11. Operation and Control of the Units (i)(cont'd.)

the separate gasket is used only when the vessel has no stainless steel liner.

12. Materials of Construction.

One of the great problems in high pressure high temperature processes of any kind is the development or selection of construction materials that will stand up under the operating conditions. For coal hydrogenation the primary requirements of materials for the high pressure equipment are:

(1) Hydrogen resistance at high temperature and with high hydrogen partial pressure.
(2) High tensile and creep strength at the operating temperature.
(3) Resistance to H_2S and Cl_2 corrosion.

A great amount of experimental and development work has been done in Germany in an effort to produce suitable steels, but at best a compromise must be made between the various properties listed above. Their problems were multiplied by wartime shortages of molybdenum, tungsten, and chromium. Austenitic 18-8 Cr-Ni steel was fairly satisfactory, but the tonnage were so great that Germany could not supply the high chromium and nickel requirements.

The early experimental work on the hydrogenation process was done with vessels of various carbon steels, but hydrogen attack was severe and the vessels failed in a very short time.(31) Low alloy chrome nickel steels were then used, but nickel appeared to decrease the hydrogen and H_2S resistance of the alloy. Molybdenum was then substituted for nickel, and gave better alloys with less alloying metal. About 0.5 percent Mo gave high temperature strength properties equivalent to 2.0 percent Nickel. Krupp P469 (N6) was the first steel of this type. In chronological order, steels N6, N8, V 2AED, and N10 were developed, each being an improvement over previous material for high temperature high pressure hydrogen service. Then, during the war, N 8V and N9 were used to save critical alloys, but were not nearly so resistant to corrosion as the earlier steels.

12. Materials of Construction. (cont'd.)

Attached diagram 652 from the IG Farbenindustrie Ludwigshafen Works presents some of the characteristics of the materials mentioned. The "Dauerstandfestigkeit" is the maximum load at which the elongation does not exceed 0.001 percent per hour in a period of 25-35 hours after the beginning of the test, and the total elongation does not exceed 0.2 percent after 45 hours.

The steels used in the hydrogenation plant were classified according to general type and the purpose for which each was used.

Table I, at end of this report, lists the manufacturers, chemical analyses, physical properties, heat treatment and field of usefulness of the various steels of each group.

"S" steels are ordinary carbon steels. They do not withstand high temperature or hydrogen attack, but they are useful for flanges, bolts, cold piping and fittings, lens rings, gaskets, and structural supports. There appears to be little new in the "S" steels either in manufacture or in application.

"N" steels are the high temperature steels and are the most important group. The structural steels, NO, NOS, NO4, N2, CV, are characterized by about 1 percent Cr content and are used for stressed pieces which are not directly in contact with hydrogen or corrosive materials.

The N1 and N5 to N10 alloys contain more Cr, usually 3 or 6 percent and are the hydrogen resistant group of the low alloys. The heat treatment of this group is quite critical, and consists of heating to the austenitic region, quenching, and annealing. These steels have great mechanical strength at high temperature and are resistant (but by no means immune) to chemical attack.

N-1 steel is used almost exclusively for pressure vessels containing hydrogen, but it is not suitable for use at temperature above 250° C, because above this range hydrogen does attack the carbon and weaken the grain boundaries. For this reason all high pressure, high temperature vessels

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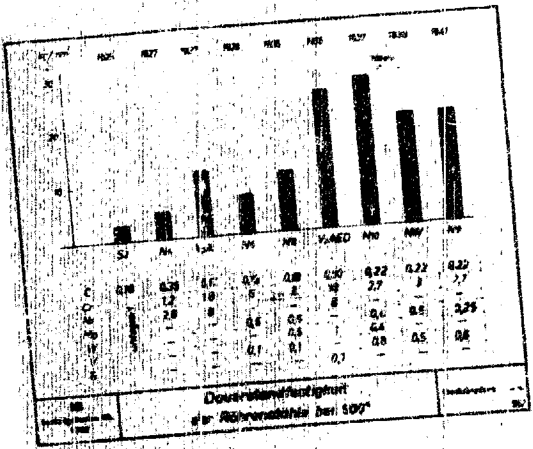


[illegible] 550 [illegible]

[illegible]stigkeit.

