High-Temperature Shift Converter Problems

Two specific case histories of failures follow a general review of the operating conditions in the four designs of ammonia plant shift converters

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The reason for this discussion is that our company has had cracks in the bottom heads of two high-temperature shift converters. These units were made for two different engineering contractors by different manufacturers, and they operate at different temperatures and pressures.

Inasmuch as I have spent most of the last 35 years in chemical plant operations, I am not an expert in anything. I know my limitations in methallurgy, pressure vessel design, and equipment fabrication. I will, therefore, point no fingers nor form any conclusions.

The vessels to be described are catalytic units which convert carbon monoxide to carbon dioxide, which involves reacting the carbon monoxide with steam. This is a classic text-book reaction called the carbon monoxide-water-hydrogen shift. The vessels in which this reaction is carried out have been called shift converters. Back between the two big wars and shortly thereafter, this was done at low temperature and with frequent catalyst changes. This was when gas was principally and expensively manufactured from coal.

With the advent of cheap natural gas, more wasteful high-temperature shift converters with their more rugged catalysts were, for a period, used almost exclusively. This use of high-temperature shift converters only resulted in higher methanation loads and higher synthesis loop purging. With the better gas pre-purification methods in the 1950's, most of it more efficient sulfur removal, a combination of high- and low-temperature shift converters came into use.

Reference to shift converters in the remainder of this discussion means *high-temperature* shift converters. The operating conditions in the four designs of shift converters the CF Industries now uses will be reviewed and then the two failures will be discussed.

CF Industries operates ammonia plants with shift converters designed by the following companies: D.M. Weatherly, a centrifugal plant; Pullman-Kellogg, a centrifugal plant; Chemical Construction, and C&I/Girdler, each reciprocating plants. The shift converters operate under the following temperatures and pressure conditions: D.M. Weatherly, 440 lb./sq.in.gauge at 850°F; Pullman-Kellogg, 450 lb./sq.in.gauge at 800°F; Chemical Construction; 275 lb./sq.in.gauge at 875°F; C&I/Girdler, 155 lb./sq.in.gauge at 780°F and 240 lb./sq.in.gauge at 800°F.

The C&I/Girdler shift converters operating at 155 lb./sq.in.gauge at 750°F are fabricated from ASTM A212 steel; and all other shift converters being discussed are fabricated from ASTM A204 steel.

Hydrogen embrittlement a major cause

In the design of shift converters, the composition of the stream must be taken into consideration. The feed and outlet streams from a shift converter contain a high mole fraction of hydrogen and consequently a high partial pressure of hydrogen. In choosing a material, one must protect against hydrogen embrittlement. Hydrogen embrittlement can be described as a condition where the metal loses its ductility as a result of the absorption of hydrogen. If the hydrogen partial pressure is high enough at elevated temperatures, it will attack steels, causing decarburization.

When hydrogen embrittlement occurs, the tensile strength decreases, the material becomes brittle and will crack and sometimes blister. The mechanism of hydrogen embrittlement involves hydrogen permeating the steel and reacting with impurities to form other gases as well as molecular hydrogen in the void spaces. The hydrogen may also react with iron carbide or carbon in solid solution to form methane, which cannot diffuse out of steel. This adds to the hydrogen pressure already in the void spaces and creates high stresses which ultimately result in failure of the material.

The best defense against hydrogen embrittlement in shift converters is to select an alloy steel with carbide stabilizer elements such as chromium and molybdenum. The data normally used to select this material is the "Nelson Chart." This chart, seen in Figure 1, shows in graphic form the safe operating limits for carbon and alloy steels in contact with hydrogen at high temperatures and pressures. It can be used by utilizing the partial pressure of hydrogen in the flowing stream versus the operating temperature of the

