Trend towards large capacity plants emphasizes the need to adequately guard against brittle fracture risk

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The current building boom of large capacity ammonia synthesis plants emphasizes the problem of adequately guarding against brittle fracture risk. The concern is greatest for high-pressure carbon steel equipment operating in the temperature range from ambient down to -20 F, since the customarily used ASME and and ASA Codes do not prescribe specific safeguards in this range. Below this limit, safeguards are called for in the form of mandatory impact test and stress relief requirements. The heavy thickness of process equipment demanded by 500-1,000 ton/day single train plants increases the possibility as well as the consequence of brittle failure. The risks will rise further with the continuing trend toward ever larger plants and higher synthesis pressures.

Fortunately, there have been no known in-service fractures of heavy-wall, high-pressure ammonia plant equipment, although failures during hydrostatic testing have occurred. However, the growing number of plants springing up all over the world certainly increases the statistical probability of a failure. On the bright side, we witness the growing awareness on the part of industry to the need for extra requirements for materials selection, fabric ation, and inspection. Similarly, we can look forward to the probable adoption by the regulatory code bodies of more stringent minimum requirements. Such revisions are being actively considered for ASME Section VIII (Unfired Pressure Vessels) and the ASA Pressure Piping Code Section B31.3; others, notably ASME Section III (Nuclear Vessels) and API Standards 620 and 650 (Low Pressure and Atmospheric Storage Tanks) already incorporate special rules to guard against brittle fracture at ambient temperatures.

Brittle fracture considerations

Appraisal of the brittle fracture risks and hazards in ammonia synthesis plants reveals them to be greater than in most other chemicat industry installations. There are several reasons for this, involving considerations of temperature, pressure, equipment size, steel thickness, and not least, the dangerous nature of ammonia and hydrogen rich process gases. The release of large quantities of toxic, flammable substances has long been a major concern of this Safety Committee and needs no further elaboration. However, attention has been concentrated on the effect of massive spills of liquefied product ammonia in the event of catastrophic failure of large storage tanks, some up to 30,000 tons capacity.

Failure of process equipment could be equally or perhaps even more disastrous in view of the high pressures and hydrogen content of synthesis loop atmosphere. There are several large diameter, high-pressure vessels and exchangers with associated piping operating narrowly above -20 F, i.e., barely over the limit where impact testing is mandatory according to Code. Yet, it is precisely such heavy-wall construction which is most prone to brittle fracture. Greater thicknesses raise the brittle-ductile transition temperature of steel and, moreover, reduce its notch-impact strength at a given temperature, as compared to thinner parts. Also, heavier sections are more rigid and hence less able to accommodate local over-stresses. Finally, there is also increased likelihood of undetected manufacturing and fabrication flaws; this applies particularly to forgings, some of which have sections over 12 in. thick in typical 1,000 ton/day plant equipment.

Brittle fracture experience

Experience and experiment have shown that brittle rupture of vessels characteristically proceeds suddenly and with explosive force. The awesome spectacle of such a violent disintegration is illustrated by the failure of an ammonia converter during hydrostatic testing, which is the subject of another paper presented in this Manual." Photographs of the ruptured vessel and a two-ton fragment are reproduced in Figures l and 2, It can be assumed that had the vessel been filled with a compressible fluid such as air or synthesis gas, the rupture would have resulted in even greater fragmentation and missile energy. Your attention is directed to the complete absence of thinning or other evidence of local yielding, typical of brittle or cleavage fractures.

This introduction to the problem of brittle fracture may sound alarming and create the impression that disaster is imminent. Such is not the case, as is borne out by the reassuring fact that brittle fracture failures are extremely rare. This favorable experience is highly significant if one considers that practically all existing industrial equipment, structures, pipelines, ships, railroads and even automobiles are constructed of ordinary, non-impact tested carbon steels which, during cold winter days, are probably in or even below their brittle transition zone. What is the explanation for this seemingly paradoxical success?

