Kirk-Othmer Encyclopedia of Chemical Technology.

HIGH PRESSURE TECHNOLOGY

During the nineteenth century the growth of thermodynamics and the development of the kinetic theory marked the beginning of an era in which the physical sciences were given a quantitative foundation. In the laboratory, extensive researches were carried out to determine the effects of pressure and temperature on the rates of chemical reactions and to measure the physical properties of matter. Work on the critical properties of carbon dioxide and on the continuity of state by van der Waals provided the stimulus for accurate measurements on the compressibility of gases and liquids at what, in 1885, was a surprisingly high pressure of 300 MPa ($\sim 3,000$ atm or 43,500 psi). This pressure was not exceeded until about 1912.

1. High Pressure in the Chemical Industry

The use of high pressure in industry may be traced to early efforts to liquefy the so-called permanent gases using a combination of pressure and low temperature. At about the same time the chemical industry was becoming involved in high pressure processes. The discovery of mauveine in 1856 led to the development of the synthetic dye industry which was well established, particularly in Germany, by the end of the century. Some of the intermediate compounds required for the production of dyes were produced, in autoclaves, at pressures of 5–8 MPa (725–1160 psi).

A pressure process for synthesizing ammonia from nitrogen and hydrogen was patented in 1881, and a modification using pressures up to 10 MPa (1450 psi) was described in 1901. However, it was not until 1904 that the full significance of pressure as a means of increasing the yield of ammonia was properly appreciated. It was soon apparent that autoclaves designed for batch processing could not be used to handle large volumes of gas continuously at pressures up to 20 MPa (2900 psi) and temperatures in the region of 500°C. The modern form of reactor designed to withstand what were then abnormal working conditions was soon developed. Between 1910 and 1913 the Badische Analin and Soda Fabrik (BASF) constructed the first commercial ammonia plant at Oppau. Since then many variations have been made to the original process primarily in catalyst composition, in type of feedstock and method of generating synthesis gas, and in operating conditions. In 1921 a modified process which operated at 100 MPa (14,500 psi) was produced, but this was never popular and to this day most ammonia plants have been designed to operate at pressures in the range 15–35 MPa (2200–5100 psi) (see Ammonia).

Other important chemical processes such as the synthesis of methanol and urea were developed in Germany. By 1923 BASF was manufacturing methyl alcohol by the catalytic reduction of carbon monoxide by hydrogen at 20–30 MPa and 390–425°C. A large number of so-called high pressure plants which were in operation throughout the world have been replaced by the low pressure process, 5–10 MPa, developed by ICI in 1966 (see Methanol). In all urea synthesis plants NH_3 reacts with CO_2 to form ammonium carbamate which is simultaneously dehydrated to give urea. This synthesis, first carried out at the Leuna works of IG Farben, is now performed in reactors in which the pressure ranges from 13–30 MPa and the temperature from 180–200°C depending on the process (see Urea).

Imperial Chemical Industries (ICI) operated a coal hydrogenation plant at a pressure of 20 MPa (2900 psi) and a temperature of 400–500°C to produce liquid hydrocarbon fuel from 1935 to the outbreak of World War II. As many as 12 such plants operated in Germany during World War II to make the country less dependent on petroleum from natural sources but the process was discontinued when hostilities ceased (see Coal conversion processes, liquefaction). Currently the Fisher-Tropsch process is being used at the Sasol plants in South Africa to convert synthesis gas into largely aliphatic hydrocarbons at 10–20 MPa and about 400°C to supply 70% of the fuel needed for transportation.

Following the discovery of polyethylene by ICI in the early 1930s, work went ahead first on the design of a pilot plant and then of a commercial plant, commissioned late in 1939, for the continuous production of polymer at a pressure of 150 MPa (22,000 psi) and a temperature of 170°C. Because the operating pressure was about four times that employed in the majority of the ammonia and methanol plants in use at the time the engineering problems in the design of the plant were considerable. Furthermore, process design proved difficult because of the need to remove the high heat of polymerization. By the mid-1940s a number of alternative processes had been designed by E. I. du Pont de Nemours & Co., Inc. and Union Carbide in the United States and BASF in Germany. These processes all operated at high pressure but differed in the way in which the heat of polymerization was removed. ICI and Du Pont used stirred reactors, known as autoclaves, in which the heat of reaction was used to raise the temperature of the incoming stream of ethylene containing small quantities of initiator. Union Carbide and BASF developed tubular reactors in which the heat of polymerization is removed by coolant circulating through jackets surrounding the reactor.

The two main types of process for the production of low density polyethylene (LDPE), the stirred autoclave and the tubular reactor, have been modified in many ways to enlarge the range of products that can be made and to increase conversion. The introduction of low pressure processes for the manufacture of high density polyethylene (HDPE) in the late 1950s and those for the manufacture of linear low density polyethylene (LLDPE) in the years following 1968 have reduced the dependence of the plastics industry on high pressure processes for some types of resin, but as long as there is a need for LDPE and copolymers such as ethylene-vinyl acetate (EVA), high pressure processes will continue to be of importance. It is estimated that the current annual production of LDPE throughout the world exceeds 15×10^6 t (see Olefin polymers).

1.1. Other Industrial Applications

High pressures are used industrially for many other specialized applications. Apart from mechanical uses in which hydraulic pressure is used to supply power or to generate liquid jets for mining minerals or cutting metal sheets and fabrics, most of these other operations are batch processes. For example, metallurgical applications include isostatic compaction, hot isostatic compaction (HIP), and the hydrostatic extrusion of metals. Other applications such as the hydrothermal synthesis of quartz (see Silica, synthetic quartz crystals), or the synthesis of industrial diamonds involve changing the phase of a substance under pressure. In the case of the synthesis of diamonds, conditions of 6 GPa (870,000 psi) and 1500°C are used (see Carbon, diamond, synthetic).

Very high dynamic pressures can be produced in material by shock waves generated by exploding charges adjacent to the material; this technique is used for welding, forming, and metal cutting operations (see Metallic coatings).

1.2. Technological Aspects

The many and varied industrial applications of high pressure make it necessary to be selective; here consideration is confined to the techniques used in the design and safe operation of continuous chemical processes operating at pressures above about 20 MPa (2900 psi). Authorities responsible for national pressure vessel and piping codes give detailed design procedures for vessels and piping systems, but until recently little consideration was given to providing guidance for the design of plants to operate at pressures above 70 MPa (10,000 psi).

Since the 1940s the design of the various processes for the manufacture of LDPE has had to be based on first principles and modified in the light of experience. For reasons of industrial secrecy, very little was published about the detailed design of the equipment used, particularly the compressors, which were of vital importance in determining the capacity and operating pressure of the reactors. In the 1990s there are continuous processes working at 350 MPa (51,000 psi) and there is no reason why, if required, this pressure could not in favorable circumstances be increased.

2. Design of Thick-Walled Cylinders

Loss of containment of chemical process vessels operating at high pressures is a rare occurrence, and when it happens it is likely to have been caused either by gross deformation or fatigue cracking. Gross deformation may result from the inability of pressure relieving devices fitted to the vessel to reduce the pressure generated within the vessel by a deflagration or rapid decomposition with sufficient speed. The resulting overpressure may rupture the vessel, particularly if its strength is weakened as a result of high temperature produced simultaneously. Alternatively the deformation may be confined to a critical part of the vessel, such as a removable closure, and result in leakage.

Repetitive loading of high pressure components by repeated application or generation of pressure, or as a result of mechanical vibration, may cause fatigue cracks to propagate through the wall thickness of the component so that leakage ensues. However, if the material of construction lacks toughness the crack may propagate only a small distance through the wall thickness before fast fracture intervenes and the component fails catastrophically.

Much information is available on the deformation and fatigue behavior of simple thick-walled hollow cylinders; the more important aspects necessary for an understanding of the techniques used in the design of modern chemical process plant are given in this section. However, it must be remembered that most process vessels are not simple hollow cylinders; they are provided with removable closures, pipe connections, side holes, etc. The shape of these features is such that it is difficult to obtain an analytical solution to the stresses induced in them by the application of internal pressure. Since the 1970s great progress has been made in the use of finite element techniques to analyze the stresses in fittings, such as screwed closures, and in components where the stress distribution is modified by the presence of cracks.

2.1. Elastic Behavior

In the following discussion of the equations relevant to the design of thick-walled hollow cylinders, it should be assumed that the material of which the cylinder is made is isotropic and that the cylinder is long and initially free from stress. It may be shown (1, 2) that if a cylinder of inner radius, r_i, and outer radius, r_o, is subjected to a uniform internal pressure, P_i, the principal stresses in the radial and tangential directions, σ_r and σ_t, at any radius r, such that $r_o > r > r_i$, are given by

$$\sigma_r = \frac{P_i}{k^2 - 1}\left(1 - \frac{r_o^2}{r^2}\right) \qquad (1)$$

$$\sigma_t = \frac{P_i}{k^2 - 1}\left(1 + \frac{r_o^2}{r^2}\right) \qquad (2)$$

where the diameter ratio $k = r_o/r_i$.

The third principal stress, that in the axial direction, σ_z (Fig. 1), depends on whether the cylinder wall resists the force acting on closures attached to the ends of the cylinder or whether the force is opposed by some

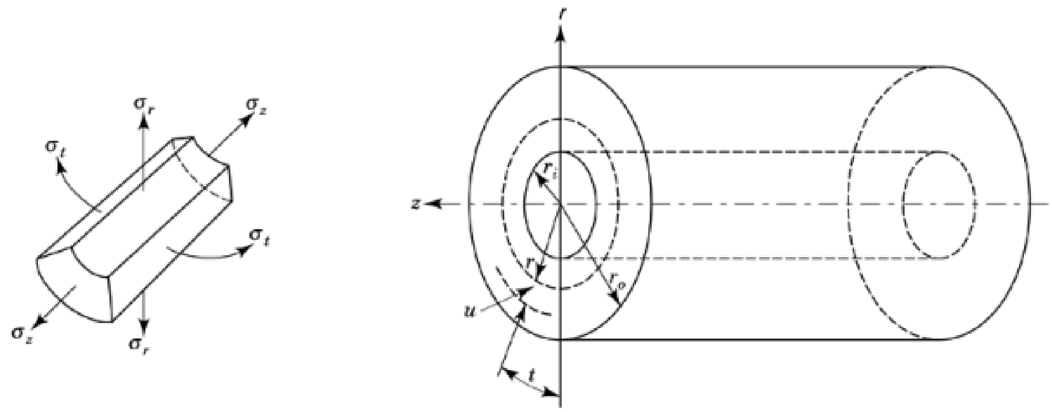

Fig. 1. Principal stresses acting on small element of cylinder wall at radius, *r,* when the cylinder is stressed elastically by internal pressure, P_i (3).

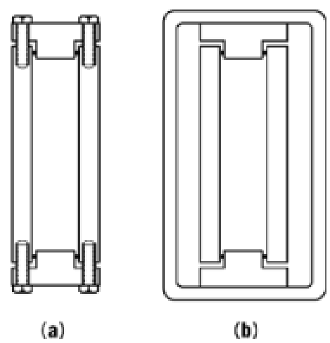

Fig. 2. (**a**) Closed-end condition; (**b**) open-end condition (4).

external support. The former method is the most common, the cylinder being fitted with removable closures attached by nuts and bolts, studs, or other coupling devices, so that the cylinder is said to be sealed under closed-end conditions (Fig. 2**a**). The second method makes use of one or two floating heads which allow the cylinder to expand or contract freely in the axial direction. The force on the heads arising from the pressure inside the vessel is then resisted by some external support and in this case the vessel is said to be sealed under open-end conditions (Fig. 2**b**). This arrangement has seldom been used for pressure vessels in the chemical industry, but is sometimes employed in the autofrettage process of strengthening components and to seal vessels used for isostatic compaction.

The stress in the axial direction of a cylinder sealed under closed-end conditions is given by

$$\sigma_z = \frac{P_i}{k^2 - 1} = \frac{\sigma_t + \sigma_r}{2} \qquad (3)$$

Under open-end conditions, neglecting the small frictional force between the bore of the cylinder and the sealing rings,

$$\sigma_z = 0 \qquad (4)$$

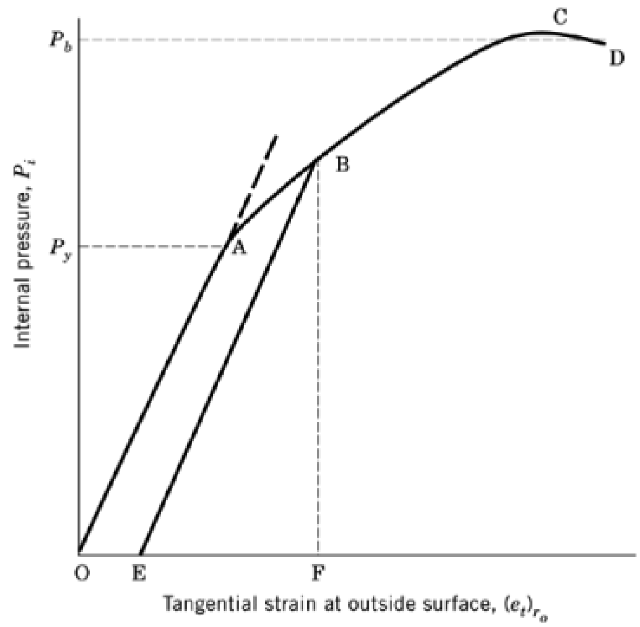

Fig. 3. Pressure expansion curve for thick-walled cylinder made of ductile material (5).

All cylinders analyzed in this article are sealed under closed-end conditions unless stated otherwise.

Equations 1 to 3 enable the stresses which exist at any point across the wall thickness of a cylindrical shell to be calculated when the material is stressed elastically by applying an internal pressure. The principal stresses cannot be used to determine how thick a shell must be to withstand a particular pressure until a criterion of elastic failure is defined in terms of some limiting combination of the principal stresses.

2.1.1. Yield Pressure

Figure 3 shows the pressure-expansion curve of a thick-walled cylinder made of a ductile material. In this figure, the strain in the tangential direction at the outside surface of the cylinder has been plotted against the internal pressure as the latter is slowly increased. From O to A the cylinder behaves elastically and if the pressure is released it will return to its original dimensions. At A the material at the bore reaches its elastic limit, and the corresponding pressure is known as the yield pressure, P_y. As the pressure is further increased, plastic deformation progresses through the wall thickness until somewhere between A and C the cylinder becomes completely plastic. At C a condition of instability is reached and localized bulging takes place. Finally the cylinder ruptures at some slightly lower pressure, D.

Early in the twentieth century it was considered prudent to design the shells of pressure vessels so that they operated within the elastic range of the material at all times. To that end designers arranged for the working pressure to be less than the yield pressure and the ratio of the latter to the former was regarded as the factor of safety with respect to yielding. This philosophy continued with the introduction of the pressure vessel codes but, as is shown later, the factor of safety with respect to yielding is expressed as the ratio of the yield strength of the material to the maximum permitted design stress generated by the internal pressure.

The state of stress in a cylinder subjected to an internal pressure has been shown to be equivalent to a simple shear stress, τ, which varies across the wall thickness in accordance with equation 5 together with a superimposed uniform (triaxial) tensile stress (6).

$$\tau = \frac{\sigma_t - \sigma_r}{2} = \frac{k^2}{(k^2 - 1)} \left(\frac{r_i}{r}\right)^2 P_i \qquad (5)$$

The maximum shear stress occurs at the bore and is given by

$$\tau = \frac{k^2}{K^2 - 1} P_i \qquad (6)$$

If it is assumed that uniform tensile stress, like uniform compressive stress (7), has no significant effect on yield, then the yield pressure of a cylinder subjected solely to an internal pressure may be calculated from

$$P_y = \tau_y \frac{(k^2 - 1)}{k^2} \qquad (7)$$

where τ_y is the yield strength of the material in torsion.

Equation 7 predicts the correct yield pressure only if the material is isotropic, the cylinder free from residual stress prior to the application of pressure, and sufficiently long, eg, more than five diameters, for there to be no end effects.

Although a torsion test is simple to carry out, it is not commonly accepted as an integral part of a material specification; furthermore, few torsion data exist in handbooks. If, as is usually the case, the design needs to be based on tensile data, then a criterion of elastic failure has to be invoked, and this introduces some uncertainty in the calculated yield pressure (8).

2.1.2. Criteria of Elastic Failure

Of the criteria of elastic failure which have been formulated, the two most important for ductile materials are the maximum shear stress criterion and the shear strain energy criterion. According to the former criterion, $\tau_y = \sigma_y/2$ and from equation 7

$$P_y = \frac{\sigma_y}{2} \frac{(k^2 - 1)}{k^2} \qquad (8)$$

For the gun steels often used in the construction of high pressure vessels, the latter criterion is favored (9) according to which, $\tau_y = \sigma_y/\sqrt{3}$. Hence from equation 7

$$P_y = \frac{\sigma_y}{\sqrt{3}} \frac{(k^2 - 1)}{k^2} \qquad (9)$$

It may be seen from equation 7 that even if the wall of an initially stress-free cylinder is infinitely thick, $k = \infty$, the yield pressure cannot exceed τ_y. The wall thickness of the cylinder is not used very efficiently since, provided the pressure is sufficiently high, the inner layers may be on the point of yielding whereas the outer are comparatively lightly stressed. Furthermore, the thicker the wall the more inefficiently is the strength of the steel utilized. The yield strength of steels which can be forged and uniformly heat treated is such that the yield pressure of a cylinder having a bore of, eg, 350 mm is restricted to about 200 MPa (29,000 psi). To achieve a higher yield pressure steels having a greater yield stress would be required. Alternatively, the inherent strength of the steel may be used more effectively by prestressing cylinders to ensure a more uniform stress distribution under load.

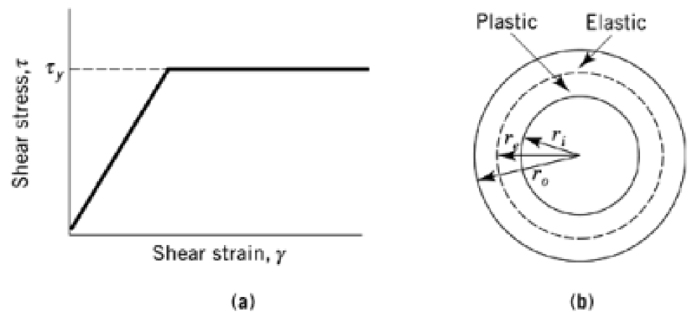

Fig. 4. (**a**) Shear stress diagram for elastic ideal plastic material; (**b**) partially plastic thick-walled cylinder.

2.2. Partially Plastic Thick-Walled Cylinders

As the internal pressure is increased above the yield pressure, P_y, plastic deformation penetrates the wall of the cylinder so that the inner layers are stressed plastically while the outer ones remain elastic. A rigorous analysis of the stresses and strains in a partially plastic thick-walled cylinder made of a material which work hardens is very complicated. However, if it is assumed that the material yields at a constant value of the yield shear stress (Fig. 4**a**), that the elastic–plastic boundary is cylindrical and concentric with the bore of the cylinder (Fig. 4**b**), and that the axial stress is the mean of the tangential and radial stresses, then it may be shown (10) that the internal pressure, P_e, needed to take the boundary to any radius r_e such that $r_i < r_e < r_o$ is given by

$$P_e = \tau_y \left\{ 1 - \left(\frac{r_e}{r_o}\right)^2 + \ln\left(\frac{r_e}{r_i}\right)^2 \right\} \qquad (10)$$

The resulting shear stress distribution while the internalpressure is acting shows the extent of yielding at radius r.

$$\textit{in the plastic region} \qquad r_i < r < r_e, \qquad \tau = \tau_y \qquad (11)$$

$$\textit{in the elastic region} \qquad r_e < r < r_o, \qquad \tau = \tau_y\,(r_e/r)^2 \qquad (12)$$

If it is assumed that yield and subsequent plastic flow of the material occurs in accordance with the maximum shear stress criterion, then $\sigma_y/2$ may be substituted for τ_y in the above and subsequent equations. For the shear strain energy criterion it may be assumed, as a first approximation, that the corresponding value is $\sigma_y/\sqrt{3}$. Errors in this assumption have been discussed (11).

Assume pressure, P_e, needed to take the elastic–plastic boundary to radius r_e corresponds to point B (see Fig. 3). Then provided the cylinder unloads elastically when the internal pressure is removed, ie, unloading path BE is parallel to OA, the residual shear stress distribution is as follows.

$$\text{when } r_i < r < r_e, \qquad \tau = \tau_y - P_e \frac{k^2}{(k^2-1)} \left(\frac{r_i}{r}\right)^2 \qquad (13)$$

$$\text{when } r_e < r < r_o, \qquad \tau = \tau_y \left(\frac{r_e}{r}\right)^2 - P_e \frac{k^2}{(k^2-1)} \left(\frac{r_i}{r}\right)^2 \qquad (14)$$

The effect of subjecting a thick-walled cylinder to a pressure greater than the yield pressure and then releasing the pressure is to put the material adjacent to the bore of the cylinder in compression while the outer layers remain in tension. On subsequent repressurization the cylinder will, to a first approximation, retrace the unloading path BE (see Fig. 3) so that the cylinder withstands elastically a pressure equal to that applied originally.

2.3. Collapse and Bursting Pressure

If the pressure is sufficiently large to push the plastic–elastic boundary to the outer surface of the cylinder so that the fibers at that surface yield, then there is nothing to restrain the wall, and the cylinder is said to collapse. With an ideal material which does not work harden the collapse pressure, P_c, sometimes called the full plastic flow pressure, the full overstrain pressure or the full thickness yield pressure, would be the bursting pressure of the cylinder. It is given by equation 10 when $r_e = r_o$ thus

$$P_c = 2\tau_y \ln k \qquad (15)$$

Little error is introduced using the idealized stress–strain diagram (Fig. 4**a**) to estimate the stresses and strains in partially plastic cylinders since many steels used in the construction of pressure vessels have a flat top to their stress–strain curve in the region where the plastic strain is relatively small. However, this is not true for large deformations, particularly if the material work hardens, when the pressure can usually be increased above that corresponding to the collapse pressure before the cylinder bursts.

An approximate procedure for estimating the stresses and strains in a partially plastic cylinder, which uses actual stress–strain data for the material and takes account for dimensional changes, has been devised (12, 13). More important, this procedure, which is based on shear stress–strain data obtained in a torsion test, may also be used to estimate the bursting pressure. Tension data may be used but the method is less accurate, particularly at large strains, where the specimen may have necked (8, 14). It is assumed that the stress system is one of simple shear and that the material is incompressible, the internal pressure corresponding to any given bore strain, and hence the pressure expansion curve, may be computed (15). Figure 5 shows the calculated pressure expansion curves for cylinders of various diameter ratios made of Ni–Cr–Mo steel EN25 (BS970-826M31) (16). At the peak pressure the decrease in strength of the cylinder due to wall thinning is just counterbalanced by the increase in strength due to work hardening of the material of which the cylinder is made. It has been observed that if the pressure in a cylinder made of a ductile material is increased slowly, bursting may not occur at the peak pressure and that the cylinder may continue to expand at a reduced pressure prior to bursting. The peak pressure reached during a burst test is often known as the ultimate bursting pressure (16).

