Cracking in High Temperature Shift Converter

Continued depressing experience with three large pressure vessels made of 0.5 percent Mo steel alloy has led to specifying 1 percent Cr Mo instead, plus other changes.

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Stress corrosion cracking in equipment that handles liquid ammonia is a very serious hazard which, nevertheless, can be minimized. Much has been written on this subject over recent years and work is still in progress.

The first part of this article will review the situation in very general terms including the incidence of cracking, the probability of contamination being present, and what Imperial Chemical Industries Ltd. (ICI) is doing about it. The second part relates to measurements of the oxygen content of the ammonia in a new 12,000-ton tank during the purging and commissioning period. Facts on what goes on during such an operation have been sadly lacking.

Liquid ammonia has been handled in steel equipment for at least 50 years. It was only about 1960 that it was recognized as being capable of stress corroding some steels, and the paper by Loginow and Phelps *(1)* dealing with the cracking of small agricultural tanks is the start of the story. As is well known, it was shown that ammonia did not cause cracking unless it was contaminated with oxygen (and perhaps CO_2) and that addition of about 0.2% water inhibited the cracking.

No more incidents were reported until the T1 road tanks had been in service a few years and were found to be cracking: this led to further work and culminated (in the USA) in the Department of Transportation (DOT) 1975 regulations, which required 0.2% water to be present in all ammonia transported in quenched and tempered (QT) high-strength steel tanks. Ammonia not containing 0.2% water was to be transported in stress relieved non-QT tanks.

In Denmark, where all ammonia is imported, the chance discovery of fabrication cracks in a new storage vessel about 1969 led to existing vessels being re-examined. Though some manufacturing defects were discovered, a high proportion of the vessels were found to contain stress corrosion cracks. This has led to tanks in other European countries and elsewhere in the world being examined more critically than before, and more cracking has been found.

A large number of companies have co-operated in sharing information on the incidence of stress corrosion cracking by sending reports to one of the authors (Dr. A. Cracknell), who periodically summarizes and distributes it. Some details are given below.

Sixteen sponsoring companies in a group

Under contract to a group of 15 European and one Japanese sponsors, the Fulmer Research Institute embarked in 1971 on a program to tie down the factors which controlled cracking of the ordinary steels used for large and small storage tanks, which in the USA had been regarded as free from trouble. American co-operation was invited but no one joined in. The programmed work has been concluded; many specimens of ordinary steels cracked, but the delineation of the critical region of composition has not been as successful as hoped, partly because it is not sharply defined, partly because it is at the edge of the range of variables it was planned to explore. This work will be published.

Over the same period Radd and Oertle *(2)* published work in which by an indirect route they concluded that oxygen was an injibitor of stress corrosion by ammonia. This conclusion is in conflict with practical experience and with the other laboratory investigations, and it is not accepted.

Later work was done by Deegan *(3)* and supported Phelps' original views, with an unexpected additional point; it is necessary for both oxygen and nitrogen to be present for stress corrosion to occur. Nitrogen is present in ammonia "as produced" and since the common contaminant is air, nitrogen is always likely to be present with oxygen.

The Fulmer work was based on redistilled ammonia, the purest available, but said to contain 50-70 ppm. nitrogen. As the effect of nitrogen was not suspected when the work started it was not treated as a variable, and the results neither confirm nor deny the effect of nitrogen. Deegan was clearly able to get the nitrogen content so low in relation to the oxygen content that its absence changed the behavior.

Ammonia is made in production plants, it goes via pipelines or transport tanks to storage: it may be transported again to customer storage, and it is then used in a variety of ways. There are highly significant differences between the conditions and steels used in contact with it during these various stages.

Ammonia is formed as gas in the production unit converter, and the exit gases are roughly 3:1 hydrogen and nitrogen, 20% ammonia, some 3-10% methane and argon, and traces of other gases, at a total pressure of 150-350 atm. The gas is cooled to say −10°C/+20°C depending on the design, and the ammonia condenses and is collected in the catchpot.

In a modern unit the catchpot is quite a large vessel, and high-strength steels are economic. Quite a number of catchpots are of multilayer construction with the circumferential welds not stress relieved, and some use steels of 70,000 lb./sq.in. yield for the core tube and the layers, and have hardnesses above 300 Hv. near the welds.

