SAFETY PROBLEMS OF UREA PLANTS

Feedback from a wide variety of experiences provides operating tips and information in the important area of urea plants

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One of the things we talked about at the Minneapolis meeting in 1965 was the problem of safety valves in urea plants and the ease with which they plug up. Subsequent to that meeting we bought and installed a steam jacketed safety valve. It was put on our first state decomposer. Prior to this meeting we had used a system of injecting water through a very small diameter stainless steel tube right up into the throat of the safety valve. This is a troublesome thing to maintain. If the water flow through this small tube is interrupted, it quickly blocks up and can't be cleared again until you take the safety valve off. So we have tried a steam jacketed valve.

The valve appeared to be satisfactory for a number of months, then finally an occasion occurred where it should have blown and it didn't. It was taken off and found to be plugged up.

In retrospect, there is one thing that occurred to me that we didn't do that may or may not have contributed to the fact that the valve was plugged up. We did not inject any steam in the outlet passage of the safety valve. I know this is the practice in a number of plants.

One of the newer urea plants that just started a few months ago in the Pacific Northwest, used a system of frangible discs under the safety valves. They had reported difficulty that when the frangible discs blew and the safety valve lifted, it almost never reseated because pieces of the frangible disc got stuck under the seat.

Measuring condenser corrosion

One of the tools that we have found to be very useful in measuring corrosion of condensor tubes, or vaporizor tubes, or reboiler tubes, that are non-magnetic is the Probilog. For those of you who are familiar with it this picks up pits, cracks, holes, etc., and you get a tape record when you pass this instrument down through the tube.

There has been some mention in the literature recently of a new device similar to this which is effective on tubes which are magnetic. This was called the Ferrolog. None of the companies in our area who normally supply such services are able to give us any assistance on renting or giving us service with this device.

Discussion

R.B. Moore (Air Products): Recently we had occasion to use this Ferrolog in our plant on a very badly corroded exchanger. We engaged the services of a specialist. The instrument gave a good indication of the pattern of corrosion in this exchanger. We were quite pleased with its performance.

Q. Were these steel tubes?

Moore: Yes. It was difficult to get an exact measurement of the metal loss, but you can get a good indication of which tubes are worst.

Q. Is there a company name and address available for the instrument?

A. Guralnick Associates, San Francisco.

Gasket design and crevices (Walton)

Another area touched on at Minneapolis was the problem arising where you have urea and carbamate solutions with the gasket design causing crevice corrosion conditions. Normally where flexitallic gaskets are used on man heads or hand holes, the I.D. of the gasket is greater than the I.D. of the nozzle. This gives you a very nice built-in crevice, as it were, and we have experienced in some cases, severe crevice corrosion at this point.

I believe I suggested at that time that some consideration might be given to changing gasket design or devise a gasket which would get around this problem.

This was also a problem in ring type joints in piping, particularly where you have a ring joint which lays on its side rather than being in the horizontal piping run. For instance, we had considerable trouble with a valve bonnet ring gasket, where the valve instead of standing upright was in a horizontal position, or the stem was.

We have been slow to get around to changing this gasket design ourselves. We are about to try, I think it is the C.G. I. series of flexitallic gaskets which have to be specially ordered so that the inner ring is the same I.D. as the nozzle. This will help to fill up this crevice but it probably won't seal it.

Another filler material that has been suggested is Cerafelt. This is a rather inert material and can be jacketed with a thin 316 jacket or similar material and used as a filler.

Discussion

R Reed (Girdler Corp.): I would like to suggest that consideration be given to the use of silicone rubber materials such as General Electric and Dow Corning are producing.

We have tested these materials with urea and urea solutions and they are quite stable even up to relatively high temperatures, and those materials could be used to seal such crevices and perhaps protect the material from allowing the urea solutions to get into that space.

Painting a problem (Walton)

In the SunOlin urea plant and in many others, painting is a problem: maintenance of the plant, maintenance of the structural steel, etc. There is a problem of keeping paint on the structures.

In our particular plant, it may be a little worse than others in that we are next door to a plant that makes a number of different acids, the prevailing wind blows from them to us, so that the pH on the surface of our steel work, such as the prill tower, may change several times a day from being very alkaline to being acid.

I would like to report that we started about four years ago trying double-dipped galvanizing for when we added structural steel members, ladders, platforms, stair treads, piping and so on. This appears to be quite satisfactory in this very difficult atmosphere.

There are some who feel that it would also be very helpful to paint the galvanized material in addition to this.

