necessitated very great changes in chemical engineering materials of construction. A century ago most of the apparatus and equipment used in the manufacture of chemicals was constructed of wood, iron, copper, and various siliceous materials. Today, because of the much greater volume of chemical manufacture and because of the more complex and corrosive chemicals employed, other constructional materials are called into service. Some must be chosen not only for their corrosion resistance but also for their resistance to high temperatures.

This is truly the age of new metals and complex alloys. No large chemical plant can hope to operate successfully without installations of nickel, silico-irons, nickel-chromium-steels, antimonyl lead, etc. It is quite possible that many of these will give way in the future to more suitable ones.

The purpose of this paper is to outline the developments made in chemical engineering metals and alloys. It is not the writer's intention to omit or disparage the use of glassware, rubber, plastics, and other non-metallic materials, useful as they are; but space permits only what the title of this paper implies. A later article will discuss the use of the non-metallic materials.

REQUIREMENTS FOR METALLIC MATERIALS OF CONSTRUCTION

In choosing the proper metals for an installation or piece of equipment the following factors are generally considered important:

1. Cost
2. Chemical or Thermal Resistance
3. Physical Properties

Cost is probably the most important. Were it not for their high cost, platinum and gold would find considerable use in various chemical operations; their high cost, however, precludes their use except in some isolated cases.

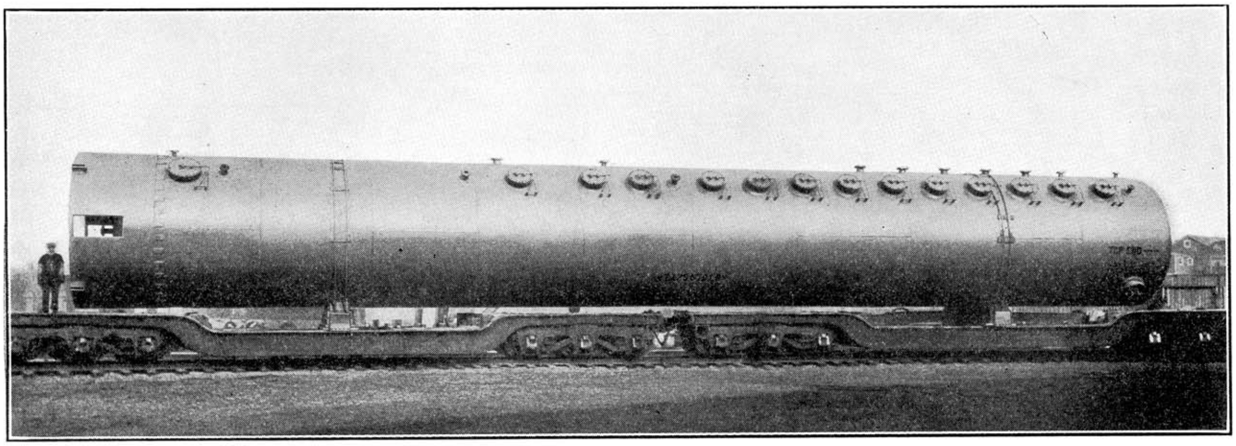
The second most important factor is the chemical or heat resistance of a metal. Obviously, if it is not resistant to the conditions imposed upon it, the material will corrode and ultimately be destroyed. Not only does the corrosion of a metal necessitate the early replacement of that metal but the products of corrosion may so contaminate the processed materials that they become unfit for sale or use. Sometimes a metal corrodes so slowly that it could be used a long time before replacement would be necessary, but its use is impractical because the products of the slight amount of corrosion contaminate the processed chemicals. A good example of this is in the manufacture of phosphoric acid for foodstuffs. From the point of view of equipment life, a certain chromium-nickel-molybdenum-iron alloy is satisfactory as material for the apparatus used in processing this acid. It is slightly attacked, however; and this results in a minute contamination which strict specifications forbid. The very interesting part of this story is that in its place a cheaper iron-silicon alloy is used which does not resist the solutions nearly so well but whose contaminating iron or silicon does not happen to be forbidden by the specifications. If a metal or alloy is not resistant to chemical or thermal action as specified for a certain use then it cannot be used.