Figure 1. Brittle failure of an ammonia converter during shop hydraulic test. Shell material is 5% in. thick low alloy steel. (Courtesy British Weiding Research Assn.)

The answer is that brittle failure will result only from the combined presence or action of several factors, only one of which is the negative effect of low temperature on ductility. The necessary conditions are local tensile loading above the yield point, a crack-like

^{.&}quot;Brittle Fracture of Ammonia Converter". W. D. Clark and K. G. Mantle.

stress intensifier and the inability of the material to deform plastically at temperature. With pressure equipment, the likelihood of failure is further reduced through thermal and mechanica] stress relief, the latter an automatic bonus obtained during hydrostatic testing. Before exploring the various precautionary measures prescribed by regulatory Codes and individual companies, let us interrupt for an elementarv review of brittle fracture.

Figure 2. Two ton fragment of failed vessel in Figure l thrown 152 ft. Hydrostatic pressure at time of failure was 5,000 Ib./sq.in. (Courtesy British Weiding Research Assn.)

Brittle fracture fundamentals

Brittle fracture of steels is by no means a new phenomenon but has been widely recognized and diligently explored for several decades. Set off by numerous instances of ships breaking in half during World War II. there has been intensive research, its findings documented in hundreds of industry. government. university. and technical society reports. We shall review briefly lundamental concepts of brittle fracture and attempt to clear up some common misconceptions about it. It is the intent to confine this review to practical aspects. and deliberately side-step the intricacies and controversies of fracture mechanics.

Brittle fracture describes a mode of failure of normally ductile material, characterized by practically no measurable stretching or deformation, much like ruptures of cast iron, glass, and ceramics. The conspicuous absence of significant plastic yielding distinguishes brittle or cleavage fractures from the usual ductile or shear type fracture normally associated with steel failure from overloads. One outstanding characteristic of brittle failures is that they can occur at relatively low nominal stress, usually well below the nominal yield point. Another earmark is the sudden and rapid crack propagation which may proceed with sonic speed and result in explosive energy release.

The combination of suddenness. violence. and the absence of any preliminary warning signs makes brittle fracture probably the most treacherous form of material failure. Since there is no discernible change in micro-structure of physical properties prior to failure. incipient brittle fracture defies detection by any known inspection tooi or technique. This sets it apart from other causes of failure such as overheating, corrosion, hydrogen fissuring, carbide precipitation, sigma formation, etc., all of which cause detectable structural changes in the metal.

Temperature most important variable

The single most important external variable influencing the brittle fracture behavior of steels is temperature. This relationship is illustrated in a schematic diagram (Figure 3) which depicts an idealized transition temperature curve (Charpy impact energy versus temperature) for ferritic materials such as carbon and low alloy steels. Actual numbers are deliberately omitted because they depend very significantly on the kind of steel and a variety of metallurgical factors. Note that Cr-Ni stainless steels (austenitic microstructure) and most non-ferrous metals do not exhibit this drop-off in impact strength with decreasing temperature. Remember also that exposure to low temperatures does not cause permanent impairment of metal properties. The drastic reduction of ductility and

impact strength is fully recoverable by warming the steel above its transition temperature range.

The typical impact-temperature curve divided the diagram into three broad, arbitrarily demarcated temperature zones. The center one is defined as the so-called transition temperature zone because it marks the transition from predominantly ductile to predominantly brittle type fractures. Some steels show a much less clearly defined and less abrupt drop in impact resistance as the test temperature is lowered. Note incidentally that the once popular term 'transition temperature' is ambiguous and its use is therefore discouraged. Originally, transition temperature was taken as the temperature corresponding to an impact strength of 15 ft.-lb. (Charpy keyhole notch), an established ASME Code criterion for distinguishing notch-tough from notch-brittle materials.

Figure 3. Impact strength-temperature curve for ferritic steels.