The high-pressure heat exchanger in which the ammonia actually condenses may be built using forgings of similar steels. A multiplicity of lower pressure vessels handle the ammonia as it is let-down and used for in-plant refrigeration. There are also various pumps, control valves etc. The steels used are usually the conventional carbon manganese steels; and welds are not usually stress-relieved unless the code demands it on a general "thickness" basis or from brittle fracture considerations.

Cracking in production units. Very little trouble which might be ascribed to stress corrosion has been reported in production units. Class and Gering *(4)* reported cracking in a special forged high-pressure (HP) catchpot in 1963 after six years of service. This was a 1¼% Cr-Mo steel heat-treated to over 94,000-lb./sq.in. tensile strength. They also report failure of Cr-Mo springs (460 Hv, equivalent to about 250,000 lb./sq.in.).

In-plant storage is distinguished from customer storage in that chances of contamination of the ammonia, which is piped direct from the production unit, would seem very small. All units have what may be considered "in-plant storage" vessels of one sort or another, made of fairly low strength steels, and some have large pressure spheres or refrigerated vertical tanks.

Cracking in in-plant storage. There are three reported cases of stress corrosion of pressure spheres fed directly from a production unit.

Transport tanks include road and rail tanks designed to withstand the vapor pressure of ammonia at ambient temperature, and also ship tanks which may be designed either for full pressure, or for operation with refrigeration to keep the pressure low. Weight is an important factor with road and rail tanks especially, and high-strength steels are used. Even so, in Europe this tends to mean a proof strength rarely exceeding 65,000 lb./sq.in. whereas in the USA, the T1 tanks had over 100,000 lb./sq.in. Some Malayan rail tanks have been made of 9% Ni steel. Because of the vibration problem etc. it has always been a requirement in the UK that road and rail tanks should be stress relieved even when of low strength (30,000 lb./sq.in. yield) steel. This had not been a requirement in the USA.

Cracking in transport tanks. This has been a major problem with Tl in the USA, and there has been some trouble elsewhere. It is discussed along with cracking in storage tanks in a later section of this article.

Customer storage tanks vary from small or large horizontal tanks and small spheres operating at ambient temperature to 1,000 to 5,000-ton spheres operating at e.g. −10°C and 30 lb./sq.in., and fully refrigerated vertical tanks. The steels used would not be classed as "high-strength" because for the bullet design the pressure is not at a level that would make such steels economic; and for spheres and vertical tanks site-welding makes high-strength steels inappropriate. The steels used for such tanks do not exceed about 50,000 lb./sq.in. yield, and many are nearer 30,000 lb./sq.in. yield. Cracking is discussed later.

Oxygen and water are important factors

The following paragraphs relate to the oxygen and water contents of liquid ammonia, which are vital factors in stress corrosion. No data is available on nitrogen content. In early work it was suspected that CO_2 contamination increased cracking and that oil might reduce it, but laboratory work has not shown that these are important and they are not discussed.

The analysis of ammonia for water and elemental oxygen is important in relation to the danger of cracking. There is no difficulty in getting reliable results for the water contents that are of interest, say 50 to 5,000 ppm. The oxygen content of interest in relation to high-strength steels in ammonia of low water content is 1 ppm. or less, and this is at the bottom limit of established analytical methods. A variety of samples have been taken from the production plants at Billingham, and analysis has shown around 1 ppm. in spite of great care in purging sample bottles and the apparatus.

From the chemical aspect it is unbelievable that 1 ppm. can be present in, eg. the HP catchpot. Based on the partition between gas and liquid, *if* there were 5 ppm. in the circulating gas in the loop, the content in the condensed liquid is estimated at 0.04 ppm. w/w/. The 5 ppm. in the gas arises from an analytical determination of "less than 5 ppm." The gas has, however, come through HTS, LTS, and methanator and the catalysts would be expected to ensure combination of any oxygen with the vast excess of hydrogen.

Data is available on a catalyst similar to LTS catalyst: in a nitrogen 3% hydrogen mixture, at 300°C it would reduce the oxygen content from 3% to 10 ppm., and would be expected to reduce lower oxygen contents in the same ratio. The methanator catalyst is expected to be comparable. The ammonia converter catalyst may not be fully effective in those loop designs where the make-up gas is added after the converter but before the catchpot, but the oxygen partial pressure in equilibrium with Fe/FeO is 10^{-30} atm.