Various other factors often have a great deal to do with the choice of material for construction. Very often a balance is struck between an expensive alloy which is resistant and a cheaper one which is not resistant. Many of the more expensive alloys have scrap value which is a good selling point over inferior and cheaper alloys. If the process is in rapid stages of development and improvement, a manufacturer is justified in being reluctant about installing permanent equipment. The same reasoning applies if the market indicates that a lower demand for a certain product is in sight. In such cases more inexpensive and less resistant materials are employed.

In order that a metal or alloy may be fabricated into equipment it must possess properties which permit such fabrication. The desirable physical properties are: machinability, weldability, strength, workability, castability, etc. Some alloys like the silicon-irons and high chromium alloys can be successfully cast, but because they are hard and brittle cannot be machined or worked. Such alloys, which are not amenable to working, can often be cast and ground into intricate shapes and designs. Most of the industrial alloys can be worked and machined with comparative ease, however.

In order to obtain the greatest corrosion resistance some fabricated alloys must be properly heat-treated.

This topic will be discussed more fully later. In recent years the weldability of a material has become more and more important. The advantages of a weld over a riveted or crimped joint should be obvious. Welding, however, often produces a strip along the weld which is more subject to corrosion than the surrounding metal. This difficulty is eradicated by proper heat treatment after the welding operation. Welding has become such a successful art that almost any metal or complex alloy of any size can be joined and finally heat-treated without impairing any of its physical properties or lowering its chemical resistance. Figure 1 shows a huge bubble tower and gas-oil accumulator constructed of $1^1/_4$-inch steel plate. This tower, which is 93 feet high, weighs over 300,000 pounds!



Courtesy Babcock and Wilcox Co.

FIGURE 1.—HUGE BUBBLE TOWER FOR OIL REFINING CONSTRUCTED OF STEEL

Chemical plant equipment is constantly being made larger and larger for the sake of efficiency and economy. The apparatus units are so large in many cases that they must be fitted together outside the fabricating plant. Most of this fitting is done by welding, followed by subsequent heat treatments in enormous annealing furnaces.

In concluding this section one can say that the future points toward cheaper and more resistant alloys bearing better physical properties. The age of alloys has just started; many are the wonders for the future.

CLASSIFICATION

Metallurgists are not satisfied with any one scheme for classifying the various alloys. They speak of ferrous and non-ferrous alloys, however, and that classification seems as good as any for a starting point. For the purpose of this paper it may be justifiable to make a classification for those metals and alloys which have a special significance to the chemist and chemical engineer, as:

Ferrous	*Non-ferrous*
1. steels, wrought, and cast iron	1. aluminum
2. silicon-irons	2. copper, brasses, and bronzes
3. chromium-iron ("stainless steels")	3. lead
4. chromium-nickel-iron ("18-8")	4. nickel and Monel metal
	5. nickel-chromium alloys
	6. rare and miscellaneous metals and alloys

Over ninety-nine per cent. of all installations make use of the metals and alloys given in this classification, although there are a number of metals and alloys not included that find certain isolated uses in the chemical industry. It must be remembered that the use of a certain metal or alloy in a certain process does not necessarily imply that it is the only one that can be used or that it is the best in use. Manufacturers are constantly finding a certain alloy to be more economical or effective than another which they have been using for years.

THEORY

The electrochemical theory of corrosion gives us very definite and useful information concerning the probable behavior of metals in various corrosion media. It tells us, for example, that the metals above hydrogen in the electrochemical series have a tendency to displace hydrogen from solutions according to the Nernst equation. (For a discussion of the mechanics of this theory see the writer's papers in the March, April, and May numbers of the JOURNAL OF CHEMICAL EDUCATION for 1933.) In chemical industry one is concerned with many concentrated acid solutions possessing a very great tendency to dissolve metals with the evolution of hydrogen. If one examines again the class of metals and alloys used in chemical industry he will find that most of them are those which occur above hydrogen and should be easily corroded or dissolved. This truly appears anachronistic, but nature in her display of phenomena has endowed these metals with the protection of self-forming, insoluble, surface-covering films, known to the electrochemist as passive films.

Because of the phenomenon of passivity the large scale chemical industry is possible; without it chemical manufacture would have to be confined to apparatus constructed of glass, ceramics, rubber, rare metals, etc. However, not all metals above hydrogen possess the ability to form passive films, nor are such films formed in all corroding media. Aluminum is insoluble in concentrated nitric acid but not in hydrochloric or sulfuric; the silico-irons are insoluble in sulfuric acid but not in sulfuric containing chlorides; lead is insoluble in dilute sulfuric acid but not in concentrated; while iron and steel are soluble in dilute but not in concentrated sulfuric acid.