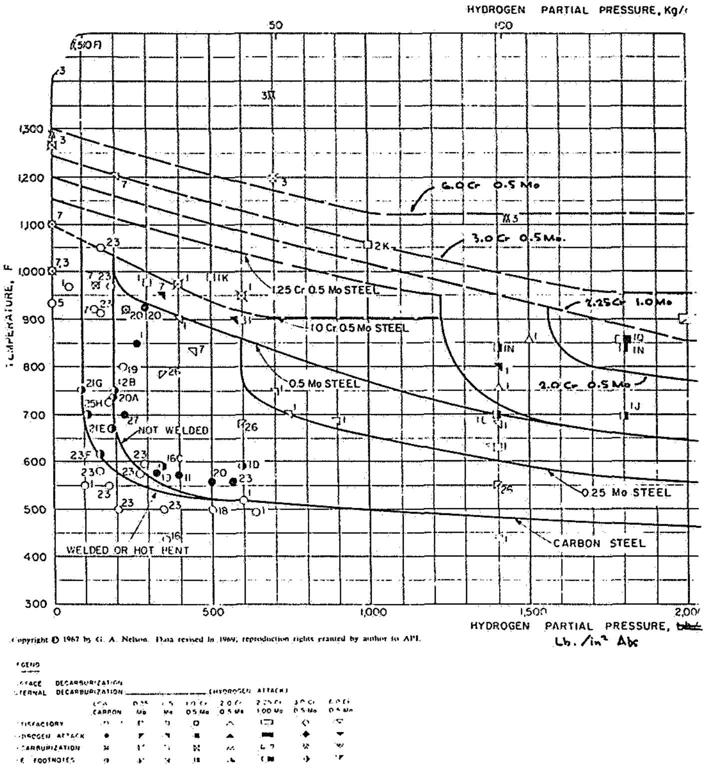

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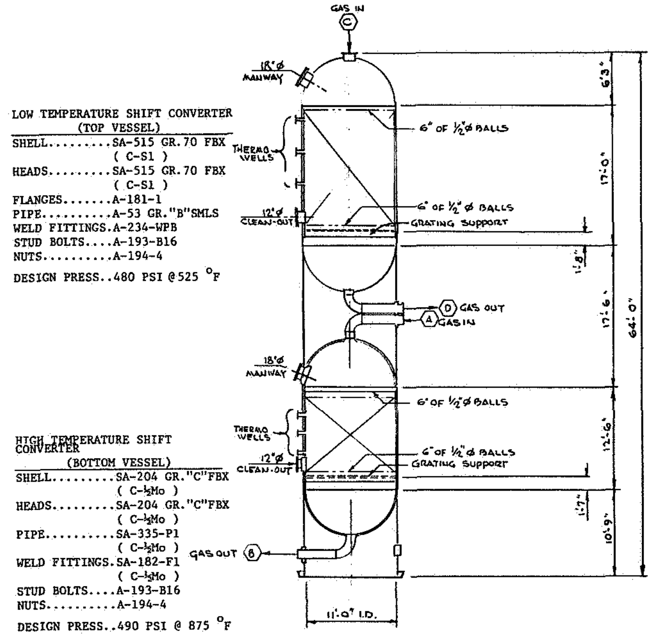
Figure 1. Nelson Chart: operating limits for steels in hydrogen service.



LOW TEMPERATURE SHIFT CONVERTER
(TOP VESSEL)
SHELL.........SA-515 GR.70 FBX
(C-Si)
HEADS.........SA-515 GR.70 FBX
(C-Si)
FLANGES.......A-181-1
PIPE..........A-53 GR."B"SMLS
WELD FITTINGS.A-234-WPB
STUD BOLTS....A-193-B16
NUTS..........A-194-4
DESIGN PRESS..480 PSI @525 °F

HIGH TEMPERATURE SHIFT CONVERTER
(BOTTOM VESSEL)
SHELL.........SA-204 GR."C"FBX
(C-½Mo)
HEADS.........SA-204 GR."C"FBX
(C-½Mo)
PIPE..........SA-335-P1
(C-½Mo)
WELD FITTINGS.SA-182-F1
(C-½Mo)
STUD BOLTS....A-193-B16
NUTS..........A-194-4
DESIGN PRESS..490 PSI @ 875 °F

OPERATING CONDITIONS

STREAM	A	B	C	D
PRESSURE PSIG	440	435	430	425
TEMPERATURE (°F)	770	850	435	460

FLOW RATE (LB MOLE/HR)

STREAM	CH_4	CO_2	CO	H_2	N_2	INERTS	DRY TOTAL	H_2O	WET TOTAL
A	22.8	553.2	905.8	3948.6	1578.9	20.2	7027.5	4039.7	11067.2
B	22.8	1211.2	245.8	4606.6	1578.9	20.2	7685.5	3381.7	11067.2
C	22.8	1211.2	245.8	4606.6	1578.9	20.2	7685.5	3381.7	11067.2
D	22.8	1427.2	29.8	4822.5	1578.9	20.2	7901.3	3165.8	11067.2

SHIFT CONVERTER

Figure 2. The shift converter that sustained cracking in the bottom head.

vessel. Most modern shift converters utilize a carbon-0.5% moly (molybdenum) steel as specified in ASTM A204. This was the material used in both shift converters which had failures.