CO_2 pressure cylinder corrosion

Another problem which has occurred during the past year is the problem of corrosion in the fourth stage CO_2 pressure cylinders.

I gather other people are having similar problems. We have had some correspondence with the manufacturer of our compressor as to method of repair. This seems to be a very difficult question.

The corrosion is in the valve port of the compressor cylinder at the gasket surface. It is pit-type corrosion. We have tried the usual things, filling in with Devcon, Smooth-On and things of this sort. This lasts for a short time and then blows out and disappears.

The cylinder is cast steel, but the manufacturer is very leery of trying to repair it by welding. He feels that to do so would be to invite warping and possible damage of the cylinder.

We are considering the possibility of using the metalocking technique for repairing this pit. I might say the cost of a new cylinder is in the order of $11,000. It is probably desirable economically, also from the standpoint you can't buy these things overnight, to see if some repair can be made.

We have corrosion on both the suction and discharge sides. It is particularly puzzling to figure out why we would have it on the discharge side where it is hot and no condensate there.

Discussion

D. Stockbridge (Southern Nitrogen: I am going to comment on some experience we had with Southern Nitrogen. We had a CO_2 maching going to the neighborhood of 3,000 lbs. The problem we had was in the fourth stage suction valve which operated at around a 1,000 lb., and this is in the area of the critical pressure of CO_2.

The manufacturer of the compressor was concerned and brought in some experts who represented the manufacturer who had supplied the separator.

It was this expert's opinion that possibly the corrosion or erosion could have been due to liquid CO_2 With this in mind and also thinking myself that it might be water not being contained by the separator, we put in a heater to heat the CO_2 between stages, with the idea of vaporizing either water or liquid CO_2. This did no good. If anything, it made it a little worse.

While we were engaged in this rather empirical research method, we were buying cylinders on the frequent basis of about every six months; the manufacturer of the compressor would not allow welding due to the reason already mentioned. However, we were able to send some of these cylinders back to the manufacturer and they had them built up by plating of iron into the affected areas and then remachining. This was satisfactory.

We tried some other things. We lined the ports with various grades of epoxy paints. This helped some but, of course, you can't maintain a film behind these gaskets and this is the area that was most affected.

We also lined with stainless steel. These looked very much like a tin can made very carefully to fit closely inside this area and sealed it in there with epoxy. This helped also but did not solve the problem. Then eventually we tried a combination pulse dampener and moisture separator. We took off the pulse bottles that were supplied with the compressor and installed these combination pulse dampeners and separators which were considerably longer and a little larger than the original pulse bottle.

After we installed these we experienced very little more corrosion. We get a little bit but nothing like what it was before, and we found that we were getting as much water out of this type of separator as we were out of the other. We left the other in, so we had both. And I believe that it is due, at least on the suction side, to moisture.

G. Midkiff (Cooper-Bessemer): This, situation has come increasingly to our attention in the past two or three years, partly because of the higher pressures being used. The early CO_2 machines operated at quite low pressures.

On this particular item of corrosion, we feel that the separation has a great deal to do with corrosion that will be experienced in the cylinders. As experienced at Southern Nitrogen, a change in separation equipment was very effective. We had another installation where we put additional separation into the system. This was on a five stage machine. We did it on the fourth and fifth stages. This separation, along with other thermodynamic considerations, seemed to make a great improvement in the operation. In this one situation, the high pressure cylinder, had a valve arrangement that was being changed out about 24 to 48 hours on a regular basis. The plant engineer and myself spent quite a few days scratching our head and worrying about this. I will say they were very patient with us in working out this problem. However, through these thermodynamic considerations and additional separation equipment, we were able to eliminate this corrosion.

The particles we feel that caused a great deal of trouble were extremely fine particles that may pass through conventional separators. If we can dry up the stream or take out very fine particles, we feel that this corrosion in large part, will be eliminated.

Our experience has shown this to be on the suction side of the machine and I was interested very much in your comments that this is starting to show up on the discharge side. But as far as the suction side is concerned, perhaps consideration could be given to making the cylinders bottom suction and top discharge. The particular cylinders that Nort Walton is talking about, are such that valves can be switched or you can turn the cylinder either way and make a top discharge and bottom suction. Of course, this means associated piping changes. But by doing this, you then tend to eliminate the possibility of this crevice corrosion down in the lower gasket areas around your valve seat. Also up around the gasket area on the top side, any condensate would then tend to move down under the lower regions back out into the piping, so maybe all you are doing is transferring the problem from the cylinder back out into the piping, but it is a little easier I think to work on corrosion out in the piping system as compared to the compressor cylinder.