The validity of Manning's method (12, 13) for predicting the pressure–expansion curve of thick-walled cylinders up to their ultimate bursting pressure has been experimentally confirmed, at room temperature, for a 0.15% C steel, a 0.3% C steel and a Ni–Cr–Mo steel EN25 (BS970-826M31) and on two alloy steels EN25 and EN40 (BS970-722M24) and a carbon steel EN3 (BS970-M26) up to temperatures of 370°C (18). In addition, ICI has provided data on 3.5% NCMV steel cylinders having a diameter ratio of 1.61 at 20°C and 350°C (15). Based on some of the earlier tests it was suggested (14, 16) that the following equation might be used to estimate the bursting pressure of thick-walled cylinders.

$$P_b = 2\sigma_u \frac{(k-1)}{(k+1)} \qquad (16)$$

Bursting tests have been carried out on nearly a hundred thick-walled cylinders made of carbon, low alloy, and stainless steels, together with some nonferrous materials. The diameter ratio of the cylinders varied from

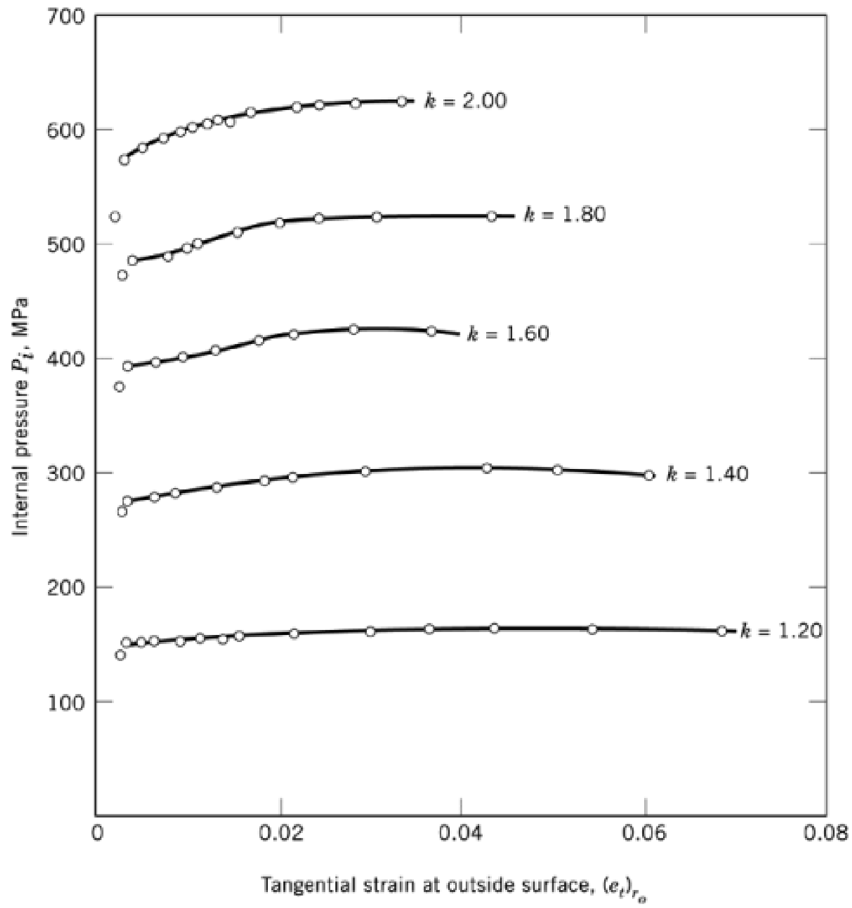

Fig. 5. Internal pressure expansion curves for cylinders of EN25 (16, 17); $k=r_o/r_i$. To convert MPa to psi, multiply by 145.

1.75 to 5.86, and some tests were carried out at 660°C. An analysis of the results (19) showed that 90% of the cylinders burst within ±15% of the value given by equation 17.

$$P_b = \frac{\sigma_y}{\sqrt{3}} \ln k \left(2 - \frac{\sigma_y}{\sigma_u}\right) \qquad (17)$$

Plots of the bursting pressures of the Ni–Cr–Mo cylinders (EN 25) vs k derived from equations 16 and 17 show that neither equation is in such good agreement with the experimental results as is the curve derived from Manning's theory. Similar conclusions have been reached for cylinders made of other materials which have been tested (16). Manning's analytical procedure may be programmed for computation and, although torsion tests are not as commonly specified as tension tests, they are not difficult or expensive to carry out (20).

2.4. Prestressed Cylinders

Two considerations of importance in the design of a thick-walled cylinder to operate at high pressures are the initial yield pressure and the bursting pressure. Whereas the yield pressure approaches the yield shear stress of steel asymptotically as the diameter ratio increases, the bursting pressure continues to increase monotonically;

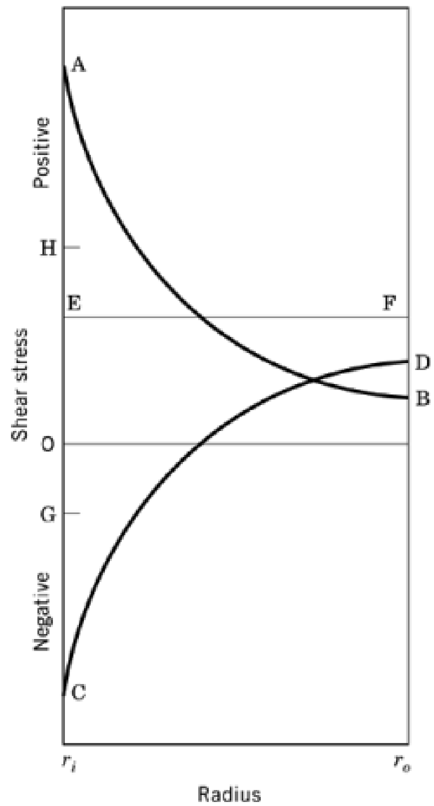

Fig. 6. An idealized example of prestressing (21). See text.

hence the margin between the initial yield and bursting pressure gets larger as the diameter ratio increases. Unless the tensile strength of the steel is changed, nothing can be done to affect the bursting pressure of a cylinder of given diameter ratio. On the other hand, the pressure to cause initial yielding of the bore of the cylinder can be raised by developing compressive stresses at the bore prior to the application of pressure, a technique known as prestressing.

The potential benefits of prestressing may be seen from Figure 6, in which curve AB represents the distribution of shear stress across the wall of an initially unstressed cylinder generated by an internal pressure *P*. If the cylinder could be prestressed in such a way that the stress distribution prior to pressure, *P*, being applied were to be given by curve CD, then the resultant distribution of shear stress when the cylinder is under load would be represented by line EF obtained from the algebraic summation of curves AB and CD. One effect of the prestressing would be to produce a more uniform resultant stress across the wall thickness at the design pressure; another would be to lower the maximum shear stress at the bore. Figure 6 shows that a prestressed cylinder behaves elastically provided the stress at C induced by prestressing, or that at E induced by the working pressure, do not exceed the yield strength of the material of construction. If it is assumed that the shear yield stress of the material in compression is the same as that in tension, then the maximum internal pressure which a prestressed cylinder, having a diameter ratio $k > 2.2$, could withstand elastically would be twice as large as that which an initially stress-free cylinder of the same radius ratio could withstand.

A more important effect of prestressing is its effect on the mean stress at the bore of the cylinder when an internal pressure is applied. It may be seen from Figure 6 that when an initially stress-free cylinder is subjected to an internal pressure, the shear stress at the bore of the cylinder increases from O to A. On the other hand, when a prestressed cylinder of the same dimensions is subjected to the same internal pressure, the shear stress at the bore changes from C to E. Although the range of shear stress is the same in the two cases (distance $OA = CE$), the mean shear stress in the prestressed cylinder, represented by point G, is smaller than that for the initially stress-free cylinder represented by point H. This reduction in the mean shear stress increases the fatigue strength of components subjected to repeated internal pressure.

In practice a uniform distribution of the working stress cannot be achieved, but it may be approached by various methods of construction such as compound shrinkage, tape winding, and autofrettage which have their origin in the design of ordnance.

2.4.1. Autofrettage

The process of overstraining a thick-walled cylinder by applying an internal pressure in excess of the yield pressure, so as to develop a favorable residual stress distribution to increase the range of internal pressure which the cylinder can withstand elastically, is known as autofrettage. It is a French word meaning self-hooping, first used in 1906 to describe a procedure for strengthening gun barrels. However, it was not until World War II that the process was widely used for this purpose, and it now plays an important role in the design of high pressure plants. Since the 1960s, the value of autofrettage in increasing the initial yield pressure of a plain cylinder has been almost completely overshadowed by its widespread use in increasing the fatigue strength of components, some of which are of complex shape.

The pressure expansion curve of a thick-walled cylinder undergoing autofrettage is shown diagrammatically in Figure 7. If the autofrettage pressure represented by point B is released, the unloading curve is more or less straight and parallel to the elastic line OA. The permanent strain at the outside surface is represented by distance OC. If the pressure is now reapplied, the loading curve is initially parallel to the elastic line and the pressure corresponding to point D is sometimes known as the reyield pressure. When the pressure approaches the maximum value of the previous loading, the stress–strain curve bends over and continues as if the process has not been interrupted at B. This behavior is typical when the degree of overstrain is small; however, if the pressure is increased to point F, such that more of the wall thickness is overstrained, then the slope of the unloading curve decreases as the inner layers yield in compression. The decrease in the yield strength of the material in compression, resulting from plastic deformation in tension, is known as the Bauschinger effect, and the assumption that the cylinder unloads elastically from the autofrettage pressure may lead to a higher estimate of the residual stresses than is realized in practice.

The pressure external expansion relationship for a thick-walled cylinder and the subsequent distribution of the residual stresses when the autofrettage pressure is removed may be calculated from material properties obtained from torsion tests on a small number of thin tubes (23). Using this procedure, the residual stresses in cylinders made of EN25 induced by autofrettage have been calculated and compared with those measured experimentally, using the Sachs boring-out technique, and with those calculated on the assumption that the cylinders unloaded elastically. It was found that with cylinders having a diameter ratio of about 2.4, autofrettaged to take the plastic–elastic boundary to the geometric mean radius, the residual stress at the bore of the cylinder was only about 65% of that expected had the release been elastic.

Quenched and tempered low alloy steels, often used for vessels, have a low strain hardening coefficient and a significant Bauschinger effect. Although other methods have been proposed to allow for the Bauschinger effect (24–27), when calculating the reyield pressure and the residual stresses in autofrettaged plain cylinders, none has yet achieved widespread acceptance. In addition to the Sachs boring-out technique, a number of other experimental methods, some nondestructive, are available for determining residual stress distributions (25).

Low temperature heat treatment, usually in the range 250–300°C, was given after the autofrettage of guns as it was thought to reduce the hysteresis loops, shown in Figure 7, and restore elasticity (28). Although tests (23) have shown that it does have a slightly beneficial effect, the problems of controlling it on all but the

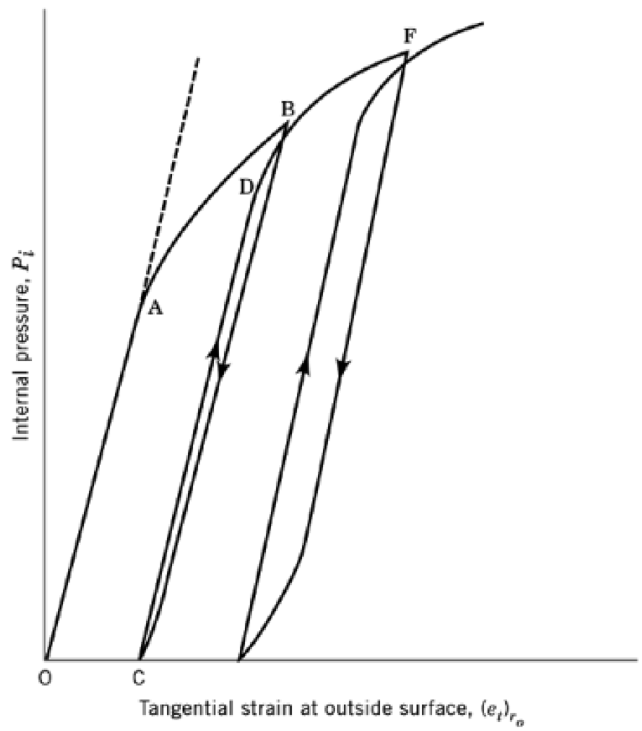

Fig. 7. Pressure expansion curve of a thick-walled cylinder undergoing autofrettage (22).

smallest of specimens have cast doubts on its value for long pipes and large vessels. At higher temperatures residual stresses induced by autofrettage may be relaxed unless the component is made of creep-resistant material (29).

The autofrettage process is usually controlled by measuring the strain in the tangential direction on the outside surface of the component while the pressure is acting and again after it has been removed. If the component is long, as with a length of tube, it may be necessary to record the strain at a number of points along the length. Since the autofrettage pressure may be two or three times the working pressure of the component, special arrangements may be needed to withstand the end load generated by the autofrettage pressure. Precautions and techniques used in the autofrettage of components for reciprocating compressors at pressures up to 1.3 GPa (189,000 psi) have been described (30) and the freezing pressures of pressure transmitting oils at room temperature have been measured (31).

Autofrettage of small bore tubes can be effected by pushing highly polished and generously lubricated oversized drifts or balls through the bore. The process can be controlled by measuring the tangential strain at the outside surface of the tube, and, if a number of passes are used, a very good bore finish is achieved. Residual stresses developed in tubes ($k = 2.5$) 300 mm long, having a bore diameter of 27 mm made of 2.5% Ni–Cr–Mo steel (EN26) as a result of forcing oversized tungsten carbide balls through the bore, have been measured experimentally (29).

2.4.2. Compound Shrinkage

In its simplest form (Fig. 8**a**) compound shrinkage consists of machining the inner radius of an outer component *I*, $(r_i)_I$, so that it is smaller than the outer radius of an inner component *II*, $(r_o)_{II}$. The difference between the

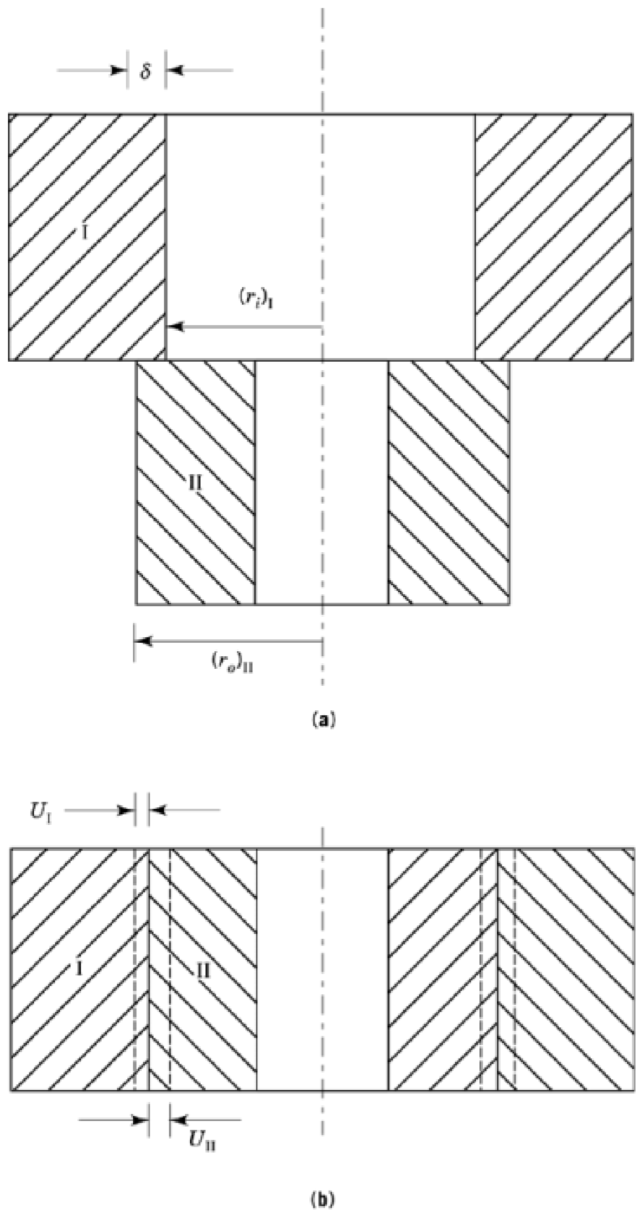

Fig. 8. Compound cylinders (**a**) before and (**b**) after assembly. Not to scale.

two is known as the radial interference δ. To assemble the cylinders, outer component *I* is heated and/or inner component *II* cooled so that the outer component can be slipped over the inner as shown in Figure 8**b.** When the temperature of the assembly returns to ambient, a compressive stress (pressure) is generated across the interface which simultaneously compresses the inner and expands the outer component and, in so doing, displaces radius $(r_i)_I$ by U_I and radius $(r_o)_{II}$ by U_{II}. Unfortunately, it is difficult to carry out this operation without setting up stresses in the axial direction (32).

The residual shear stress distribution in the assembled cylinders, prior to the application of internal pressure, may be calculated, from pressure P^*, generated across the interface. The resulting shear stress distribution in the compound cylinder, when subjected to an internal pressure P_i, may be calculated from the sum of the residual stress distribution and that which would have been generated elastically in a simple cylinder of the same overall radius ratio as that of the compound cylinder.

In a correctly designed and assembled compound cylinder the stresses are all within the elastic range; however, if the interference is too large the inner component can yield in compression or the outer component in tension. On the other hand, if the internal pressure is too high the inner or outer component can yield in tension.

The radial interference, δ, necessary to achieve pressure P^* may be calculated from the radial displacements U_{I} and U_{II} generated during assembly, assuming that the shrinkage is carried out without generating an axial stress in either component.

It may be shown (33) that when the inner surface of a cylinder made of n components of the same material is subjected to an internal pressure, the bore of each component experiences the same shear stress provided all components have the same diameter ratio. For these optimum conditions,

$$k_1 = k_2 = k_3 \cdots = k_n = k_o^{1/n} \qquad (18)$$

The yield pressure of the multicomponent cylinder isgiven by

$$P_y = \tau_y n \frac{\left(k_o^{2/n} - 1\right)}{k_o^{2/n}} \qquad (19)$$

and plottedin Figure 9 in dimensionless form against the overall diameter ratio k_o with the number of components, n, as parameter. It might appear possible from Figure 9 to design a cylinder to withstand very high internal pressures if both the number of components and the overall diameter ratio k_o were large enough. However, this cannot be done because the residual shear stress at the bore of the vessel after assembly would be so large that the material would yield. If it is assumed that the shear yield stress is the same when the material is stressed in compression as it is when stressed in tension, then the maximum internal pressure which the multicomponent cylinder can withstand without yielding is given by

$$p_y = \frac{2\tau_y\left(k_o^2 - 1\right)}{k_o^2} \qquad (20)$$

Provided the design is such that it can be represented by coordinates which fall within the unshaded area, then the residual stress will not exceed the yield strength of the material. When the cylinder is built up of n components of the same material, it can be shown (35, 36) that the interference per unit radius required for all cylinder mating operations is given by

$$\frac{\sigma}{r} = \frac{2P_i}{nE} \qquad (21)$$

where ς is the interference of the components in contact at radius r, P_i is the internal pressure, n the number of components, and E the modulus of elasticity.

To utilize fully the strength of the inner member it should be stressed from the yield point in compression to the yield point in tension. From Figure 9 it is seen that if the members are initially stress-free at least three must be employed to make this possible.

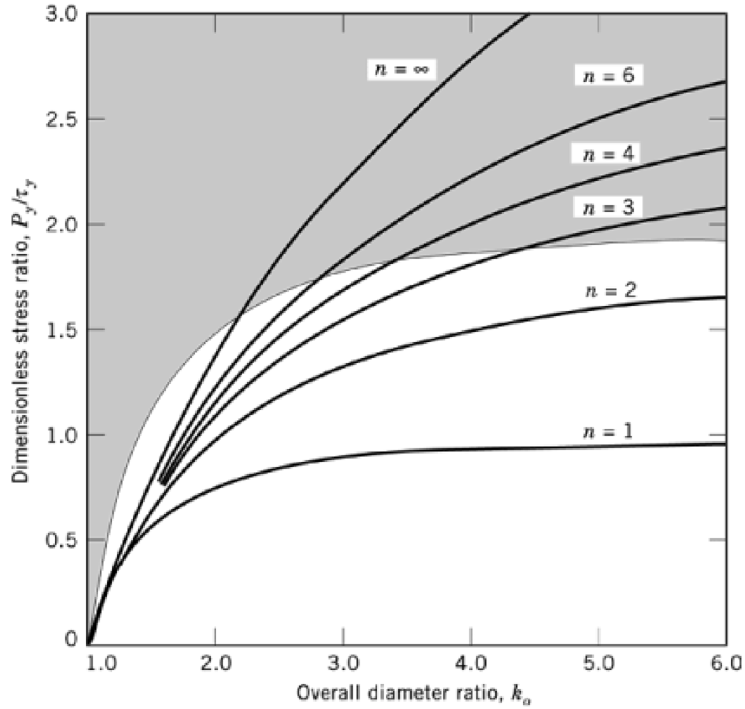

Fig. 9. Yield pressure of multicomponent vessels designed for optimum conditions (34).

In practice compound shrinkage is often used to prestress a high strength or corrosion-resistant liner. The optimum radius ratios of components of different yield strengths have been shown (37, 38) to be

$$\frac{\tau_{y_1}}{k_1^2} = \frac{\tau_{y_2}}{k_2^2} = \frac{\tau_{y_3}}{k_3^2} = \text{etc} \qquad (22)$$

The maximum internal pressure, subject to the avoidanceof reversed yielding, is then given by

$$P = \tau_{y_1}\frac{k_1^2 - 1}{k_1^2} + \tau_{y_2}\frac{k_2^2 - 1}{k_2^2} + \cdots \tau_{y_n}\frac{k_n^2 - 1}{k_n^2} \qquad (23)$$

If all the components have the same elastic constants,the condition for reversed yielding is the same as that given by equation 20.

This optimum condition is designed to ensure that the bores of all components yield at the same time. If the cylinder is subjected to fatigue conditions, it has been suggested (39) that a better design criterion would arrange for the maximum normal stress, which controls fatigue crack propagation, to be the same in each component.

When the components are shrunk together there is a limitation on the temperature difference that can be employed. The upper temperature must not exceed the tempering temperature of the outer members and the lower temperature is limited by the dew point of the atmosphere, otherwise water condenses on the cooled component. It is also necessary to have a clearance of about 1 mm/m diameter to facilitate assembly. It is difficult to carry out the shrinkage operation without compressive axial stresses being generated in those components which are cooled, and tensile axial stresses being generated in those components which are heated, prior to assembly. During use the components in tension tend to contract in length; those in compression expand so as to relax the axial stresses. The resulting strains are unimportant unless, as with some compressor components, the ends of the compound assembly are lapped to provide sealing surfaces. If a compound vessel is to be used under conditions where the heat flux changes rapidly over the length of the vessel, such as during start-up and shut-down of a reactor, it is important to anchor the inner component to the outer at one point along their length so as to avoid relative movement of the components as a result of thermal ratcheting. The difficulties of shrinkage may be reduced, at least in the case of relatively small components, if the components are tapered (using an angle less than the angle of friction) and pushed together in a press.

Probably the largest compound vessels built were two triple-wall vessels, each having a bore diameter of 782 mm and a length of 3048 mm designed for a pressure of 207 MPa (30,000 psi). These vessels were used by Union Carbide Co. for isostatic compaction; unfortunately the first failed at the root of the internal thread of the outer component which was required to withstand the end load (40). A disadvantage of compound shrinkage is that, unless the vessel is sealed under open-end conditions, the end load on the closures has to be resisted by one of the components, which means that the axial stress in that component is high.

Although compound shrinkage has occasionally been used in the manufacture of pressure vessels for the polymerization of ethylene, its main application in the chemical industry has been in the construction of components, such as packing cups for reciprocating compressors, which are subjected to fatigue conditions or to the manufacture of compressor cylinders with wear-resistant liners made of brittle materials. Since these liners are made of hard materials such as tungsten carbide, which have poor tensile properties, it is necessary to ensure that they are never subjected to tensile stress. The differences in the modulus of elasticity and in Poisson's ratio between tungsten carbide and steel must be taken into account when calculating the required interference. The coefficient of thermal expansion of tungsten carbide is approximately 7×10^6 per $^\circ$C compared with 12×10^6 per $^\circ$C for steel; provided the shrinkage requirement can be kept below about 2 mm/m, a worn or damaged liner can usually be made to drop out of its outer mantle by heating the assembly through about 450°C.

2.5. Composite Vessels

2.5.1. Wire-Wound Vessels

Wire-winding was used extensively in the manufacture of large guns, but is seldom employed for chemical process vessels mainly because of the difficulty of providing the vessel with sufficient strength in the axial direction. However, this problem does not arise if, as in the case of some isostatic presses, the vessel is sealed under open-end conditions when the advantages of pretressing by wire winding can be realized (41, 42).