HIGH PRESSURE 325 Atm

Applications of the Working Materials

Temp. Stage	Operating Temp. C	Nominal Range	Applicable Material for Tubes	Formed Pieces	Blind Flanges	Screw Flanges	Bolts	Nuts	Lenses
I	0-200	6-16 16-160 200	St.45.29 St.35.29	S2	S2	S1	S3 K4Mo K1,K1MS	S3	S2
II Now 200 - 400°C	200-400	6-200	N8A	N8A	N8A	K4MS,K1, K1MS	K4MS,K1, K1V,K1CV K1MS	S3	N5A
II Previously 200-480°C	200-480	6-200	N8	N8	N8	K3,K3CV	K3,K3CV	S3	N5
III Now 400-510°C	400-510	6-200	N9	N9	N9	K3CV K3	K3CV K3	S3	N5A N6
III Previously 480-510°C	480-510	6-45 58-200	N8 N8V,N10	N8 N8V,N10	N8 N8V,N10	K3,K3CV K3,K3CV, K5,K5V	K3,K3CV K5,K5V	S3 K1MS,K3 K1V,K1CV	N8 N8A

HIGH PRESSURE 700 Atm

Applications of the Working Materials

RESTRICTED

Temp. Stage	Operating Temp. °C	Nominal Range	Applicable Working Materials for Tubes	Formed Pieces	Blind Flanges	Screw Flanges	Bolts	Nuts	Lenses
I	0-200	6-16 24-160 except 135 135	K2M K2	S3 S3	S3 K4MS K1 K1MS	S1 K1 K1MS	S3 K4MS K4MS K6	S3 S3,K1, K1V,K1CV	S2 S3
II Now 200-400°C	200-400	6-45 58-160 except 135 135	N8A	N8A	N8A	K4MS,K1 K1MS K4MS,K1 K1,K3 K3CV	K4MS,K1 K1V,K1MS K4MS,K1,K1V K4MS K6	S3 S3,K1,K1V K1CV	N8A N8 N8A
II Previously 200-420°C	200-420	6-160	N8	N8	N8	K3,K3CV	K3,K3CV	S3	
III Now 400-510°C	400-510	6-16 24-45 58-160	N9 N10,N8V N9	N9,N8V N8V	N9,N8V N5V	K3CV K5,K5V K7	K3CV K5,K5V K7	S3 K3,K1V K1CV K1MS	N8A N8
III Previously 420-510°C	420-510	6-160	N10W	N10	N10	K7 K5,K5V	K7 K5,K5V	K1MS K3,K1CV	N8A

12. Materials of Construction. (cont'd.)

of this material contain internal insulation or cooling surfaces to maintain the shell at a lower temperature than the process materials.

N6 was the first preheater tube material that could be used to replace 18-8 Cr-Ni steel.(34) It was not entirely satisfactory due to low creep strength and a low resistance to hydrogen attack, but some N6 preheater tubes were still in service in Leuna during the war.

N8 was first used about 1935. It is a 3 percent Cr alloy with ½ percent tungsten, and is cheaper as well as stronger than N6 at the preheater operating temperature. N8 has somewhat lower high temprature strength than 18-8 Cr-Ni steel, and requires particularly careful heat treatment, but it is still considered satisfactory for 325 atm. preheater tubes.