One problem that develops in the compressor cylinder, is that in these cylinders you have some cross bores and also have liner bores. These are held to close tolerances during the manufacturing procedure. If any welding is done in any of the adjacent areas, there is a question whether you can hold these bores true during the welding process or during any stress relief afterward. We have some feelings that perhaps that you can't hold these within the allowable dimensions, that they may go out of round. So this is our concern in trying to do any welding in the cylinder at a method of repair.

Iron plating has been accomplished on some cylinders. However, I might add that it's a very long process involving several months. You may say, why is this so? The reason that we have found is the cylinders that come back will have various degrees of corrosion on them, and we do not know at the time we get the cylinders just exactly how much metal is going to have to be taken out up around these valve pockets. Once this is determined, then of course, the pockets can be machined. We then would send this to a plating concern to have it iron plated, but there is a limit as to the amount of plating that is desirable to be put on at any one time. So when the plater reaches this limit, he will then send the cylinder back for additional remachining to take out the excess layers of this metal and then, after we have machined it, of course, there is a matter of sending it back up to the plater. Well, this can involve maybe two, three, or four different operations and transportation which does eat up a considerable amount of time. So we don't suggest this as a rapid method of repair. It is one which we have done and shows possibilities, but if, as in most cases, you are interested in getting these cylinders repaired in the shortest possible time and getting your plant back on the line, about the only thing we could suggest in this regard is purchasing a spare cylinder while the damaged cylinder is being repaired. Of course, this involved quite an outlay of dollars.

We have looked at this situation of a sleeve. I don't know whether anyone has done this in the field. We have looked at this and we are reluctant to put this sleeve in because we would have to machine out up around the valve cap and to drop the sleeve down around the gasket area. In doing this you have to then watch the stresses you get into on your valve cap bolting.

So there are some definite limitations as to what can be done on the repair of these cylinders. We would suggest, just basically at this time, to certainly watch your separation equipment, being sure that it is getting these very fine particles out of the system. If you anticipate some difficulty in this regard, then perhaps investigate other types of separation equipment.

Q. Is there any reason metallizing can't be used to fill the pits which then could be machined?

Anon.: We have used this metallizing technique very successfully in the first stage following the condenser. We seal with an epoxy resin, and it has worked out very fine. I have only one note of caution. You want to use a combination of Metco 1 and Metco 2, which gives a good machineability over the hard Metco 1.

Carbamate corrosion (Walton)

Carbamate corrosion is always a problem. I would like to relate the fact that in the past year we have had failure by cracking of welded Schedule 160 Elbows on the discharge of a high pressure carbamate pump. The cracks appear in the weld and in the heat affected zones and adjacent to the longitudinal welds in these welded elbows.

The solution that we have gone to, is to go to seamless elbows in this case, which doesn't sould like much of a solution because you still have your circumferential welds, but strangely, they were not affected. We did not have cracks in any circumferential welds in this piping.

One of the things that we tried in this piping is the use of aluminum rings for the ring-type joints. Unfortunately, the aluminum that was bought for this was 2024-H-12 which contains 4½% copper, and when the ring was taken out after two weeks' use, you can see there is very severe corrosion where the carbamate wetted the inside of the ring. So-warning, if you are going to use aluminum in carbamate service be sure it is an aluminum that does not contain this much copper; preferably not more than a tenth of a percent.

Another thing which occurred to us in the past year is the water jacket on our reactor, or autoclave, cracked all the way around, right at the lower expansion joint. We had stopped using the water jacket for heat transfer purposes and, of course, this means, particularly in the wintertime, this jacket in the expansion joint is more stressed than it would normally be if it is in operation. One day in zero degree weather, this cracked all the way around.

Bulk warehouse problems

Another thing came up in our plant this year which I think is a very definite safety problem. Our bulk urea warehouse and bag urea warehouse is a pretty large building. We have storage capacity in the bulk warehouse for presumably 10,000 tons. This gives a roof area which is a good many square feet.

This roof is covered with corrugated aluminum sheets. We noted early this year that the sheets were coming loose, and when we had a good wind, they rippled like the waves in an ocean. There was considerable concern that an extra good wind would come along and blow some off and they would fly around the area and possibly decapitate somebody when they approached the ground level.

We hired a "giraffe" and inspected this roof pretty carefully from the underside and where we could reach it from the top. We found that many of the stainless steel bolts which are screwed into the purlines, were snapped off. On looking further, we found that when the roof was installed the holes which were bored in the aluminum sheets were of the same diameter, or a slightly greater diameter from the bolts themselves.