The only sources of oxygen are slip in the secondary reformer, and air additions to CO_2 removal systems. On plants cleaning up the gas by a liquid nitrogen wash unit, the oxygen content of the nitrogen would seem important but in such plants the make-up gas sees the ammonia converter before the catchpot.

It is therefore believed that the oxygen content of the ammonia "as made" is nearer to 0.0001 ppm. than to 1 ppm., and analytical methods (and perhaps sampling techniques) are quite incapable of such measurement. Work on a new method of analysis is being done at Billingham and may permit a major improvement.

The water content of ammonia "as made" depends on the elimination of water vapor from the wet make-up gas and is affected by the efficiency of compressor aftercoolers and catchpots, and cooling water temperature. It normally runs at 100 to 3,000 ppm. The low oxygen content is believed to account for the immunity of production plant equipment even though some of it would be expected to be as sensitive as Tl steel.

Contamination and ways to minimize it

In any situation where ammonia is put into transport tanks and from the transport tanks into consumer's site storage, there is a risk of contamination with air. At the least, the air in the flexible filling arms, couplings, etc., will be swept into the tank. At the worst, if the tank being filled starts full of air and no measures are taken to purge the air, contamination can be high.

Usual practice is to sweep out the air with ammonia gas until tests show that little air remains, then to raise the pressure and feed in liquid, continuing to vent gas, and finally to gag the vent so that the liquid feed no longer vaporizes. Details depend on whether it is acceptable to chill the bottom of the tank to −33°C, the temperature which would result if ammonia was allowed to vaporize freely. The amount of ammonia used in purging can be considerable, and difficulties can be encountered in disposing of the contaminated ammonia vapor. Obviously purging can be done badly, and perhaps it often is. Practically no data is available on the results achieved.

Transport tanks are normally returned for refilling containing a little liquid ammonia, and at pressure. The only contamination during refilling should be that inherent in the connections. Internal examination of the tank for cracks creates the situation requiring purging.

Tanks on ships are of various types but as regards contamination (neglecting any other cargoes shipped) are not different from the usual pressurized transport tank or the refrigerated storage tank.

Contamination can occur in two types of static storage tanks: those operating below normal ambient temperature and those operating at ambient. Cold storage tanks suffer a degree of heat inleak; therefore some degree of boil-off occurs continually. Because of the high partition ratio of oxygen, the boil-off will tend to remove oxygen. This boil-off is either used in consumer units or is compressed, refrigerated, and returned to the tank.

The refrigeration cycle separates the inerts (O_2, N_2, CH_4, etc.), and they are not returned to the tank. Any tank operating cold, therefore, has a built-in mechanism which will reduce the concentration of contaminants in it. It is noteworthy that these contaminants become concentrated in certain parts of the refrigeration system—the compressor catchpot, etc.—and not surprising that one or two cases of stress corrosion have been reported in this area.

It is common practice to couple a tank to be filled by two lines, one to convey the liquid and the other to return any boiled off ammonia to the source. This gas balance line will convey to the supply tank any air, etc., in the tank being filled, which may contaminate the main tank. This is a possible explanation of the cracking of three spheres mentioned above which were fed only by the output of a producing plant.

Cracking in storage and transport vessels

After 1970, when the first reports of cracking in storage vessels came out of Denmark, Imperial Chemical Industries, Ltd. (ICI) agreed with the other members of the (UK) Chemical Industries Association Working Party on the Handling of Ammonia to collect reports on the examinations of storage and transport vessels and periodically to circulate the information to the participating companies.

It was hoped that an examination of this data would give an appreciation of the extent of the problem and perhaps suggest ways in which cracking might be avoided. Though initially only European companies contributed information, more recently companies in Australia, Japan, and South Africa have taken part. Summaries of the information collected have been circulated in 1971, 1973, and 1976 to the cooperating companies and to others who have expressed an interest.

Very few companies in North America have taken part in this exercise, and perhaps as a consequence all the vessels included in the 1976 survey had yield strengths below 70,000 lb./sq.in. and many were below 50,000 lb./sq.in. In spite of the relatively low strengths, a high proportion (60 out of 93) were said to contain cracks of varying degrees of severity. None had leaked or ruptured and all appear to have continued in service after weld repairs, after simply grinding out the cracks, or at a reduced pressure after grinding.