V-notch test preferred

Nowadays, the Charpy V-notch test is preferred to the keyhole notch test as an index for measuring relative resistance to brittle fracture. The reason is that the V-notch more directly simulates crack-like flaws and weid defects and thus yields better correlation with brittle fracture service experience and NDT." The characteristic S-shaped curve in Figure 3 could also be constructed by plotting variables other than energy against temperature. Two such in common use are the lateral expansion behind the notch, and the ratio of cleavage (granular) vs. shear (fibrous) fracture, as observed from broken impact test specimens.

Transition temperature zones for non-impact tested pressure vessel carbon steels generally fall within the range from -20 to +100 F,; impact test strength levels vary between approximately 1-5 ft.-lb. for 100% brittle fracture and 40-100 ft.-lb. for 100% ductile fracture.

NDT refers to Nil Ductility Temperature as measured in the Drop Weight Test, ASTM E208-66T, in which full thickness precracked plates are struck by a falling weight at a series of temperatures. The highest temperature at which the specimen fractures is termed the Nil Ductility Temperature. This test, developed by the Naval Research Laboratory, has shown excellent correlation with service failures (Weiding Research Council Bulletin No. 88, May. 1963).

Alloy steels, especially in the quenched and ternpered condition, may reach upper plateaus exceeding 100 ft.-lb., showing the direct influence of yield strength on energy absorption. The lower end of the curve levels off at *^lk* to 2 ft.-lb., which signifies that even completely brittle material requires a certain minimum energy for fracture to occur. The small spread of impact values in the lower plateau merely indicates that little energy is required for a completely brittle fracture.

The broad range of attainable upper levels of impact strength forewarns us to interpret cautiously any test readings obtained at only a single temperature level. For example, the long-standing ASME criterion of 15 ft.-lb. Charpy keyhole is at best applicable to low-strength carbon steels and by no means assures satisfactory brittle fracture resistance for stronger carbon and aüoy steels. In fact, for such high-strength materials, 15 ft.-lb. may be in the lower range of the transition zone, as well as below the NDT.

The usefuiness of impact type tests for evaluating brittle fracture characteristics and behavior gives the impression that dynamic loading is a prerequisite for this mode of failure. This is a common misconception which has lulled many people into a false sense of security. Static loads definitely can and do cause brittle fracture. particularly in the presence of sharp-edged stress raisers and triaxial stress patterns. Another point to remember is that even carefully operated equipment may occasionally be subjected to sudden, unexpected high local stresses arising from hydraulic, pneumatic or mecnanical impact forces.

Factors other than temperature

There are many factors other than temperature which affect the brittle fracture behavior of a steel, let alone a complex piece of equipment. Some of these exert a direct influence on the temperature at which the material undergoes the brittle-ductile transition; among them are alloy content, deoxidation practice, microstructure, thickness. and heat treatment. Other important but harder to measure factors include defect size and shape, as well as various fabricational aspects like forming technique, cold straining and strain aging, weiding practice, and post weid heat treatment. The great influence of weiding is brought out by the fact that the majority of brittle failures have initiated at or near weids.

The manner, extent and rate of loading also play a major role in determining whether or not a structure will resist brittle fracture in service. This covers not just the level of applied and residual stress but, more significantly, the magnitude and direction of locally intensified stresses, particularly by impact loads. Obviously, these are closely dependent on design and fabrication details. Equipment geometry and configuration affect the ability to deform plastically and redistribute stress; this pertains especially to the attachment and reinforcement of massive components such as large nozzles. The high degree of constraint, multi-axial stress distribution and presence of weids at such locations combine to create potential initiation sites for brittle cracking.

It is apparent that most of these variables are closely interrelated and therefore it is hardly surprising that brittle fracture behavior does not lend itself to rigorous mathematical analysis. The directional effect of individua! factors with respect to either raising or lowering susceptibility toward brittle fracture is tabulated in Table 1. No attempt is made to rate them in order of importance nor to indicate their complex interdependence. Nevertheless, this simple tabulation may help non-metallurgists recognize and assess those provisions in Codes and specifications which relate specifically to minimization of fracture risk.