It is unfortunate that so little is known concerning the phenomenon of passivity. Although our experience with the nature of some metals and alloys in various media has given us considerable information as to the probable resistance of other metals or alloys, there is as yet only one infallible rule for determining the adaptability of a metal or alloy, and that is—try it! Certain self-evident rules can be often applied. If, for instance, a high chromium-iron alloy is resistant to crude phosphoric acid and a 20% chromium-iron alloy only slightly resistant, then one can be pretty certain that a 12% chromium-iron will not be very resistant. Again, if nickel is fairly resistant to hydrochloric acid and chromium not resistant, alloys rich in the former will be more useful for solutions of this acid than alloys rich in the latter. Although generally correct, such conclusions may be misleading because of the minutiæ of factors that are involved and not considered.

On the other hand, if a metal or alloy is desired for processing a mixture, for example, of acetic and hydrochloric acid, one would not know what to recommend without actually testing the various metals and alloys in this mixture. One may guess, and guess correctly, at some alloy, but the chances are so great against successful guesses "backed by reason" that it does not pay. Too often metals are tested against a specified solution, recommended for service, only to fail in actual use, as manufacturers are keenly aware. For instance, if a metal is desired for phosphoric acid, tests are carried out at different concentrations of the pure acid and at different temperatures, and on the basis of the results a final recommendation is made. However, the tests are made in pure acid, while the acid used in processing is not pure (in one instance it contained one half per cent. hydrofluoric acid, which makes it a much more corrosive solution than the pure acid); consequently, the chances that the recommended alloy will stand up are very poor.

The eager desire of the metal salesman to sell his products "with hopes" and the laxity of the user in defining the conditions under which the metal will be used have caused much grief for both parties. Some time ago the writer wrote to a number of manufacturers of metals and alloys asking for samples resistant to a certain solution. Over sixty different samples were obtained, thanks to the kindness and interest of these concerns, but only two were found fairly resistant and one resistant! Writing to the several companies processing this solution the author found twenty alloys and metals in use amid much grumbling and discontent.

It may be correct to say that for every process there is one, and only one, metal or alloy which works best. All others, then, must be inferior in a lesser or greater degree. It is up to the metallurgist and chemical engineer to find which is best. To date, this job has not been done thoroughly, although the future indicates that it must and will be efficiently accomplished.

II. FERROUS METALS AND ALLOYS

IRON AND STEEL

Iron and steel, being relatively inexpensive and possessing desirable physical properties, are used more, where conditions permit, than all the other metals and alloys put together. Iron and steel are used not only with the less corrosive substances but often with the strongest acids. This is due to two reasons, first, the low replacement cost for iron and steel equipment and second, the fortunate passive behavior of iron in various media.

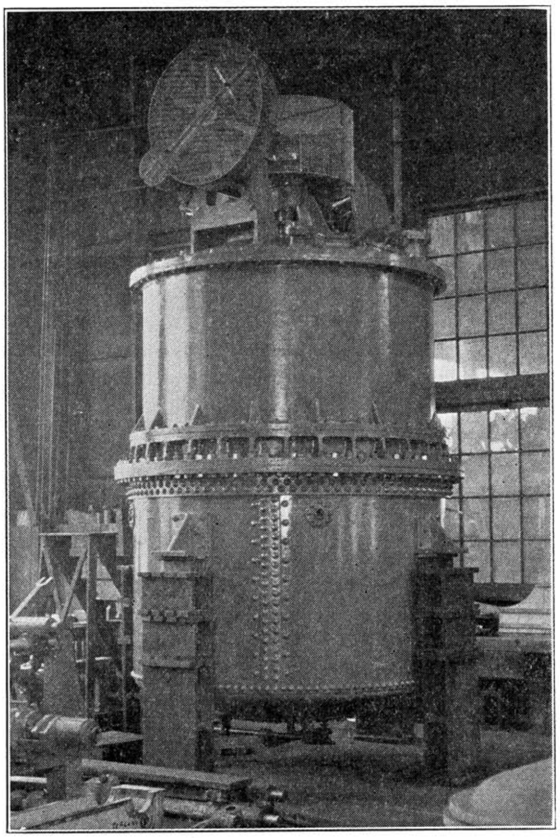
Aside from their use for general plant constructional equipment, iron and steel are used for equipment and apparatus designed for water and steam, weak electrolytic solutions, water-free gases and liquids, alkaline and ammonia solutions, solid and liquid caustic, molten aluminum, zinc and brass, petroleum and its products, and concentrated nitric and sulfuric acids, and their mixtures. The use of iron and steel for jacketing and reinforcing more resistant materials is steadily becoming more common. Figure 2 illustrates a large mixing kettle for processing phenolic compounds which is constructed chiefly of cast iron and is reinforced with a sheet-steel jacket.

