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Nitrogen wash incident

Process safety modifications include replacement of carbon steel pipe subjected to low temperatures, better instrumentation and control systems.

On the afternoon of March 12, 1960, approximately 70 ft. of a schedule 40 carbon steel line containing H_2 at a pressure of 325 lb. was suddenly subjected to liquid N_2 temperatures causing the line to rupture with explosive violence. Despite the fact that fragments were thrown in all directions with sufficient force to embed themselves into the lagging of adjacent equipment, no one was injured and little damage was done to nearby lines or equipment.

Just prior to the line rupture, the operation of the N_2 wash system had not been stable or satisfactory. In fact, only 4 hr. earlier it had been necessary to back feed gas out of the boxes because of cold warm-ends on the heat exchangers.

After the cold warm-ends had recovered, feed gas was reintroduced and shortly thereafter trouble began. The first symptoms of trouble were cycling temperatures and gas compositions from the wash column. As had been done many times in the past, control instruments were placed in manual in an effort to break this vicious temperature and composition cycle that was obviously becoming more extreme as time went on. Finally, the temperature alarm in the carbon steel piping sounded, which indicated that the temperature had fallen to −20°C.

The operator pressed the toggle switch in the 60 point potentiometer to read the temperature, and found it to be −120°C and falling rapidly. He

Upper level operating platform after the line rupture at DuPont's nitrogen wash unit.

immediately took emergency corrective action by diverting the flow through another parallel heat exchanger, but it was too late. The temperature continued to fall and in 15 to 20 sec. had reached −140°C at which time the line ruptured. The field operators responded well to the emergency and had the boxes valved off with purge N_2 flowing into the feed-gas lines before the head count was completed.

What happened and why?

The rather exhaustive investigation on the part of DuPont and Air Products revealed that the trouble probably started at the time the feed gas was first withdrawn from the boxes. At that time, the N_2 scrubbing column (a sieve-plate column) dumped, and a 100% liquid level existed in the base of the column. Shortly after the column had dumped, the level fell to 60% and the operator assumed that the automatic level control valve had disposed of the excess liquid.

However, what actually happened when the level exceeded 100% was that liquid N_2 backed up into the upper impulse line to the level controller. This impulse line was not back bubbled with purge N_2. The liquid in the impulse line gave the false level signal that indicated a somewhat normal level when actually the column was at a level greater than 100%. During the 2 to 2½ hours in which feed gas was not in the boxes, the liquid N_2 reflux to the scrubbing column was not reduced since the level did not appear to rise abnormally. Undoubtedly, the column was nearly full of liquid when feed gas was reintroduced.

The initial warm feed gas that entered the base of the column caused heavy boiling and entrainment of liquid in the overheads line. The first low temperature alarm that the operator observed was caused by the cold gas preceding the liquid. By the time he had selected the proper toggle switch and read out the temperature, liquid was already leaving the box and entering the carbon steel lines.

An instant before the line ruptured, a sudden pressure rise was noted in the carbon steel line. This pressure rise was caused by liquid N_2 vaporizing rapidly in the relatively warm piping. Thus, the carbon steel was simultaneously subjected to a rapidly increasing pressure and a very heavy thermal shock. It is not at all surprising that the rupture was a violent one.

It was the conclusion of all investigating parties that the operator took the proper action; but once liquid N_2 had entered the carbon steel lines, all control was out of his hands and there was nothing he could do to prevent the inexorable progression of events.

Process modifications

The plant was shut down for a number of weeks while the damage was cleaned up and extensive modifications made to the warm-end piping as well as the instrumentation associated with the cold boxes.

All of the carbon steel piping that could be subjected to low temperatures, that is, the purified H_2, the recycle N_2, and the waste gas lines leaving the boxes were replaced with type 304 stainless steel piping. The carbon steel lines leading to the compressors joined the stainless steel lines 6 ft. downstream of a stainless steel automatic block valve. A stainless steel back-pressure control valve was installed some distance upstream of each block valve to maintain the desired pressure on the system and vent the excess gas to a stainless steel stack. Each of the stainless steel automatic block valves was tied to the signal of the proper thermocouple in the warm ends of the final exchangers in the boxes.

The instrumentation was so arranged that at −10°C a panel alarm would sound to indicate not only that a low temperature was imminent at the exit of a heat exchanger, but also in which exchanger the trouble existed. If the temperature continued to fall, a low temperature trip set at −20°C would automatically close the proper block valve to prevent cold gases from passing from the exterior stainless steel piping into the carbon steel piping leading to the compressors. Of course, when this automatic block valve closed, the stainless steel back-pressure control valve would then vent the cold gases up the proper stainless steel stack to the atmosphere. A so called "panic" button also was installed in the control room so that

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the operator would not have to rely upon the automatic interlocks if he saw the temperatures getting out of hand.

In an effort to obtain earlier knowledge of impending temperature upsets on the warm ends, alarms were installed on the thermocouples in the lines leading to the final heat exchangers within the cold boxes. Also, all of the points on the 60-point potentiometer were duplicated with new recording thermocouples. Thus, the operator would have before him a visual record of all critical ΔT values within the cold equipment. Likewise, the five new thermocouples that were installed on the manifolds of the five warm ends leaving the boxes were fed to a high speed recorder which monitored and printed out each temperature every 5 sec.

