HYDROGEN FIRE

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In our Millhaven Plant we use hot potassium carbonate to remove the bulk of CO_2 and H_2S from the process gas stream. The scrubbing system is single stream, composed of CO_2 absorber, a regenerator and a single stage double suction 500 hp, 3600 rpm centrifugal pump with a similar spare unit.

Prior to the accident flow to the absorber was controlled by an automatic flow valve located in the common discharge line of both pumps. The pumps were isolated from the common suction line by means of a single gate valve which was normally kept open to keep the spare pump flooded. The pump discharge was isolated by means of a check valve and a gate valve which was normally closed.

The method of switching pumps was to partially open the discharge block valve on the pump to be put on line, start the pump, partially close the discharge valve on the pump coming off line and shut down the pump. Because of the size of the valve and pressure, it was not possible to close the discharge valve completely in time to prevent cavitation. Therefore, we had to shut down the pump and rely on the check valve to prevent back flow.

On 7th April, 1961, a routine pump switch was being made in order to repair a leaking nipple on the operating pump. As soon as the operating pump was shut down, flow was lost. An immediate check showed the pump which had just been taken off line was running in reverse. An attempt was made to restart the pump, but the pump motor, unable to overcome the reverse momentum, failed on overload, and the pump continued to accelerate in reverse. The area was abandoned seconds before the pump motor and pump destroyed themselves. The pump packing glands failed, allowing process gas to escape into the pump room. Two or three explosions resulted, followed by an intense local fire. The fire was extinguished by dropping purification pressure and introducing nitrogen. The flow valve in the main line was shut to reduce the back-flow of gas.

Cause determined

Following the accident, we discovered that the 1/8 stainless steel washer holding the check valve disc to the yoke had worn and allowed the disc to drop enough to foul the valve bottom, thus jamming the valve in the open position. This allowed unimpeded back-flow.

To reduce the chance of such a check valve failure re-occurring, we ground all sharp edges on the yoke to reduce wear, and also installed a thicker stainless washer.

We were forced to operate on one pump until June, when we installed a new motor and pump. The discharge piping was altered as follows:

A flow control valve was installed on the discharge of each pump. Their purpose, besides acting as a flow control valve on the operating pump, was to act as a discharge block valve on switching pumps.

By means of a small control panel near the pumps, the control of carbonate flow is taken over from the main control board. The manual block valve is opened on the idle pump and the pump is started. The flow is increased on one pump and decreased on the other pump by means of the pneumatic flow valves until the flow control valve is shut on the pump coming off line. The pump is then shut down. As you can see, the pumps are always started and stopped against a closed valve, eliminating the tremendous hammer caused by the check valve closing. Secondly, since the manual discharge valve is not used as a throttling valve, there is less wear and it is more reliable as an isolation valve when required.

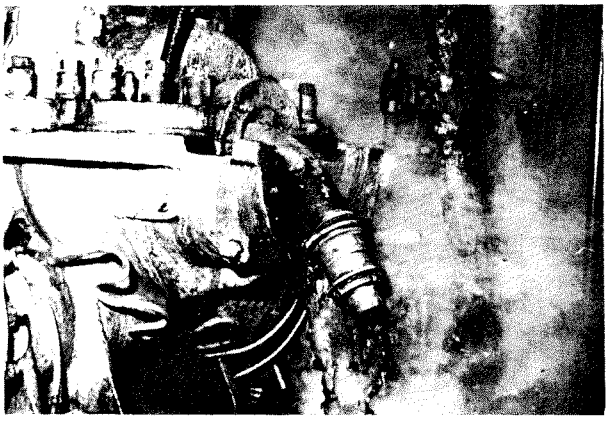

Figure 1. Note how shaft softened on 1,200 U.S.E. PM pump.

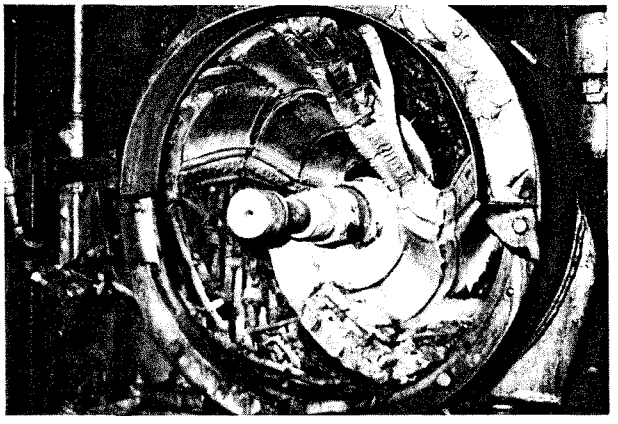

Figure 2. Induction motor damaged was 500 h.p., 4,150 volt, 3,600 rpm.