It would be futile to attempt any precise differentiations between iron, wrought iron, and steel. Cast iron may be said to contain several per cent. carbon and various impurities. A typical analysis would be: 2.0–4.5% carbon, 0.7–3.0% silicon, 0.1–0.3% sulfur, 0.1–3% phosphorus, 0.2–1% manganese, and traces of other impurities. It is quite hard and brittle; these characteristics make it suitable only for castings which will not be subject to shock or impact. Wrought iron is made from cast iron by oxidizing most of the impurities out of the former in a basic furnace. It is soft, tough, and malleable and possesses a fibrous structure because of slag inclusions. Steel is generally considered as a form of iron containing less than 2% carbon and being susceptible to hardening through heat treatment.

Because of the ease of casting and because of its cheapness, cast iron is used where conditions permit. It finds uses in the manufacture of caustic pots, although the use of nickel or nickel-cast iron is considered to be better. Figure 3 illustrates a large reaction kettle constructed of cast iron for the manufacture of a dyestuff. Cast iron is also used to a great extent for molten aluminum and its alloys, zinc, brass, solders, copper, and several other metals and alloys.

Wrought iron, though being gradually replaced by mild steel, possesses excellent resistance to water. This property is probably enhanced by its high silica content. On the other hand, the high silica content is responsible for the lack of resistance of wrought iron to molten alkali and strong caustic solutions.

The excellent physical properties of steel and its ease of fabrication make it a very desirable metal for construction where corrosion is not severe. The phenomenon of passivity permits most steels to withstand strong sulfuric and nitric acids as well as their mixtures (mixed acid). Nitric acid can be handled if it is over 65% HNO_3; below this concentration the iron ceases to retain the passive state and passes into solution very readily. Sulfuric acid can be handled in iron equipment when it is from 78–98% H_2SO_4. Sulfuric acid or mixed acid ($HNO_3 + H_2SO_4$) containing more than 20% water attacks most steels because at these lower concentrations they are not rendered passive. Iron and steel containing much silicon are selectively corroded



Courtesy Buffalo Foundry and Machine Co.

FIGURE 2.—REACTION VESSEL CONSTRUCTED OF STEEL AND CAST IRON

at the grain boundaries by sulfuric acid containing over 100% H_2SO_4 (oleum). This is due to the action of SO_3 on silicon, the latter being oxidized to SiO_2. It is therefore important that iron used with fuming sulfuric acid contain very little silicon.

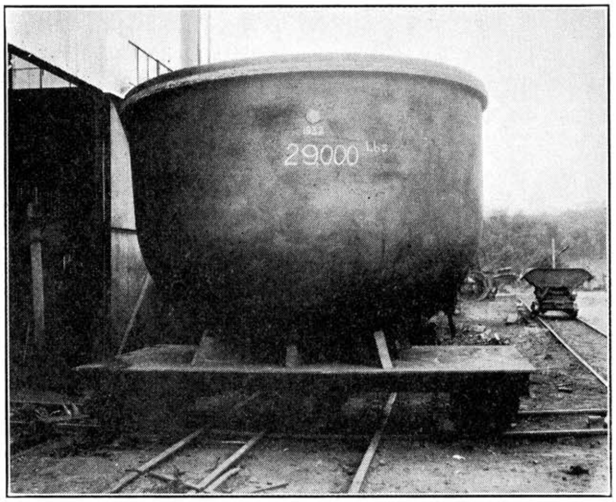
The absence of electrolytic action in the absence of water makes it possible to employ iron or steel with dry chlorine, HCl, SO_3, bromine, etc. In the alkali-chlorine industry the wet chlorine is dried by sulfuric acid, and from this point the gas is transferred, compressed, and liquefied in steel equipment without danger of corrosion. Liquid HCl gas is also transported in steel cylinders.