The liquid level impulse lines on the scrub column and the liquid N_2 phase separator, as well as the column pressure tap, were back bubbled with purge N_2. As an additional means of detecting column flooding, a properly back-bubbled recording differential pressure instrument was installed across the wash column.

Modifications satisfactory

All of these modifications have proved very satisfactory during subsequent operation. As a matter of fact, this automatic diversion system has literally saved our equipment a number of times. The ability to take low temperatures exterior of the boxes and still keep running has enabled us to uncover a number of shortcomings and make the proper modifications to the cold equipment.

I seriously doubt that by now, even at the expense of more ruptured lines, we would be operating the cold boxes safely and in a controlled manner if we did not have this ability to work through the temperature upsets, develop new operating techniques to pull ourselves out of the difficulty, and then keep going regardless of exterior cold lines. #

Questions and answers

WALTON—Rohm & Haas Co., Pasadena, Texas: After the dump valve to the flare opens, what means do you use to stop the compressor? Is a compressor shutdown device tied in with this system, or does the compressor kick off on low suction pressure?

CONKLIN: No, actually our compressors then go on automatic recycle from, for instance, a 4th stage back to 3rd, 2nd back to 1st. Should these recycle valves be slow, or any other thing happen, we do have low pressure suction trips on the machines.

ANDRIES—Spencer Chemical Co., Vicksburg, Miss.: I was wondering if you have ever had any trouble with channeling in your exchanger which would result in the same condition?

CONKLIN: No, we have had no indication that we have had channeling in any of our heat exchangers.

ANONYMOUS: What type of level indicating instrument or level sensing instrument was on this tower?

CONKLIN: The one that was on it was a DP cell.

HEPP—Sun Oil Co., Marcus Hook, Pa.: We cracked one low pressure line and although the crack was minor the manner in which we cracked it might be of some help for everyone. We believe this was cracked when the operator was putting the unit back on stream, after regenerating the exchanger. Our procedure is as follows. To put an exchanger back on, you put a crack of cold product gas through without any exchange until it cools down to a point where a thermal bump is avoided in the process when you put it in service. The operator in this case cracked this valve and, we believe, allowed it to go too long. Of course, in time, the outlet line will go on down to the inlet temperature.

Thus, you might wish to review your procedure for bringing these exchangers back in service after a normal defrost.

SVOBODA, Dow Chemical Co., Plaquemine, La.: Did you purge your differential pressure or delta p indicator on the N_2 scrubbing tower with N_2 also?

ANONYMOUS: Yes, we did. I, for one, am in Mr. Conklin's category of those who have experienced ruptures of carbon steel lines at low temperatures on both the air separation plants and the N_2 wash box. We have had numerous occasions where the defrosting lines or safety valve lines cracked, usually at welds, when they got extremely cold because of process upsets.

LAWRENCE, U. S. Industrial Chemical Co., Tuscola, Ill.: I wonder what your basis was for the statement that 6 degrees below was dangerous. It actually is, of course, about 14 degrees warmer than the code for carbon steel, and most low pressure ammonia systems operate lower than that.

ELLIS—Du Pont: Du Pont has never agreed with this minus 20° because of some experiences that we've had on carbon steel equipment. We generally divide the materials into carbon steel down to 32°F. When we go from 32°F to 0°F, we consider all the carbon steels with respect to their use and the consequence of their use in this temperature range. Below 0°F we go into specified materials with impact tests, special heat treatment, special fabrication considerations with the equipment.

ANONYMOUS: You mentioned that you dumped the liquid N_2 into the stainless steel line several times. We have always had a great concern for the thermal fatigue that might occur because of the rapid application of the cold gases to the stainless steel which has a poor thermal conductivity. We figure we can get quite a ΔT across the thickness of the material and then contractual forces occurring in the length of the line. Several companies mentioned they have dumped liquid N_2 into a brass line and into a stainless steel tank. How often have they done this and what was their experience with thermal fatigue in such a line?

KRYZER—Standard Oil (Ind.), Whiting, Ind.: The line that we use is generally cooled all the time. Because it also carries the continuous purge from our auxiliary vaporizer, we do not shock it with a large dump. It's chilled continuously.

WALTON—SunOlin Chem. Co., Claymont, Del.: We have two blow-down systems, one is a schedule 10 aluminum 2-inch line which runs about a thousand feet to the aluminum vaporizer. We have used this many times, dropping liquid N_2 out there and rich liquid bottoms from the air plant. There have been no failures in this line. It does contain expansion loops. We also have a blow-down system for the hydrogen wash box made of a stainless steel type 304. It goes to a tank (about 2½-ft. in diameter by about 4-ft. high) made of stainless steel, and is vented to a stainless steel stack. We have dumped cold liquid in here many times. The coldest material has been the bottoms of the nitrogen wash tower which is about −310°F. We have had no sign of failure in this system for over seven years.

LAWRENCE—U. S. I.: On your specs on carbon steel, do you also disagree with the code on shapely tested steel going down to minus 30 or minus 50 if it's A-300 or special type steels?

ELLIS—Du Pont: We do carry the A-300 material down to minus 50.