We have also installed a check valve and manual block valve on the discharge flow line outside the pump room. This will allow us to isolate the pump and piping under emergency conditions.

DISCUSSION

WELLS—Calumet Nitrogen: Could you give us the pressures in your absorber and in your stripper regenerator?

LAMOND—Canadian Industries: We operate the absorber around 360—365 pounds and the stripper operated with a back pressure of about four pounds.

DUNCAN—Southern Nitrogen: I would like to report that Southern Nitrogen had two similar failures approximately two years ago. We have, since these two failures, changed our check valve from the flapper type check valve to a Williams-Heager check valve. In fact, we have replaced all discharge check valves on all of our purification pumps to these type check valves and we find them very satisfactory. Also, on our big 500 pump motors, we have put a non-reversible brake on the outboard shaft of these pumps so that these motors cannot turn backwards. In other words, when you start the reversible flow, when this motor is at a real low speed, it will hold the pumps. It will not let them reverse.

LAMOND: We thought we might as well go one step further because you may stop the motor from reversing, but you cannot stop the gas and liquid from pushing back into the regenerator and possibly bursting open the low pressure lines as ours did. I did not mention that as part of the damage, but actually the bottom bed of our generator bumped and then came down and collapsed the supports. There was a tremendous surge of gas and liquid back into the regenerator. It is just not built to take it.

MASON: I was looking at that chain valve outside the building. The only time that you would need this outside valve would be when you had a large flow through there, and I question whether that chain valve would operate under these conditions.

LAMOND: Yes, it will. On a chain valve, you have a little more leverage, and, secondly, operators can put their full weight on the chain.

HAUGHTON—Du Pont: Could you give us the manufacturer's name on this brake mechanism that you use in the carbonate pump?

DUNCAN: I couldn't give you that information right now. I could certainly let you know.

GENERAL DISCUSSION

JENKINS: On our hydrogen wash box, we have a problem. Our hydrogen source is a waste refinery gas and there is some acetylene in it. We attempt to wash it out with an exchanger. However, we did get an explosion in our wash tower this January. It was a limited explosion and not very serious. In fact, nobody heard it. Suddenly, we just couldn't scrub CO out. The trays were installed with a four-inch tray space, but there was a four-foot space between two of them after the explosion so that we definitely had some force between these trays. We were thinking about installing a methanator upstream of our wash box. This would eliminate any unsaturates and clean up anything that could cause us trouble. I wonder if anybody has ever considered this before.

GRUNBERG—PROCESS DEVELOPMENT, Air Liquide: I don't see how acetylene could be responsible. On which tray of the Nitrogen Scrubbing Column did the explosion occur? On the first tray or higher up?

JENKINS: I think it was between the 23rd and the 24th of the sixty-eight tray scrubber.

GRUNBERG: It is physically impossible to find more than a very small fraction of one ppm of acetylene in that section because acetylene has a very low vapor pressure at that temperature. There is no methane left even two trays above the bottom of a scrubber column.

JENKINS: We have found it very difficult to believe ourselves and we don't say that it is acetylene. We say we just haven't found the answer and felt that perhaps elimination of all unsaturates would get us to the point where we would be much safer.

GRUNBERG: Did you say that you did not note this explosion when it happened?

JENKINS: That is correct.

GRUNBERG: I will propose an explanation for the destruction of these trays. At one time there may have been an abnormal flooding in that column and the feed gas being introduced suddenly the plant was restarted and some trays were damaged by the heavy impact of the accumulated liquid.

JENKINS: You feel that we had liquid nitrogen possibly due to some kind of blockage in the tray and that when we put in warm hydrogen that we vaporized a tremendous amount of nitrogen.

GRUNBERG: Yes.

JENKINS: This was after start-up, and of course strange things do move through cold boxes on start-up.

GRUNBERG: As you know, sometimes a level indicator cannot operate when the liquid phase reaches the top level connection.

BOLLEN: We have had freeze-up of methane in the bottom trays of our scrubbing column in the nitrogen scrub box, usually again after start-ups when the temperature of our methane condenser is a little on the warm side. And this has resulted in nitrogen hold-up. Initially, when this occurred, our operators weren't alert enough to catch it and we could build up a substantial quantity of nitrogen. This we found when it did finally break through and we had nitrogen coming out by the barrels in the bottom of the column. Now the operators are alert enough to catch it rather quickly and by fluctuating the pressure slightly in the box, you can usually shake it free and continue operating.

WEIGERS: Did the difficulty occur right after a start-up with a warm condition?

JENKINS: Yes sir.

WEIGERS: The reason I asked was that quite a few years ago, we were operating a sieve tray plant and from all appearances started it with water on the trays

in the low pressure column. This effectively blocked the gas passages and we tore 17 trays out of the column on start up. Mechanical damage is very possible.