The bare statistics do not give a fair impression of the incidence of cracking. Undoubtedly companies that have not found cracks have less interest and a lower motivation towards taking part in voluntary information sharing exercises. Moreover, 40 of the cracked vessels were from a single batch of identical rail tankers, five from another batch of nine identical tankers. If we class these groups as single "incidents," we still find that there were 17 incidents of cracking in 46 examinations reported.

The survey gives some support for the value of water additions but the evidence is not conclusive. Water certainly appears to prevent cracking of 9% Ni steel and is said to prevent cracks growing in precracked fracture mechanics test pieces.

In some cases, however, cracks have been found in spite of additions of 0.2% water, but this is always in vessels where there was a history of cracking before the water was added. It is possible that these cracks were formed during the previous service and though present at the time of the original examination, were not detected or removed.

Reports have been received of oxygen contents ranging from 0.4 ppm. to 150 ppm. Some details are given later. It is clear that oxygen can vary enormously, though sampling and analytical techniques are difficult and reported values possibly misleading.

Excluding the analysis of the ammonia, the factors considered important in stress corrosion cracking are the operating temperature, the strength of the steel (and weld metal) and whether the structure has been stress relief heat treated. To demonstrate the effects of these factors Figure 1 is a plot of the information given in the two most recent vessel inspection summaries. In it the specified minimum yield strength is plotted against the declared operating temperature using different symbols to indicate whether or not stress corrosion cracking was reported. Almost all the reports are of as-welded vessels and the few cases in which stress relief was applied are marked SR.

The strong effect of temperature on the risk of cracking is immediately obvious. Almost all the vessels in which cracks were reported operated at 0°C or above. The division is not absolute, however, for cracks have been reported in a sphere operating at $-20°C$ in Japan and while this paper was being written, of a sphere in South Africa operating at $-6°C$.

It is not at all clear if the effect of temperature is simply that the cracking reactions go faster at higher temperatures, or that cold vessels usually have associated refrigeration units which purge off suspected causative agents such as oxygen and nitrogen or whether there is some more subtle effect as suggested by G. H. Arup *(5)*; i.e., that when ammonia condenses on the walls of a tank, above the liquid level, it has a composition different from and more aggressive than the bulk liquid. This latter situation can only occur with relatively warm storage in which the ambient temperature falls below the bulk liquid temperature.

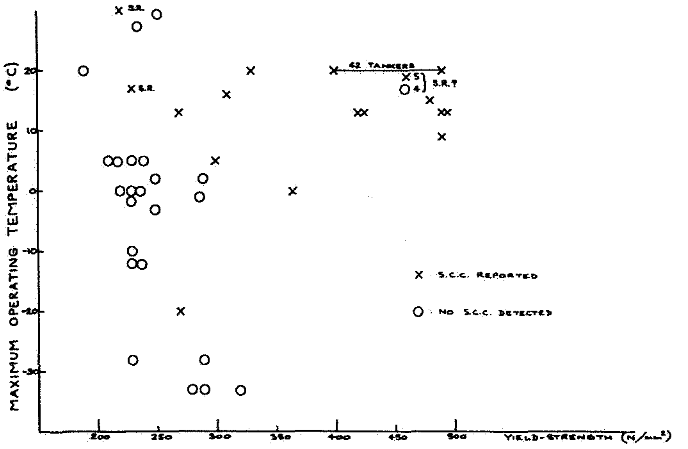

Figure 1. Effect of operating temperature and yield-strength on stress corrosion cracking of ammonia containers.

The effect of steel strength is also very marked. Cracks were reported in every as-welded vessel made from steels having proof strengths over 50,000 lb./sq.in. Steels having lower proof strengths are not immune but clearly the risks are much less.

Little or no information has been collected on stress-relieved vessels, largely because no one considered there was a risk of their cracking when made from steels having yield strengths up to 70,000 lb./sq.in. Many examinations have been made of fully stress-relieved vessels and no cracks found. Where cracking has been reported in spheres, it has always been in the as-welded parts, never in the stress-relieved plates to which the legs and nozzles are attached.