Safety Codes and Standards

Most state laws require that ammonia plant equipment be furnished to comply with various Codes and Standards. In the U.S.. the major ones are the Boiler and Pressure Vessel Code (ASME), the Pressure Piping Code (ASA) and API Standards. Pertinent paragraphs from each dealing explicitly with brittle fracture prevention are surveyed in the appended summary tables. In ammonia plant

design, the most important ones are ASME Section VIII. (Unfired Pressure Vessels), ASA B31.3 (Refinery Piping) and API Standard 620 (Low Pressure Storage Tanks).

Table 1. Factors affecting transition temperature and susceptibility to brittle fracture of carbon steel.

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SENEFICIAL FACTORS

It should be recognized that almost all of the items covered fall in the realm of materials selection and testing which, as we have seen, is only one of several contributing factors. Other important influences, i.e., those relating to design, fabrication, and inspection are difficult to evaluate and cannot be properly covered in such a simple tabulation. ASME Section VIII and ASA B31.3 put heavy emphasis on these less obvious aspects; this should be taken into account in making comparisons with documents such as API 620 and 650, which rely almost exclusively on appropriate materials selection as a safeguard against brittle fracture.

A combination of restrictive materials selection and high caliber design, fabrication, and inspection is provided in ASME Section III (Nuclear Vessels). It is considerably more conservative than Section VIII, and so far has not been applied to chemical plant construction. The prevailing trend in ASME Code Committees and Task Groups concerned with brittle fracture is in the direction of upgrading Section VIII requirements, but not necessarily to the level of Section III. This tightening-up process is already in evidence in ASME Subcommittee proceedings.

The ASA B31.3 requirements pertaining to brittle fracture protection are patterned closely on ASME Section VIII, as would be expected from the traditionally close cooperation between these two Code bodies. The most significant difference between them is in the area of stress relief below -20 F., which is mandatory only in Section VIII.On the other hand, ASA B31.3 is somewhat more conservative in the -20 to -50 F. range with respect to impact test exemptions. At temperatures of -20 F. and above, neither impose specific safeguards or materials limitations

Requirements for storage tanks

Storage tanks are designed and built in accordance with the requirements established in API Standards 620 (Low Pressure) and 650 (Atmospheric). The large single and doublé wall refrigerated ammonia storage tanks are covered by the Supplement to Standard 620, alternately referred to as Appendix \tilde{R} (the R stands for refrigerated). The comprehensive rules for selecting materials in

API STORAGE TANK STANDARDS

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ASME BOILER AND PRESSURE VESSEL CODE SECTION III - 1965

(Nuclear Vessels)

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ASA CODE FOR PRESSURE PIPING - 1966
(ASA B31.3 Petroleum Refinery Piping)

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ASME BOILER AND FRESSURE VESSEL CODE SECTION VIII - 1965

(Unfired Pressure Vessels)

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API 620 reflect the deliberate effort to provide notch-tough steels. In this respect, API 620 is indeed more progressive and stringent than ASME Section VIII. It can be argued that the API has been under greater pressure to include specific brittle fracture safeguards in view of several catastrophic failures of atmospheric storage tanks.

Since Section VIII rules cover the majority of equipment items in all domestic ammonia plants, let us briefly analyze these provisions and their limitations. The major limitaüon of Section VIII for low temperature service is that there are no special provisions to guard against the possibility of brittle fracture at temperatures above -20 F. This arbitrary temperature dividing line considers neither steel analysis nor thickness. which makes it virtually certain that a significant percentage of Code vessels operate below the transition temperature range. In the range below -20 F. where impact testing is mandatory, Section VIII still allows the use of Charpy keyhole specimens; however. it is anticipated that they will soon change over to the more significant Charpy V-notch test.

The limitations of Section VIII are best illustrated by a practical example. Consider a pressure vessel operating at -18 F. and 3.000 Ib./sq.in. constructed of 4 in. thick ASTM A212 Gr B steel. By all the presently recognized criteria, the shell material will most likely be below the ductile-brittle transition temperature range. There may be notches in the shell surface, at nozzle weids which are not radiographed, in pipe used for nozzles, and at external or internal attachments. Even the shell main seam weids which must be radiography (e.g. slag inclusions below % in. The shell stress will be 17,500 Ib./sq.in. nominally, but will be higher at nozzle attachments, notches, head-to-shell junctions. locally thinned areas, etc.