N10 steel(35) is the best low alloy material that has been found for high temperature hydrogen service, and all preheater tubes and fittings for 700 atm. service were made from it. Exceptionally high hydrogen resistance and creep strength were claimed. It has more vanadium and less chromium, molybdenum, and tungsten than N8, thus a saving was made of the most critical metals during the war. Most of the newer installations had N10 preheater tubes whether they operated at 325 atm. or at 700 atm. except where wartime necessity required the use of substitutes. If N10 is properly heat treated (heated to 1050°, cooled in air stream, annealed at 700°) the cold tensile strength can be 90-100 Kg/mm^2. Faulty heat treatment can produce a material brittle at room temperature but still satisfactory at 500-600° C. Air stream cooling in the quench gives a Brinell hardness of 220-260 compared to 240-280 by oil quench, but the Germans state that the air-cooled steel has almost twice the strength at 500-600° C of oil quenched steel in that temperature range.

N10 steel preheater tubes were in service for five years before a failure occurred that could not be traced to some manufacturing flaw. Up to that time they had considered the metal immune to hydrogen attack, but they found that

12. Materials of Construction. (cont'd.)

a very slow removal of carbon from between the grains did occur. It has been claimed that a heat treatment of the tubes after each period of not more than 10,000 hours service will prolong the tube life indefinitely. This heat treatment is presumably the same as the initial treatment.

N steels can be arc or resistance welded but gas welding is risky. The design of most large vessels avoids welding but resistance welding of preheater tubes and piping is regular practice. The welding procedure most be followed by heat treatment.

"K" steels were made primarily for 700 atm work where the "S" steels were not sufficiently strong. The "K" steels contain about 1 percent Cr and have lower Mo and higher C than the S steels.

The remainder of the steels shown have counterparts in American practice. The "RA" steels are 18-8 Cr-Ni alloys for acid and chemical resistance. The "RM" steels are 12-14 Cr steels for hardened pieces such as valve parts. 25Cr-20 Ni alloys are the non-oxidizing, flame-resistant steels. Alloys containing 1-5 percent nickel are used for heavy duty forgings such as piston rods, and for low temperature service. The final groups are the surface hardening and nitriding steels.

Hydrogen sulfide corrosion becomes progressively more severe as the temperature rises. Under the pressure and temperature conditions of coal (or tar) hydrogenation H_2S attack on ordinary carbon or low chrome steels is quite rapid. For instance, the Billingham plant of I.C.I. uses 4" thick low chrome steel liners in the converters and they estimate their life at about 5 years. The hydrogen sulfide cannot be eliminated because it forms during the conversion and because it is necessary to have some of this gas present to preserve the sulfide catalyst used in gas phase operation. A 14 percent chrome alloy withstands the conditions imposed, but due to the difficulty involved in fabricating large pieces from this material the Germans sometimes made their liners for converters and hot separators from 18-8 Cr-Ni steel.

12. Materials of Construction. (cont'd.)

It was found that brass containing at least 37-42 percent zinc has very high H_2S resistance, but of course brasses cannot be used at the high temperatures involved. In one set of German experiments they made a series of iron-zinc and nickel-zinc alloys containing up to 50 percent zinc to see if such alloys would be H_2S resistant. (It is interesting to note that these alloys were made under 60 atmospheres nitrogen pressure because of the high vapor pressure of zinc at the melting point of iron or nickel.) Alloys containing as much at 15 percent zinc were not attacked by H_2S but, as might be expected, the alloys were too brittle to be of any practical use. However, these experiments led to the vapor galvanizing of parts such as heat exchanger tubes and liners, a procedure that apparently proved to be satisfactory and is still used. They also galvanized 13 percent Cr converter internal parts. The vapor galvanizing is accomplished by holding the parts in zinc vapor for 25 hours at 870°C., thus forming a very thin crust of Fe-Zn protective alloy.

Chlorine and chlorine compounds form some hydrochloric acid under the conditions of hydrogenation. No practical construction material will withstand this attack, therefore when chlorine is present in the feed, soda ash is added to neutralize the acid.