The use of iron for electrodes in many electrolytic processes is very common, its chief use being as cathodes in the alkali-chlorine industry whereby salt solutions are electrolyzed. In the electrolysis of sodium hydroxide solutions for the production of oxygen and hydrogen, iron is sometimes used for the cathode. The Edison storage cell also makes use of iron cathodes.

Courtesy Lynchburg Foundry Co.

FIGURE 3.—REACTION VESSEL FOR DYE MANUFACTURE

In recent years there has been a great tendency to investigate and use steels containing low percentages of nickel, molybdenum, copper, chromium, silicon, and vanadium. Figure 4 shows a large caustic pot for boiling down caustic solution. Such pots are often made of iron alloyed with small amounts of nickel. The indications are that such additions improved the chemical resistance for certain purposes as well as the physical properties in general. The petroleum industry has some very severe corrosion- and heat-resistance problems which still remain unsolved. In the cracking of oils to produce lighter fractions, the use of the proper metal for the cracking tubes is a difficult problem. The unfortunate tendency for the tubes to burst is well known. The advantage of the straight steel or low alloy steel tubes, such as 5% chromium, lies in the fact that any tendency which they may have for failure announces itself by a swelling and the operator can then "cut them out." The disadvantage of the higher



Courtesy Lynchburg Foundry Co.

FIGURE 4.—CAUSTIC POT MADE OF SPECIAL ALLOY CAST IRON

alloys of iron is due to their failure without any preliminary warning.

The use of iron and steel at higher temperatures is limited because of the rapid rate at which oxygen and iron react as the temperature is increased. The action is direct, with the formation of a non-adherent oxide scale. The rate of reaction increases very rapidly above 200°C. For temperatures above this point special alloys are called into use. These will be mentioned later.

THE SILICO-IRONS

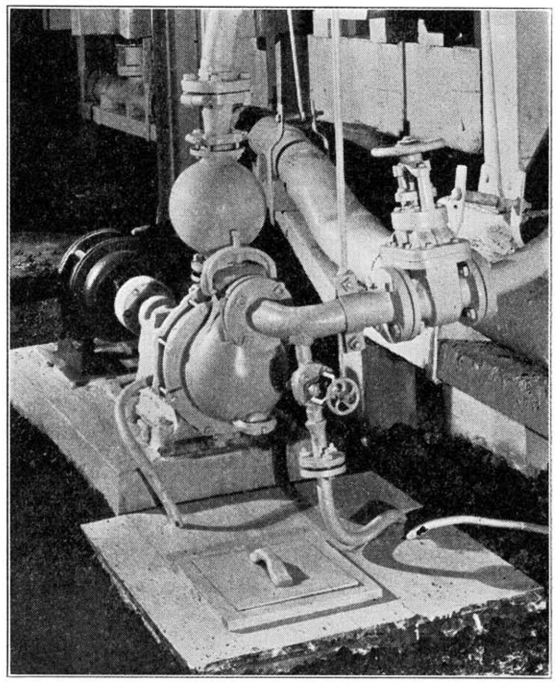
The addition of silicon to iron produces no beneficial effects until about 13% has been introduced. Alloys of about 14% to 17% silicon seem to be the ideal compositions for corrosion resistance. The addition of over 17% silicon produces a slight lowering in chemical resistance.

The earliest manufacture of the silico-iron alloys was attended by a great number of difficulties, chiefly physical in nature. It is now known that the iron and the alloying agent must be low in impurities, such as sulfur and phosphorus, in order to produce successful castings. The casting temperatures as well as the cooling rates are also very important. The alloys are very hard and brittle and are difficult to machine or work. All fabricated equipment or apparatus must be cast into the desired form and then ground with abrasives to the proper fitting. Figure 5 illustrates a Duriron pump set up for ammonium sulfate solutions.

Duriron and Corrosiron are the trade names for the most important silico-iron alloys used in this country. The manufacturers of these alloys have been very successful in fabricating them into apparatus of desired shapes and sizes. Without doubt, these alloys are so widely used with so many corrosives that it would be simpler to list the general groups of corrosives they will not resist than those they will resist. The use of both Duriron and Corrosiron would undoubtedly be greater if they possessed better physical properties.