A ready-made candidate for fracture

The kind of vessel described appears to be a ready-made candidate for brittle fracture. Yet, hundreds of such vessels are successfully operating in oil and gas fields. and additional hundreds are installed in existing ammonia synthesis and other industrial plants. This example illustrates the point emphasized earlier that brittle fractures require the coexistence of several detrimental conditions. which is unlikely from statistical considerations. The favorable operating experience of these vessels is probably also an indication of the beneficial effects of postweld heat treatment and hydrostatic testing, both required by Section VIII.

Since it is impossible to fabricate commercial pressure equipment completely free of notches and stress concentrations, increased resistance to brittle fracture is best achieved by selecting materials which can be expected to perform satisfactorily in the presence of notches at design temperature. This is the approach presently incorporated into API 650 (Appendix D) and API 620. and is also being considered by ASME Special Committees. The Nuclear Code (ASME Section III) goes still further by requiring impact tests for all ferritic steels regardless of service temperature.

In the area of materials selection, the most promising improvernent insofar as resistance to brittle fracture is concerned is the development of steels with enhanced noten toughness, such as ASTM A516 for plates and A524 for pipe. These specifications include requirements for high Mn/C ratio, fine grain steel making practice. and heat treatment, all known to improve resistance to brittle fracture. Unfortunately, comparable specifications have not vet been developed for forgings.

Another approach toward minimizing brittle failures lies in reducing allowable stresses for low temperature applications. Both ASME Section VIII and ASA B31.3 are in fact doing this for temperatures below -20 F. Impact tests are not required if allowable are 40% and 15% respectively of their room temperature value. This restriction maintains applied nominal stresses in the 2,000-7,000 Ib./sq.in. range which is below the level at which brittle fractures would be expected to propagate. Except for thin-walled shells, this approach is clearly uneconomic.

What the industry practice is

Progressive industry thinking and practice is leading the way toward greater conservatism and safety in the realm of brittle fracture prevention. The trend is set by leading designers, fabricators, and users of large, critical pressure equipment, most of whom adhere to self-imposed standards more rigorous than the ASME Section VIII Code rules. This discrepancy is accounted for by the normal time lag between the evolution of new practices and their eventual recognition and adoption by the Code.

There is general agreement among the large ammonia producers that the existing Codes should be supplemented to provide added protection against brittle fracture 'n process and storage equipment. Such supplemental requirements are not imposed arbitrarily but are applied with discrimination according to the anticipated service conditions. the degree of hazard and the potential damage. The following listing of typical additional requirements and safeguards is a conglomerate, compiled from various company specifications design standards, and shop practices. For sake of conformity, they are sub-divided into the same categories employed in the Code, i.e., Materials, Design, Fabrication, Inspection, and Testing.

1. Materials

Materials are ordered to specifications which provide reasonable expectation that the notch toughness will be satisfactory at the lowest design temperature of the equipment. Optimum assurance is, of course, attained by ordering the material to conform to impact test requirements at or below design temperature.

a. Materials Selection - As design temperature decreases and thickness increases, plate materials are selected from the following specifications, listed in order of expected increasing resistance to brittle fracture:

A parallel ranking of common piping materials would be A53, A106, and A524, the last being the most resistant.

b. Impact Testing - Impact testing is required for pressure parts below some arbitrary temperature limit, typically 0 F., $+32$ F., or $+60$ F. While some companies may impose these limits for all materials and thicknesses, most restrict it to heavy plates and forgings and to high-strength steels. Impact test requirements are increasingly based on Charpy V-notch rather than keyhole specimens, reflected in the typical requirements cited below:

2. Design

Weids are specified to be full penetration and free from undercuts and surface defects. Blind root fillet weids are not allowed, in order to guard against the introduction of harmful notches in welded connections, joints, and attachments.