Recently, there have been reports from two companies of cracks being found in stress-relieved vessels. In one case, cracks were found in the welds of five out of nine identical rail cars. At one time it seemed significant that the cracks were at the same end of the vessels, suggesting non-uniform temperatures during heat treatment. This now seems less likely because five different fabricators were later found to have been involved. The proof strength of the steel was 66,000 lb./sq.in., much lower than that of Tl steel but presumably high enough to represent a risk unless 0.2% water is added to the ammonia.

The other two cases reported by a Japanese company are not explainable in this way. Both occurred in vessels made of the same low-strength steel (yield strength 31,000 lb./sq.in.) and had similar dimensions but were fabricated with a nine-year interval between them. The extent of the cracking was relatively small—600 mm. long × 0.2 to 0.6 mm. deep in one case, and 16 mm. long × 4.5 mm. deep in the other. And, though cofirmed by microscopical examination as stress corrosion cracking, they must probably be ignored as evidence of the many hundreds of stress-relieved low-strength steel vessels which have shown no signs of cracking.

Guidelines to avoid stress corrosion cracking

There is as yet insufficient evidence on which to write firm rules that will guarantee the avoidance of stress corrosion cracking. Any such rules will have to account for the operating temperature, strength of the steel, post-welding heat treatment, and the analysis of the ammonia both in service and when the vessel is being purged of air during commissioning.

Rules governing vessels for service in ammonia plant loops with their very low oxygen contents will inevitably be different from those applied to vessels for storage and transport where there appears to be much more opportunity for contamination with oxygen.

Tentative rules for the construction and operation of vessels for storage and transport derived from the practical experience summarized in Figure 1 are given in the following, covering choice of steel, analysis of ammonia, inspection frequency, and purging of vessels.

Choice of steel is indicated in the information in Table 1. Naturally any local statutory regulations for handling ammonia or rules for the avoidance of brittle fracture must be also taken into account when making a decision.

Analysis of ammonia. The only control currently exercised over the composition of ammonia to avoid stress corrosion cracking is the addition of about 0.2% water. This is not permissible with all grades of ammonia and though efforts may be made to avoid contamination with oxygen (where water cannot be added), the incidence of cracking shows that this control is not always effective. In fact very few companies have reported that they measure the oxygen content of the ammonia in an attempt to control contamination.

Even if the oxygen were measured there is little published data to show what is an acceptable level. Therefore, guidelines have been drawn up for as-welded vessels based in part on reported industrial experience, part on the now completed work of the Fulmer Research Institute on the effect of ammonia analysis on the probability of cracking (which it is hoped will soon be published). Not all the data is consistent, so that the guidelines may be changed as further experience

Table 1. Factors involved in choice of steel

Specified Minimum Yield	Specified Minimum Strength	Maximum operating temperature	Comments
1,000 lb./sq.in.	**N.sq.mm.**		
>70	>460	Any	Do not use without taking expert advice.*
50-70	350-460	Any	Shall be stress relief heat treated.
<50	<350	−5°C and above	Shall preferably be stress relief heat treated.
<50	<350	Below −5°C	Stress relief not mandatory.

*Based on lack of experience in Europe of such high-strength steels in ammonia

Table 2. Ammonia analyses and indicated cracking experience[1]

Company[2]	O_2 ppm. w/w	H_2O ppm. w/w	Experience of cracking
P	5-15	<100	None found
Q	5-6, including argon	2,000	Many cracks in spheres. Water has not always been added.
R	118-154	200/300	Many cracks in a sphere. Cracks propagated in test pieces.
R	118-154	2.000	Cracks did not propagate in test pieces.
ICI Billingham, S	0.4-2.5	80	No cracks in storage vessels. But cracks readily form in 9% Ni steel bend test pieces.
ICI Severnside, T	2-5	200-1,300	No cracks found in spheres (−12°C).
U	1	2,400	No cracks found in sphere. in stress relieved 9% Ni rail tankers or in 9% Ni steel U bend test pieces in the tankers.

[1] In as-welded vessels made of steels with specified yield strengths less than 50,000 lb./sq.in. and operating above −5°C.

[2] Letters are codes for four companies other than ICI.

accumulates on the analysis of ammonia and the risk of cracking. Reported analyses of ammonia coupled with experience of cracks in as-welded vessels made of steels having specified yield strengths less than about 50,000 lb./sq.in. and operating above −5°C are given in Table 2.