Figure 2 shows one of the shift converters that sustained cracking in the bottom head. This vessel was fabricated from ASTM A204, Grade C, Firebox Quality plate, which is carbon-0.5% molybdenim steel. With a partial pressure or hydrogen at 198 lb./sq.in.abs., this is the proper material according to the "Nelson Chart." The design conditions for this vesslel are 490 lb./sq.in.gauge at 870°F, and the operating conditions are 440 lb./sq.in.gauge at 850°F. The vessel is 11 ft. inside diameter, and the lower head is hemispherical. The head is fabricated from seven segments, or gores, and one dollar-plate. The thickness is a minimum of 1.186 in.

In February, 1976, a leak developed in the lower head of this vessel. Investigation revealed a crack in the edge of one of the vertical welds joining the segments or gores. The cracked portion had propagated across the circumferential weld of the dollar-plate to a segment and into the base metal of the dollar-plate forming an "L" shaped crack 13 in. long.

Since it was impractical to dump the catalyst and get inside the vessel at this time, the repair was made entirely from the outside. The cracked area was removed to a total depth of 1-1/16 in. and the groove was checked by the magnetic particle method to insure removal of the cracked material. Since the skin of the vessel was still at 600°F, the weld repair was made with no further pre-heating. Each weld pass was peened, using a needle gun.

During the repair, transverse cracking was encountered in two areas. Minor transverse cracking occurred in the circumferential weld, but only to about 1/4 in. depth. An additional transverse crack was detected n the dollar-plate base metal about 1/2 in. below the circumferential weld and extending about 2 in. from the original crack. These cracks were removed by gouging to a depth of 3/4 in.

After completion of welding, the repair area and adjacent areas were again checked by the magnetic particle method to insure freedom of additional cracks. The completed weld area was field stress-relieved with an oxy-acetylene torch at 1,100°F for one hour, covered with insulation, and held for one hour. No samples were takein for metallurgical examination.

Repairs could be made only on outside of vessel

The ammonia plant was taken down for annual turnaround in June, 1976. At that time, another crack was observed on the bottom head of the shift converter. This crack was approximately 1½ in. long on the outside surface of the previously repaired area. At this time, samples were taken for metallurgical examination of both the previously repaired area and adjacent head segmental weld.

Again, accessability to the inside of the head was not possible and repairs were made from outside of the vessel by arc gouging to the root of the crack, and dye-checking to be sure all the damaged material was removed. The cracked area measured approximately 14 in. long. Transverse cracking in the lower dollar-plate base material had occurred, giving a "Y" type crack.

Since the repair had to be made from outside the vessel, a backing ring was used of the same material as the base material. The backing ring was inserted from outside the vessel. Welding was accomplished by welding from the extremities toward the center, thereby reducing the gouged out area and welding the center area last. During the welding operation, a pre-heat of 250°F to 300°F was maintained.

After the crack was filled with weld material, another small transverse crack was observed in the lower dollar-plate and extended to about 2½ in. to a depth of ¾ in. This was removed by arc gouging and was repaired by welding. The repaired area was checked with dye penetrant and no additional cracking was observed. The entire lower circumferential weld was stress relieved at 1,125°F for 1½ hr., using resistance electric heaters.

The vessel was put in service on July 17, 1976, and was visually inspected during an unscheduled plant outage on August 3, 1976. The previously repaired area was checked by the magnetic particle method and no cracking was detected.

Preliminary reports from the laboratory running the metallurigical examination have indicated no evidence of graphitization, which had been suspected; however, there seemed to be an indication of hydrogen embrittlement, particularly in the heat-affected zone of the weld. It appeared that the initial crack originated in the heat-affected zone of a segment weld and propogated across the circumferential weld of the lower dollar-plate into the base metal. The metallurgical examination also revealed a hardness differential between the weld metal, heat-affected zone, and the base metal of the vessel itself.

Except for one period of 3 min., during October, 1974, the shift converter had always operated within the design temperature and pressure limits. The exception noted was during a plant malfunction when the temperature went above the design temperature for the vessel. It is hard to reconcile this 3-min. excursion as the cause of hydrogen embrittlement in the heat-affected zone of the weld on the lower head.