3. Fabrication

a. Impact tests of weids and heat affected zones is required

in weiding qualification procedures for temperatures higher than -20 F, especially for high-strength materials and for heavy sections. The minimum test result criteria norally parallel those established for base material.

b. Postweld heat treatment is specified for all thicknesses, in order to reduce residual stresses from weiding and forming operations.

4. Inspection

Magnetic particle inspection, dye penetrant inspection, and ultrasonic inspection of plates, forgings, and weids are specified as a supplement to mandatory radiographic inspection. The intent is to discover defects, seams, sub-surface laminations, slag inclusions and other flaws or defects which can become focal points for brittle fracture.

5. Testing

The metal temperature during hydrostatic test is specified to be higher than the expected minimum temperature at which the material will be ductile to prevent brittle fracture during the test. For mild carbon steels, typical temperature-thickness limits are as follows:

The limits recognize the effect of thickness on brittle fracture, but do not take into account the influence of chemistry, miero-structure, stress relief, etc.

Precautions in new plants

In place of a conventional summary. we thought it more useful to conclude this discussion of brittle fracture hazard with some practical guidlines for minimizing it. Obviously, such a complex and controversial subject as brittle fracture does not lend itself to a set of simple, universally applicable set of rules. The task is further complicated by the fact that formulation of safety practices is influenced strongly by individual company policies and attitudes. Since new plants naturally present greater opportunities for providing fracture-safe construction, they are considered separately.

With Code requirements as a minimum, supplements should be made to materials, design, fabrication, inspection, and testing

requirements, as outlined in the section on Industry Practice. It bears repeating that these Code adjuncts ought not be applied across-the-board but selectively, to suit the individual equipment and circumstances. They are especially pertinent to equipment in the temperature range from ambient to -20 F., where the Code has no specific provision. The extent of upgrading will be influenced by technical factors such as temperature and thickness, as well as by consideration of the degree of hazard and consequences of failure.

Among the most important supplements to Codes are those aimed at providing materials that will not be brittle at design temperatures. This may be achieved by selecting improved steels (e.g. A516) or, more positively. by impact testing of materials at design temperature. Such changes will in most cases raise the cost of equipment. Additional expenses can be surprisingly large if they involve impact testing of massive components. For instance, in one recently built ammonia plant, impact testing the heavy wall forgings of a high-pressure exchanger added nearly \$25,000 to the base cost of \$100.000. Changing plate material specifications from A201, A212 or A285 to A516 will increase steel costs by 5 to 15%.

The operation most ükely to increase the possibility of brittle fracture is repair and maintenance weiding. The simple operation of weiding on a support clip to a pressure vessel will introducé residual weiding stresses at yield point level. will leave a stress raiser at the root and toe of fillet weids, and can leave the weid heat affected zone with low ductility. Careful consideration should therefore be given to weiding design and procedure, non-destructive testing, and postweld heat treatment for field weid repairs on steel equipment which will operate or be hydro-statically tested in the ambient temperature range.

Another aspect of safeguarding existing plants against possible brittle fracture accidents concerns changes in process or operaüng conditions. Thus. any decrease in temperature or increase in pressure in the ambient temperature range should consider the accompanying increased possibility of brittle fracture. This applies not just to the magnitude but equally to the rate of change of temperature and pressure. because sudden pressure surges or rapid chilling are more apt to be damaging than severe steady-state conditions.

Finally. unusually cold wintertime temperatures should be recognized as a source of increased hazard, especially for storage tanks and equipment whose metal temperatures are closely affected by climatic conditions. Any change in operation which could produce higher than normal loads should at such times be undertaken with extra caution. Similarly, deliberate effort should be made by operating personnel to prevent mechanical or hydraulic shock. The controlling effect of low ambient temperatures on brittle fracture is made evident by the fact that practically all the recorded brittle failures have occurred during exposure to cold air or water.