LAWRENCE: I disagree with Mr. Grunberg on the fact that you don't get acetylene in the scrubber. Actually, we have ethane, ethylene, and everything else in the scrubber. We found it all through the tower and the pattern of this explosion, if we may use the word, originated in the middle and worked toward the ends. It wasn't a simple blockage. We would have readily noticed a simple blockage. We never established what it was, but it is an unusual thing. It leads me to a question I wanted to ask this group on cold boxes. We have a rather firm feeling in this group that we should derime an air plant every year. On a nitrogen wash box, you don't have to derime every year as far as process reasons go, but do we feel that you should derime that box every year to remove acetylene or nitrogen oxides or other possible contaminants?

GRUNBERG: We have to deal, generally with small concentration of unknown impurities. It is a safe and recommended practice to plan a short yearly shutdown in order to derime and clean the units. Some units have been running continuously for two and a half years but this is not a safe way of operating the equipment. So, there should be a standard period between shutdowns for any plant. To save five extra days of operation in a year may often be a costly risk.

BOLLEN: We have been in the practice of shutting down and deriming our nitrogen wash box at least once every year. However, this is not done solely for safety reasons but also because operating conditions make it desirable to do so. There are usually enough interruptions and changes in feed gas flow, compressor troubles and other plant operating difficulties to cause several short shutdowns of the nitrogen wash box during the course of the year. These shutdowns, of perhaps a few hours at a time, cause changes in the operating conditions of the box which gradually reduce the rate of production from the unit.

WEILAND—Ketona Chemical: We ran, approximately two years, on our nitrogen wash system, feeding coke oven gas. We had washed parts of the system with chlorothene but had not given the system a caustic wash. Then, on the occasion of changing a valve, we found a very thin deposit of black material, so we washed the entire system with caustic and got out not a gross quantity but an appreciable quantity of black tarry material. It was not an extremely dangerous material which many of these nitrogen compounds are; but nevertheless, was enough to alarm us. We have now established a firm policy of washing the entire nitrogen wash system once a year with caustic. We wash certain parts of it with solvent but we feel that the caustic wash is more effective on these deposits which are probably reaction products between NO and acetylene. They are more effectively removed with caustic. We insist on removing them once a year.

TIXHON: It is a standard practice in Europe to derime and clean the nitrogen scrubbing unit when running on coke oven gas after having fed between 1,000 and 1,500 liters of NO into the cold box.

GRUNBERG: I agree with these two gentlemen. Coke oven gas units are cleaned once a year with a caustic solution.

HAUGHTON: We have a system that consists of a first stage CO_2 removal by hot potassium carbonate. The second stage by monethanolamine. Recently we had occasion to inspect our MEA regenerator. We found considerable corrosion in the low section of this column which is stress-relieved carbon steel shell, bubble caps and trays. The corrosion was very severe. As a matter of fact, the bottom trays had lost both bubble caps and chimneys. There was corrosion on the column wall to the extent of 3/32nds of an inch which was at the vapor-liquid interface. We have determined the wall thickness is still sufficient for its structural strength and wind loading but we are concerned about what to do about this in the future. We are considering a stainless steel column with stainless steel internals, which is not a cure. I would be very happy to hear others comment about this problem which I realize is not peculiar to us.

JENKINS: We have a clean-up system for our Girdler units. We take the slip stream through what is called a redistillation unit. We run the MEA through this batch still and the overhead then returns to the system and the underflow is the residuals that they tell us causes the corrosion. The redistillation unit was supplied to us by Girdler Corp. We don't operate ours continuously but we do operate it whenever we get any amount of impurities in our MEA.

CULP: I think there are as many experts on this as there are people in the room. We have gone through your phase of corrosion with carbon steel on the column. We have eaten stainless steel out the same way so don't count too much on that. We have had marked improvement in one plant by the uniform addition of sodium silicate. In one plant, it worked beautifully. In the other plant, it did not work at all. There was a little difference in the operation. The dirtier the MEA physically, the cleaner the tower was and the less corrosion we actually had. The nice clean system we are eating up at a very rapid rate. The silica will help, but you have to be very careful with it. I would suggest a silica content something in the neighborhood of 150 ppm, not any more than that. And it should be added uniformly and not in a "slug."

WELLS: We have used an inhibitor. It is a filming-amine type inhibitor. We have had no appreciable corrosion. I think the temperature in the bottom sections, particularly the reboiler of the stripper, is extremely important here. Ours operates at low pressure and, of course, the lower the pressure, the lower the temperature to do the stripping job. We had some trouble with the build-up of dirt and we added just a slip stream filter, filtering a little less than 25% of the amine. This has kept the system a lot cleaner, but we have noticed no change in the corrosion rate which has always been low.