It is suggested that as a minimum the oxygen and water contents of ammonia handled should be monitored regularly and the results obtained compared with the criteria given in Figure 2. (CO_2 and nitrogen should also be checked in case they subsequently turn out to be significant.)

Inspection frequency. Figure 2 is divided into three areas —*A*, *B*, & *C*—separated by lines which, according to the Fulmer work, represent constant probabilities of cracking. The reported industrial experience is superimposed on the graphs.

Area *C* represents compositions in which there is a very high risk of cracking. No vessels should operate with ammonia of these analyses.

Area *B*. There appears to be a finite risk of cracking with ammonia of these analyses but this is not proven. Company *P* appears to operate satisfactorily in this area but inspects their vessels at two-year intervals. Most companies require inspections at about six-year intervals. It is proposed that if the ammonia analyses regularly lie in this area the vessels should be inspected for cracks at least twice as frequently as is required by local regulations, but not necessarily more frequently than once every two years.

Area *A*. The risk of cracking with ammonia of these compositions is small. Except where there is reason to suspect cracking (eg., as at Company *Q*) vessels should be inspected at a frequency determined by local regulations.

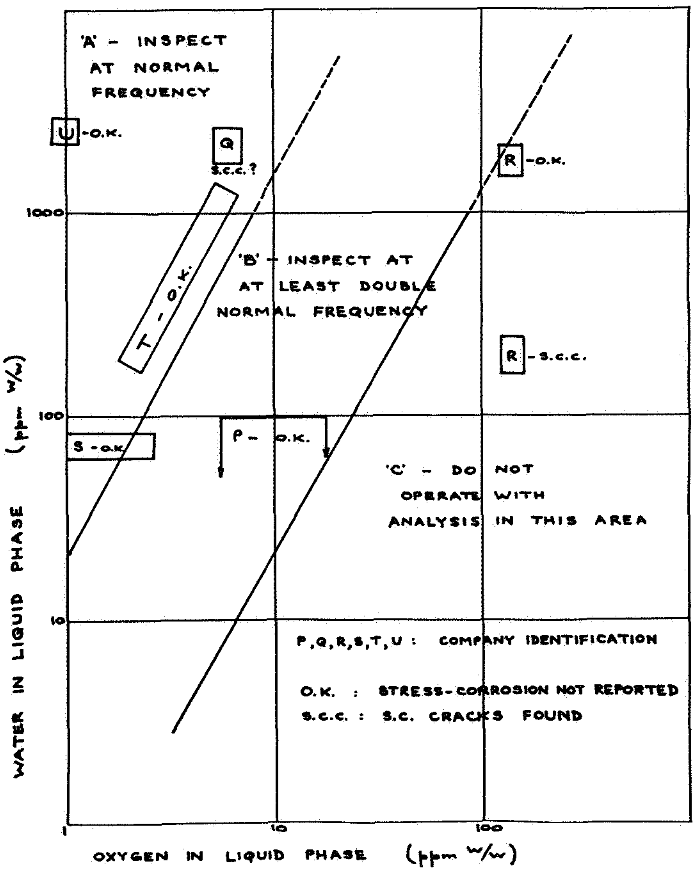

Figure 2. Reported stress corrosion cracking and ammonia analysis: proposed inspection frequency.

Too few data are available to show if these requirements are unnecessarily restrictive, but unless information is collected we shall continue to have reports of vessels being found to be cracked and not be able to pin down the cause.

Purging of vessels. An implicit assumption of the proposed guidelines is that cracking is a relatively slow process and that routine monitoring of the oxygen and water content is sufficient. Transient high oxygen contents can occur during commissioning when the vessel must be purged of air. Until it can be proved that cracking is slow, it is important to reduce the oxygen content of the ammonia as quickly as possible to the normal operating level.

Some recently collected data on the movement of oxygen during commissioning a tank are given in Part 2 of this article. This does confirm that enhanced oxygen contents occurred in the liquid phases present but not so high or as dangerous as would have been expected from the gas phase analyses. A check will be possible when another tank is recommissioned later.

Oxygen content in ammonia tank

The details given here relate to the commissioning of a third 12,000-ton tank in a complex containing two 12,000-ton tanks, each with its regrigeration unit, fed by pipeline from producing units. No. 3 tank relies on the refrigeration units of Nos. 1 and 2. No water is added to the ammonia.