The avidity with which the halogens and halogen acids attack most metals and alloys is well known. The straight silico-irons are no exceptions in this respect. As previously mentioned, the action of strong alkali and molten caustic upon silicon is rather pronounced. It is evident then that these alloys are not to be used with such substances. Further, the heat conductivity of these alloys is not as good as that of cast iron. Consequently, apparatus constructed from large castings is very sensitive to rapid temperature changes. These silico-iron alloys are, also, not recommended for very high pressures except for smaller apparatus.

Very recently a new silico-iron alloy appeared bearing a composition of 13.5 silicon, 3.5 molybdenum, and 1.0 nickel. This new alloy, called Durichlor, possesses exceptional resistance to hydrochloric acid and is probably the only alloy existing which resists this corrosive



Courtesy The Duriron Co.

FIGURE 5.—DURIRON PUMP FOR PUMPING AMMONIUM SULFATE LIQUORS

at all concentrations and temperatures. This resistance is attributed to a protective compound film which forms on the surface after a definite period of exposure. An interesting bit of information relative to this alloy is that it was not developed specifically for the purpose of resisting hydrochloric acid but was made in an attempt to improve the properties of Duriron, its HCl-resisting properties being discovered later.

THE CHROMIUM AND CHROMIUM-NICKEL IRONS AND STEELS

These series of alloys are of relatively recent origin, dating from about the start of the World War. Today (known to the man on the street as "stainless steels") they are probably more common than any other series of alloys. Actually, they are far from being stainless; a more appropriate designation would be "corrosion and heat resisting" steels.

The alloys having the greatest importance in these series may be classified as follows:

Cr-Fe	Cr-Ni-Fe
Low Cr (11–15%)	High Cr—Low Ni (less than 3%)
Medium Cr (17–20%)	"18-8" (18 Cr-8Ni)
High Cr (24–30%)	High "18-8" (20–27 Cr-12–24 Ni)
	High Cr-Ni (27 + Cr − 14 + Ni)

Many other alloys of chromium, nickel, and iron do exist, but those above seem to be of the greatest importance.

The properties and consequent uses of these alloys may be explained without taking too many liberties with the governing fundamentals by saying that all these alloys are resistant because of their tendency to form insoluble oxide coatings. The addition of both nickel and chromium improves the chemical resistance, the chromium additions having no effect until 11% chromium is reached. As the nickel and chromium contents are increased the chemical resistance against most corrosives improves correspondingly.

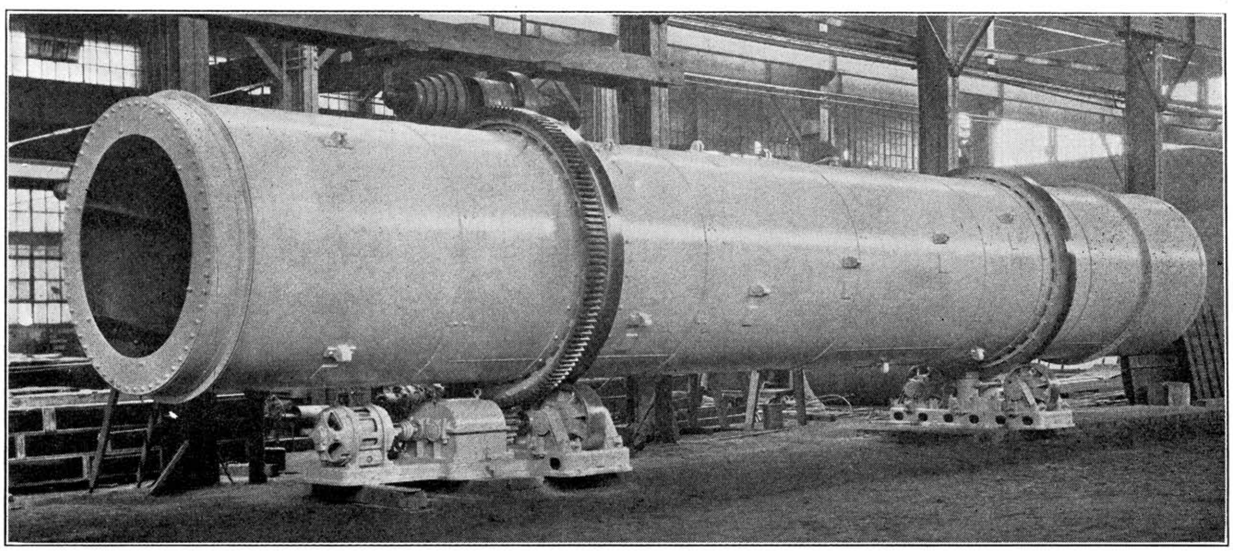
With the straight chromium-iron alloys an increase in chromium (over 11%) improves the chemical resistance while the physical properties become poorer. On the other hand, the opposite effects are noted for the carbon contents of such alloys. It is therefore important to get a balance between the chromium and carbon percentages in order to have an alloy which will have good chemical resistance as well as desirable physical properties. In this way a 12% chromium alloy may have a 0.10% carbon content; an 18% alloy may have a 0.25% carbon content; and a 27% alloy may have a carbon content as high as 0.75%. In cases where hardness and strength are not as important as chemical resistance the carbon content is lowered. The chromium-iron series crystallizes in the body-centered cubic system, commonly called the ferritic state; this is characteristic of a soft annealed iron. Heat treatment rarely improves its physical properties, because of the great tendency for chromium to crystallize only in the body-centered cubic system.