Erosion is a serious problem in much of the equipment and piping. It can be traced to one or the other of two sources in most instance. One source is abrasive material in suspension in the fluids being processed, such as ash, sand and catalyst in the coal paste, the sump phase liquids, and in the sludge recovery system. Wear in the paste pumps is combatted by using surface hardened metals and nitrided plungers and valves, and by low plunger velocity. The return bends of the sump phase preheaters suffer much damage and hardened inserts, usually of 12-14 percent chrome steel, are often placed inside the outer wall of the fitting. Valves have hardened seats and discs, and are designed so that the flow is streamlined as much as possible. Heat exchanger tube sheets are approached with long conical sections which reduce solid deposition as well as erosion on the ends of the tubes. Stuffing boxes are equipped with

12. Materials of Construction. (cont'd.)

flushing oil connections, and are flushed continually while in service.

The second type of erosion is due to high flow velocities of fluids, especially mixtures of vapor and liquid, through pressure release points. This condition is partially combatted by the design of the unit and the equipment. Expansion is carried out through expansion engines or in several stages. Expansion valves have turbulence chambers with slightly restricted openings on the outlet. Piping is installed undersized in order to take part of the pressure drop. Where it is necessary that a considerable pressure drop be taken across a valve, the seat and disc are made replaceable and of some abrasion resisting material such as tungsten carbide or tungsten-titanium carbide. Two pressure reducing stations are always installed in parallel, with shutoff valves one each side of each expansion valve so that it can be removed from service for replacement or repairs.

Hydrogen attack on steels(37) is a particular type of corrosion, causing decarburization at the grain boundary, and it is of such great importance in high temperature high pressure operation that it is considered separately. The mechanism of the attack is the slow hydrogenation of the carbon in the steel to methane. This takes place primarily in the matrix rather then in the crystals, and greatly diminishes the strength of the steel. The reaction velocity for any given steel increases with the temperature and with the hydrogen partial pressure. The resistance of steels to hydrogen attack varies from that of carbon steel, which is quite sensitive even at 200°C, up to stabilized 18-8 Cr Ni austenitic alloys which are practically immune over the entire range of temperature used in the process.

Due to the great cost of austenitic stainless steel, low alloys were developed which would have sufficient hydrogen resistance for particular purposes. These are the "N" steels. N4 could be used for 325 atm H_2 up to 400°C and N6 and N8 up to 600°C. The use of 700 atm pressure dropped these permissible temperature ranges and forced the development of N10.

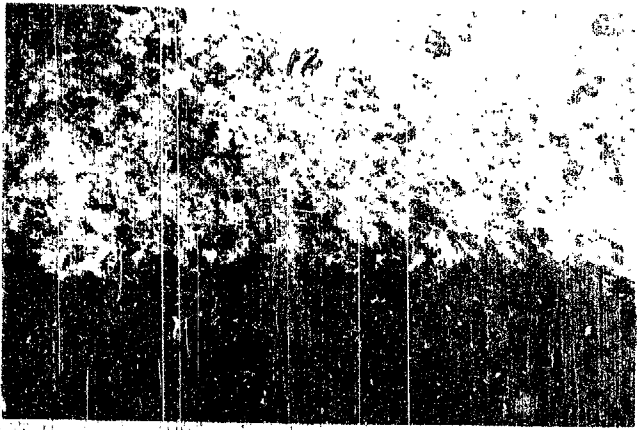
12. Materials of Construction. (cont'd.)