Figure 3 shows the second shift converter which failed in service. This vessel was fabricated from ASTM A204, Grade B, Firebox Quality plate, and was put in service in late 1963. The design conditions for the vessel are 275 lb./sq.in.gauge at 900°F. Operating conditions are 274 lb./sq.in.gauge at 815 to 875°F. With a partial pressure of hydrogen of 96 to 97 lb./sq.in.abs., it falls within the range of the material selected in accordance with the "Nelson Chart." The vessel is 9 ft., 6 in. inside diameter, and the minimum thickness of both the shell and ellipsoidal heads is 1-5/16 in.

The sketch in Figure 3 and detail in Figure 4 show experienced in this vessel; the first two at the lower manway and the third in the bottom head on the outlet nozzle.

In April, 1968, a leak was discovered in the vicinity of the bottom manway on the shift converter. When the insulation was removed, it was found that the vessel had cracked at the toe of the fillet weld attaching the reinforcing pad to the vessel. The reinforcing pad was fabricated from ASTM A204, Grade B, Firebox Quality plate and was

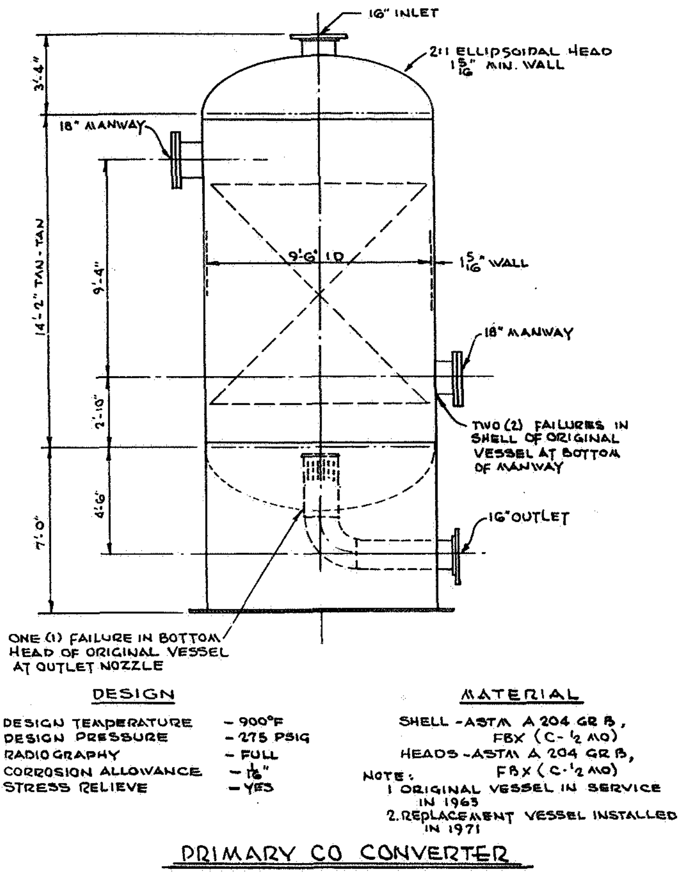


Figure 3. The shift converter that sustaind three failures, two at the lower manway, and one in the bottom head on the outlet nozzle.