Figure 3 shows the essential features. Table 3 gives the analyses at the times indicated: the analysis points are marked on Figure 3. No measurements of flows are available.

The sequence of operations was as follows:

1. Gas Purge: Gas from No. 1 tank top was passed to the top of No. 3 and to atmosphere from a temporary stack from the bottom of No. 3. The requirement was to exceed 90% ammonia in the exit gas: in fact 97% was reached.
2. No. 3 closed, pressurized with ammonia to about 0.5 lb./sq.in. gauge, and checked for leaks.
3. Meanwhile, the No. 1 refrigeration system liquid and purge gas was analyzed to get baseline data.
4. Cooldown. Sprayed liquid ammonia ex No. 1 tank

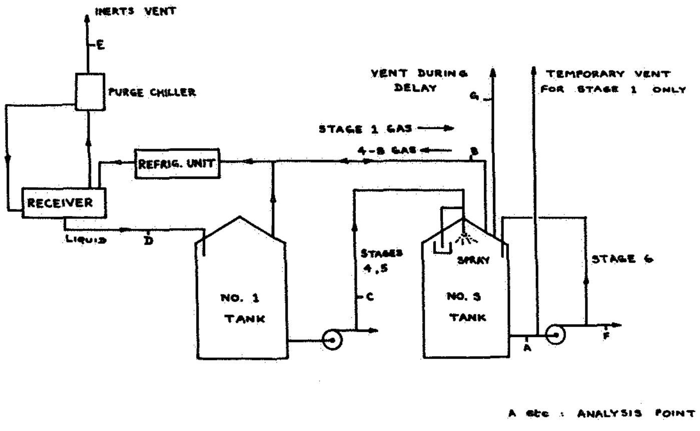

Figure 3. Simplified diagram for commissioning procedure.

Table 3. Oxygen analyses in 12,000-ton ammonia storage tank

				Analyses ppm. V/V oxygen							
				E	D	A	B	C	F	G	
				Exit No 1 Refrig. Unit.							
Stage	Date	Time	Tank Temp °C	Purge Gas	Liquid	Tank bottom gas	Tank top gas	Liquid feed ex No. 1	Export from No. 3	Top vent	
1 Gas	15.7	—	—	—	—	start	—	—	—	—	
Purge	17.7	14.15	—	—	—	80% NH_3	—	—	—	—	—
	20.7	—	—	—	—	97% NH_3	—	—	—	—	—
3 Baseline	15.7	11.00	—	—	—	—	—	0.4	—	—	—
No 1 Refrig	17.7	19.00	—	550	0.5	—	500	—	—	—	B figures are gas feed from No 1 Tank
unit	18.7	11.00	—	350	0.5	—	320	—	—	—	
	18.7	19.30	—	—	—	—	500	—	—	—	—
	21.7	11.00	—	300	0.7	—	—	—	—	—	—
4 Cooldown	21.7	15.00	20	5,400	5.3	11,000	4,200	—	—	—	Layering causes difference A-B
	21.7	17.00	4	—	—	—	—	—	—	—	
	21.7	19.00	0	4,800	4.4	14,000	3,000	0.5	—	—	—
	22.7	00.00	-12	6,800	2.1	—	—	—	—	—	—
	23.7	05.00	-30	—	—	—	—	—	—	—	Probably liquid on bottom
Delay	23.7	19.00	—	—	—	—	—	off	—	4300	Unplanned delay
	28.7	19.00	—	—	—	—	—	off	—	1900	Gas vented at G
	29.7	13.30	—	—	—	—	—	off	—	1100	—
Restart	31.7	00.15	—	2500	2.0	—	860	0.8	—	—	—
	31.7	16.00	—	8,300	4.1	—	730	—	—	—	—
	1.8	03.30	—	8,400	1.4	—	730	—	—	—	—
5	1.8	19.15	-33	2,950	2.3	—	600	0.9	—	—	Definite liquid on btm.-float lifts
	2.8	10.30	-33	2,850	3.4	—	1,250	0.8	—	—	—
	3.8	11.00	-33	5,100	3.3	—	570	—	—	—	Six feet liquid in tank
	4.8	10.30	-33	9,400	5.9	—	500	—	—	—	—
	5.8	11.00	-33	2,800	1.9	—	530	—	—	—	—
	6.8	15.30	-33	2,800	2.7	—	460	—	—	—	—
6	9.8	15.30	-33	—	—	—	—	—	0.4	—	export pump
	10.8	14.30	-33	—	—	—	—	—	0.4	—	recirculation
	17.8	—	—	3,400	0.7	—	660	—	—	—	—