2.5.2. Tape-Wound Vessels

In 1937 it was suggested (43) that lack of axial strength in wire-wound vessels might be overcome if the vessels were reinforced with interlocking tape, and in 1938 IG Farben produced the first Wickelkorper or tape-wound vessel. In this process a forged or welded inner tube was set up in a special lathe and spiral grooves were cut in the outer surface to match tongues in the tape (Fig. 10**a**). Before wrapping was commenced on the lathe, one end of the tape was welded to one of the dummy ends of the inner tube. As the tape unwound from a spool, it was heated electrically to 800–900°C and immediately after winding cooled first by jets of compressed air then by cold water. After the first layer of tape had been completely wound the end was welded to the other dummy end. The beginning of the next layer was then welded to the first layer so that it overlapped the joints of the underlying layer (Fig. 10**b**). Succeeding layers were similarly wrapped until the required wall thickness, up to 380 mm, was obtained. The theory of compound shrinkage shows that the residual contact pressures between 10 or more components are sufficiently small that they could be achieved by the tension generated as a result of the contraction of the tape and the wrapping tension. Flanges were screwed or shrunk on the layers, after

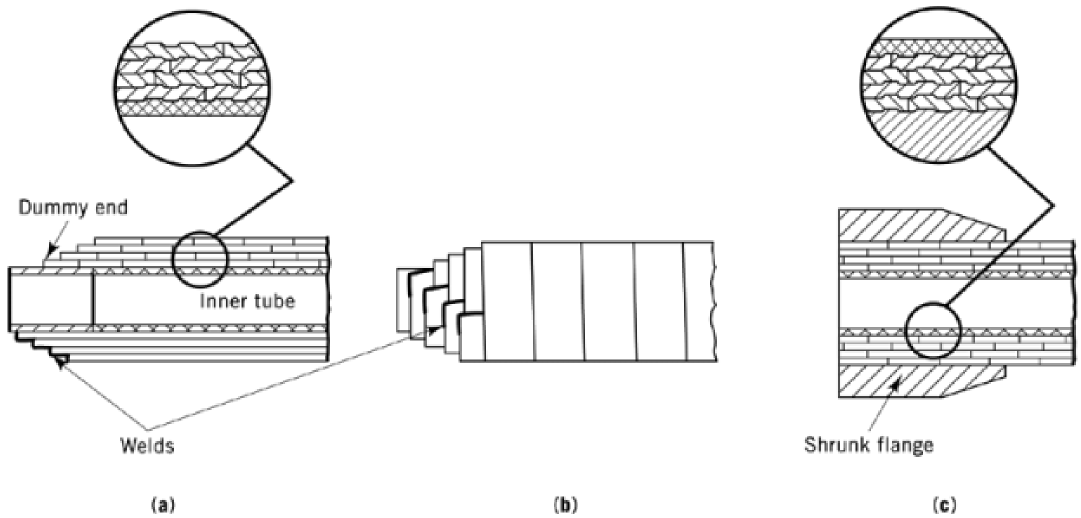

Fig. 10. Detail of tape-winding process (44). See text.

which the dummy ends were cut off and the vessel machined to its proper length, as shown in Figure 10**c.** Tried methods for attaching cooling/heating coils to the outside surface of tape wound vessels are available.

The theory of tape-wound reinforcement and the calculated residual and working stress distributions in the radial and tangential directions in a typical vessel used for coal hydrogenation have been presented (45, 46). By the end of World War II over 200 vessels for service at 30–70 MPa (4350–10,000 psi) had been made, the largest being 18 m long and 1.2 m internal diameter. Since then vessels have been manufactured for use as pulsation dampeners in LDPE plants, some of which have been in operation at pressures of 276 MPa (40,000 psi) since the 1950s (46). Few tape-wound vessels similar to those described have been made outside Germany (47).

2.5.3. Multilayer Construction

An alternative method of construction developed since 1931, first by A. O. Smith Corp. and subsequently used in Europe, consists of wrapping and welding successive layers of thin steel plate round an inner cylinder (48, 49). The original objective was to produce a thick-wall from much thinner material, thereby easing the task of ensuring sound material throughout. Later, multilayer vessels were found to have greater elastic strength than was expected because of the residual stresses produced by a combination of wrapping tension and weld contraction and are reported to be used at pressures up to 250 MPa (36,000 psi) (50). Current practice assumes that the residual stresses are generated by the transverse weld shrinkage in the longitudinal seams but analyses of the problem (50–52) show that many other factors are involved. The ends of the layer built shell are scarfed so that closures of conventional design may be welded on to them. The relief provided by the movement of the individual layers prevents the development of internal stress; hence heat treatment of the circumferential welds which may be as much as 400 mm thick is not required.

The main advantages of multilayer construction are that it (*1*), reduces the risk of fragmentation; (*2*), resists the growth of flaws from one layer to another; and (*3*), enables leakage of the inner layer to be detected if the outer layers are provided with vent holes (53).

Multilayer vessels burst at about the same pressure as initially unstressed vessels of the same diameter ratio made of the same material (54). A bursting test was carried out on a special multilayer vessel manufactured by Krupp which consisted of an inner layer 5 mm thick, three middle layers 10 mm thick which had not been welded along their longitudinal seams, and an outer shell 5 mm thick. Friction between the layers was such that the bursting pressure was three-quarters that of a normal vessel of the same materials and dimensions (55). The bursting pressure of a model vessel of 307 mm bore diameter, made of seven 3-mm thick layers in which the longitudinal seams of the inner five layers were staggered over 60° and tack welded at a few points to keep the layers in contact, was only 4% below that calculated for an equivalent monobloc vessel (56). Similar experiments, including fatigue tests, have been carried out by other workers on model vessels (52, 57).

2.5.4. Helically Coiled Vessels

These were developed in the 1970s in Japan, China, and the former Soviet Union and are produced by winding long strips of metal plate 900–1800 mm wide around a core tube at an angle of 15–30° by means of pressure and guide rolls, using a procedure similar to the winding of a coil spring. After the vessel is fabricated, outer wrapper sheets are used to enclose the helically coiled courses, the spring effect of which greatly improves the axial strength of the vessel (58).

2.6. Effect of Temperature on Design

In gas separation processes high pressure equipment is needed to operate at temperatures considerably below atmospheric, whereas some heterogeneous gas reactions have to be carried out at high temperatures to make them economically feasible. Both high and low temperatures have an effect on the mechanical properties of metals. In general, the ductile properties, and in particular the toughness and impact strength, of most low alloy steels, decrease sharply as the temperature is reduced and care has to be taken over the choice of materials if low temperature embrittlement is to be avoided. On the other hand, the yield and tensile strength of steels decrease as the temperature increases and allowance has to be made for this in estimating the static strength of a thick-walled cylinder at temperatures above ambient. Above about 350°C, creep starts to become an important factor with Ni–Cr–Mo steels of the sort used for high pressure applications, and the stresses in the wall of the vessel and its deformation are no longer independent of time. In addition to the effect of temperature on mechanical properties, temperature gradients, generated in the walls of vessels as a result of applied heat or of heat liberated by exothermic reactions proceeding within the vessel, cause thermal stresses which may need to be considered when estimating the stresses in a thick-walled cylinder subjected to both internal pressure and heat flux.

2.6.1. Thermal Stresses

When the wall of a cylindrical pressure vessel is subjected to a temperature gradient, every part expands in accordance with the thermal coefficient of linear expansion of the steel. Those parts of the cylinder at a lower temperature resist the expansion of those parts at a higher temperature, so setting up thermal stresses. To estimate the transient thermal stresses which arise during start-up or shutdown of continuous processes or as a result of process interruptions, it is necessary to know the temperature across the wall thickness as a function of radius and time. Techniques for evaluating transient thermal stresses are available (59) but here only steady-state thermal stresses are considered. The steady-state thermal stresses in the radial, tangential, and axial directions at a point sufficiently far away from the ends of the cylinder for there to be no end effects are as follows:

$$\sigma_r = -\frac{\beta}{2}\left[\frac{k^2}{k^2-1}\left(1-\frac{r_i^2}{r^2}\right)-\frac{\ln(r/r_i)}{\ln k}\right] \qquad (24)$$

$$\sigma_t = -\frac{\beta}{2}\left[\frac{k^2}{k^2-1}\left(1+\frac{r_i^2}{r^2}\right) - \frac{\ln(r/r_i)}{\ln k} - \frac{1}{\ln k}\right] \qquad (25)$$

$$\sigma_z = -\beta\left[\frac{k^2}{k^2-1} - \frac{\ln(r/r_i)}{\ln k} - \frac{1}{2\ln k}\right] \qquad (26)$$

where $\beta = \alpha E \Delta T/(1-\upsilon)$; $\Delta T = T_i - T_o$ is the steady-state temperature difference between the inner radius r_i and the outer radius r_o; α is the coefficient of thermal expansion; E, Young's modulus; and υ, Poisson's ratio.

In the derivation of equations 24–26 (60) it is assumed that the cylinder is made of a material which is isotropic and initially stress-free, the temperature does not vary along the length of the cylinder, and that the effect of temperature on the coefficient of thermal expansion and Young's modulus may be neglected. Furthermore, it is assumed that the temperatures everywhere in the cylinder are low enough for there to be no relaxation of the stresses as a result of creep.

Figure 11 shows the thermal stresses in an austenitic stainless steel pipe having a diameter ratio of 2, when subjected to a temperature gradient of 100°C arising on the one hand from internal and on the other from external heating. The thermal stresses in the axial direction, unlike those induced by internal pressure, are not constant across the wall thickness. Furthermore, the axial stress is not always the intermediate principal stress, so that care must be taken in evaluating the maximum shear stress. The tangential stress at the bore may be compressive or tensile, depending on whether heat flows from the inner to the outer wall or vice versa. Thus, when a vessel is heated internally, the thermal stresses oppose the pressure stresses, whereas when it is heated externally they augment them. This is illustrated in Figure 12 where the principal thermal stresses shown in the previous figures have been combined to give the distribution of the shear stress across the wall thickness, for the case of internal heating and that of external heating. Superimposed on this figure is the distribution of shear stress, neglecting the thermal stress present which arises from an internal pressure of 138 MPa (20,000 psi), together with the resulting working stress given by the algebraic summation of the thermal and pressure stresses.

Seldom is the temperature difference across the wall thickness of an item of equipment known. Since large temperature gradients may occur in the boundary layers adjacent to the metal surfaces, the temperature difference across the wall should not be estimated from the temperatures of the fluids on each side of the wall, but from the heat flux using equation 27

$$\Delta T = Q \ln k / 2\pi\lambda \qquad (27)$$

where Q is the rate of flowor heat from the cylinder per unit length and λ is the thermal conductivity of the metal.

2.6.2. Creep of Thick-walled Cylinders

The design of relatively thick-walled pressure vessels for operation at elevated temperatures where creep cannot be ignored is of interest to the oil, chemical, and power industries. In steam power plants, pressures of 35 MPa (5000 psi) and 650°C are used. Quartz crystals are grown hydrothermally, using a batch process, in vessels operating at a temperature of 340–400°C and a pressure of 170 MPa (25,000 psi). In general, in the chemical industry creep is not a problem provided the wall temperature of vessels made of Ni–Cr–Mo steel is below 350°C.

The stress system within the wall of a pressure vessel under creep conditions does not lend itself to simple analysis because of the continual redistribution of stress which occurs as creep takes place. Consequently, the

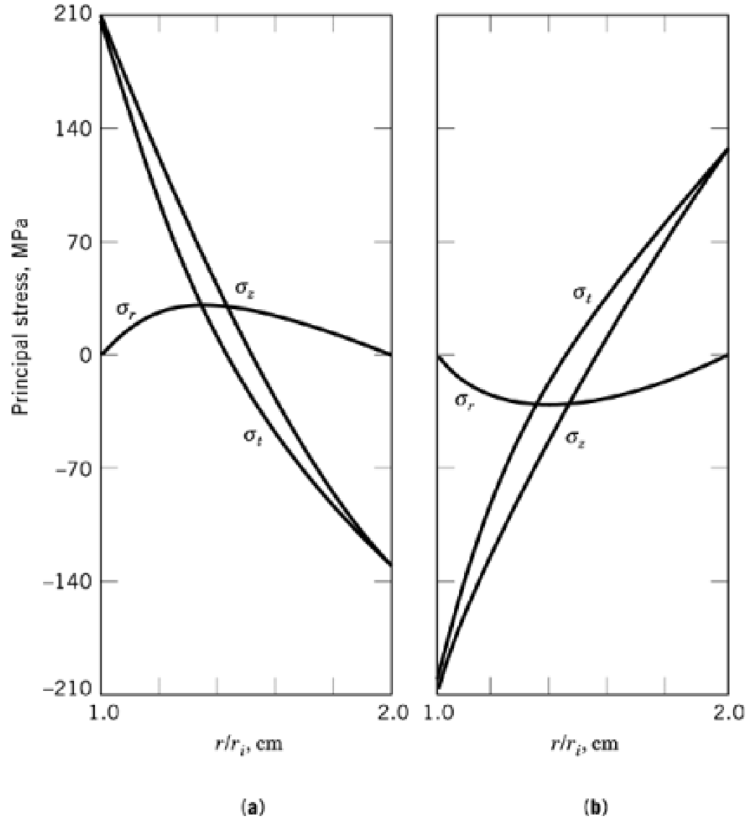

Fig. 11. Principal stresses induced in a cylinder of $k=2$ by a temperature gradient of 100°C: (**a**) maximum temperature at outside surface; (**b**) maximum temperature at inside surface (61). To convert MPa to psi, multiply by 145.

calculation of the rate of deformation of a thick-walled cylinder subjected to internal pressure undergoing creep poses many problems (63). From results of pressure creep tests (64) on cylinders, of diameter ratio 2, made of 0.19% carbon steel at 450°C, it was concluded (65) that a previously outlined procedure (66, 67) provides a satisfactory correlation between tension and thick-walled creep data in the secondary region of creep. Subsequent (68) pressure creep tests were made on cylinders of 2.5% Ni–Cr–Mo steel (EN25) having a diameter ratio of 1.67 at pressures of 309–340 MPa (45–49,000 psi) and the results correlated (69, 70). Before vessels can be designed with confidence to operate at high pressures in the creep range, more reliable experimental data against which the various theories may be tested is required.

2.6.3. Creep Rupture

The results from creep rupture tests on tubes under internal pressure at elevated temperatures (71, 72) may be correlated by equation 16, in which ς_u is replaced by ς_{cr} the tensile creep rupture stress after time t at temperature T.

$$P_b = 2\sigma_{cr}\frac{(k-1)}{(k+1)} \qquad (28)$$

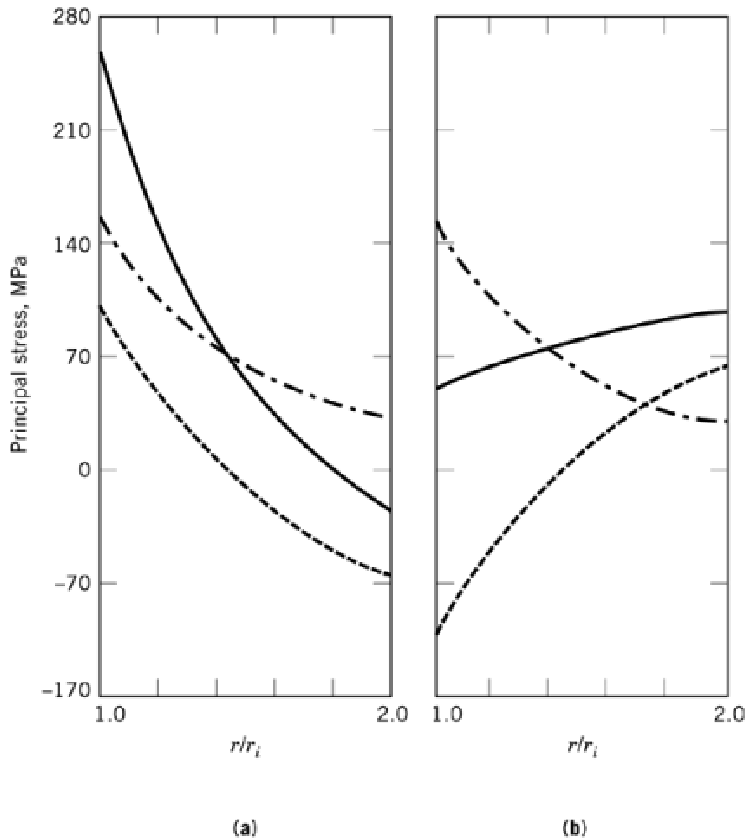

Fig. 12. Pressure and temperature stresses in a cylinder, $k=2$, subjected to a steady temperature gradient of 100°C and an internal pressure of 138 MPa (20,000 psi): (**a**) maximum temperature at outside surface; (**b**) maximum temperature at inside surface (62). (– – – – – –), Thermal stress; (—— – —— –), stress due to pressure; (–), combined pressure and thermal stress.

Short-term (100 h) internal pressure creep rupture testsof small bore cylinders having diameter ratios of 3 to 4, made of a number of different refractory metals, have been investigated at temperatures in the range 900–1300°C (73).

2.6.4. Internal Heating

In many high pressure gas reactors, where for economic reasons it is essential to operate at a high temperature, special provision is made by heat exchange or direct cooling to keep the inner walls at a temperature low enough to minimize creep. One way of doing this is to allow the cool gas entering the reactor to flow between the inner surface of the vessel and an insulated layer on the outside of the reaction chamber. Thus the outer vessel, which has to withstand the internal pressure, is at a relatively low temperature, while the inner reaction chamber, which is maintained at a high temperature, is not subjected to an unbalanced pressure.

With a batch process, such as hot isostatic compaction (HIP), heat exchange as used in a continuous reactor is not possible, and it is common practice to provide a furnace within the pressure vessel which is thermally insulated to ensure that the temperature of the vessel does not rise above 300°C. Most HIP operations involve gas pressures in the range 70–200 MPa (10–29,000 psi) and temperatures of 1250–2000°C, occasionally 2250°C

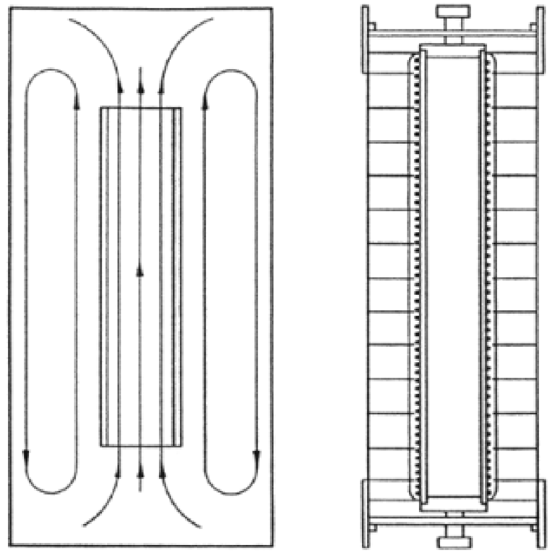

Fig. 13. (**a**) Convection currents around electrically heated furnace tube; (**b**) furnace construction to minimize convection (78).

(74). The pressure vessel may have a bore diameter from 27 to 1524 mm (75) and is nearly always provided with threaded closures sealed with O-rings made of elastomer provided the temperature is low enough.

In the 1950s, serious problems were experienced in the design of furnaces (qv) to prevent unrestrained gas convection currents which gave rise to very large temperature gradients (76, 77) and made furnace control difficult. Figure 13**a** represents convection currents around an electrically heated furnace tube in an enclosure pressurized by gas. To achieve a uniform temperature over the central section of tube shown in Figure 13**b,** the furnace was wound in four sections so that the power input to each section could be varied independently. Covers were fitted to the top and bottom of the tube to prevent gas flowing through it, and the charge within the furnace was surrounded by fine dense alumina powder of low permeability. Convection currents on the outside of the tube were largely prevented by a series of impermeable baffles, the volume between the baffles being filled with alumina powder. The performance of the furnace at temperatures up to 1250°C and helium gas pressures of 100 MPa (14,500 psi) was satisfactory (79).

During the 1960s, improvements in furnace design made possible the replacement of helium by less expensive argon. A convection furnace, widely used since about 1976, heats the dense gas and transfers heat by natural convection to the workpiece above. A linear is used to provide a path for the gas to flow (Fig. 14**a**) and circulation helps to achieve a uniform temperature throughout the work area. In the forced circulation furnace (see Fig. 14**b**) high heating and cooling rates may be achieved. Convection furnaces are favored because, for a given vessel diameter, the work cavity is larger and the heating elements are less susceptible to damage during the loading/unloading process.

The workpiece volume of production HIP equipment ranges from 0.05 to 2.5 m^3 but seldom exceeds 1.5 m^3, and the most common materials for the elements of the furnaces are graphite, molybdenum, and Ni–Cr alloy (75). To ensure that the temperature of the vessel is sufficiently low to enable O-rings made of elastomer to be used to seal the upper and lower closures, it is necessary to cool the vessel wall. This can be done by pumping coolant through helical passages of a liner shrunk into the bore of the vessel or through cooling coils attached to the outside of the vessel. The need, for process reasons, to use argon containing oxygen in HIP

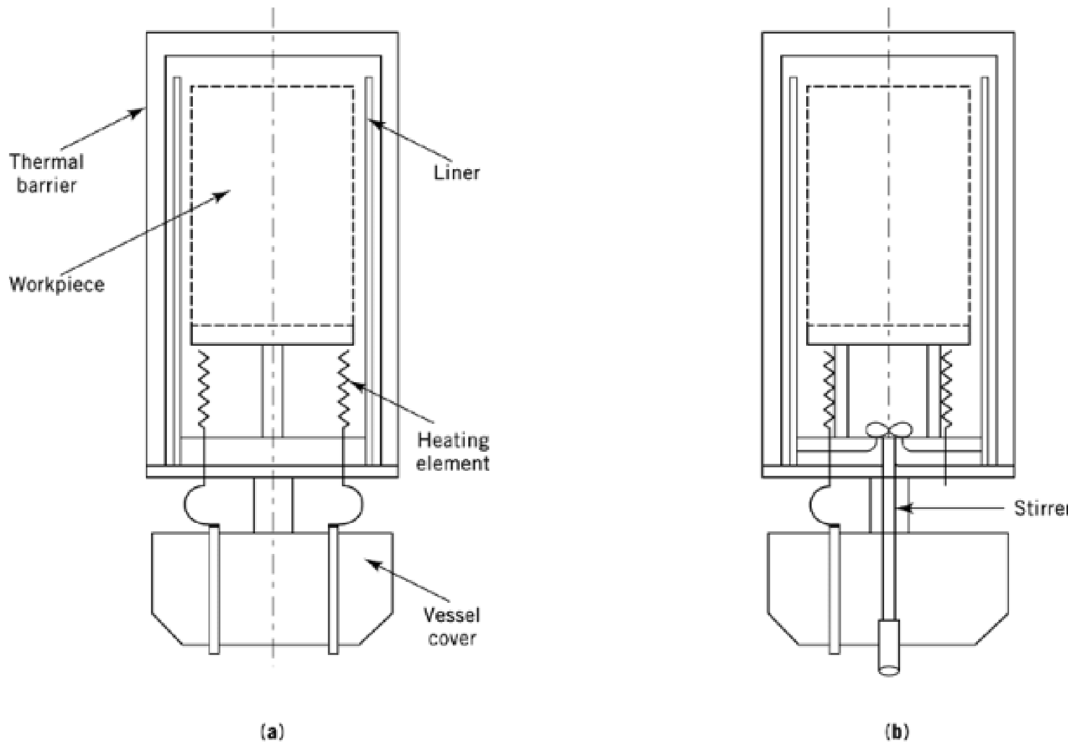

Fig. 14. (**a**) Workpiece heated by natural convection; (**b**) workpiece heated by forced convection (80).

furnaces for super-conductive materials has generated a need for oxygen compatible furnaces, vessels, seals, and pumps (79).

2.6.5. Fatigue

Fatigue, or the failure of metals under repeated application of a stress insufficient to cause failure on the first application, was recognized in the middle of the nineteenth century. However, it was not until the mercury lute compressors, used by ICI in their process for polymerizing ethylene, failed unexpectedly after only several months of operation that engineers became aware that fatigue data, which relate to simple kinds of loading, eg, reversed bending, may not be directly applicable to the design of equipment subjected to repetitions of internal pressure (81).

After World War II, at the University of Bristol, a machine was developed (usually known as a Bristol-type machine) to study the fatigue strength of tubular specimens subjected to a pulsating internal pressure generated by reciprocating a plunger within the specimen, the internal space being filled with oil (82, 83). The early machines were capable of speeds in excess of 15 Hz which enabled them to generate 10^7 cycles in a week of continuous operation. With specimens of the size shown in Figure 15, the maximum cyclic pressure, which could be varied by changing the stroke of the plunger, was limited to 350 MPa (51,000 psi). However, both specimen bore size and maximum cyclic pressure have been increased as similar machines have been built and developed at a number of facilities in the U.K. and United States. One of the latest is designed for operation at pressures up to 700 MPa (101,000 psi) at speeds up to 16 Hz (85).