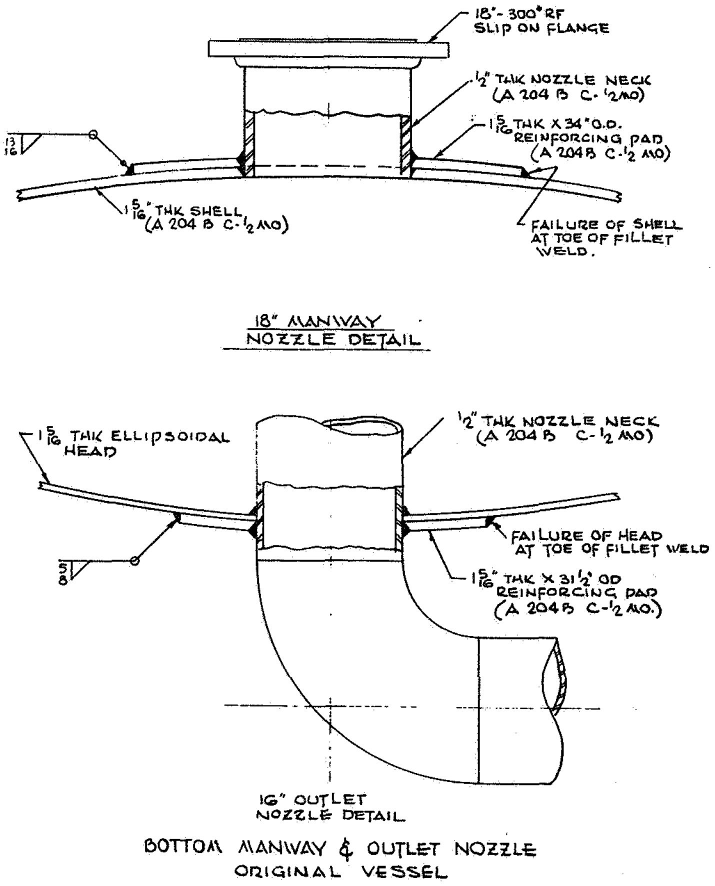


Figure 4. Details of failure sites in shift converter shown in Figure 3: manway nozzle above, and outlet nozzle below.

1-5/16 in. thick and 34 in. outside diameter. The crack extened approximately 120° around the circumference of the reinforcing pad.

The plant was taken down, the crack was ground out to within 1/16th-in. of the inside wall, and repaired by welding. No outside preheat was required since the vessel wall was approximately 300°F during the repair procedure. Each weld pass was peened to relieve the stresses, and therefore no external stress-relieving was done following the repair. The vessel was put back on line following the repair.

Repair procedures prove effective

In July, 1969, a leak was again discovered around the bottom manway of the shift converter. Removal of the insulation showed that cracking had again taken place along the toe of the fillet weld connecting the reinforcing pad to the vessel wall. This crack had started in the end of the area repaired in April, 1968, and continued on around the circumference of the reinforcing pad fillet weld. The crack was again ground out, repaired by welding, and dye checked.

The welding procedure was the same as the repair for the original crack. During the plant turnaround in the fall of 1969, the catalyst in the primary shift converter was changed. When the vessel was empty and clean, the repair was inspected internally. It was found that good penetration had been mad with all of the repair welding and that no new cracking showed from the inside wall.

It was still decided to grind out the area of repair from inside to a depth of approximately ¼ in., and tie welding in from the inside to the repair welds which had been made from the outside. This was done using the proper preheating and welding procedures, ground smooth, and dye-checked. No cracks were found following this repair.

A third failure in this vessel occurred in June, 1970. At that time a leak was found within the skirt of the shift converter, and the ammonia plant was taken down. When the insulation was removed, a crack was again found in the toe of the fillet weld of the reinforcing pad on the 16-in. outlet nozzle. The crack extended approximately 180° around the circumference of this fillet weld. The reinforcing pad was made of the same material as the vessel and was 1-5/16th in. thich by 31½ in. outside diameter.

Welding repairs were made using proper welding procedures and preheat; and following repairs the area was dye-checked for additional cracking. No additional cracking was found and the unit was put back on line. As with the second crack in the bottom, an internal check was made on the bottom head during the turnaround in the fall of 1970. This involved grinding out from the inside to tie into the repair weld which had been made from the outside. Dye-checking of this repair showed no further cracking either internal or external.

It was felt that the cracking had been caused by the sharp change in section from the thick reinforcing pad to the thick shell. This would act as a stress riser due to the difference in stiffness of the heavy pad and head or shell compared with the head or shell alone. With the sharp change in section, heat concentrations would be built up resulting in overstressing and failure from thermal fatigue.