into the top of No. 3 at a rate which caused No. 3 to cool at about 5°C/hr. The required rate was estimated at about 0.75 t/hr but was not measured. Control was on the tank metal temperature as indicated by a thermocouple which was about 6 ft. up the wall instead of at the bottom as planned. The vapor generated was taken by No. 1 refrigerated unit and the liquid returned to No. 1 tank. Analysis was done at intervals on samples from various points.

During this stage there was an interruption in the ammonia feed at a time when there was probably liquid already present on the tank bottom but not showing on the level gauge. This liquid was allowed to vaporize through a vent on the tank top. Spraying was resumed, and when it was clear that the tank bottom was at −33°C the spray was bypassed and liquid from No. 1 fed in until there was about 6 ft. liquid in No. 3.

5. The No. 3 export pumps were then commissioned, using the spill back line. Regular analyses were continued.

The analyses in Table 3 were by methods regarded as the best available at present, and have a reproducibility of about ±3%, with calibration on large bottles of gas mixed under pressure. Liquid was sampled after thorough purging by repeatedly trapping a known volume of liquid between valves and allowing it to vaporize completely into a known large volume. Details of the techniques are available and will be published. Even so the analyses varied with time in an unexpected manner. There are no other known sources of oxygen to the tanks or refrigeration units.

The ratio between oxygen in the liquid and the gas purge from the refrigeration unit would be expected to be constant but this is not found. It varied from 500:1 to 5,000:1. In particular it was less than 1,000 during the "baseline" measurements, but 5,000 at the end of the period. One possible explanation is that there is a constant error in the liquid samples; i.e., zero oxygen is measured as about 0.5 ppm./V/V. This would fit the fact that determinating of oxygen from the production unit catchpot show about 0.5 ppm. as against the very much lower figure that would be expected.

The data suggest that No. 3 tank had liquid ammonia on the steel surface with a significant oxygen content only over the period 22.7 to about 28.7. After this period the vented gas had only 1,000 ppm. oxygen, which suggest eg. 3 ppm. O_2 in the liquid. If the feed of liquid had not been interrupted, the concentration would have fallen more quickly by dilution. Ten days later the oxygen was very low.

The observations on the streams from the refrigeration unit show, as expected, that the returned liquid carried appreciable oxygen back into the tank system, though the significance of this depends on the flow rate and its relation to other flows into and out of the tanks which would dilute it, on which measurements are not available.

Future work plans

One of the first uses of No. 3 tank will be to permit emptying and full inspection of No. 2 tank, last inspected in 1969. After inspection, No. 2 will be recommissioned using a procedure similar to that described above; and it is hoped to make similar observations but get more details or estimates of flow rates and also water contents. Similar data will also be obtained in relation to other types of tank, and it is to be hoped that other operators will do similar work. Only by such investigations will it be possible to decide whether the cracking found results from general exposure conditions during the life of the tank or from severe conditions produced during the commissioning period.

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CLARK, W.D.

DISCUSSION

L.A. ZEIS, Pullman Kellogg: You have a statement about the Nelson chart which says—in conclusion #1D, "The resistance of half percent molybdenum steel to hydrogen attack appears to be less than the Nelson curves suggest." I'd like to comment to say that the type of cracking which you reported in the last two vessels, and that which Dr. Liebe described, is not the Nelson chart type of hydrogen attack.

True, it's damage in the presence of hydrogen but there appears to be an embrittlement which can be transitory depending on the conditions. It's not necessarily a permanent type of damage if it's handled properly. —I would like your comment as to whether or not there has been some actual decarburization or damage which the Nelson chart does describe.

CLARK: There has been no decarburization, so-called hydrogen attack, which the Nelson curve deals with, on the inside surface of the vessel at any point that we've found. That aspersion on the steel is based from, I think, Japanese work which suggested that the Nelson curve is a little bit optimistic. It has had stones thrown at it by other people. I don't like it much either, so fine, let's not argue any more, let's use 1% chrome-moly which is better. I'm afraid that's the way our minds are working.