These alloys show excellent resistance to nitric acid, being probably unexcelled for this purpose, They are also used in contact with various kinds of fruit juices, as well as with many of the weaker acids, such as acetic. The mineral acids such as hydrochloric, crude phosphoric, and sulfuric corrode these alloys readily, although phosphoric has little effect upon the higher chromium alloys. Figure 6 shows a large rotary drier constructed of "stainless steel" which is employed for drying a corrosive metallurgical product.

The addition of one to three per cent. nickel to the chromium-irons and steels tends to improve the physical properties greatly. A very large number of such alloys are used where high temperatures are employed. They can be used at temperatures around 1500°F. without danger of disintegration or warping. Figure 7 illustrates a large SO_2 blower whose impeller is constructed of nickel-chrome steel.

The most important alloys of the entire chromium-iron and nickel-chromium-iron series are the "18-8" alloys containing 18% chromium and 8% nickel. In contrast with the straight chromium-iron alloys these alloys are austenitic by virtue of the tendency to crystallize in the face-centered cubic system under the proper heat treatment. The presence of carbon then is not necessary or desired; in fact, the tendency is to try to remove every trace of graphitic carbon because of the dangers of intercrystalline corrosion.

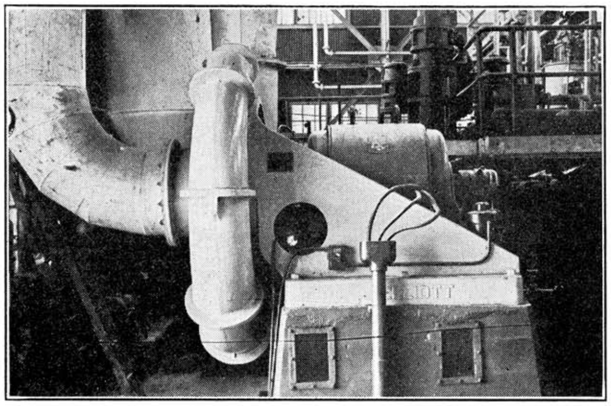
The tendency for these alloys to precipitate carbides at the grain boundaries upon cooling and give local points for local-action corrosion has been a problem worrying the manufacturer and alloy user for years. This type of corrosion, commonly called intercrystal-



Courtesy Struthers-Wells Co.

FIGURE 6.—"18–8"-LINED DRIER FOR CORROSIVE ORES

line corrosion, intergranular corrosion, or embrittlement, is characterized by a tendency for corrosion to confine itself chiefly to the grain boundaries and thus to cause eventual disintegration of the alloy.



Courtesy Elliott Co.