In Figure 16 the maximum shear stress at the bore of cylinders made of a 2.5% Ni–Cr–Mo steel EN25 T, generated by repeated internal pressure, has been plotted against the number of cycles to failure for cylinders,

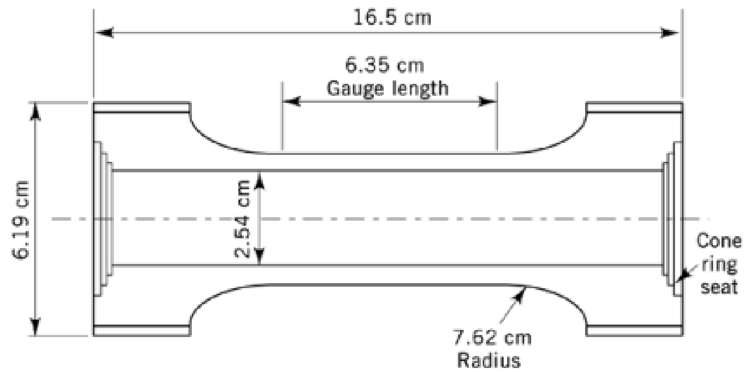

Fig. 15. 2.54 cm (1 in.) bore diameter fatigue test specimen (84).

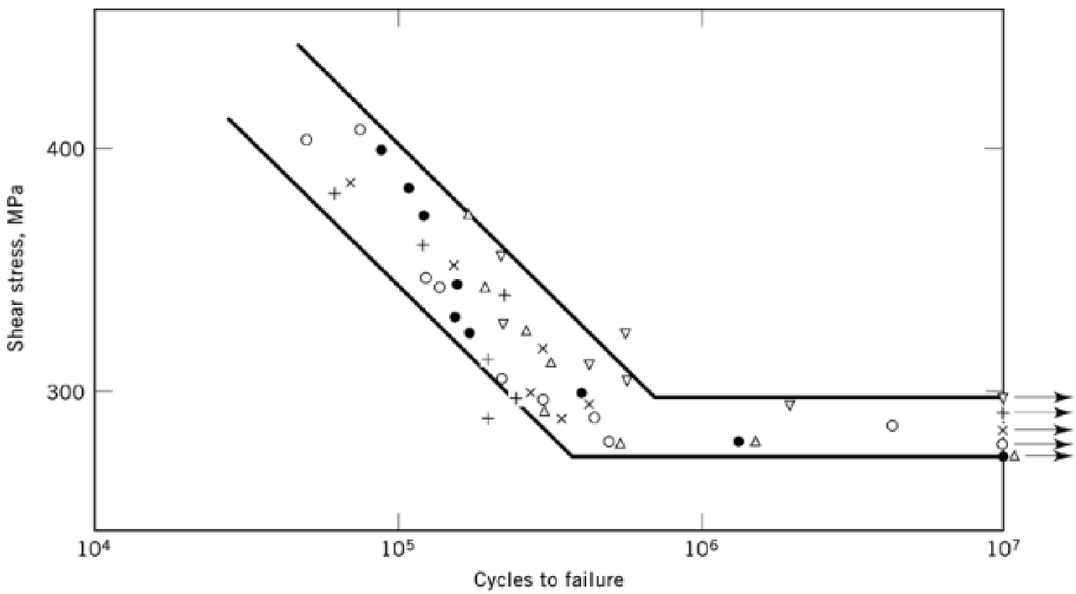

Fig. 16. Maximum shear stress at bore vs number of cycles to failure for specimens of EN25 T steel at various k values. +, k=1.2; ○, k=1.4; ×, k=1.6; △, k=2.0; △, k=3.0 (83). To convert MPa to psi, multiply by 145.

of six different diameter ratios in the range 1.2 to 3.0 (83). After machining, the bore of each specimen was honed to a smoothness of 0.025–0.1 μm or better, before being stress relieved in vacuo to remove the residual compressive stresses generated by the honing process. Tests discontinued after 10^7 cycles are indicated on Figure 16 by an arrow. The results for each diameter ratio show considerable scatter, which is normal for all fatigue tests, but there is a well-defined fatigue limit at a bore shear stress of about 270–300 MPa (39,000–43,000 psi). A cylinder made of the same material, having the same mechanical properties and bore surface finish designed so that the shear stress at the bore is less than the fatigue limit, should under conditions of repeated internal pressure last indefinitely. In practice, because of the statistical nature of fatigue and the differences between the test samples and an actual cylinder, the shear stress at the bore has to be limited to, eg, 0.3–0.5 of that at the fatigue limit to increase the probability of the cylinder lasting indefinitely.

Similar correlations, based on the shear stress at the bore of the cylinder, were found with the following ductile materials tested (82–88): mild steel, EN25 T, EN25 V, EN40 S, EN56 C, 18-8-Ti stainless steel, and maraging steel. Cylinders of titanium (82), beryllium copper (86), and an aluminium alloy (82) failed to give consistent results (86). There was no clear indication of a "knee," ie, fatigue limit, with these materials and the endurance limit or cyclic stress to cause failure in a defined number of cycles, such as 10^7, was reported.

The composition of the materials tested, their heat treatment, and their static and fatigue properties have been reviewed (89). Because fatigue results for cylinders of different diameter ratios subjected to repeated internal pressure can be correlated on the basis of the maximum bore shear stress, it might have been expected that this stress at the fatigue limit would correspond to the fatigue limit for the material in repeated torsion. However, it was found that the limit for the pressure tests was much lower than expected. Attempts to relate the limiting shear stress at the bore of the cylinder to the fatigue or endurance limit of the material in other forms of loading, eg, torsion, were not successful, and it was necessary to adopt an empirical approach. With the exception of EN56 and titanium, the ratio of the range of shear stress at the bore at the fatigue limit of 10^7 cycles to the ultimate stress $\Delta\tau_{r_i fl}/\sigma_u$ lies between 0.36 and 0.27. Thus it appears that the limiting maximum shear stress which can be endured indefinitely at the bore of a plain cylinder is about one-third of the ultimate tensile stress at least up to tensile strengths of 1 GPa (145,000 psi). If the material is markedly anisotropic the ratio $\Delta\tau_{r_i fl}/\sigma_u$ may be smaller (90).

A number of workers (90, 91) concluded that the reason the fatigue results under pulsating pressure were lower than expected was due to the ingress of oil into incipient microcracks at the bore surface. There is a good correlation (eq. 29) between the range of repeated internal pressure ΔP , which must not be exceeded if fatigue initiation is to be avoided, and the range of repeated stress for the material of construction at the fatigue limit in uniaxial tension $\Delta\sigma_{fl}$ (91).

$$\Delta P = \frac{\Delta\sigma_{fl}\left(k^2 - 1\right)}{2k^2} \qquad (29)$$

The uniaxial specimen should be cut so that its axisis tangential to the cylinder.

2.6.6. Nature of Failure

Fatigue cracks in a thick-walled cylinder of ductile material generated by pulsating internal pressure are very different from those produced by static loading in which the pressure is gradually increased to the bursting point. In the latter case, fracture nearly always takes a spiral course across the wall thickness (maximum shear stress trajectory), and is preceded by considerable plastic deformation. On the other hand, with a plain cylinder, a fatigue crack initiates and propagates from inclusions intersecting the bore surface and usually spreads outward in all directions in the axial–radial topicplane so that its shape is approximately semicircular. If the cylinder is made of ductile material, the crack usually continues to propagate across the wall thickness until it intersects the outside surface and leakage ensues. The crack at the outside surface is so fine that it is difficult to detect with the naked eye. The fracture surfaces, revealed when the tube is broken open, are found to be smooth with a rippled appearance characteristic of fatigue. This type of behavior is sometimes known as leak before break. On the other hand, if the material lacks toughness, the propagation of the fatigue crack may be interrupted part way through the wall by the intervention of fast fracture, resulting in what is sometimes known as the break before leak mode of failure.

The life of a component, as measured in a fatigue test, is the number of cycles needed to initiate a crack and cause it to propagate across the wall until it intersects the outside surface or until fast fracture intervenes.

2.6.7. Mean Stress

The fatigue strength of plain bored cylinders (Fig. 15) was established using repeated pressure cycles, in which the pressure increased to a specified maximum value and then dropped almost to zero, thus making the mean stress half the maximum. Using a test machine in which both the mean stress and the range of stress could

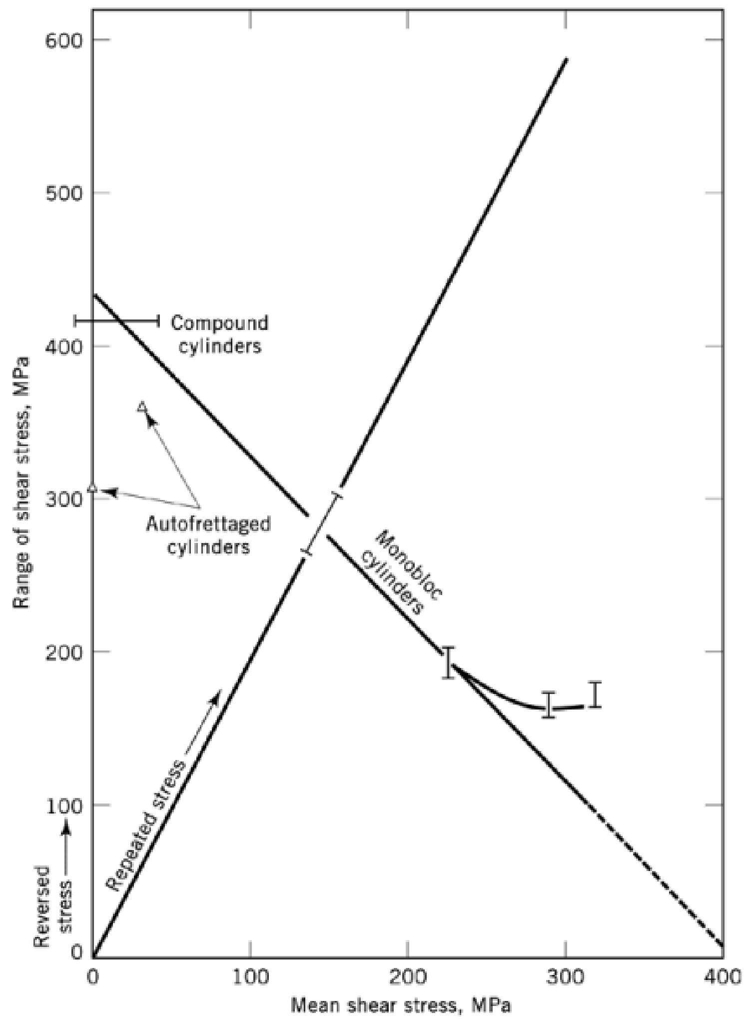

Fig. 17. Effect of mean shear stress on the fatigue strength of EN25 for life of 10^7 cycles (92). To convert MPa to psi, multiply by 145.

be varied, it was found, in the life range 10^6 to 10^7 cycles, that the fatigue strength of thick-walled cylinders, $k = 1.8$, of EN25 depended not only on the maximum range of bore shear stress, but also on the associated mean shear stress (92) or the mean normal stress on the plane of maximum shear (93). Assuming the critical stress to be the mean shear stress at the bore, then as this increases, the fatigue strength as measured by the maximum bore shear stress to cause failure in 10^6 to 10^7 cycles, decreases as shown in Figure 17. The reversed stress condition (zero mean stress) was achieved using specimens around which an outer mantle was shrunk. The fatigue strength of autofrettaged cylinders is increased relative to that of a nonautofrettaged cylinder, as a result of the reduction in the mean shear stress brought about by overstrain. However, the increase is not as large as expected because of the Bauschinger effect. It has been suggested that residual stresses induced by autofrettage are significantly altered by cyclic loading (92), but this is not thought to be so at temperatures low enough for there to be no relaxation of residual stress due to creep.

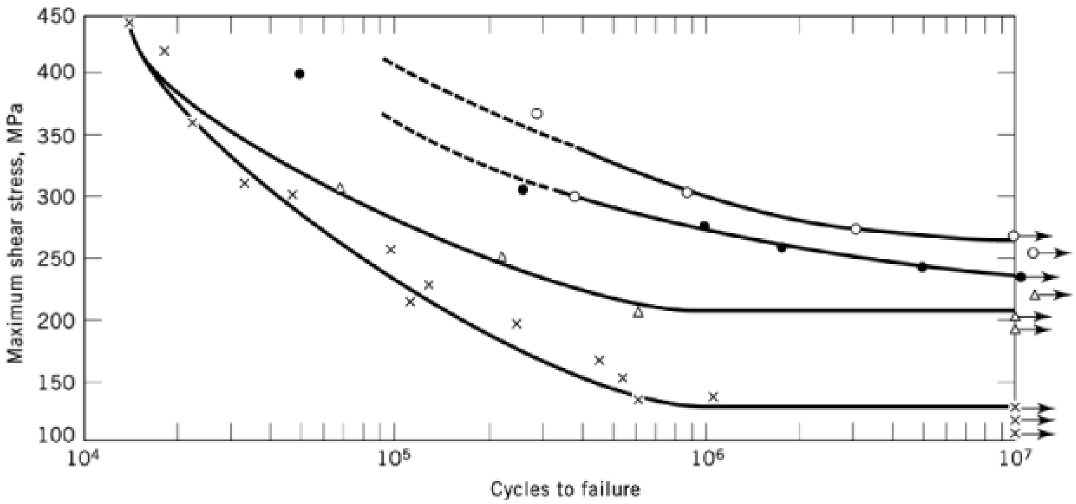

Fig. 18. Repeated pressure tests on autofrettaged EN25 steel cylinders, $k=2.25$, with cross-bores (86, 96). △, Autofrettaged at 324 MPa; •, at 552 MPa; ○, at 665 MPa; ×, normal cross-bore cylinders. To convert MPa to psi, multiply by 145.

One of the effects of autofrettage is to raise the mean stress on the outside surface of a thick-wall cylinder, subjected to a pulsating internal pressure, above that for a similar nonautofrettaged cylinder. If there are design features, such as threads, grooves, or severe metallurgical defects, to concentrate the stress at the outside surface, a fatigue crack may propagate from that surface to the bore surface leading to a reduction in fatigue life. The effect of diameter ratio, degree of autofrettage, stress concentration, and internal pressure on the fatigue life of cylinders subjected to a repeated internal pressure on a Bristol machine have been measured (94). The specimens were made of AISI 4340, heat treated to give a nominal yield strength of 1100 MPa (160,000 psi), and the autofrettage was carried out mechanically using the swage method. A combination of shot peening and a reduction of the stress concentration of notches on the outside surface has been shown to be very effective in increasing the fatigue life of autofrettaged cylinders, of a design of interest to ordnance engineers, when subjected to hydrostatic fatigue loading (95).

2.6.8. Cross-Bores

The results of tests (87, 88) carried out on specimens with a small radial cross-bore made of EN25 T which were stress-relieved indicate that the fatigue limit is at a shear stress of 136 MPa, as compared with 288 MPa for a cylinder without a cross-bore. This gives an actual fatigue strength reduction factor of 2.1 compared with a theoretical shear stress concentration value of 2.5 (89). The benefit of autofrettaging cross-bore specimens of the same design is shown in Figure 18, in which the specimens were autofrettaged at various pressures and subsequently given a low temperature heat treatment at 250°C for 1 h (86).

A considerable reduction in stress concentration could be achieved by using a cross-bore which is elliptical in cross-section, provided the major axis of the ellipse is normal to the axis of the main cylinder. A more practical method of achieving the same effect is to have an offset radial hole whose axis is parallel to a radius but not coincident with it (97, 98). Whenever possible the sharp edges at the intersection of the main bore with the cross bore are removed and smooth rounded corners produced so as to reduce the stress raising effects.

2.6.9. Short Life Tests

To cause thick-walled cylinders to fail in less than 10^4 cycles, larger internal pressures than those generated by the Bristol machine are required and low cycle, high stress fatigue studies are usually carried out by piping pressure from an intensifier to the component or components under test (99). When the set pressure is reached, a valve is opened and the pressure drops to near atmospheric after which the cycle is repeated. Alternatively, the intensifier is used as a jack to reciprocate a ram within an oil-filled space (88, 100). About 10–20 cycles per min can be achieved using an hydraulic drive, but pressures of 1 GPa (145,000 psi) can be achieved in specimens of small volume (99) or 300 MPa (43,500 psi) in vessels having a bore of 300 mm (100, 101). The hazards and safeguards of fatigue tests on large vessels have been reported (102).

Short life tests have been carried out at Watervliet Arsenal (99) on autofrettaged cylinders, autofrettaged cylinders with subsequent low temperature heat treatment, and nonautofrettaged cylinders made of AISI 4340 steel with a nominal ultimate tensile strength of 1100 MPa. The cylinders which had an internal finish varying from 0.4 to $>3\ \mu$m (16 to 125 micro inches) were tested in the open-end condition. Tests on cylinders with diameter ratios of 1.4–2.0 showed that autofrettage improves the fatigue life at lower pressures but had no effect at the higher pressures where the lives were very small. Further results obtained in the range 10^3–10^5 cycles on smooth and rifled bore autofrettaged and nonautofrettaged cylinders with diameter ratios varying between 1.2 and 2 made of material roughly equivalent to AISI 4330 steel have been reported (103).

2.6.10. Increased Tensile Strength

Because the limiting maximum shear stress that can be endured by a thick-walled cylinder indefinitely is about one-third of the ultimate tensile strength, it might be thought that increasing the tensile strength would be a good way to increase the fatigue strength. Fatigue tests on cross-bored cylinders of EN25 in various states of hardness (104) show that the fatigue limit is raised as the ultimate tensile strength increases, but at much higher pressures and shorter lives the higher strength cylinders survive for fewer cycles than those of lower strength. Most of the failed cylinders of the two highest tensile strengths suffered fast fracture of increasing severity as the pressure increased, whereas those cylinders having the lowest tensile strength all failed as a result of fatigue cracks with no fast fracture. For fatigue cracks associated with the cross-bore configuration a small increase in fracture toughness from 77 to 88 MPa $\sqrt{\mathrm{m}}$ is sufficient to ensure that the fatigue crack penetrates the wall before fast fracture intervenes. For long plane fronted cracks of the sort found in rifled gun barrels, material with a much higher fracture toughness is needed to prevent fast fracture.

2.6.11. Surface Treatments

Any surface treatment which sets up compressive stresses in the bore layers of a cylinder increases its endurance to high cycle fatigue. Such treatments include peening, nitriding (83), honing, etc. Nitriding produces a very hard case which is also helpful in preventing the initiation of fatigue cracks, providing the components does not contain areas of stress concentration which would result in strains sufficiently large to cause the case to crack when the component is stressed. Finishing operations which might leave scratches on the bore surface should be avoided, particularly if the scratches are parallel to the axis of the cylinder.

2.6.12. Cumulative Damage

Pressure vessels may be subjected to a variety of stress cycles during service; some of these cycles have amplitudes below the fatigue (endurance) limit of the material and some have amplitudes various amounts above it. The simplest and most commonly used method for evaluating the cumulative effect of these various cycles is a linear damage relationship in which it is assumed that, if N_1 cycles would produce failure at a given stress level, then n_1 cycles at the same stress level would use up fraction n_1/N_1 of the total life. Failure occurs when

$$n_1/N_1 + n_2/N_2 + \cdots + n_i/N_i = 1.0 \qquad (30)$$

The linear damage rule takes no account of the orderin which the stress cycles are applied.

2.6.13. Fracture Mechanics

Linear elastic fracture mechanics (qv) (LEFM) can be applied only to the propagation and fracture stages of fatigue failure. LEFM is based on a definition of the stress close to a crack tip in terms of a stress intensification factor *K,* for which the simplest general relationship is

$$K = Y\sigma\sqrt{\pi b} \qquad (31)$$

where ς is the nominal stress normal to the crack plane, b is the crack depth, and Y is a constant containing material and crack shape parameters.

The use of the single parameter, *K,* to define the stress field at the crack tip is justified for brittle materials, but its extension to ductile materials is based on the assumption that although some plasticity may occur at the tip the surrounding linear elastic stress field is the controlling parameter.

One of the most important applications of LEFM is to estimate the critical crack or defect size which causes fast fracture to occur. This occurs when the value of K in a structure becomes equal to the plain strain fracture toughness, K_{IC}, of the material; the critical crack size, for a given stress and fracture toughness, is then given by equation 31.

Lack of accepted stress intensity factors for internally pressurized components has, until recently, limited this application. The factors are a function of the size and shape of both cracks and high pressure components as well as modes of loading (91). Stress intensity factors can be derived analytically for some simple geometries, but most require the application of advanced numerical methods (105–107). Alternatively they may be determined experimentally (108).

Standard procedures for fracture toughness testing of materials give reproducible values of minimum fracture toughness, but little guidance is available for incorporating these values into the design process (109). A design philosophy for the avoidance of unstable fracture in high pressure components based on LEFM has been given (91); for all practical combinations of yield stress and fracture toughness an LEFM analysis proves conservative except in the case of very thick-walled components.

This belief is supported by the results of burst tests on tubular specimens made of AISI 4335 tempered to various fracture toughness levels from 65–120 $\mathrm{MPa}\sqrt{\mathrm{m}}$ and precracked to a radial depth of half the wall thickness. For the lowest tempering temperature it was found that the burst pressure, at the onset of fast fracture, was 22% higher than that expected on the basis of a careful LEFM analysis, whereas at the highest tempering temperature the discrepancy was 100%. Apparently the conventional requirements for plane strain fracture toughness testing are not adequate for internally pressurized thick cylinders because of the enhanced plasticity generated by the pressure acting at the tip of the crack.

Another important application of LEFM is the rate of growth of a fatigue crack under cyclic loading. This is also controlled by the stress intensity factor through an equation of the following form (110):

$$\frac{db}{dn} = C\,(\Delta K)^m \qquad (32)$$

where db/dn is the crack growth/cycle or crack growth rate, ΔK is the range of stress intensity, and C and m are material constants. Knowledge of crack growth rates in components, in which it is difficult to prevent crack initiation, are of value in establishing inspection frequencies to ensure that the crack is not allowed to reach critical size.

Irrespective of whether unstable fracture or subcritical crack growth is being considered, reliable values for the stress intensity factors are required. Those for single semielliptical or straight fronted cracks located on the inside or outside surfaces of a nonautofrettaged cylinder are straightforward to calculate. Multiple flat fronted cracks of equal depth, multiple unequal flat fronted cracks, and multiple flat fronted cracks with one crack deeper than others have been studied (111). Cracks initiating in complex regions of a vessel, such as blind end corners, cross-bore corners, or the root of threads in a threaded closure, are difficult to calculate. In addition, the problem becomes much more complicated when residual stress fields created accidentally or deliberately, as with autofrettage, need to be considered.

One aspect of pressure vessel design which has received considerable attention in recent years is the design of threaded closures where, due to the high stress concentration at the root of the first active thread, a fatigue crack may quickly initiate and propagate in the radial–circumferential plane. Stress intensity factors for this type of crack are difficult to compute (112, 113), and more geometries need to be examined before the factors can be used with confidence.

Another possible mode of failure for this type of vessel is the growth of a fatigue crack in the radial–axial plane, which may grow from a pre-existing defect at the bore surface or initiate in the usual way. Because the growth of such a crack to a critical size can represent a significant portion of the fatigue life, it would be advantageous to be able to estimate this. The parameters which need to be considered are cylinder size, and diameter ratio, initial crack depth and shape, the allowable crack depth, the cyclic internal pressure, and the residual stress field induced by autofrettage (114).

3. Design of Removable Closures

3.1. Pressure Vessels

Closures usually consist of three elements: a cover to the opening in the vessel, a coupling device holding the cover in position against the internal pressure, and a sealing ring or gasket between the cover and the vessel. The sealing ring or gasket is nearly always made of a softer material than the vessel and end cover so that when it is tightened to make an initial pressure tight seal, it deforms and follows the irregularities in the mating surfaces closely. Thus deformation is almost entirely confined to the sealing ring which may be replaced as necessary.

An alternative method of making a pressure-tight seal between a vessel and its cover is to develop such a high compressive stress between the two components that they yield along a narrow, axisymmetrical, circular band of contact. By this means the asperities on the mating surfaces are smoothed out and what is usually described as a metal-to-metal seal is formed. This technique makes it difficult to refurbish the mating surfaces of large vessels and it is almost entirely confined to fittings used for connecting small-bore pipelines and to sealing adjacent packing cups or valve components in reciprocating compressors.