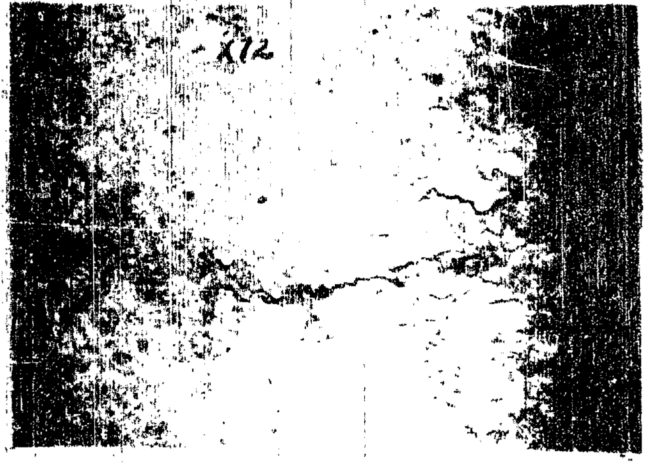
The first report of tests published by F.K. Nauman in 1938 (Stahl und Eisen, pg 1239) stated that N10 was unaffected by 200 atm hydrogen at 600°C in 100 hours. The failure by hydrogen attack of N10 preheater tubes after several years of service caused additional study of the effect. It was found that chemical analysis alone did not mean much with regard to hydrogen susceptibility, but fabricating and operating conditions played a considerable part. Many steels showed evidences of attack only after 400-600 hours and some only after 1000 or more hours. Heat treatment was an important factor, and in general, air quenched steels were found to be more resistant than oil quenched. These tests indicated that resistance increased with a decrease in unstable carbides in the matrix and with less dissolved carbon in the ferrite, also, that complete immunity is not attained by ferritic-pearlitic steel containing as high as 6.5 percent Cr., but that grain boundary failure will occur in time.

The following four figures show micrographs of N10 tubes which failed in 700 atm. service in the hot section of a preheater after approximately 11,000 hours service. The two photographs with a magnification of 12 diameters show the fissures caused by hydrogen attack which ultimately result in failure of the tube. These fissures are typical of hydrogen attack on any steel. The two micrographs with a magnification of 125 diameters emphasize the deterioration at the surface in contact with the hydrogen. The etched sample in particular shows the effect of the decarburization on the steel grain structure.

The following figure shows bend tests of samples taken from one of the tubes which failed. The samples from left to right are taken: from the inner tube surface, with the immediate surface removed, 0.2 mm removed, 1 mm removed, middle of tube, outside of tube. It can be seen that the attack penetrated less than one millimeter over the tube as a whole.

Results of experiments led the Germans to believe that the life of N10 steel preheater tubes could be prolonged indefinitely by giving them a heat treatment after each


X14


X12

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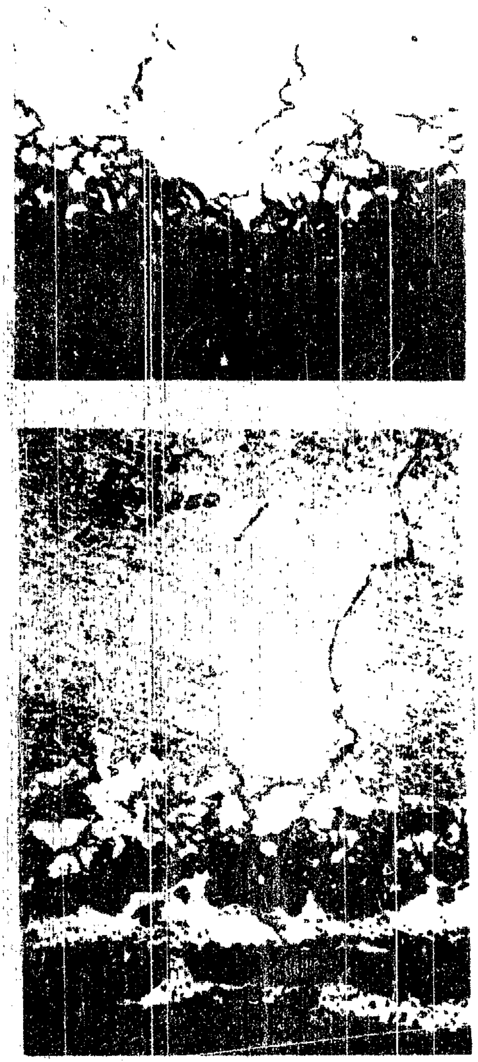