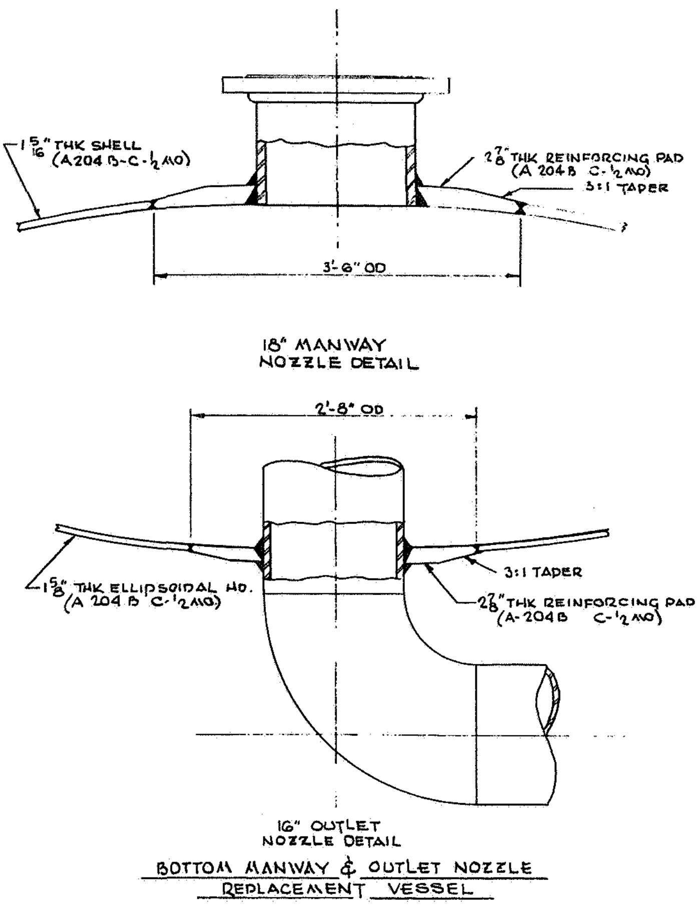


Figure 5. Details of replacement vessel showing new bottom manway (above) and outlet nozzle (below).

A new vessel was ordered in 1970 to replace the existing shift converter. On the basis of our theories regarding the cause of cracking, a different type of reinforcing pad was used. As seen in Figure 5, the reinforcing pads were made from 2-7/8-in. thick ASTM A204, Grade B, Firebox Quality plate, and tapered at 3-to-1 down to the 1-5/16 in. thick vessel wall or head wall. They were then flush welded into the wall or heads. This was done on the inlet, the outlet, and the two manways. The design eliminated the sharp section change and provided a much improved stress pattern. This vessel was installed in the fall of 1971 and is still in operation today.

Following installation of the new shift converter with the redesigned reinforcing pads, we were able somewhat to confirm our theories regarding the failures. It was found that some refiners had experienced very similar failures on the fillet weld connecting the reinforcing pads to vessel walls on coking drums. They had corrected this by gently tapering the outside edge of the reinforcing pad and then using a gentle tapering weld to attach the outside edge of the reinforcing pad to the vessel. This is another method for reducing the sharp change in section.

It is interesting to note that the original vessel was modified using this new design reinforcing pad and has been in operation since 1973 as a low-temperature shift converter.

As stated at the beginning, I have made no firm conclusions regarding these failures. The reason for the discussion is not to hypothesize on why the failures occured, but rather to make everyone aware of critical design factors that must be taken into consideration for the design of high-temperature shift converters for use in an ammonia plant. #

LAWRENCE, J.A.

DISCUSSION

Q. What were, once aqain, the operating conditions for the two shift converters that experienced failure?
LAWRENCE: The Weatherly converter was 440 lb./sq.in. gauge at 850; the Chemico converter was 375 lb./sq.in. gauge at 875.
Q. Were these actual operating conditions of design conditions?

LAWRENCE: These were actual operating conditions.
JACK BRENNAN, Chemical Separations Corp.: I'm President of the company which is the manufacturer of the ion exchange system that was just shown on those 10-15 slides. I think it's right for Mr. Lawrence to advise immediately those present about this problem. I think it would be a greater service, since I was at the site within five hours afterwards, to give the probable cause or at least the preliminary indications of the cause, and also for the benefit of the people here what at the moment it looks like the way the process was being operated.

I had my technical director and inventor of the process, Irwin Higgins, my vice president of commercial and process operations, Randhir Chopra, and my chief engineer, Bob Lamb, with me and we were at site for about four hours on Friday afternoon, the day of the accident. The system is built specified to use 22% nitric acid as a regenerant chemical. We interviewed the operator, we interviewed the shift department supervisor in the laboratory; I spoke to the plant manager, and I think—Mr. Lawrence—it would be a service to tell the people present also that the unit was at the last hour of its operation, and I think a sustained period before that, although I don't know that, was operating at over 9 molar nitric acid which is 45% concentration. The system is designed to use 22%. That was over twice what we designed the system for, and I think it's a service to this group to know that. The process was not being operated properly when the detonation took place.

I'd also like to add that my people were in touch with all other operators of similar nitric acid process shortly after the accident. We have 11 of these systems around the country—and we've never had any explosion problems with any other one. One has been in operation ten years. Any my people would like this audience to know that we were in touch with every one of our customers within two or three hours after we were told about the explosion. And we will keep people advised on anything that we know about the problem.