3.1.1. Sealing Rings

Gaskets or sealing rings may be of the compression type or the self-sealing type. Figures 19**a** and **b** shows two compression-type gaskets in which the initial stress across the jointing faces decreases as the internal pressure in the vessel increases. To a first approximation these joints remain pressure tight as long as the compressive stress along the sealing paths on each face of the gasket is greater than the pressure to be resisted. Thus the maximum pressure that this type of gasket is capable of withstanding is determined by the initial compressive stress that can be developed across the sealing surfaces. This imposes severe limitations on the pressure which can be sealed even when, as in Figure 19, the gaskets are fully confined.

Self-sealing types of ring in which the stress across the jointing faces is automatically maintained at a higher value than the pressure to be sealed are almost exclusively used for chemical process vessels designed for pressures above about 20 MPa (2900 psi). These rings are sometimes known as unsupported area or Bridgman seals, following Bridgman's development of the unsupported area principle (116) in the 1920s to seal pressures of 1200 MPa (174,000 psi) in laboratory equipment.

3.1.1.1. Lens Ring. The lens ring joint in Figure 20**a** illustrates the principle by which self-sealing is achieved; the ring, usually of steel, seats between conical surfaces and receives no lateral support, except that

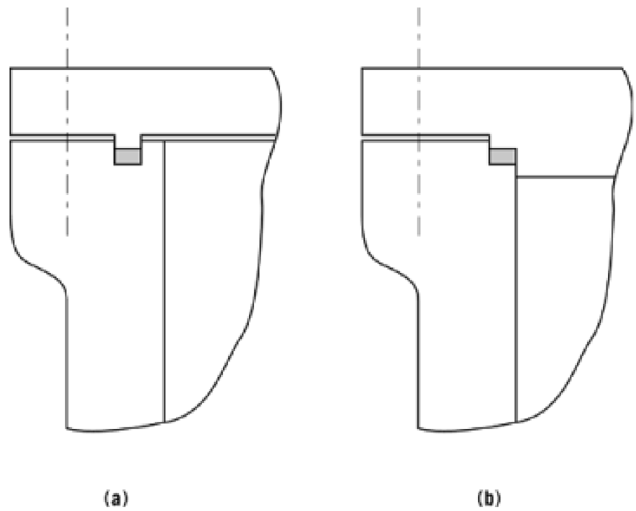

Fig. 19. Fully confined gasket joints (115). See text.

provided by the line contacts with the body of the vessel and its cover. Once an initial seal has been formed, the pressure on the inside surface of a correctly proportioned ring causes a compressive stress to be developed across the sealing surfaces which is always greater than the internal pressure. There is a small axial component of the load across these surfaces which increases that generated by the internal pressure and has to be resisted by the coupling device. If the included angle of the conical surfaces is increased the ring may yield and collapse inwardly when the joint is tightened initially. In the case of the conically shaped D-ring shown in Figure 20**b,** this may be prevented by providing a spigot on the underside of the end cover to support the ring. Note the use of a soft material interposed between the ring and the mating surfaces to facilitate the making of an initial pressure tight seal and the grooves to ensure that the internal pressure has unrestricted access to the inside surface of the ring.

3.1.1.2. Delta Ring. This triangular section ring (Fig. 21) is used extensively in the United States. To prevent it from collapsing during initial tightening, it is located in grooves in the body of the vessel and the end cover in such a way that the combined depth of the grooves is slightly less than the height of the ring. A relatively small coupling force is required to make the initial seal, and contact between the flanges prevents the ring from being crushed when this force is exceeded; hence the initial sealing stress is determined by the geometry of the ring and grooves. Under load the inner face of the ring is subjected to the internal pressure and the self-sealing effect comes into play. Another ring which makes use of the self-sealing principle is the metal lip sealing ring shown in Figure 22**a.** On initial tightening the inward movement of the ring is prevented by the reinforcement profvided by the rim, which is compressed between the head and body of the vessel.

3.1.1.3. Wave Ring. The ring shown in Figure 22**b** has two crests which are slightly greater in diameter than the recesses in the vessel and end cover. To make an initial seal the ring has to be forced or sprung into position; this is often done by cooling it and allowing it to expand in the recesses. The ring, usually made of hardened steel, is highly finished and polished, as are the recesses in each of the mating components. To avoid damage when fitting the ring, the entrance to each recess is provided with a lead-in and the ring is coated with suitable lubricant or flashed with a soft metal to facilitate making an initial pressure-tight seal. There is no axial component of the force generated by the stress across the seating surfaces, and the self-sealing property of the joint is fully effective. Unlike the lens or metal lip sealing rings the wave ring accommodates itself to the

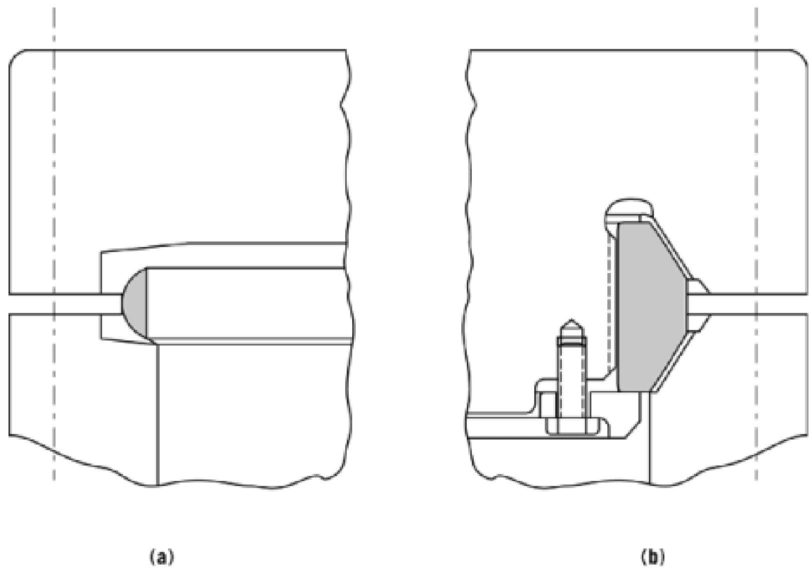

Fig. 20. Lens rings (117). See text.

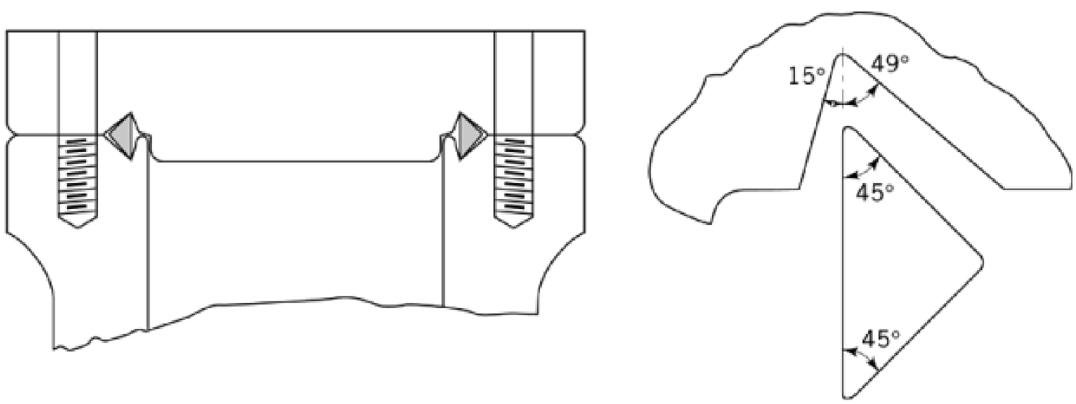

Fig. 21. Delta ring (118). See text.

radial expansion of the joint without relative movement at the lines of contact and provides accurate location of the end cover relative to the vessel.

3.1.1.4. O-Ring. Although these are not used to seal vessels for continuous chemical processes, they are widely used in other applications such as isostatic pressing. Figure 23 shows an elastomeric O-ring in its undeformed state, backed up by a chamfer or miter ring to prevent the extrusion of the elastomer into the gap between the head and body of the vessel when the internal pressure is applied. For the seal to work the antiextrusion ring must have a high yield strength to enable it to maintain its shape under maximum pressure conditions. Provided the geometry of the recess is such that sufficient initial squeeze is applied to the O-ring and it is backed up by an antiextrusion ring, it continues to work to very high pressures. The maximum operating temperature for elastomeric materials is limited to about 200°C; at higher temperatures PTFE may be employed provided some device, such as a spring, is used to give the polymer the required elasticity.

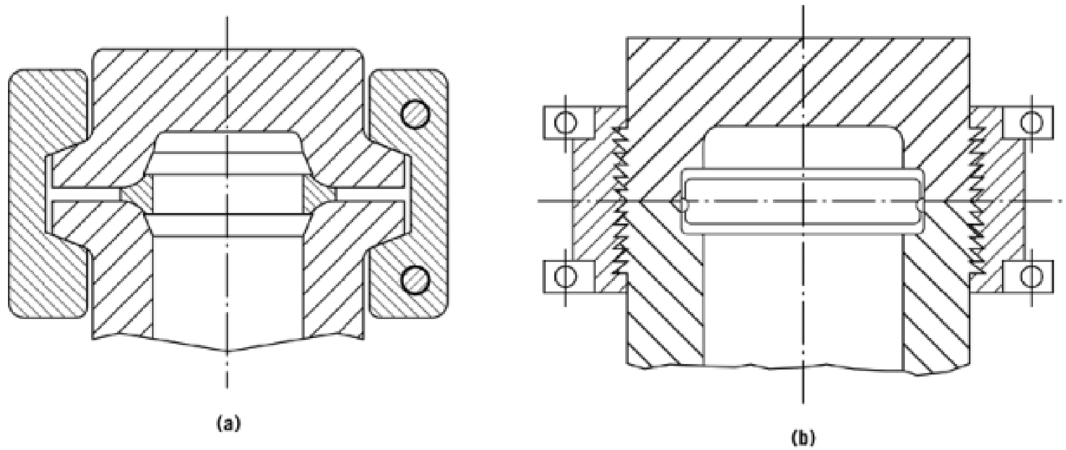

Fig. 22. (**a**) Metal lip sealing ring (119); (**b**) wave ring (120).

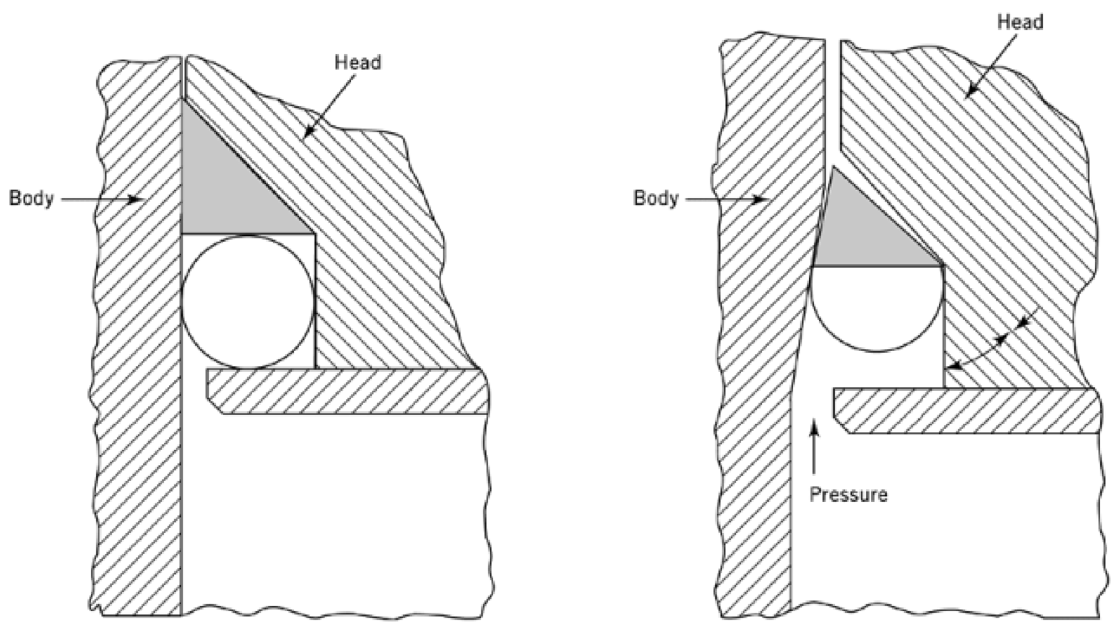

Fig. 23. O-ring backed up by miter ring to seal vessel (121).

3.1.1.5. Bridgman Seal. With the exception of the lens ring, the initial stress across the sealing surfaces of all the self-sealing gaskets described is governed by the geometry of the closure. Should the joint leak it cannot be tightened more and usually has to be remade. With the Bridgman-type closure shown in Figure 24, the functions of taking the end load and making an initial pressure-tight seal can be separated. Nuts, A (Fig. 24), enable the vessel to be tightened easily without heavy sledging of the large nuts, B, required to resist the end load. The high stresses set up in the gasket may deform the inner surface of the vessel, making it difficult to remove the end plug, and provision is usually made for its extraction by means of jack bolts, C.

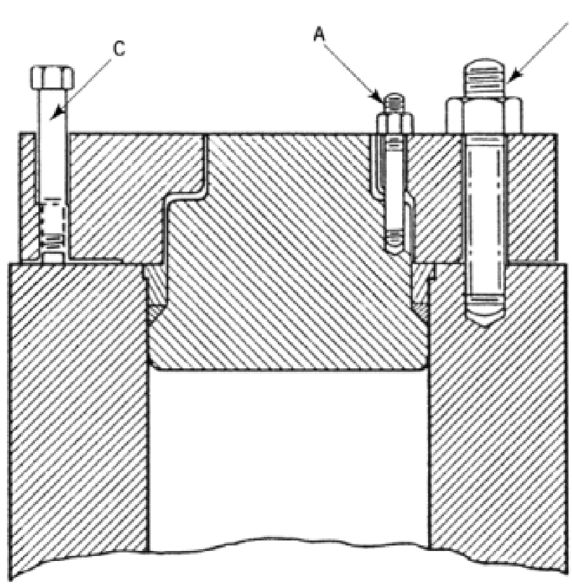

Fig. 24. Bridgman-type closure (122). See text.

3.1.2. Coupling Devices

Usually the coupling device has to withstand not only the stress produced by the internal pressure acting on the cover, but that produced by the initial tightening of the seal. With some self-sealing gaskets such as the wave ring, the only stress which has to be considered is the former but with others, such as the delta and the lens rings, there is a small wedging effect in addition to the initial tightening up stress.

3.1.2.1. Bolted Flanges. Probably the oldest method of coupling is the use of bolted flanges; the flange may be integrally forged with the body of the vessel or alternatively welded or screwed to it. In designing a flanged closure, the aim is to reduce the diameter of the bolt circle so that the coupling action of the nut and bolt is as near vertically above the gasket or line seating as possible, thereby reducing the required thickness of the end cover as well as reducing the overall diameter of the closure. A limit is imposed by the necessity of providing adequate room to tighten the nuts.

3.1.2.2. Screwed Plugs. Vessels for isostatic pressing, made in the mid-1950s, were provided with screwed plug closures. Isostatic pressing, whether carried out hot or cold, is a batch operation, and these closures are compact, inexpensive to manufacture, and can be opened and closed easily. Because the thread on the screwed plug is in compression and that on the vessel in tension, it is nonuniformly loaded along its length. The stress acting at the root of the first engaged thread may be 10 times that at the thread remote from the seal. One of the earliest failures occurred in a vessel, having a bore of ca 450 mm, in which the crack propagated, from the first thread, across the wall of the vessel in the radial tangential plane as a result of axial bending (123). This failure led to Sopwith's analysis (124) of the distribution of load in screw fastenings being used to predict the effect of changing many of the screwed plug parameters. Photoelastic tests on model vessels, in which both the thread and vessel parameters were changed, showed that the experimentally measured peak stresses at the root of the first thread were higher than those predicted (123).

With the help of photoelastic (125) and fatigue (126) studies on models of specific screwed plug closures, many design changes have been proposed. For example, different thread forms such as acme and buttress have been used. The root radii of the threads have been increased and the undercut adjacent to the first active thread modified to reduce stress concentration; the length of the thread has been increased to obtain a more even distribution of load, the angle and pitch of the threads have been varied, and the threads have been ground to introduce residual compressive stresses. A novel arrangement, known as a resilient thread (127), makes use of a spiral wound spring to take the place of the protruding portion of the threads, and fit closely into opposing grooves in both the vessel and closure.

The development of finite element methods, since the late 1960s, has made possible the exploration of a wide range of variables relevant to the design of screwed plug closures. Work (126, 128–132) on the stress at the root of the first loaded thread, where most failures occur, and the load distribution along the thread length has led to the conclusions that the load carried by the first three threads decreases considerably as the number of active threads increases to 20, and the load carried by the second thread, f_2, is approximately 75% of the load on the first thread, f_1, and that on the third thread, f_3, about 60% of f_1, that on the first thread, regardless of the number of threads.

Empirical equations have been proposed (133) which enable a combination of thread and vessel parameters to be chosen to minimize the stresses at the root of the first three active threads. The load distribution along the thread is sensitive to machining tolerances and temperature differentials (134) and it is clear that threaded vessels should not be used for high cyclic service without rigorous and frequent inspections (135).

3.1.2.3. Quick Opening Devices. Breech block, tapered or interrupted thread, or pinned closures are often used when an end cover has to be removed quickly, as with some isostatic presses (126, 136), or to enable the end cover to be removed easily after the vessel has been heated to high temperatures.

3.1.2.4. Vickers-Anderson Coupling. Whenever possible it is desirable to take the end load on the outside of the vessel, since this is less highly stressed than the inside. One way in which this may be done is with the Vickers-Anderson coupling. The end cover is secured by means of a collar which is usually made in three segments drawn together by means of tangential bolts (Fig. 25**a**). The joint may be sealed by any of the self-sealing gaskets previously described and in Figure 22**a** a metal lip sealing ring is shown. The contact pressure to effect the initial seal is obtained by machining a shoulder with an external conical face on to the body of the vessel and the end cover and clamping them together with the collar, which is counterbored with corresponding conical surfaces. The angle of the cones should be less than the angle of friction of the mating metallic surfaces, so that the tangential bolts do not carry any stresses; however, for reasons of safety the bolts are usually designed to withstand the separating forces which would be generated in the absence of friction. The stresses in the critical regions of a closure of Vickers-Anderson type, in which eight hydraulically operated clamp jaws were used to secure the end cover of an isostatic compaction vessel having a bore of 610 mm at pressure up to 138 MPa (20,000 psi), have been estimated (123, 139).

3.1.2.5. Buttress-Shaped Grooves. The cones of the Vickers-Anderson coupling may be replaced by a series of parallel grooves of buttress section machined on the outside surface of the vessel and its end cover, which mate with similar ones counterbored on the inside of a split collar as shown in Figure 22**b.** This arrangement is only possible for a ring such as the wave ring which requires no initial end load to make a pressure-tight seal. Instead of the three component split collar shown in Figure 25**a,** two half laps may be used as in Figure 25**b.** This closure has formed the basis of the commonly adopted design for the largest autoclaves used for LDPE production, although there are variations in the number and size of the buttress grooves employed. Some vessels use a split collar to engage with a buttress-shaped thread and so overcome the problem of ensuring that the buttress grooves are of uniform pitch. Seals for vessels commonly used in the German chemical industry at pressures of 30 to 400 MPa (4350–58,000 psi) have been reviewed (140).

3.1.2.6. Yokes. The need to couple the end cover to the body of the vessel may be avoided if yokes, external to the vessel, are used to resist the load arising from the internal pressure acting on the closures. However the necessity to move the vessel out of the yoke and remove one of the closures to gain access to the inside of the vessel limits its use for chemical process equipment. Yokes may be pinned, welded, bolted, or wire wound. Both the vessel and yoke may be wire wound (136).

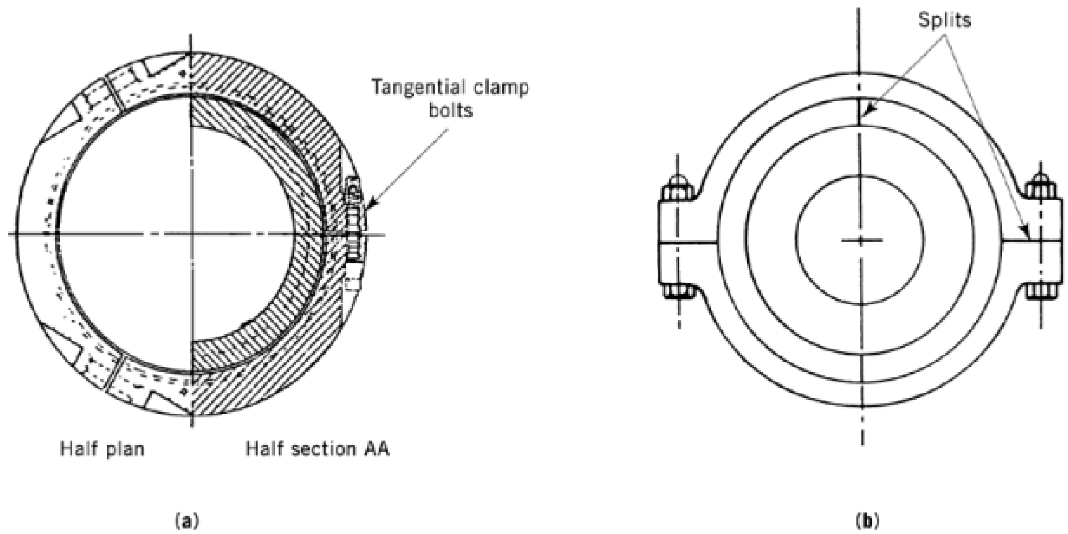

Fig. 25. Split collar coupling (137, 138). See text.

3.1.3. End Covers

Generally it is desirable to have as few openings as possible in the walls of a vessel, and to this end it is customary to accommodate ancillary equipment, such as stirrer glands, pipe connections, and small fittings for measuring instruments, in the more lightly stressed end cover.

3.2. Tubes

Tubes having a wide range of bore sizes are required to operate at pressures in the region of 150–300 MPa (22–44,000 psi). Small bore tubes, say 3–15 mm dia, are used to supply lubricant to the packing cups of secondary compressors, initiator to reactors, etc, while larger bore tubes, say 25–75 mm bore dia, are used to connect compressors to reactors and for the construction of coolers and tubular reactors.

3.2.1. Union Connectors

Collar and cone-type connectors (Figs. 26**a** and **b**) are nearly always used to connect small bore tubes at pressures up to about 400 MPa (140). The included angle of the end of the tube is 55–57° and that of the seat 60–61° so that when the gland nut is tightened into the connector a metal-to-metal seal is formed along a narrow band of contact between the end of the tube and the connector. Union connectors for small bore tubes at pressures of 500 MPa and above usually employ lens rings.

3.2.2. Loose Screwed Flanges

The ends of tubes having a bore greater than about 12 mm are usually threaded and coupled together with loose screwed flanges designed in accordance with the ASME procedure. Cone rings, lens rings, or metal lip sealing rings may be used to make the seal between the ends of adjacent lengths of tube. For ease of assembly the cone ring in Figure 26**b** (140) is located in a recess in the flange which is concentric with the outside diameter of the tube. However, since the bore of the tube may not be concentric with the outside diameter, it is necessary to establish a sealing diameter at the end of the tube, which is larger than the tube bore, concentric with the outside diameter, and blended into the bore. In spite of this preparation the cone ring requires less machining on the ends of the tubes than a lens or metal lip sealing ring. To achieve optimum performance with

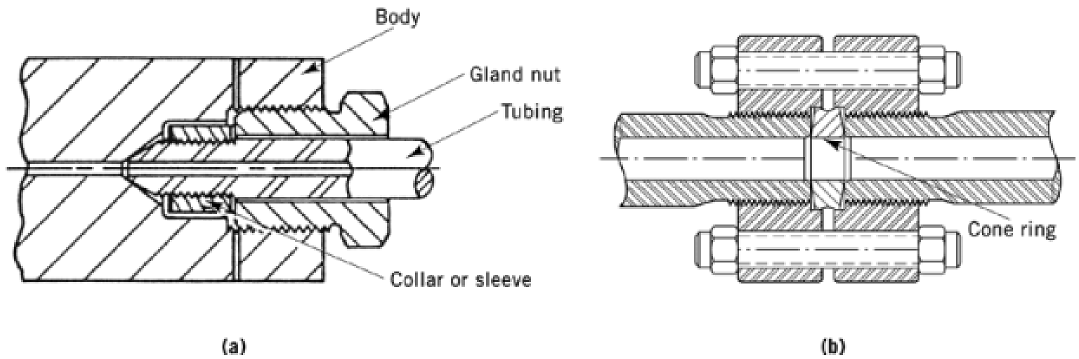

Fig. 26. Joints for tubes. See text.

a cone ring or lens ring, the stud bolts which provide the coupling force to effect the initial pressure-tight seal are often tightened hydraulically. This is not necessary with the metal lip sealing ring because the ends of the pipe are forced into contact with the rim of the ring and the joint cannot be overtightened. Unlike the cone ring or lens ring the metal lip sealing ring does not suffer if the tube is subjected to a bending stress. On the other hand, it may be difficult to spring the pipes sufficiently far apart to replace a metal lip sealing ring should it be necessary. Seals for pipes commonly used in the German chemical industry at pressures of 30 to 400 MPa (4350–58,000 psi) have been reviewed (140).