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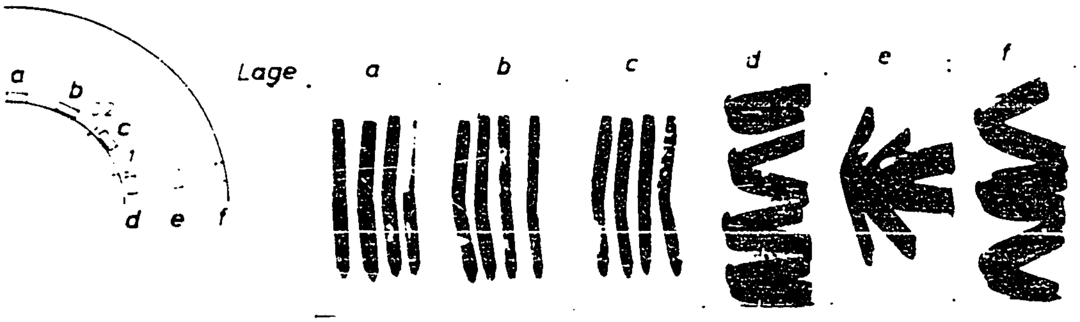


a = Innenrand unbearbeitet
b = Innenrand abgezogen
c = 0,2 mm v. Innenrand entfernt
d = 1 mm v. Innenrand entfernt
e = aus der Mittelzone
f = vom Außenrand

Form der Biegeproben 8 × [illegible] mm

Bend [illegible] on [illegible] from [illegible] which Failed
In [illegible] Atm. High Temperature Hydrogen Service.

12. Materials of Construction.(cont'd.)

10,000 hours service. Apparently the heat treatment re-established the carbon equilibrium in the steel of the inner tube surface, but it is not clear just how this was accomplished.

A thorough study of the use of columbium to replace the carbon for blocking grain slippage in the steel was proposed as a possible method of developing a completely hydrogen resistant low alloy steel. These experiments were not carried out due to wartime shortage of manpower.

The German creep strength test consists of putting a series of constant loads on test pieces held at the specified temperature for periods of 45 hours each. The creep strength (Dauerstandfestigkeit) is the greatest load in Kg/mm2 at which the creep velocity does not exceed 1/1000 percent per hour during the 25-35 hour period and the total extension in the 45 hours does not exceed 0.2 percent. It is claimed that this test is reproducible and extremely useful as a method of evaluating creep strength in a short term test.

A second method of evaluating high temperature strength is a plot of different constant loadings at constant temperature against the number of hours elapsing before the fracture of a given material occurs. This is known as the load-time curve (Belastungs-Standzeitlinien), and is usually plotted on both rectangular and log-log coordinates. Two types of these plots are shown in the attached figures. The first two (marked Abb. 4 and 5) show curves for a 0.91 percent Ni, 0.78 percent Cr, 0.94 percent Mo steel at 300°, 400°, 500°, and 600° C., plotted with the two types of coordinates. The second pair shows the curves for 500° C of five different chrome steels, including V2AE, N9, a 20 percent Cr. steel and two low alloy Cr-Ni steels.

The following figure (Abb. 18) shows the loading, time to fracture, elongation, and reduction in area beneath photographs of test pieces of a steel corresponding to N10 composition which were broken under the various loads. It is interesting to observe the changing appearance of the

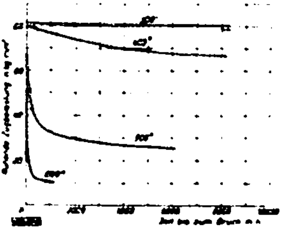


Abb. 4. Belastungs-Standzeitlinien von Stahl 14 (0,20% C, 0,91% Ni, 0,78% Cr, 1,04% Mo) bei verschiedenen Temperaturen in metrischer Darstellung

