PROBLEMS IN SHUTTING DOWN AND STARTING UP

Rapid pressure rise in autoclave ruptured relief seal above 6,000 lb. pressure; start-up heaters have built-in restrictions which can cause trouble

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We ran into difficulties unexpectedly in the startup phase of a new urea plant. Using old-time tested operating procedures, we shut down with a safe pressure of about 2,000 lb. / sq.in. and bottled up the 6,000 lb. / sq.in. autoclave. Some 12 or 14 hours later, we were surprised when the autoclave head seal relieved at something over 6,000 lbs. Had it not been for the particularly fortunate circumstance in the relief of this seal, we could have had a serious situation on our hands.

When the unexpected thus happens, everybody gets into the picture trying to find out what happened. I think we have pretty well earmarked just what did happen. I would like to pass the information along to everyone else in order to prevent a catastrophe.

This clave was about 4 ft. in diameter and 50 ft. tall designed for high pressures in connection with the Allied-CPI urea process. We were in a startup phase and, as is common in many urea plants, on shutdown the block valves tend to leak a little. Our relief valves are on the inlet side for convenience in purging with ammonia. It is a practice among some operators while shutdown to let the inlet and the outlet valves freeze themselves and then just let the clave remain sealed with hot water circulating in the jacket and holding that water at constant temperature. We can thus hold claves for a month or more.

From 2,000 to 6,000 lb.

On this occasion, we were running along and had a small blockage in a tower. We took the pressure down to 2,000 lbs. and closed the autoclave off, and this time as in the past let it remain with automatic control of the circulating jacket temperature. The temperature in the jacket only wandered 10° in this whole time and 10° isn't a lot to look at. Finally, when the seal blew, at the same time a block on the inlet valve cleared, and our recording pressure gauge jumped from 2,000 lb. / sq.in. to over 6,000 lb./ sq.in. How did it get to 6,000 lb. / sq.in. on only a 10 degree temperature swing?

We found the answer in the triple point of ammonia. We had shutdown on a high ammonia ratio in operating dislocation. If you examine the triple point or the critical value on ammonia it can be seen that the liquid phase in the reactor will undergo something like a 30% expansion in 10 F. just below the critical. The same thing is true of water. If we had shutdown at 4,000 lbs. above the critical pressure, we would have been all right -- 10 would have just made a slight change.

We just happened to get under this critical triple point as is possible, particularly with the newer urea processes running at higher ammonia ratios. There is a tendency to start up at a high ammonia ratio and this is where one can get into trouble.

I imagine there are other critical points that can bother us but this was a specific instance that surprised us all.

Startup heaters

I think we all need to examine the startup heater situation very thoroughly. Nobody has said anything about it up to now and I can see why some people have to maintain an inherent silence but we are not involved directly so we can call people's attention to it.

Elsewhere there have been two fatalities, two serious accidents, and we had our own experience in which we again had a golden angel on our shoulders. Except for the fortunate circumstance, we could have had a heavy loss and a real serious personnel situation.

Today with large fired startup heaters and the extreme push for economy, designers have tended to restrict the number of valves, the firing protection, and the stability of flame pattern. Nothing wrong was done in our plant but we have cut a little too close, with the result that there are some rather serious problems to consider.

In this particular case, the circular shape and the construction entirely in 1/4 in. and 3/8 in. carbon steel, resulted in making this quite a restricted container. The entire upper section including the stack separated and went up some 30 ft. Fortunately, it came crashing down on a vacant roadway. Had the fall been on the other side, it would come across all of our high pressure synthesis lines, all our converter exchangers, and fracture could have occurred with ignition and an uncontrolled release of some 300,000,000 B T U.

Corrective measures taken

We have taken some corrective measures—putting pilots in our burners, providing explosion hatch reliefs, and tying the top down so it won't come off again. We would just like to call this to everyone's attention as this is an item that could create a real major catastrophe and it needs to be reviewed by each party in their own plant.

There are other things that concern us about this design area. For example, the coils are being specified with a low order of heat resistance. In other words, the coils in a startup heater are not of stainless steel type 310 or something that can take heat. They are just a high-chrome iron and even a flow is interrupted for any reason, you can expect a coil failure in terms of minutes. We need to have interrupting interlocks so if the flow stops for any reason the firing is cut off. If we examine the new larger plants, there is a tremendous venting of the syn-gas through any failure. This doesn't apply just to the startup heater but it is a point to consider.

In our particular plant, for example, we calculate a release of 520 million B T U in a few minutes through a furnace system with active ignition and only designed for about 35 million an hour. You can see where this makes a real mushroom of flame and poses some problem in getting these things sealed off.

Discussion

Paul Meyers (Kaiser Agricultural Chemicals): We had a failure happen, I believe twice. It was a methanator heater explosion. It resulted from a loss of flow through a methanator heater, a 900 lb. system, and resulted in not a disastrous fire by any stretch of the imagination, but it was quite spectacular. It lit up the sky. People in a drive-in movie three miles away were quite impressed with the fire and light that we put out at Kaiser Agricultural Chemicals.

But, it was a failure caused primarily by insufficient flow or lack of flow through the methanator at that time. This did happen to us twice. Of course, since then we have put in the interlocks, etc. on the system, so this should not happen to us again.

Q. Would you mind detailing a little bit what you did to keep it from happening again?

Meyers: If I may on that, I have somebody who is more qualified than I, and I would like to call on him. That is, the Ammonia Plant Superintendent, Mr. Wilbur Smith.

Wilbur Smith (Kaiser): We had two tube ruptures caused by loss of process gas flow.

We now have an interlocked safety system with a secondary lock-up using a process flow transmitter, pre-set to trip on low flow.

For complete protection, we added a high temperature alarm and trip circuit on the heater stack, and a thermocouple welded to a tube in the fired zone of the heater. The thermocouple has a high temperature alarm circuit, pre-set to alarm just above operating temperature.