In thinking what happens when the sun comes up on this roof, or let's say, it has been a hot day or a hot sun and you get a sudden shower, we realized there could be considerable movement of these sheets due to expansion and contractions. It was felt that this possibly was the cause of the failure of so many of these tie-down bolts.

Another possibility for this failure may be the explosion we had in the hydrogen compressor which I related I think two years ago, because at that time we know the blast went through the door of the warehouse as it knocked the tripper off the track there, and we felt that might have contributed to these bolt failures. So in any event, we have devised a method of repair.

I also might mention, and I am sure this had nothing to do with the explosion, that where the sheets lap over each other, right at the joints, we seem to have pinhole corrosion. So we tried to do two things at once here. At all these laps we are going to insert between the two sheets a piece of Corrulux, or similar plastic material, and make a sandwich at that point. Then we are going to bolt, or rebolt, wherever the bolts were broken, to the purlines but the hole in the aluminum and Corrulux or polyvinyl sheet, is to be appreciably larger than the diameter of the bolt. Above that there is to be a rather heavy Neoprene or Hypalon washer of a durometer that is reasonably soft Shore A 60. This will allow some movement of these roof sheets when you have conditions that give expansion and contraction, without putting a great deal of shearing stress on the bolting system. We feel that this should be of considerable help.

Discussion

Q. Were these bolts examined to determine the mode of failure?

Walton: It was felt it was a sudden fracture due to overstress. There is not any necking down, so it appears to be, more or less, a brittle fracture.

D. Speed (Huntington Alloy Div.): We have seen similar failures of stainless steel tie-wires, for example, in the building construction field where they use stainless. One of the most dramatic example was Florida's Power and Light transmission lines between Miami and Key West which were all hung with stainless steel cables and stainless bolting and tie-wires. They failed, and this has all been traced back to stress corrosion cracking. Crevice corrosion forms where the bolts tied into the poles. If you have ever seen these bolts manufactured you would understand the reason why because where they were cold-headed, the failures were right beneath where the shank of the bolt and the head formed, extremely high stresses were generated here.

The solution, of course, came out to be that you simply solution annealed these bolts after they were cold-headed. It eliminated the problem entirely.

I personally don't think the aluminum could generate that much strength to shear the stainless. I think the aluminum would go first.

Discussion

Ralph V. Green (DuPont Co.): I have one or two items. One is similar to the problem you had with roof panels. We are all aware I think of the hydroscopic nature of urea and the fact that it picks up moisture, but we are not always aware of the dangers that might come from this property.

We have found that our transite roof panels have become loosened by deposits of urea which occurred in the handling areas of the plant when these deposits become moist and expanded. In order to avoid the repetition of this hazard, we periodically hose down these areas of the plant.

The other item which I wanted to mention concerns the fact that the plant has to periodically clean the sewers in the urea plant. About twice a year we open up these sewers with high velocity water jets in order to get them to operate properly.

Q. You don't hose down the underside of the roof, do you, when the warehouse is empty?

Green: The building is hosed down so as to remove any urea dust deposits. This is on the underside where the transite comes into contact with the roof supports.

Ferrite content (Walton)

Ferrite content of 316 stainless steels was discussed to some extent at the Minneapolis meeting. Since then I have reviewed the literature on the subject and I find there are very conflicting statements in the literature. There is one article which indicates that in order to keep from having corrosion in 316 stainless that you should keep the ferrite content below 1%.

There is another article which states that in order to gain the most corrosion resistance on 316 stainless, you should be in the order of 5% to 15% ferrite content.

There is one vendor of urea plants which has very strong feelings about ferrite, in that they incorporate in the purchase specificiations, that it must meet certain ferrite contents.

Discussion

C.L. Glover (Solar Nitrogen): We operate under the same Stamicarbon specifications as Columbia Nitrogen, which are - 11-½% Nickel, 2.2% Molybdenum, 17-18% Chromium, 2% Maximum Ferrite, and .03% Maximum Carbon.

We have found after some six years of operating experience that when the Ferrite content in the metal exceeds 2½%, for example, 3 to 4%, we experience serious corrosion on valves in carbamate service.

On the other hand, our let-down valve on the urea reactor contains less than 1% Ferrite, approximately 12% Nickel, and 17% Chromium. This particular valve has been in urea-carbamate service for three years and shows evidence of little or no corrosion.

The stem and seat of our reactor let-down valve is made of 316 ELC and the valve packing is of the teflon-chevron type. The stem and seat give reliable service for a period of one year. We also experienced stem breakage in this valve and attributed the failures to corrosion which in turn was initiated by a graphite impregnated packing.