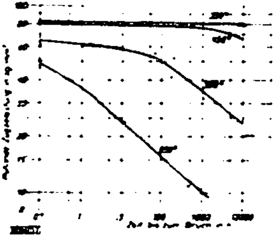


Abb. 5. Belastungs-Standzeitlinien von Abb. 4 in doppelt logarithmischer Darstellung

Abb. 4 und 5

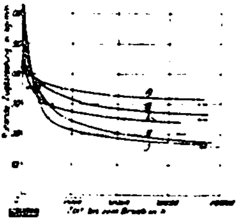


Abb. 6 Belastungs-Standzeitlinien von Stählen verschiedener Zusammensetzung bei 500 °C in metrischer Darstellung

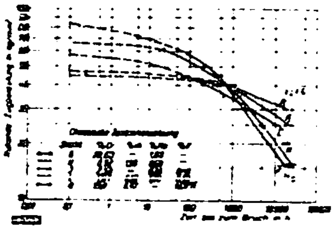
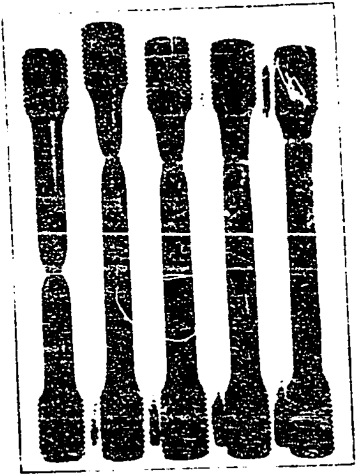


Abb. 7 Belastungs-Standzeitlinien von Abb. 6 in doppelt logarithmischer Darstellung

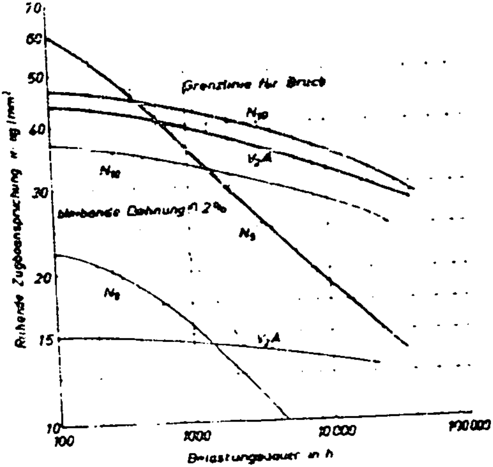
bb. 6 and 7



[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Zeit bis zum Bruch	h	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Bruchdehnung	%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Brucheinschnürung	%	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Abb. 18. Veränderung von Bruchdehnung und Brucheinschnürung mit zunehmender Belastungszeit bei 500° C von Stahl K (0,10% C, 2,71% [illegible], 0,53% Mo, 0,74% V und 0,48% W)

Abb. 18. M10 Cert [illegible] S.



Tr[illegible] creep tests of
[illegible] steels.

12. Materials of Construction. (cont'd.)

fracture after increased periods of time. The next figure shows the relation between the break point and the loading which produces an elongation of 0.2 percent after various periods under tension at 500°C. The poor qualities of wartime substitute N9 as compared to N10 are plainly shown.

The following tables are taken from Technical Report No. 57-45 of the U. S. Naval Technical Mission in Europe, and shows the uses of the principal materials in high pressure equipment.

It should be noted that N8 and N9 would both be replaced by N10 for new construction when alloying metals are available in the necessary quantities.

Internal parts and liners for the vessels are not listed above, but austenitic 18-8 Cr-Ni still is the preferred material, with 18 percent Cr steel as the best substitute.

Austenitic stainless steel is also preferable for pressure shells, but N1 is satisfactory when precautions are taken to avoid metal temperatures of over about 250° C. It can be noted that no cases of failure of pressure shells have been found, although on a few occasions vessels have been blown out of the cells by gas explosions in the cell space.

On the whole, the German development and selection of steels appear to be satisfactory in conjunction with their equipment design.