4. Manufacture of Pressure Vessels

4.1. Steels for Forged Vessels

The choice of steel for early forged pressure vessel bodies and closures was influenced by ordnance practice. In the U.K. vessels built during the 1950s were made of a 2.5% Ni–Cr–Mo steel EN25 (BS970-826M31), a gun steel which could be heat treated to achieve uniform strength throughout the wall thickness while retaining adequate ductility and transverse impact strength. As more highly stressed vessels were needed to minimize the size of forging for a given reaction volume, the Ni–Cr–Mo–V steels found favor because increased strength could be achieved without loss of ductile and impact properties. It is unlikely that 3.5% Ni–Cr–Mo–V steel will be replaced (141) for the production of large forgings, and much information is available on the mechanical properties of forgings of this material.

In the United States similar gun steels, 2300 series nickel steels and Ni–Cr–Mo–V steels, are widely used for forged pressure vessels. ASTM specification A508 first issued in 1964 covers quenched and tempered vacuum-treated carbon and low alloy steels for pressure vessels (142), but it was not until 1975 that the ASTM issued specification A723 to cover three grades of Ni–Cr–Mo–V steel for pressure vessels, containing approximately 2, 3, and 4% Ni, in six classes of tensile strength from 795 to 1310 MPa (143). Tensile, impact, and axial fatigue properties have been reported on large forgings of A723 in three directions (144).

The effects of variations in composition, cleanliness, structure, and mechanical properties of electroslag remelted (ESR) 35NiCrMoV12.5 steel have been reported. This steel which lies between Grades 2 and 3 of ASTM specification A723 is widely used in Europe (145).

4.1.1. Forging Process

The prime reason for forging is to shape the component, but it also improves the properties of the steel (qv). The introduction of large electric arc furnaces and the development of liquid steel degassing techniques in the late 1950s made possible the manufacture of large forgings which were less susceptible to hydrogen flakes or hairline cracks. These days ingots are relatively free from porosity; the final portion of the steel to freeze, which is high in carbon and sulfur, is contained within the head which, like the bottom of the ingot, is discarded prior to forging. Suitable forging techniques can greatly lessen the differences in the ductile properties of the steel in the longitudinal and transverse directions by breaking up inclusions and working the steel in more than one direction.

One such technique, once widely used in the U.K., is hollow forging. This consists of heating to forging temperature an ingot, the core of which has been removed, and forging it on a massive mandrel so that the metal is squeezed out circumferentially and worked in the direction to resist internal pressure. However, the process cannot be carried out unless the final minimum internal diameter is at least 300 mm and, even then, only if the overall length is less than about 2000 mm (146). Hollow forging longer cylinders may require several heats, with the result that parts of the forging are heated to forging temperature and not reworked. This results in local grain growth which is difficult to refine by heat treatment and which may lead to a degradation of the mechanical properties.

A more satisfactory procedure, which ensures work in all three directions, involves upsetting the ingot in the axial direction followed by drawing down and shaping to size. This enables the whole forging to be hot worked thereby reducing grain size and ensuring that it is relatively uniform. As a consequence of the upsetting treatment, better transverse properties are achieved in the final heat treatment.

Gun steels are generally used in a quenched and tempered condition which means heating the forging to about 850–920°C, followed by quenching in oil or, with 3.5% Ni–Cr–Mo–V steel, water. The steel is then extremely hard and brittle, but by tempering, ie, heating again usually in the range 500–650°C, the tensile strength is reduced, whereas the ductility and impact strength are improved. The mechanical properties of the forging are determined from test specimens cut from prolongations on the ends of the forging, after it has been demonstrated that heat treatment has been carried out satisfactorily. After preliminary surface machining, ultrasonic inspection is used to ensure that no harmful internal cracks or concentrations of nonmetallic inclusions are present (141). A second ultrasonic inspection, made before finish machining but after final heat treatment, enables the forging to be examined before cross-bores, grooves, etc, which would interfere with the examination, have been machined. After finish-machining all surfaces are subjected to a magnetic particle examination before the vessel is assembled and pressure tested. On completion of pressure testing the vessel is dismantled prior to a final magnetic particle and ultrasonic check.

4.1.2. Remelting Processes

Vacuum arc remelting (VAR), which came into prominence in the early 1960s, provides material almost completely free of oxide inclusions and in which the crystal size and the directional properties are both remarkably uniform and dissolved hydrogen, oxygen, and nitrogen are greatly reduced. The remelting process consists of preparing, from a cropped ingot, a rough machined solid cylinder, which is progressively fused by an electric arc under high vacuum, after which the material resolidifies to form a new ingot. To manufacture stirred reactors for polyethylene production from VAR steel would require a remelted ingot larger than that readily available and, since satisfactory reactors have been forged using stream degassed steel, the process has not been widely used for such vessels. However, VAR steel is often specified for components to work under severe conditions, such as those which form part of high pressure reciprocating compressors.

An alternative process is electroslag remelting (ESR). More oxide inclusions are found in ESR steel than in VAR steel, but their size and distribution are such that they normally have no noticeable adverse effect on properties (141).

4.2. Design of Forged Vessels

Out of concern for public safety, organizations within many industrially developed countries have been given the responsibility of issuing and maintaining codes of practice for the design, construction, and testing of unfired pressure vessels. In the United States it is the American Society of Mechanical Engineers (ASME); in the U.K. it is the British Standards Institution (BSI).

4.2.1. ASME Boiler and Pressure Vessel Code

The ASME Boiler and Pressure Vessel Code is published in 11 sections. Section VIII, which is concerned with rules for the design of unfired pressure vessels, was first published in 1925 and since 1968 it has been issued in two parts, Division 1 (147) and Division 2 (148), the latter being known as the Alternative Rules.

4.2.1.1. Division 1. Below the creep range, design stresses are based on one-fourth of the tensile strength or two-thirds of the yield, or 0.2% proof stress. Design procedures are given for typical vessel components under both internal pressure and external pressure. No specific requirements are given for the assessment of fatigue and thermal stresses.

4.2.1.2. Division 2. With the advent of higher design pressures the ASME recognized the need for alternative rules permitting thinner walls with adequate safety factors. Division 2 provides for these alternative rules; it is more restrictive in both materials and methods of analysis, but it makes use of higher allowable stresses than does Division 1. The maximum allowable stresses were increased from one-fourth to one-third of the ultimate tensile stress or two-thirds of the yield stress, whichever is least for materials at any temperature. Division 2 requires an analysis of combined stress, stress concentration factors, fatigue stresses, and thermal stress. The same type of materials are covered as in Division 1.

4.2.2. Limitations of ASME Code

In its present form Section VIII of the code contains disclaimers for its application to high pressure. Division 1 requires additional consideration for pressures above 20 MPa (3000 psi); although Division 2 is not restricted to a particular pressure, in practice, some additions to or deviations from the rules may be necessary to meet the design principles and construction practice required for high pressure vessels. The limitations of Division 2 (149) are as follows: (*1*) restriction of the maximum allowable stress to one-third of the ultimate tensile strength does not permit utilization of the inherent strength of the steel to the extent that has been reliably demonstrated to be reasonable and prudent; (*2*) materials of higher ultimate tensile strength than 932 MPa (135,000 psi) and of higher yield strength than 828 MPa (120,000 psi) are currently not listed in the code; (*3*) prestressing produced by compound shrinkage, autofrettage, or other means cannot be taken into account when assessing the fatigue strength of a vessel.

In 1979 because neither Division of Section VIII was suited to the design of high pressure vessels, the ASME Board on Pressure Technology, Codes & Standards approved the establishment of a Special Working Group for high pressure vessels under the ASME Subcommittee on Pressure Vessels (Section VIII). The main design criteria, which are likely to be incorporated in a new Division of Section VIII, have been set out (149).

4.2.3. Design Criteria

Traditionally the yield pressure has been regarded as an important design criterion because it is the largest pressure to which an initially stress-free cylinder may be subjected without the cylinder suffering any permanent deformation when the pressure is removed. Customarily, calculation of the yield pressure has been based on measurements of the tensile rather than the shear yield strength of material of construction. If it is assumed that the material yields in accordance with the shear strain energy criterion of failure, then the yield pressure is given by equation 9. From this equation, even for an infinitely thick-walled vessel ($k = \infty$), which is free from stress prior to the application of pressure, the yield pressure is limited to $\sigma_y\sqrt{3}$. If a factor of safety against yield of, eg, 2.5 is used, then for a vessel to withstand a pressure of 200 MPa (29,000 psi) a material with a tensile yield of 866 MPa (125,600 psi) would be required for an infinitely thick-walled vessel, or 1155 MPa (167,500 psi) for a vessel with $k = 2$.

Thus, to increase the yield pressure, the designer is tempted to use an excessively high strength steel with much lower transverse impact strength. Manning, who was responsible for the design of the vessels used by ICI in their LDPE process, realized that a low transverse impact strength was undesirable in that it could lead to what he referred to as brittle fracture, now known as fast fracture. Consequently he decided to adopt a factor of safety of 2.5 against bursting based on room temperature data and a factor of safety of 1.5 against yield, with an additional requirement that the transverse impact strength as determined by an Izod test should exceed 34 J ($25\text{ft}{\cdot}\text{lbf}$). It was required that the vessel be proof tested to the yield pressure.

To a first approximation the materials normally used for high pressure vessels behave in an ideal elastic–plastic manner and the collapse pressure is given by equation 15. If the factor of safety of 2.5 based on the bursting pressure is applied to the collapse pressure, then for a design pressure of 200 MPa (29,000 psi) and $k = 2$ the tensile yield stress, based on the assumption that the material yields in accordance with the shear strain energy criterion, would be 625 MPa (90,600 psi) which is much less than the value of 1155 MPa quoted for a factor of safety of 2.5, based on the yield pressure. In reality the bursting pressure is a little higher than the collapse pressure as most high strength steels exhibit some strain hardening.

Figure 27 shows the initial yield, collapse, and bursting pressure for EN25 used in the early autoclaves. Adopting Manning's proposals gives the two lower curves which show that, up to a radius ratio of about 1.7, the design is dictated by the lower curve based on bursting pressure and above this radius ratio the curve based on yield pressure is critical. For a vessel of this material with a design pressure of 200 MPa a radius ratio of 1.8 is needed. At 300°C the bursting strength is reduced by 10% compared with atmospheric temperature tests (18). So the actual factors of safety against yield and bursting of 1.5 and 2.5 adopted by Manning were, under operating conditions, somewhat reduced.

For an impact strength of 34 J ($25\ \text{ft}{\cdot}\text{lbf}$) the equivalent fracture toughness (150) is approximately 120 MPa$\sqrt{m}$. The fracture toughness dictates the critical size of crack above which fast fracture intervenes, so the smaller its value the smaller the critical crack and hence the greater significance of the transverse impact requirement specified by Manning.

These design rules have been extensively used by ICI since the 1940s and as far as is known there have been no catastrophic failures (151). More recently it has been proposed (152) that the factor of safety with respect to yield be reduced to 1.25 and the factor with respect to bursting to 2.25. If the initial yield and bursting pressures are based on data at the operating temperature, which might be as high as 300°C, then it is suggested that these factors can be further reduced to 1.0 and 2.0, respectively. At present, static design of high pressure vessels is based almost exclusively on the estimated bursting or collapse pressure of the vessel together with the fracture toughness properties of the material of construction.

Autoclaves of 250 L capacity built during the 1950s were made of 2.5% Ni–Cr–Mo steel having an ultimate tensile strength (UTS) of 965 MPa. Later, as the required volume increased, 3.5% Ni–Cr–Mo–V steel having a UTS of 1112 MPa was used. Probably the largest vessels currently in use are about 1.25 m external diameter and up to 10 m long with a nominal output of 150,000 t/yr (151).

5. Manufacture of Tubing

In the early polyethylene plants built by ICI, high pressure tube up to 3 m long was made from 12–14% chromium steel to BS 970 EN56C (now grade 420837). These tubes were made from bored bar by a number of cold reducing operations. Subsequently, tubes were made in material equivalent to EN56C by several companies in the United States using a cold pilgering process. Tubing made by tempering cold reduced bored round bars had a transverse Charpy impact strength of less than 5 J at $-17.8°\text{C}$ and failed in a break-before-leak manner (153).

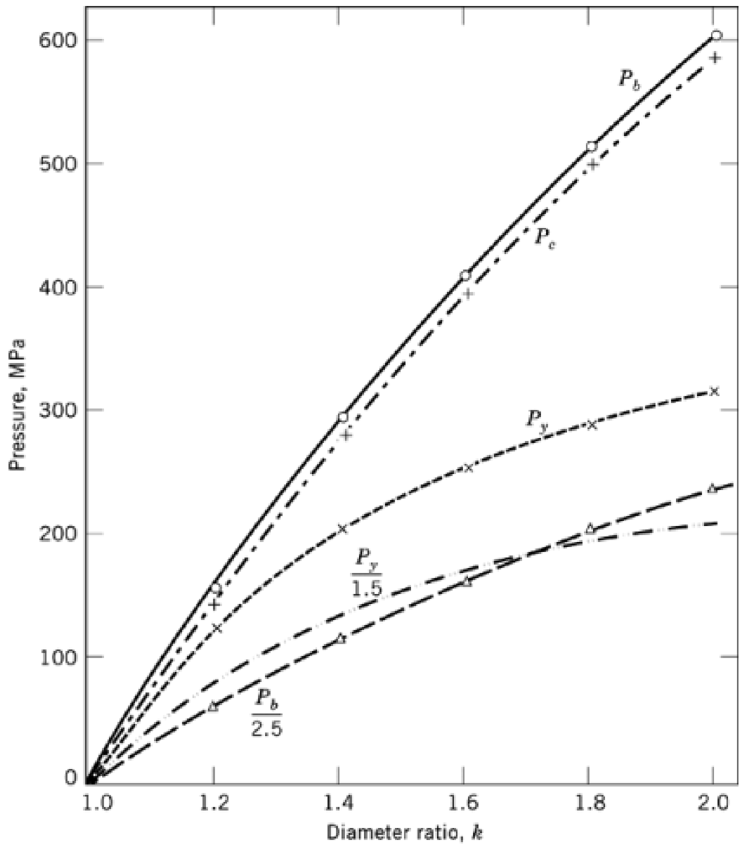

Fig. 27. Bursting (P_b), collapse (P_c), and yield (P_y) pressure for thick-walled vessel of EN25 (138). To convert MPa to psi, multiply by 145.

In the late 1950s the Timken Co. began to produce tubes 10 m long in AISI 4300 series steel. The process starts by piercing a billet, which is then hot rolled or hot Assel elongated to reduce the outside diameter to the required size. This tubing may then be finished, heat treated, and sold as hot worked tubing. Alternatively, the hot worked tube may become the hollow for subsequent cold reduction by cold pilgering. After cold pilgering the tube is finished, heat treated, and sold as cold reduced or Rotorolled tubing. A fine bore finish can be achieved by honing.

Defects such as hot tears or laps, quench cracks, localized overheating during stress relief, and corrosion may occur during the tubemaking process (154). Magnetic particle, ultrasonic, and visual inspection techniques are used to ensure that relatively few tubes enter service with significant defects.

5.1. Design Criteria for High Pressure Piping

Since 1984 the Chemical Plant and Petroleum Refinery Piping Code, ASME B31.3, has included rules for the design of high pressure piping systems. If the new rules are to be used, all the requirements in Chapter IX must be met. In the context of the code, high pressure is considered to be pressure in excess of that allowed by the appropriate ANSI B16.5 Class 2500 flange ratings, about 45 MPa (6500 psi) at room temperature. Reference must be made to the latest edition of the code for full details of the requirements which have been reviewed

(155); only those aspects to ensure that the piping has adequate static and fatigue strength and that it is made of material with acceptable toughness are considered here.

5.1.1. Static Strength

For a straight pipe the internal design pressure, *P,* is given by

$$P = \frac{S}{1.155} \ln \left(\frac{d + 2T}{d + 2c} \right) \qquad (33)$$

where $S = 2\sigma_y/3$ is the basic allowable stress for the material of construction, d = inside diameter of the pipe, c = sum of mechanical allowances (thread or groove depth plus corrosion and erosion allowances), and T = the pipe wall thickness.

If the sum of the mechanical allowances, *c,* is neglected, then it may be shown from equation 15 that the pressure given by equation 33 is half the collapse pressure of a cylinder made of an elastic ideal plastic material which yields in accordance with the shear stress energy criterion at a constant value of shear yield stress $\tau_y = \sigma_y \sqrt{3}$.

5.1.2. Fatigue Strength

Alternative approaches to fatigue design are under consideration by the ASME Special Working Group on High Pressure Vessels for inclusion in the High Pressure Vessel Code which is under development. Other than this writing the allowable amplitude of alternating stress is determined from the ASME Boiler and Pressure Vessel Code. Credit is not allowed for favorable compressive mean stresses such as those induced by autofrettage or shot-peening, unless it can be demonstrated by testing or successful service experience that the design is adequate and that it is consistent with the design criteria in Chapter IX.

5.1.3. Fracture Toughness

In an effort to ensure that all piping components have sufficient toughness to resist fast fracture in the presence of a through-thickness crack, minimum Charpy V-notch impact values have been specified in the code. The values range from 20–95 J ($15 - 70$ ft·lbf) depending on the wall thickness of the component, the specified minimum yield strength of the material, the direction in which the test specimen is cut, and the number of tests carried out. For example, the average of three Charpy V-notch impact values on specimens, cut in the transverse direction from a tube having a bore of 25 mm ($k = 2.625$), made of steel having a minimum specified yield strength of 965 MPa, is required to be 40.7 J (30 ft·lbf) at the lowest metal temperature at which the component will be subjected to a stress greater than 41 MPa (5945 psi).

6. Low Density Polyethylene Process

6.1. Autoclave Process

When exothermic polymerization of ethylene is carried out in a stirred reactor, it is difficult to transfer much heat through the wall, and cold ethylene is passed continuously into the polymerizing mixture to maintain a constant temperature in the range 200–300°C and a pressure of 150–300 MPa (22,000–43,500 psi). Maximum conversion of ethylene to polymer is determined by the temperature difference between the incoming gas and the reacting mixture, and the need to achieve high conversion and throughput requires the reaction temperature to be set fairly close to the temperature at which ethylene decomposes into carbon, hydrogen, and methane. The decomposition is strongly exothermic and, once started, it proceeds very rapidly and might cause a pressure increase sufficient to rupture the vessel were it not for the pressure relief provided. Furthermore, if the hot products of the decomposition reaction are not cooled sufficiently before being vented, they may explode when they come into contact with the atmosphere and produce what is known as an aerial decomposition.

6.1.1. Stirrer

Initiator may be introduced into the cold ethylene feed or directly into the reactor at one or more points. To control the reaction temperature closely and avoid hot spots caused by nonuniform dispersion of the initiator, which might result in a decomposition, it is necessary to achieve good mixing of the polymerizing fluid from one end of the reactor to the other and rapid mixing of the cold ethylene with this fluid. The turbulence necessary to accomplish this requires a high stirrer speed with considerable power input. Stirrers which are prone to attract a buildup of polymer need to be avoided, not only because they become unbalanced and vibrate making fatigue failure more likely, but also because the polymer deposits undergo graft polymerization which degrades the product.

A rotary stirrer driven by an induction motor housed within the vessel was an integral part of the ICI process. Figure 28 shows a general arrangement of the 250 L autoclave introduced in 1943 in which the stirrer motor housing was coupled to the reaction vessel, both being designed for the same pressure. The shaft from the motor passed through the stem connecting the two components and was coupled to the stirrer (not shown), which extended over the length of the reaction space. Cool ethylene entered the top of the motor housing and passed through the gap between the rotor and stator down the stem containing the shaft into the reaction space. Development of a satisfactory stirrer involved extensive flow visualization and mathematical modeling; from an engineering point of view, many of the early problems stemmed from decompositions caused by local overheating or breakage of stirrer bearings.

The use of an internal motor has found wide acceptance even for the very large autoclaves now in service, although Du Pont has used an external motor with a shaft passing through high pressure glands (157).

6.1.2. Heating and Cooling

The body of the autoclave is heated by steam or other fluid to bring it up to reaction temperature and enable the process to be brought on stream as quickly as possible. The heating jackets may be of the separate compartmental clamp on type or they may be welded directly to the outside of the vessel. End covers to the autoclave may have machined passages to allow them to be heated. Once the reaction is established cooling fluid may be passed through the jackets to remove some of the heat of polymerization.

6.1.3. Protection against Overpressure

A decomposition propagating through the large mass of ethylene contained in a stirred reactor leads to a high rate of rise of temperature and pressure. To protect the reactor from excessive pressure, without having to resort to a large vent area, requires the pressure relieving device to act quickly and open at an overpressure which is as small as practicable. The early autoclaves used by ICI were protected by hydraulically balanced safety valves which were held closed by constant oil pressure. As soon as the pressure in the vessel increased significantly above the operating pressure, an oil relief valve lifted allowing the safety valve to open. In the case of the 250-L autoclave shown in Figure 28, the safety valves were housed in the recesses located round that part of the vessel provided with the cross-bore (156). Although a bursting disk was fitted in the oil system to accelerate the opening of the safety valve, it was still relatively slow in operation and was replaced by precisely machined bursting caps which, when the pressure significantly exceeded the operating pressure, failed in tension (158). The end of the bursting cap which becomes detached is caught in a dead-ended hole in-line with the exhaust port. Other types of bursting and shear element can also be used, provided the element which fails as a result of overpressure is located as close to the bore of the vessel as possible and that the material of construction does not creep significantly at the operating temperature. It may be necessary to provide a number of bursting elements to secure the required vent area with a large autoclave. The steel surrounding

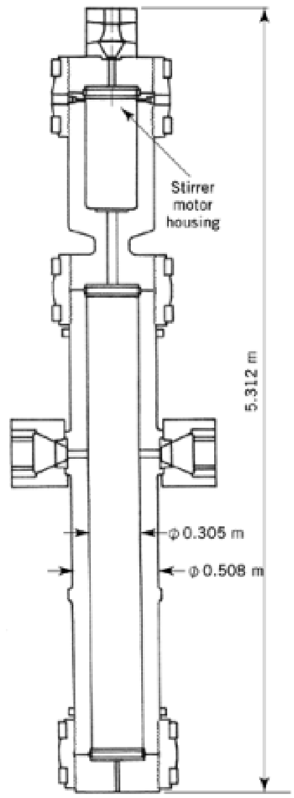

Fig. 28. General arrangement of 250-L autoclave (ICI) (156).

the exhaust ports through which the products of the decomposition reaction pass at sonic velocity when the pressure relieving device opens would be subjected to severe decarburization and cracking were it not for the replaceable sleeves fitted in the ports.

The autoclave is not the only component of an LDPE plant which may be exposed to a decomposition. Local hot spots in a secondary compressor may initiate a decomposition reaction; consequently it is necessary to protect these units from serious overpressure by pressure relieving devices and to release the products of the decomposition reactions safely. The problem of the aerial decomposition referred to earlier has been largely overcome by rapidly quenching the decomposition products as they enter the vent stack.

6.2. Tubular Process

Tubular reactors vary in length and may be as much as 1000 m long. They are constructed by joining together lengths of high pressure tubing, $\sim$10 m long, with a bore diameter in the range 25–75 mm and a radius ratio of about 2.5. To reduce the ground space required, the reactor is usually of zigzag or serpentine construction, adjacent straight lengths of tubing being joined by return bends or loops. The tubes are jacketed so that they can be heated or cooled by passing suitable fluids through the jackets. The first part of the reactor, which may be a quarter of the total length, is used to preheat ethylene to 100–200°C. A small amount of initiator is then injected continuously into the reactor and the heat of polymerization raises the temperature to 250–300°C. After the temperature of the polymerizing ethylene has been reduced by transferring heat through the wall of the jacketed tube, more initiator may be introduced at a second initiation point, and after further cooling yet more at a third point. Multiple point initiation serves to increase the percentage conversion of ethylene to polyethylene but it increases the length of the reactor. Further increases in conversion may be obtained if side streams of cold ethylene are introduced into the reactor, but in this event it may be necessary to use tubes of a number of different bore sizes so as to maintain the velocity through each section of the reactor approximately constant.