VAN WINKLE: Ken Moore of Atlantic Refining wrote a very good paper in which he described a technique for continuously measuring the corrosion rate. One of the problems encountered when you start to "cure" a corrosion problem is knowing when you start accomplishing your purpose. These probes can be installed and are a resistance device where the cross-section of the probe determines the electrical resistance.

WALKER: I believe these probes go under the name of Corrosometers. They come in tubular solid wire type probes. They also have strip type probes. Depending on your use and your rate of corrosion, you pick your probe.

MARRIAM—Grace: We have had practically every known type of corrosion in MEA System and have made every conceivable effort to eliminate this corrosion. One of the things we used was these corrosion probes

in an effort to check our corrosion and the effectiveness of our test. What we found was that in using these corrosion inhibitors, they inhibit the corrosion on the probe to a very fine degree and it looks as though you are doing a marvelous job. In the meantime, your tower disappears. One thing that we have noticed, however, is that our bubble cap trays which are cast iron are untouched. The tower, however, which is carbon steel, (sometimes lined, sometimes not lined with stainless) disappears at a rapid rate. However, we noticed that the pattern of corrosion is a washing corrosion at the downcomers and one of the ways that we tentatively stopped it on the tower was to install cast iron wear plates in these spots.

HAYS—U. S. I.: I was going to mention previously that we have planned to begin monitoring the corrosion with a Corrosometer but after these comments, I am beginning to wonder. Did you just discontinue using the probes or did you find a means where you could get an idea of fates in your vessels with the Corrosometer probes?

MARRIAM: Luckily, at the same time we were using this electronic type of probe, we also had the standard samples put through the nozzles so we could check the corrosion this way. We continued this. This does give us a very good indication of the location of the corrosion as well as the rate.

WELLS: We have used similar probes on our cooling water at a number of spots from time to time and occasionally we have gotten spotty results both ways. In general, the pattern with probes has given us a pretty fair picture of what the corrosion actually is in the equipment.

WALKER: We did find one trouble in an MEA system where we had a high corrosion rate. The degradation of products which contained the iron seemed to plate out on the probe and these unfortunately conduct electricity so instead of your resistance going up in your probe, it goes down in your probe, indicating you aren't corroding your system.

HAYS: Has any one had any problems with rain coolers? At U. S. I., we have the Vilter rain coolers, and we are beginning to get in trouble on corrosion. Also, we have had quite a bit of trouble with the flange connections. Of course, we are getting quite a bit of external corrosion and right now, we are looking for a new design for welded headers. I understand there are some with all welded headers in service now. On materials of construction, I also had another question. In our cold box, we have had some gasket troubles on the large flanges of the columns—low pressure columns in particular. We have been using Garlock 900 gaskets, and we have had some leakage trouble. We plan to go to glass-reinforced Teflon. Has anyone had any experience with that particular type gasket? Our concern with Teflon, of course, is with "cold flow," but our understanding of this particular gasket is that it is almost eliminated and you can get up to 1200 to 1400 psi compression stress on these gaskets.

TIXHON: When we started our cold boxes up at Brockville Chemicals, Liquid Air tried some Teflon gaskets but none of them could withstand the low temperature and we, therefore, had to replace them.

MACKAY: I would like to know if anybody has any experience to report on the use of transition joints between aluminum and stainless steel as compared to flange connections.

KEITH: We began working on a transition joint of the type described about ten years ago. The first joints developed were a compressive joint which employed a stainless sleeve, an aluminum muff which was "shrunk" on and then another stainless "car" on the outside which in turn was "shrunk" on and then it was put in a press and compressed. It was peened, and hammered and banged on, and we did everything to try to get them not to leak. When we first put them in service, it worked pretty good. After a very few months, they started to leak a little. Recently we have been able to come up with a unit which actually employs a metallic bond between the stainless and the aluminum. We have had those in service in pressures ranging from atmospheric to 1500 pounds and ranging down to minus 320°F. They have been installed and in operation since about the early part of 1958. They have been installed in two commercial plants that we have built and, so far as I know, we have had no difficulty with them at all. They do not leak. They have shown no evidence of any fracturing. We have cycled them under laboratory conditions and now in commercial conditions from ambient temperatures to minus 320 both under pressure and not under pressure and thus far we have had no problems with them.

BOLLEN: Would you care to comment on the range of sizes which are available? I understand that transition joints for pipe as large as 8" have been made and I have heard that such joints are now in production for 12" pipe.

KEITH: The last I knew they were making it in eight-inch sizes and I think now that they are in production up to twelve inches.

PENROD: There was reference to the use of gaskets within the cold box. I have some very definite convictions which we can back up by good, continued operation. It is that any place where you can avoid having a flange of any kind, it is better not to have it. I believe that it is beneficial to use a welded joint everywhere you can. In other words, keep any mechanical joint where you are depending upon bolts or torque to hold them together out of the cold box.