(b) Insulation(39)

There were three principal classes of service where insulation was required in the high pressure hydrogenation units. The first consisted of coverings for pipe lines and fittings; the second was the internal insulation employed inside of the pressure vessels to maintain the shell temperature below 250° C: and the last was the protection of steel work to prevent buckling in case of fire.

12. Materials of Construction (h)(cont'd.)

For pipe coverings in the range of 100 to 250° C. an insulation called Diamag, which was a Magnesium carbonate, Kieselguhr, asbestos mixture in a 60 - 25 - 15 ratio, was employed. This material was used for low pressure steam lines and pipes which were not carrying very hot fluids. In the temperature range of 400 - 450° C. glass wool or rock wool was commonly used on hot gas and high pressure steam lines. A sheet metal housing outside of the pipe was packed with the wool to a density of about 180 kg/m^3 for glass wool and 240 kg/m^3 for rock wool. At these densities the respective thermal conductivities at 200° C were 0.063 and 0.954 KCal./meter (hr)(°C.).

At temperatures over 450° and up to 300° C a diatomit insulation was used. This material was a kieselguhr produced by a low temperature burning. It had a compression strength of 6-8 kg/cm^2, a density of 450 kg/m^3 and a thermal conductivity of 0.08 Kcalories/meter(hr)(°C) at 100° C. An asbestos cement of 4 percent asbestos, 90 percent kieselguhr and 6 percent alumina plus a binder was commonly used to fill in the cracks and produce a smooth surface. When the lines were to be protected against possible fires, a thin iron sheath was placed on the outside of the insulation and held in place by galvanized iron bands.

As has been previously described, the inside of the hot, high pressure vessels such as the converters, heat exchangers, and hot separators were insulated in order to keep the external wall temperature below 250° C., and thereby prevent hydrogen embrittlement. A harder grade of Diatomit made by burning Kieselguhr at a higher temperature was used for this purpose. The compression strength of the Diatomit blocks was 25 kg/m^3, and the thermal conductivity was 0.12 K.Cal/meter(hr)(°C.) at 100° C. At 200-300 atmospheres pressure the conductivity of the oil saturated Diatomit rose to 0.4 - 0.8 k.Cal/meter(hr.)(°C.). In practice the vessels were lined with blocks of the insulation about 65 m/m thick, and asbestos cement was employed to fill up the cracks. The cement had a thermal conductivity essentially the same as that of the Diatomit.

In order to protect the structural steel work in the

12. Materials of Construction (b)(cont'd.)

stalls from buckling in the case of fire, the supports for the converters and connecting girders were insulated. A layer of Diatomit blocks about 65 m/m thick was laid around the outside of the structural steel and held in place by a wire mesh. A coating of 15-20 m/m of cement was applied over the top to protect against weather and to make a smooth finished surface. Other structural steel members were also covered with either brick or Diatomit and finished with a cement coat. These precautions helped to prevent more serious accidents in the case of fires, since the steel could stand intense heat for 30 minutes or longer when so protected.

The following table No. IV shows the I.G. Farbenindustrie application of various types of insulating materials for different applications. The ordinates show the temperature ranges and the services, while the blocks show the type of material and the thickness for different diameters.

13. Conclusions.

In a planned economy and in anticipation of war, a nation may artificially stimulate the production of potentially strategic materials. In this light the chronological development in Germany of the high pressure hydrogenation processes are of interest. The earliest commercial plants were the Haber units for the hydrogenation of nitrogen to ammonia. Developed prior to 1913, this process made Germany independent of Chile saltpeter imports for explosives production during World War I.

The experience gained in design and operation of these units proved helpful when the Germans expanded their search for materials and started in the early 1920's to hydrogenate carbon monoxide to methanol. The designs of auxiliaries, safety precautions, and materials of construction could be applied directly, and the designs of the converters, heat exchangers, and separators, could, with suitable modification, be used. Thus the Germans had two large scale high pressure processes in operation prior to the next expansion