As the percentage conversion increases, the polymer has a greater tendency to form a second phase on the bore surface of the reactor where it reduces heat transfer and makes temperature control of the polymerizing mixture difficult. To increase the flow velocity through the reactor and slough the polymer from the wall, the pressure at the exit to the reactor is rapidly reduced from its maximum operating value of $\sim$300 MPa to $\sim$200 MPa (29,000 psi) every few minutes. The depth and frequency of the so-called bump cycle varies widely from plant to plant. In addition, there is a superimposed small high frequency cyclic pressure from the compressors; hence fatigue is of primary consideration in the design of a tubular reactor.

6.2.1. Tubing

Results of a large number of fatigue tests on tubing in the as received (pressure tested) and autofrettaged states and also a few tests on pipe bends have been reported. These tests were carried out at high mean pressure with a superimposed cyclic pressure to simulate the conditions in LDPE tubular reactors with periodic let-down in pressure (159). At a mean pressure of 207 MPa (30,000 psi) autofrettaged tubes withstood a range of cyclic pressure at the fatigue limit in excess of 310 MPa (45,000 psi), which means that under the conditions similar to those of the test, such tubes can withstand being cycled from 52 to 362 MPa (7500–52,500 psi) indefinitely (160).

Tests cannot be used to estimate actual service life because laboratory test conditions, particularly in the absence of transient and steady state temperature gradients through the tube wall, are not identical to those used in the LDPE process. Nevertheless a comparison between components A and B in the laboratory, coupled with a knowledge of how component A behaves in the plant, will usually enable an estimate to be made of how B is likely to perform under the same operating conditions. Comparative fatigue tests have proved to be a valuable tool in assessing the effect of heat treatment, anisotropy, surface finish, degree of autofrettage, etc, in the development of tubes and components for the LDPE tubular process.

6.2.2. Autofrettage

To achieve the required fatigue strength the tubes have to be autofrettaged to induce favorable residual stresses. The degree of autofrettage used by different manufacturers varies from that needed to take the elastic–plastic boundary a small distance through the wall to a pressure which may be 75% of the burst pressure of the tube. When high autofrettage pressures are used, the process is usually controlled by measuring the strain on the outside surface at, eg, three points along the length of the tube. Provided the variation in tensile strength along the length of each tube is small, this procedure ensures that each tube is subjected to a similar degree of autofrettage irrespective of the strength of the individual tubes. Tubes may be hot or cold bent provided the radius of the tube center line is not less than 10 times the nominal tube outside diameter. Any heat treatment required after cold bending is carried out before autofrettage.

Relaxation of the residual stresses induced by autofrettage at 720 MPa (104,400 psi) in reactor tubes ($k = 2.4$), of AISI 4333 M6 at a uniform temperature of 300°C has been studied and it was concluded, on the basis of creep tests for 10,000 h, that after 5.7 years 60% of the original stress would remain (161).

6.2.3. Heating and Cooling Jackets

The tubes of a tubular reactor are surrounded by heating or cooling jackets which are interconnected. In some early designs the jacket was fixed to the tube at one end and a gland was provided at the other to allow for thermal expansion. To obviate inevitable leaks at the moving gland the modern trend is to fix a flexible jacket at each end, either by welding to the outside of the tube or by welding to rings which are shrunk on to the outside surface of the tube.

With many reactors only the straight lengths of tube are water jacketed; however, processes are now available for continuously bending jackets round preformed high pressure bends so that no welding is required except at the jacket to tube ends. Care is needed in the design of the supports to the reactor; otherwise thermal expansion may induce large bending stresses in the tubes. At the same time, it is necessary to ensure that the reactor does not vibrate under the influence of the cyclic pressures and generate axial bending stresses.

6.2.4. Side Inlets

Some early tubular reactors were fitted with T-blocks, to provide side inlets for pressure and temperature measurement, initiator injection, etc. A large number of these forged blocks were required; furthermore, they were heavy and expensive because they had to be large enough to take the stud bolts needed to join the block to the adjacent tubes. An alternative arrangement is to put the cross-bore through the sealing ring (162). Unfortunately the fatigue strength of the cross-bored sealing ring, which is subjected to an axial compressive stress in the direction of the main bore, is less than that of a cross-bored block in which the axial stress is tensile, and special precautions have to be taken to ensure that the fatigue strength of the cross-bored sealing ring is adequate.

6.2.5. Protection against Overpressure

The problem of protecting a tubular reactor from high pressures generated by decompositions is not as serious as with a stirred autoclave because the much smaller mass of ethylene contained in the tube leads to a slower rate of rise of pressure. The first line of defence against overpressure is usually one or more externally controlled dump valves (162) such as that shown in Figure 29 for an operating pressure of 320 MPa (52,000 psi) fitted to a tube of 60 mm bore. In addition rupture disks are usually provided at various points along the length of the reactor, but these cannot be set to burst at a pressure close to the operating pressure. This is because the temperature is not constant along the length of the reactor and because it may be necessary to replace the rupture disks on a preventative basis, if failure due to fatigue caused by the periodic let-down cycle is to be avoided. Rupture disks are often housed in Y blocks with a generously radiused intersection to avoid fatigue (163). All the fittings such as that shown in Figure 29 and the blocks required to house the bursting disks must be designed so that the dead space is as small as possible, otherwise the space itself may become a source of decompositions.

If the speed with which ethylene is passing through a tube is comparable to the speed with which the decomposition reaction travels through the ethylene, then one or other of the fronts where the decomposition is occurring will be stationary relative to the tube. Under these conditions the tube will be heated to a very high temperature rapidly and fail at a pressure much lower than the burst pressure of the tube at ambient temperature.

6.3. Initiator Pumps

Initiator, usually a mixture of organic peroxides dissolved in solvent, may be injected into the reactor through a sparger using hydraulically driven intensifiers or multicylinder mechanically driven pumps. With intensifiers in which the piston is relatively slow moving, it is essential to ensure that the flow of initiator is not interrupted at the end of each stroke. In principle, while initiator is being discharged from intensifier 1 the piston in intensifier 2 has to precompress the liquid to the discharge pressure, so that when intensifier 1 has completed its stroke intensifier 2 can take over without any interruption to the flow. Unfortunately, some of the control systems used to synchronize the operation of the intensifiers, which may be single or double-acting, are not easy to maintain and an interruption to the flow may result in a decomposition or loss of reaction at the sparger fed by that pump.

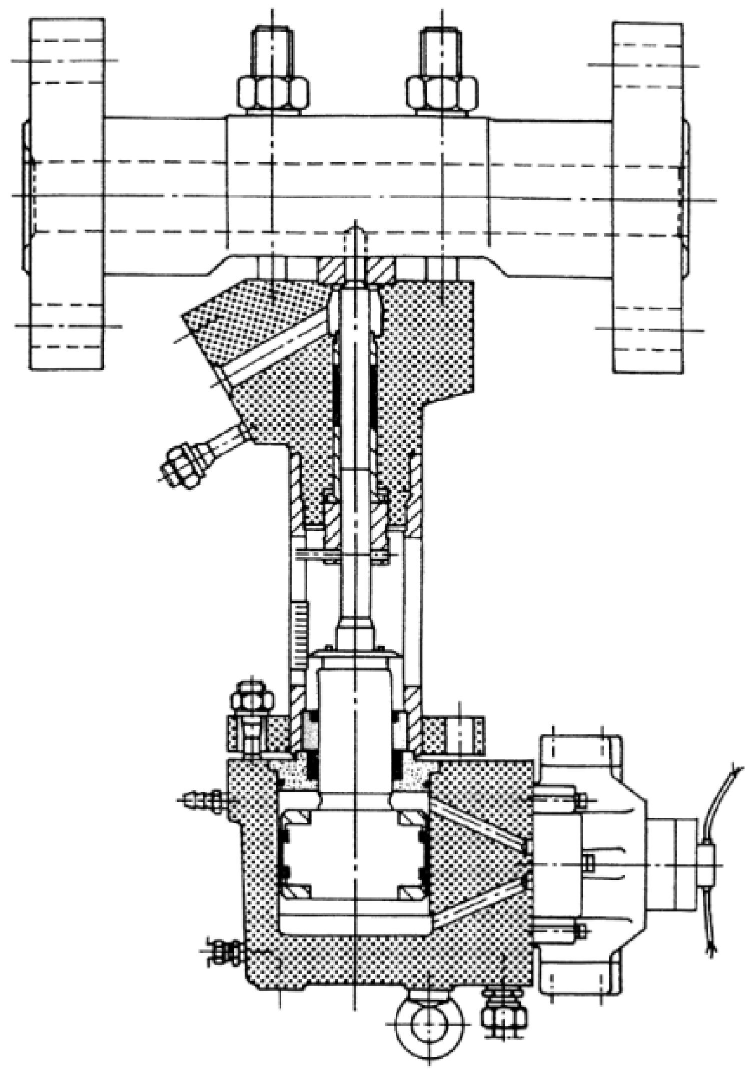

Fig. 29. Dump valve (Uhde) (162).

Many initiators attack steels of the AISI 4300 series and the barrels of the intensifiers, which are usually of compound construction to resist fatigue, have an inner liner of AISI 410 or austenitic stainless steel. The associated small bore pipework and fittings used to transfer the initiator to the sparger are usually made of cold worked austenitic stainless steel. The required pumping capacity varies considerably from one process to another, but an initiator flow rate 0.5 L/min is more than sufficient to supply a single injection point in a reactor nominally rated for 40 t/d of polyethylene.

The biggest problem associated with high pressure reciprocating pumps is that of satisfactorily sealing the plungers. To avoid excessive rate of wear a liquid film must be maintained between the plunger and the packing and, if this cannot be done by the fluid being handled, separate lubrication must be arranged. The plungers in the intensifiers are usually sealed using stationary chevron or U-type packings in which the liquid under pressure deflects the limbs of the U to provide the seal. Packing rings are often made of filled polytetrafluoroethylene (PTFE), which has low friction coefficient and good resistance to attack from solvents, such as benzene, toluene, hexane, etc, used to dissolve the organic peroxides. The rings held between suitably shaped steel rings are compressed by a plug being screwed into a recess at the end of the cylinder. Some peroxides deposit solid material during the compression process, which is difficult to control; this has an adverse effect on the life of the packing and the operation of the valves which are usually of the ball or double ball type. The valves may be accommodated in the pump body itself or more usually in a separate head attached to the body.

Because of the problems of securing an uninterrupted flow, some manufacturers have developed mechanically driven pumps of three or more throws. Some of these pumps avoided the use of conventional chevron-type packing by arranging for a stationary lubricated sleeve or bushing to be hydraulically tightened round the plunger so as to effect a satisfactory seal. Some of the difficulties in developing metallic lip clearance seals for high pressure reciprocating pumps operating on oil have been described (164) (see Pumps).

6.4. Reciprocating Compressors

Prior to 1895, when Linde developed his air liquefaction apparatus, none of the chemical processes used industrially required pressures much in excess of 1 MPa (145 psi) and the need for a continuous supply of air at 20 MPa provided the impetus for the development of reciprocating compressors. The introduction of ammonia, methanol, and urea processes in the early part of the twentieth century, and the need to take advantage of the economy of scale in ammonia plants, led to a threefold increase in the power required for compression from 1920 to 1940. The development of reciprocating compressors was not easy; little was known about the effects of cycles of fluctuating pressure on the behavior of the limited number of materials of construction which were then available, and failures of high pressure cylinders, valves, and gland packings occurred frequently.

Although the advantages of centrifugal compressors, one of which was the delivery of oil-free gas, had been recognized since 1926 (165) two problems had to be solved before they could be used in ammonia synthesis plants. First, the discharge pressure had to be raised, and second, the throughput of the compressor had to be decreased. It was not until 30 years later that a centrifugal machine was used in an ammonia plant; it operated at about 15 MPa and was followed by a single-stage reciprocating compressor to raise the gas to the final pressure. Further development, pioneered by Clarke Brothers in the United States, resulted in centrifugal machines capable of compressing synthesis gas to 30–40 MPa being used in all new single-stream plants having an output of 600 t/d or more. By the early 1960s only methanol and urea plants made use of reciprocating compressors. The development, by ICI in the late 1960s, of the supported copper oxide catalyst made possible the synthesis of methanol at pressures in the range 5 to 10 MPa with the results that centrifugal compressors could be used for all but the smallest plants.

The discovery of polyethylene created a need for compressors capable of compressing ethylene to about 150 MPa (22,000 psi). Initially the type of compressor used for this duty was based on a technique used in the laboratory (166), whereby ethylene was compressed from 25 (3600 psi) to about 150 MPa by an oscillating mercury piston contained within a U-tube, the movement of the mercury needed to compress the gas being produced by high pressure oil acting on one side of the mercury column. Although it accomplished its purpose by ensuring a steady production of polyethylene during the war years, it was not until World War II that any real progress was made in the development of reciprocating compressors suitable for pressures of 150 MPa.

GHH or Maschinenfabric Esslingen, as it was then, produced the reciprocating compressor used by BASF in its first polyethylene plant in 1942. GHH probably manufactured the first commercially available compressor in 1948, followed by Burckhardt in 1951. With the licensing of the LDPE process and the rapid development of the market for polyethylene, both ICI and its licensees gave up their attempts to develop their own compressors and sought to collaborate with selected compressor makers in the development, first, of machines capable of generating pressures of 150 MPa and later of larger machines for higher pressures. Feedback of operating experience from users provided technical know-how which enabled the makers to establish a virtual monopoly in the manufacture of these compressors. Each manufacturer developed machines which differed from those of his competitors, and users were reluctant to introduce alternative designs into their plant, with the result that comparatively little has been disclosed about the detailed design and performance of the different machines.

However, some of the more important techniques in high pressure engineering which made possible the increase in throughput of reciprocating compressors from $4-5$ t/h at a pressure of 125 MPa (18,000 psi) in the early 1950s to 120 t/h at a pressure of 350 MPa (51,000 psi) can be considered.

6.4.1. Hypercompressors

In an LDPE plant a primary compressor, usually of two stages, is used to raise the pressure of ethylene to about 25–30 MPa and a secondary compressor, often referred to as a hypercompressor, is used to increase it to 150–315 MPa (22,000–45,700 psi). The thermodynamic properties of ethylene are such that the secondary compressor requires only two stages and this results in a large pressure difference between the second stage suction and discharge pressures.

The principal problems which had to be solved in the development of secondary compressors for higher operating pressures and throughputs were restriction of ethylene leakage past the plunger or piston to an acceptable level without jeopardizing the life of the elements used to seal the plunger or piston; and the avoidance of fatigue failure of high pressure components such as the cylinder and valves. In a compressor cylinder the stress fluctuates cyclically between a minimum and maximum corresponding to the suction and discharge pressures. A compressor running at 5 Hz completes 10^7 cycles in about 23 days of continuous operation; hence design must be based on high cycle fatigue data.

In addition to these mechanical problems there are two aspects of the compression process which relate specifically to ethylene. First, there is a tendency for small amounts of low molecular weight polymer to be formed and, second, the gas may decompose into carbon, hydrogen, and methane if it becomes overheated during compression. Cavities in which the gas can collect and form polymer, which hardens with time or in which the gas can become hot, need to be avoided.

6.4.2. Sealing Arrangements

Moving or stationary friction seals are used to make an acceptable seal between the reciprocating piston or plunger (the terms are used interchangeably), and the stationary cylinder. Moving seals make use of piston or sealing rings which are attached to the piston and reciprocate within the cylinder, whereas stationary seals make use of sealing elements through which the plunger moves. The former is known as the ring on piston, and the latter as the packed plunger arrangement.

6.4.2.1. Ring on Piston. Figure 30 shows a secondary cylinder of an Ingersoll Rand (Dresser Rand) compressor built in the 1960s in which the plunger is sealed with a ring on piston arrangement (167). Figure 31 shows the details of two typical piston ring assemblies used by Burckhardt, which consist of pairs of sealing rings with each of the rings covering the slot in the other, and an expander ring behind the pair, which also seals the gaps in the radial direction (168). Special grades of cast iron, bronze, or a combination of both are used for the rings; cast iron or steel are employed for the expander. Tungsten carbide has been found to be the most satisfactory material for cylinder liners in which sealing is effected by piston rings of the type described. However, because this material is weak in tension, it is essential to prestress the liner in compression by shrinking it into an outer mantle. To ensure that prestressing is not reduced as a result of the relative thermal expansion between the tungsten carbide liner and the outer steel cylinder into which it is shrunk, it is necessary to cool the cylinder as shown in Figure 30.

Lubrication of piston rings in a hard liner is achieved by injecting oil into the suction stream or outer end sleeve (see Fig. 30) but this is not always satisfactory because compressed ethylene is a good solvent for mineral oils and very little oil reaches rings other than the first one or two. The temptation to use larger amounts of lubricant has to be resisted as the oil usually has an adverse effect on the properties of the

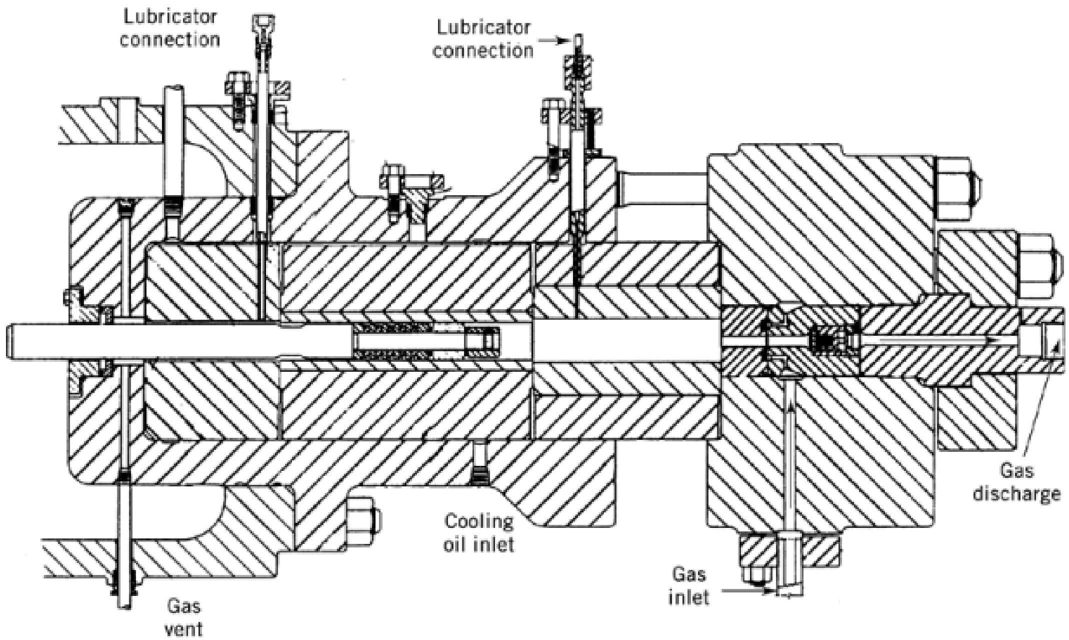

Fig. 30. Secondary cylinder with piston rings.(Courtesy of Dresser Rand (167).)

product. Furthermore, if the product is to be used for food packaging, the lubricant has to be acceptable to the health authorities, and special lubricants with less satisfactory lubricating properties must be used in as small a quantity as possible (168). Fortunately, low molecular weight polymers carried by the recycle gas are reasonably good lubricants and supplement lubricant injected into the suction gas; on the other hand, too much polymer of higher molecular weight causes the rings to stick in their grooves. Maintaining conditions for good lubrication of piston rings is difficult to achieve. Experience has shown that rings in the assembly do not share the pressure difference across the plunger equally; the largest pressure drop is taken by one or two rings, not necessarily those nearest the upstream pressure. When these, as a result of wear, are no longer able to hold the pressure the sealing is taken over by other rings. There is no simple rule for the number of rings to seal a given pressure, and fewer than 10 have been found adequate to seal pressures of 250 MPa (36,000 psi).

6.4.2.2. Packed Plunger. With a packed plunger, lubricant is injected directly into the sealing elements. This has a number of advantages; first, all the oil is used in lubricating the moving surfaces at critical locations; second, unlike the piston ring arrangement, there is no direct contact between lubricant and ethylene, and this reduces both the amount of lubricant required and the contamination of the compressed gas.

A typical secondary compressor cylinder with packed plunger manufactured by Dresser Rand is shown in Figure 32. Initially steel plungers were either nitrided or flame plated but most of these have been replaced by plungers of tungsten carbide available up to 300 mm diameter. Misalignment between the axis of a tungsten carbide plunger and the axis of motion of the thrust block attached to the cross-head may lead to fracture of the plunger, as a result of bending stresses, unless precautions are taken (169, 170). Sealing rings, not shown in Figure 32, are located in the recesses in the packing cups which are of compound construction. Metallic self-adjusting sealing rings of the type shown in Figure 33 are widely used. They are usually assembled in pairs, the actual rings which are tangentially split into three or six pieces being covered by a three piece radially cut section. Both, usually made of bronze with high lead content, are kept closed by surrounding garter rings. The optimum number of sealing elements is 4–5 (168). On the suction stroke, gas at discharge pressure, trapped

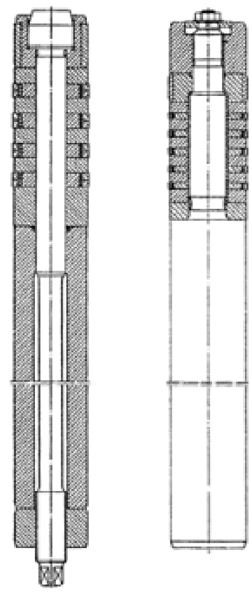

Fig. 31. High pressure pistons with piston rings (168).

in the packing cup recesses, flows toward the cylinder as the pressure drops to suction value. This backflow may result in ring and garter spring damage in those rings nearest the pressure side of the packing assembly unless a breaker ring, such as that shown in Figure 33, is used to minimize backflow. The pressure distribution along the length of such packings has been examined (172). Lubricant is supplied directly to the sealing rings by quills which pass through packing cups; each quill and its associated check valve is provided with lubricant from a separate pump. Lubricants used (subject to agreement by the health authorities) include mineral oil mixed with various percentages of polybutene, polybutene with no additives, and polyglycol. By restricting plunger velocities to $2 - 3$ m/s cylinder lives of nearly 70,000 h, with an end of life leakage of ethylene past the plunger of about 200 kg/h at a delivery pressure of 290 MPa (42,000 psi), have been achieved (151).

The packing cups, high pressure cylinder, and cylinder head are held together by tensioned bolts so that the axial stress across the carefully ground and lapped mating surfaces, finished to about 0.2 μm, is sufficiently high to prevent leakage. Duplex or triplex shrink fit construction is used to overcome the stress concentration effect of the cross-bores needed for the lubrication quills and the axial holes needed for the supply of coolant oil. Although fatigue failure in the radial–axial plane is rare, cups may fail from fatigue as a result of fretting induced by bending stresses. An assessment has been made of the stresses in packing cups at the junction of their mating surfaces and the critical value of the axial load to prevent fretting in secondary cylinders designed by Nuovo Pignone (173). Techniques used by the same manufacturer to autofrettage various components of the packed plunger design to improve their fatigue life have been described (30).

The disadvantage of the packed plunger design lies in the much larger joint diameters of the packing cups and other static cylinder parts which require higher closing forces than a comparable piston ring design. The cylinder bolts of cylinders of large bore need to be pretensioned to 10 or more times the maximum plunger load, and various hydraulic tensioning devices have been developed for this purpose. In spite of this, the superiority of the packed plunger design for secondary compressors has been generally accepted, although many primary compressors still use pistons fitted with rings.