We have the characteristic corrosion problems on the carbamate manifold used in conjunction with high-pressure, positive-displacement Union Pumps. We have experienced failures in the pump blocks and at the present time are on our second block replacement. At this time, we have on order a 329 stainless steel pump block which we expect to try within the next three months. Returning to the carbamate manifold, we have experienced no serious corrosion in valves that contained a 329 stainless steel stem and a titanium seat.

F.W.S. Jones (Canadian Industries, Ltd.): I was in Europe some little time back and encountered a manufacturer who was making electrodes which were to conform with the Stamicarbon requirements for ferrite. He informed me, and it seems to be consistent with most of the things mentioned here, that corrosion appears to peak with a ferrite content in the region of 4% to 6% ferrite. In other words, a low ferrite content is all right, below 2% --the region between 2% and perhaps 8% represents a hump in the corrosion rate curve, and as one exceeds the upper limit and goes to increasing quantities of ferrite, the corrosion rate again becomes acceptably low.

Type-329 would be a largely ferritic material. It would have large quantities of ferrite in its microstructure and this, of course, would be consistent with its javing a ferrite content substantially above this critical region of between, say 2% and 8%. Nort Walton noted that one observer suggested that below 2% would be desirable and another suggested that higher quantities of ferrite would be all right. This is also consistent with the situation in which there appears to be a critical region which needs to be avoided.

Teflon-lined valves (Walton)

Earlier I mentioned the difficulty that we have had with Teflon-lined cocks of the 6-inch size on the section of our carbamate pumps and that we had gone over to ball valves, in accordance with some recommendations that were made last year at Minneapolis.

I would like to call on Bruce Hawthorn of Sun Olin to bring you up to date on our experiences this year with let-down valves in the line from the reactor. We had a history of a great deal of trouble with these valves. In most cases the stems broke and in other cases they jammed, etc.

Discussion

Bruce Hawthorne (SunOlin Chemical): Our biggest problem was the breaking off of the plugs from stems because when this happened, it immediately stopped the flow from the reactors. We did a couple of things at the same time. We overhauled the stem guide bushing because this had corroded over a period of years. It had worn away and was allowing the plug to whip and we felt the failure was due to fatigue.

At the same time we also increased the sten size from ⅜ in. to ½ in.; the size of the plugs stayed the same. Also, we changed the metal of the plugs from 316 ELC, which it had been from the early years of the plant, to a 15-7 MOPH type. The erosion and corrosion of the plugs after two or three months was such that we could no longer maintain control of the reactor pressure and we were forced to go back to the 316 stainless which lasted approximately 9 months to a year.

We have not had any failures where the plug became separated from the stem since this work was done about a year ago.

Elevator maintenance (Walton)

There was discussion at the meeting last year on elevator maintenance problems in urea plants.

Since last year we have simplified considerably the control system on our passenger elevator on the prill tower and removed such devices as automatic leveling controls and also simplified considerably the call system, making the operation of the elevator more manual than before. This enabled us to remove an amazing amount of electrical gingerbread and whereas I can recall having to call a serviceman as often as once and sometimes more than once a day, in the past. Since the simplification of these controls, this situation has improved considerably.

Another item that we have had a problem with recently is in materials. This is the problem of the type of rubber and the reinforcement of rubber in the hot prill belt on the prill tower. We had thought that the failure of our belts -- we are on the third one -- and we had felt that the failure of the others were due to mechanical things, lumps falling on the belt, the belt getting snagged on shoes, this sort of thing. I guess now we have a feeling that perhaps it may be a temperature problem, perhaps aggravated by mechanical problems.

Miscellany

Last year there was some mention made of the fact that we found in our nitrogen that we were buying, merchant nitrogen, that we had a hydrogen content which varied between 0 and 50 parts per million averaging somewhere around 5. This seemed to be a rather new concept, that is very few people realized that it was possible to have hydrogen in this amount in nitrogen.

The reason for it appearing there, in the source of supply which we have, is still not clear. However, we have installed a deoxo catalyst unit, a very small reactor, in the line. We pass the nitrogen through that and add the proper amount of air to it. This completely and very satisfactorily removes the hydrogen from it. This is a deoxo unit in reverse of the usual way that deoxo is used. I thought this might be of interest.

One last point, the Compressed Gas Assn. has available a handbook on compressed gases which costs $20. It is published by Reinhold. If you order from CGA, you get a 20% discount if a member of that organization.