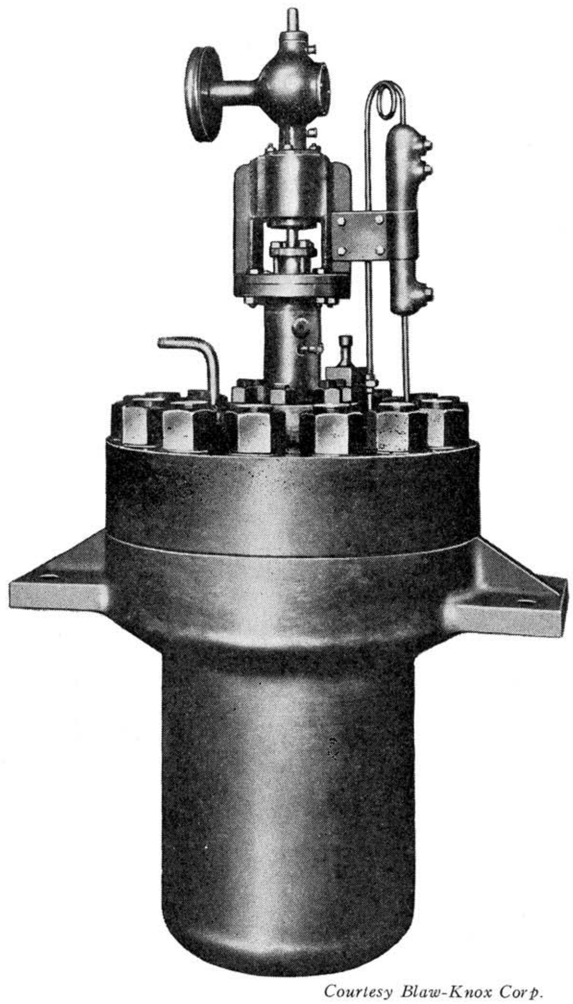
FIGURE 7.—BLOWER FOR SO_2 CONSTRUCTED OF STEEL AND NICKEL-CHROMIUM-STEEL

Intercrystalline corrosion is combated in these alloys in three ways: by limiting the carbon content to 0.07 per cent., by proper heat treatment, or by the addition of small amounts of metals such as molybdenum, silicon, titanium, or columbium which tend to hold the carbide phase in solid solution. Such alloys are called "S" alloys (the "S" signifying soft); thus a straight "18-8" alloy might be called KA_2 or "18-8" steel, while the stabilized alloy might be called KA_2S or "18-8 S." It is only fair to mention that intercrystalline corrosion is not an inherent property of these alloys only, but exists in hundreds of other metals and alloys as well. Merely because the "18-8" alloys have enjoyed such wide use has the intercrystalline corrosion study centered upon them.

Many alloys exist having the composition 24 Cr, 12 Ni, or 24 Cr, 12 Ni, 3 Mo. Such alloys are fabricated for the sole purpose of obtaining more corrosion resistance than the "18-8" or "18-8-3" alloys can offer. The alloys of higher chromium-nickel composition, such as 36 Cr–20 Ni, or 35 Ni–15 Cr, find their chief use as heat-resisting alloys.

The "18-8" alloys find most extensive uses in the chemical industry. Recently, the "18-8-3" alloys have been found very useful in the manufacture of crude phosphoric acid and in the sulfite treatment of paper pulp. The milk-handling and pasteurizing industry uses "18-8" alloys to a great extent. The breweries are also employing the alloys. While these alloys are not quite as resistant to nitric acid as the chromium-iron alloys, they are better for sulfuric acid and find a much wider use in the food-processing industries because of their better physical properties. Again, it is probably easier to state which reagents attack these alloys rather than which do not. The halogens and their acids are the worst offenders, along with most boiling acids. The molten metals also attack these alloys.

Reactions involving hydrogen or hydrocarbon at high temperatures and pressures place unusual demands upon metallic equipment. The difficulties in such reactions are due to hydrogen penetration and combination with the alloyed or precipitated carbon which result in eventual intercrystalline corrosion of a different kind. Manufacturers have avoided most of these difficulties by lowering the carbon and raising the metallic alloy contents of these alloys. Figure 8 illustrates a stainless steel autoclave for hydrogen which operates at over 3000 lb. per square inch pressure.



Courtesy Blaw-Knox Corp.

FIGURE 8.—25-GALLON HYDROGEN AUTOCLAVE WITH "STAINLESS-STEEL" LINING

These alloys can be welded, but inasmuch as the welding operation produces a temperature gradient ranging from the molten weld to the cold body of metal, carbide will be encouraged to precipitate if the alloy contains none of the stabilizing elements mentioned. The alloy must then be annealed above 1800°F. and be properly heat-treated so as to redissolve the precipitated carbide in order to retain its corrosion resistance.