With both the packed plunger and ring on piston designs it is essential that the piston or plunger be accurately centered if the seals are to be effective, and to this end guide rings are provided within the packing

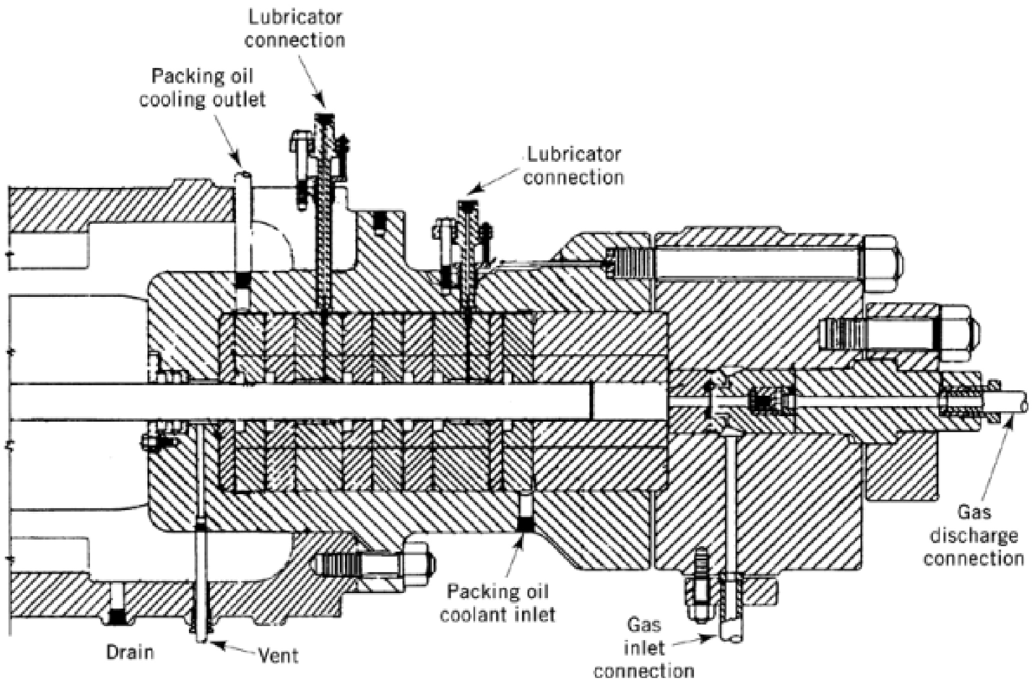

Fig. 32. Secondary cylinder with packed plunger.(Courtesy of Dresser Rand (167).)

cup assembly (see Fig. 32) and at the connection between the piston and the driving rod. At the low pressure end of the cylinder, additional seals allow gas which has escaped past the sealing rings or piston rings to be collected.

The rate of ethylene leakage past the plunger is measured for each secondary cylinder on a periodic basis, and these measurements provide valuable information on the degradation of the friction seals. The decision as to when to change a cylinder is usually based on economic considerations relating to loss of product resulting from leakage and that resulting from downtime caused by a cylinder change. The maximum rate of leakage acceptable before a cylinder change varies from plant to plant and with the demand for product.

The time the plant is down for a cylinder change may be reduced, and cylinder life increased, if the cylinder with worn packings is removed from the compressor in its entirety and replaced with one which has been assembled with care in a clean environment. Alternatively, with some designs it is possible to replace the packing cups and valve assembly as a complete cartridge.

6.4.3. Pressure Wrapped Cylinder

The pressure wrapped, sometimes called wrap around or fluid ring, cylinder aims to overcome fatigue failure of the packing cups by ensuring that they are at all times exposed to compressive stresses by subjecting their outer diameter to gas at discharge pressure. Thus, simple one piece packing cups, instead of duplex or triplex designs, can be used; however, the outer cylinder must be designed to withstand the more or less constant discharge pressure which acts on its bore. Figure 34, shows a pressure wrapped cylinder in which packing cups, A, outer end sleeve, B, and valve assembly, C, are all subjected to the discharge pressure which acts on the bore of outer cylinder, D, between static seals, E. To facilitate assembly, the packing cups are held together and joined to the outer end sleeve by tie rods, F. One of the problems in handling ethylene at high pressures is that polymer formed during the compression process may pass through the discharge valve and deposited in

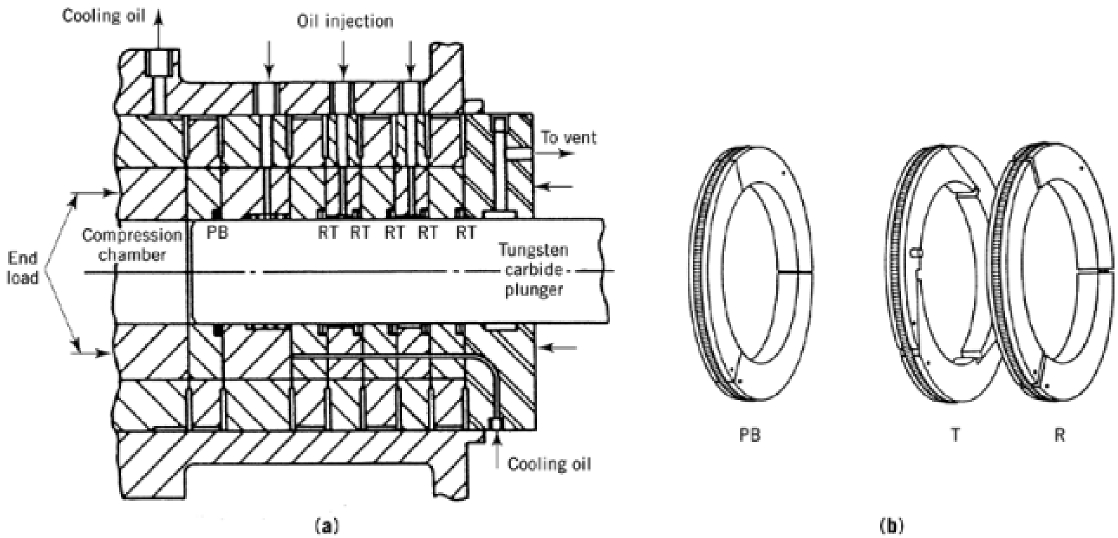

Fig. 33. (**a**) Typical secondary cylinder with packing cups (171); (**b**) stationary sealing rings for packing cups (France Products Division, Garloc Inc.). PB, pressure break; T, tangential ring; R, radial ring.

the gap between the outside of the packing cups and the inside of the cylinder. This polymer hardens with age and may make it difficult to withdraw the valve, outer end sleeve, and packing cup assemblies from the cylinder. More important, the design must be such that, if the annulus is partially blocked, the resulting transverse load cannot force one or more of the packing cups out of alignment and damage or break the carbide plunger.

So as not to decrease the strength of the outer cylinder by introducing cross-bores, in the section subjected to the discharge pressure, lubricant may be supplied to quills at the low pressure end of the cylinder and then through axial drilled holes to the appropriate packing cup. Lubricant has to be supplied at a pressure greater than the discharge pressure and fatigue failure of check valves and lubrication quills sometimes proved to be a problem until the check valves were enclosed within the cylinder. The discharge gas passed around the packing cups contributes little cooling, and additional cooling is provided by passing oil through passageways drilled in the packing cups in the axial direction.

6.4.4. Valve Design

The reliability of the suction and discharge valves is crucial to the performance of the compressor. Initially, compressor manufacturers designed cylinder heads containing radial suction and discharge valves, so that it was possible to pull a complete piston with its rings through the cylinder head without disconnecting the suction and discharge lines or removing the valves. With this arrangement fatigue proved to be a serious problem which the design, shown in Figure 35, attempted to overcome. The well radiused intersection of the gas passages with the main bore was located in a small forged core shrunk into a heavy flange and compressed axially by the cover plate so that it was subjected essentially to all-round compression (168). The head made use of the single poppet valves shown in Figure 36**a** in which the lapped mating surfaces of the three components were loaded in compression to produce a pressure-tight seal.

As the difference between the suction and discharge pressure increased, it became necessary to remove the pressure fluctuations from the area of the cross-bores and several ways of doing this have been described (168). In the arrangement shown in Figure 36**b,** the suction and discharge valves are arranged in line and the entire valve body is subjected to suction pressure on the outside; only the gas passage leading to the discharge valve is subject to cyclic pressure. Separation of suction and delivery pressure is assured by the

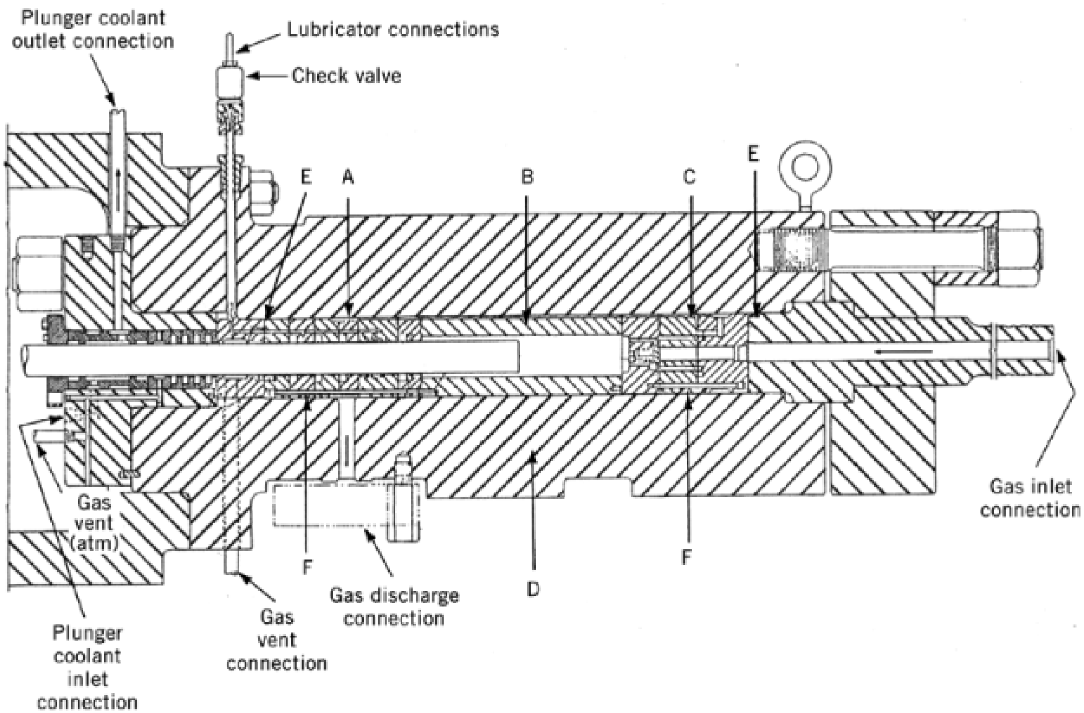

Fig. 34. Pressure wrapped secondary cylinder.(Courtesy of Dresser Rand.)

sealing ring and the entire valve is pressed on the end of the cylinder liner by the difference of pressure and the precompressed belville washers. The components of this valve assembly can be autofrettaged to increase their fatigue resistance. Other manufacturers subject the outside of their axial valves to discharge pressure, which gives added strength, and may use multipoppet valves or plate valves instead of single poppet valves. Figure 36**b,** shows an axial plate valve in which the discharge pressure acts on the outside surface of the components; such a valve might be used in the pressure wrapped cylinder shown in Figure 34.

6.4.5. Driving Mechanism

The first essential is to ensure axiallity of motion of the high pressure plunger, so as to avoid side loading of the packings and plungers which would jeopardize packing life and might result in damage or fracture of the plunger. The second requirement is to reduce the cyclic fluctuation of torque.

Basically, a vertical mechanism (Fig. 37**a**) was adopted from the design of large diesel engines and this, together with a horizontal mechanism (Fig. 37**b**), was used for some of the earliest secondary compressors. Since there is only one working stroke in two, both mechanisms suffer from large cyclic torque fluctuations. The mechanisms in Figure 37**c** and **d** give a more uniform torque diagram and the load on the small-end bearing reverses which aids their lubrication. The horizontal machine, unlike the vertical, has excellent accessibility to all parts of the drive mechanism as well as to the valves and glands; furthermore, layout of the pipework and auxiliary plant such as coolers, pulsation dampers, and separators is easier. The mechanism in Figure 37**c** which makes use of a yoke or secondary cross-head to which the plungers of an opposed pair of cylinders are attached, was adopted by Dresser Rand. The inboard cylinders are not as accessible as the outboard, but alignment is good. The arrangement has the added advantage that it is easy to incorporate a distance piece to prevent ethylene entering the crankcase, an important safety consideration, but it suffers because of its

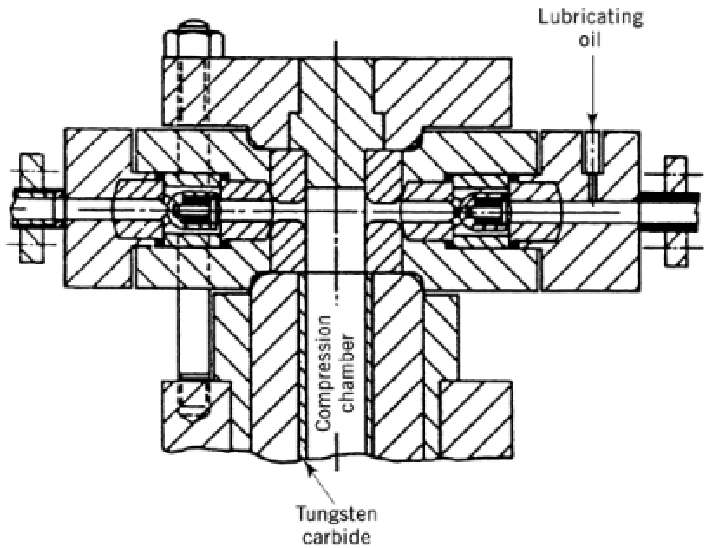

Fig. 35. Precompressed cylinder head with radial inlet and outlet valves (174).

great overall length. The most commonly adopted design is that of Figure 37**d** in which the connecting rod is connected to a cross-head which surrounds the crankshaft. The cross-head is connected to a second cross-head on the opposed high pressure cylinder. With this design the cross-head guides can be arranged in the base of the machine as is done by Burckhardt and GHH or in the plane of the center-line of the plungers which is the design adopted by Nuovo Pignone (175).

6.4.6. Capacity

As a consequence of the limitation on plunger velocity, compressors are usually slow speed with a short stroke. At the same time constructional problems limit the bore size and large capacities have to be achieved by multiplying the number of cylinders. A range of compressors with different strokes and bore diameters, based on the driving mechanism of Figure 37**d** and a module of two cylinders, has been designed by both Nuovo Pignone and Burckhardt with up to six modules, that is twelve cylinders. For example, a machine with 10 cylinders operating between a suction pressure of 25 MPa (3600 psi) and a delivery pressure of 315 MPa (45,700 psi) would have a throughput of $118,400$ kg/h and require a power input of 15.2 MW (151).

It was concluded in 1975 that centrifugal secondary compressors with a delivery pressure of 200–250 MPa (29,000–36,000 psi) would be feasible for ethylene capacities of more than $100,000$ kg/h. However, in order to replace the primary compressor with a centrifugal machine, it would be necessary to increase the throughput to $200,000 - 250,000$ kg/h (176). Rotary machines have yet to be used in LDPE plants.

6.4.7. Variable Flow Rate

Conventional variable clearance volume and valve lifting devices are impracticable at high pressures and, should it be necessary to vary the flow rate, use has to be made of variable speed electric drives or magnetic clutches. Integral steam and gas engines have been used and Burckhardt (168) developed an hydraulic drive to provide an integrated variable capacity machine, but its efficiency is less than that of a straight mechanical drive.

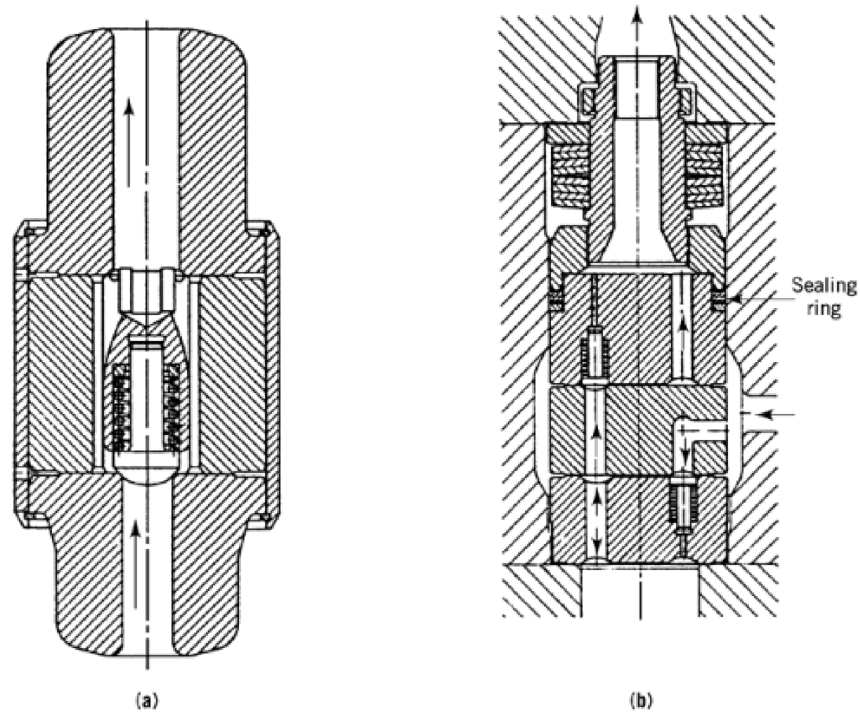

Fig. 36. (**a**) Single poppet valve; (**b**) combined inlet–outlet axial plate valve.(Courtesy of Dresser Rand (169).)

6.4.8. Operational and Maintenance Problems

6.4.8.1. Stud Tightening. A large number of screwed fastenings are used to secure the component parts of a reciprocating compressor, eg, cylinder, cylinder head, tie rods, drive rods, etc. Each of the threaded components is subjected to an alternating load, and pretensioning forms the best and simplest way of increasing the fatigue strength of the fastening. Pretensioning serves to increase the mean stress in the bolt but reduces the amplitude of the cyclic stress by an amount determined by the relative stiffness of the bolt and the parts being joined together (177). The pretension may be 80% or more of the yield stress of the bolt material based on core area. A number of methods of controlling the pretension in bolts may be used, of which measurement of the axial stretch by means of a dial indicator is the most common. In a bolted joint about 95% of the torque applied by wrenching is needed to overcome friction and less than 5% becomes useful preload. The torque needed for preload is a function of the cube of the nominal bolt diameter; hence, it becomes very difficult to preload large diameter threads properly unless some form of hydraulic stud tensioning is used.

The pretension in the bolts gradually becomes less as the contact surfaces settle down, as a result of the surface roughness peaks being smoothed out during subsequent loading cycles, and routine checking of tightness is desirable. Loss of pretension is more rapid with machine cut and ground threads than with rolled threads.

6.4.8.2. Pulsation Dampening. At the compressor discharge, the peak to peak pressure variation as a percentage of the mean pressure may be as much as 15–18%. It is seldom reduced using volume bottles because the required volume is large; hence, steps have to be taken to minimize the potentially damaging effects. Pressure pulsations induce vibrations in the downstream piping, particularly if it contains numerous bends, and it is necessary to restrain the movement of the pipe to limit the stresses, especially in bending, to a safe level. Mechanical resonance occurs if the frequency of the pressure pulsations, or one of the harmonics,

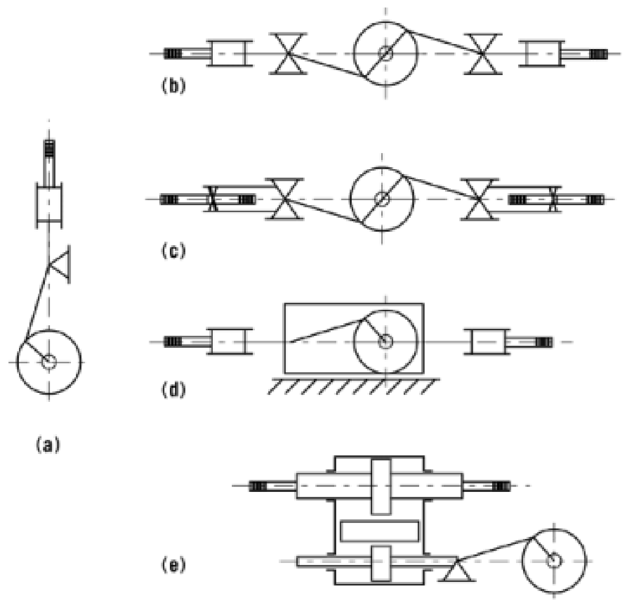

Fig. 37. Driving mechanisms used in secondary compressors (174). See text.

coincides with the natural frequency of vibration of part of the piping system. In this case selection of the correct distances between supports or the use of vibration dampers, in areas where supports cannot be used, may be necessary to reduce the amplitude of the vibration to acceptable levels. Acoustic resonance gives rise to larger pressure pulses than would otherwise be expected and, when designing a complicated piping system to operate over a range of conditions, is difficult to predict. Analogue simulation shows how the potential for resonance conditions can be minimized by altering the pipe layout and by inserting restrictions at appropriate points.

Axial bending induced by mechanical vibration may cause a pipe to fail by fatigue cracking in a transverse direction, usually at the last engaged thread behind a screwed flange. To avoid this mode of failure, which is particularly hazardous as it leads to full bore leakage, it is essential not only to reduce the amplitude of vibration of the pipe between supports to a safe level but also to monitor it periodically in the suction, delivery and interstage piping to ensure that it remains so. Advice on this subject has been given both by users (178) and by manufacturers of compressors (179, 180).

6.5. Nonlubricated Compressors

In processes such as hot isostatic compaction, gas purity is very important and diaphragm compressors, nonlubricated reciprocating compressors, or liquid pumps, are often used. In the operation of a diaphragm compressor, oil, above a reciprocating piston, flexes a metal diaphragm in a lenticular cavity, allowing gas on the other side to be sucked in and discharged through inlet and outlet valves housed in recesses (181). The diaphragm compressor is not able to handle large flow rates; the displacement of a single head ranges from 1.5×10^{-4} to $0.1\ \mathrm{m^3/s}$. Each stage is capable of a compression ratio of about 15 to 1 by virtue of the large cooling area surrounding the diaphragm; hence, fewer stages are required than would be the case for a reciprocating compressor. The weakest element is the diaphragm, which is subjected to high cyclic stresses and is easily damaged by small solid particles which may enter with the gas. Triple diaphragms with leak detection monitors ensure that oil cannot enter the gas stream, but diaphragm life is from 200–500 h depending on gas cleanliness and service conditions (182). With a batch process this may be acceptable; the alternative is to use a nonlubricated piston compressor. These are electrically or hydraulically driven, single or double stage and rated up to 200 MPa (29,000 psi). The drive fluid in the hydraulically driven compressor is segregated from the process gas and avoids contamination. Seal life is about 500–1000 h, depending on service conditions (182).

7. Safety and Testing

The engineering problems involved in the development of a safe and cost effective chemical plant such as that for the manufacture of polyethylene depend on the skill and experience of the craftsmen involved. It is common experience that high pressure work requires special skills and abilities and, even more importantly, a dogged perseverance. In particular, it requires the ability to work with high strength and frequently intractable materials which are more difficult to machine to high accuracy and surface finish. Great attention is needed to minute details in order to achieve reliability as, for instance, in the lapping of the mating surfaces of packing cups for reciprocating compressors and the installation of the sealing rings and plunger. Cleanliness in the assembly of valves and catalyst pumps, for example, is essential for their successful operation.

Reliability and safety depends not only on the craftsmen but also on the quality of the materials used in construction. Very large forgings in high strength steel alloy required for autoclaves needed considerable developments in the casting of the original ingot and its subsequent forging to achieve the high quality demanded, particularly in relation to defects. This improvement in the production of large forgings coupled with metallurgical development work has been necessary in the tube manufacturing process to produce the high quality of tubing required and the larger diameter tubing demanded as a result of the increased size of plant.

The safe operation of high pressure plant of the type described here necessitates a suitable in-service inspection program to ensure that the equipment remains within acceptable design limits. Nondestructive testing plays an important role, and dye penetrant, magnetic particle, eddy-current, and ultrasonic techniques have been widely used to detect flaws or fatigue cracks in high pressure components. A realistic approach to inspection and maintenance of high pressure equipment in polyethylene plants and the compromise which is often necessary between unreasonably rigorous standards and those dictated only by plant production requirements have been discussed (183). The need for adequate records and the extent to which in-service programs have complemented and taken account of more fundamental investigative work have been stressed (183). The concept of a structural integrity program introduced by Du Pont, as a result of its experience with high pressure operations has been discussed (184). This program is aimed at improving the general awareness of those designing and maintaining plants with unusual hazards and standards, as well as providing specific technical control in areas such as failure analysis and inspection.

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