

AIR SEPARATION AND AMMONIA PLANT SAFETY SYMPOSIUM

Transcript of unpublished proceedings from A.I.Ch.E. National Meeting, Tulsa, Oklahoma, September 25-28, 1960.

Centrifugal compressors

J. W. BUDDENBERG - Collier Carbon and Chemical Corp., Brea, Calif: We had a little maintenance problem with one of our centrifugal compressors, and I wondered if some of you had run into the same thing. We periodically had opened the nine-stage compressors and Magnaflux inspected the impellers. Each year when we made this inspection we were very happy to see that nothing was occurring except minor pitting in the impellers.

This year, after five years of operation, we found that cracks were developing on the impeller proper. Since this compressor turns at 11,000 rpm, we were quite worried about this. We are replacing these with stainless impellers of our own design. We're going to 410 stainless, and we're getting away from the riveted construction which we think is the source of the cracks. The cracks that we did notice were proceeding right along from rivet to rivet, so we are replacing the riveted construction with a furnace-brace construction. I wonder if others here inspect their high speed compressors this way, and have they found any such deterioration?

G. WEIGERS - American Cyanamid Co., New Orleans: We have centrifugals in our service that are of domestic manufacture. We Magnaflux the rotors every three years, and we have now gone through two of these inspections and so far have found no cracks that were not traced back to an initial forging problem in construction, and they were corrected without replacing the rotor.

P. C. KEITH, JR. - Hydrocarbon Research, Inc., New York: In most cycles in air separation plants, one of the things that can be done to avoid the problem of contaminating oil from expanders is to expand a material other than air. There is a sort of a moot argument that goes on as to whether you lose anything in recovery by expanding nitrogen rather than air, and this has certainly not been proven yet—at least, not to our satisfaction. If you do expand nitrogen in a low or medium pressure cycle, this nitrogen normally goes directly to waste from the expander. It provides the same refrigeration and it is out of the tower system completely. The discharge from the expander never gets to the tower; it never sees any concentration of oxygen greater than about 97%—98% nitrogen. This is, of course, one way completely around the problem.

So far as mechanical leakage of oil is concerned: we have in some cases installed expanders upright rather than in a horizontal plane, with the bearings located outside the box and down below, so any dripping or any leakage of oil leaks directly on a pad outside the cold box rather than into the cold box. The head of the expander itself is located up in an auxiliary box which is completely separate from the main cold box.

P. S. HEPP - Sun Oil Co., Marcus Hook, Pa.: We originally had expansion turbines with no positive seal between the oil loader and the air wheel, and had considerable carryover up through the labyrinth seals into the process. In the redesign of our plant, we have a seal system that is interposed between the oil wheel and the expansion wheel. A 300 pound air system is injected through orifices, and it blows out through a little bleed, and any oil leakage up past the labyrinth seals is automatically forced out this bleed. We feel it's a hundred percent effective, and the one or two times that our labyrinth seals have failed, oil has blown out this bleed, telling us we're in trouble. To the best of our knowledge, we've examined the piping to and from the expansion wheel on shutdowns and find no oil or anything, in about three years of operation. I think that you can modify this type of expander, to be completely safe.

F. G. KERRY - American Air Liquide, New York: We have centrifugal oxygen compressors for compressing oxygen to a relatively low pressure and we use ordinary mineral oil lubricants. We feel that with these particular compressors, the way they are designed and operated, there is no real hazard, providing we don't have an actual failure of the machine. We feel that the additional cost of the so-called non-flammable lubricants—and I use the term advisedly—is not justified.

I'm curious to know whether there is anybody else who uses mineral oil as a lubricant in oxygen compressors?

W. W. FETZER - Du Pont Co., Inc., Belle, W. Va.: We have handled high pressure oxygen with centrifugal compressors up to 550 pounds/sq. inch. We use mineral oil with a very extensive sealed air system, and we've had no trouble.

ANONYMOUS: As a result of one oxygen compressor fire, we have installed some very fine mesh filters in our sealing system, because one of the theories for the cause of that fire was a rust particle or some metallic particle in the sealed air system, blowing into the seals and causing overheating, which resulted in an oxygen fire—on a compressor which, by the way, was using a synthetic lubricant.

FETZER: I might add that our seal air piping is all stainless steel, and all of our high pressure piping is stainless steel, and it was all very thoroughly solvent washed before being placed into service.

J. E. HART - Dow Chemical Co., Midland, Mich.: We took some action recently that some of you with older plants might want to consider. We found ourselves with an oxygen dump tank literally within a few feet of our main operator's station. The possible hazard if we dumped a contaminated charge of oxygen bothered us. As the oxygen evaporated out of the dump tank, we would have an undesirable concentration of the hydrocarbons, conceivably getting into the flammable and explosive range. So we moved this dump tank about 200 feet away and connected it with a 3 inch schedule 10 aluminum alloy line. We've used it once since, and it's worked quite well.

KERRY: Could I ask whether you just dumped the liquid oxygen into this tank and let it evaporate gradually, or do you take any steps to heat it up to get it out?

HART: No, we just let it evaporate gradually.

D. C. LAMOND - Canadian Industries Ltd., Kingston, Ont.: I might describe an incident which occurred in our plant. We have high pressure oxygen pumps in our plant, with carbon seals. One of these pumps had been repaired and put on the line, and due to a clearance problem or for some other reason the seal apparently overheated, and we had a small fire in the seal with gaseous oxygen. In this case there was heat present, and the carbon ring provided the fuel. The damage was not severe; the fire was quite easily quenched. (We, also, have a stainless steel dump tank with stainless steel piping. We force the evaporation by the use of steam, and the steam is left on the tank after the oxygen has been dissipated to prevent an accumulation of solid hydrocarbons.)

Vaporizers

J. W. TURNAGE - U. S. Steel Corp., Monroeville, Pa.: One oxygen plant we have disposes of oxygen by using a jet ejector of a type used to supply air to ventilate tanks. A steam hose is connected to the compressed air connection of the ejector and a copper tube carries the oxygen dump into the air intake of the ejector. With the steam turned on full blast oxygen is admitted into the steam stream. Is there any experience which indicates that it is not safe to mix oxygen with a large volume of steam, vaporizing it immediately and mixing it with diluent?

F. HIMMELBERGER - Air Products, Inc., Allentown, Pa.: In a number of plants that I'm familiar with, I know that that system is being used and used satisfactorily. There is one weakness to be considered. That is that the steam must be applied first and the system must be kept warm. The possibility of plugging the system due to residual water condensing in the line and freezing the system must be eliminated. If a steam vaporizer seems to be the best approach, a system in which intimate contact between the oxygen and the steam is avoided is preferable. However, the steam injector with direct contact has been used satisfactorily in a number of places. In these cases, some type of alarm should be used to make sure that the system is warm, and that steam is flowing properly before the oxygen is permitted to flow.

KERRY: Is your only fear of such a system the possibility of freezing and breaking steam lines?

HIMMELBERGER: Yes. To be more inclusive, the fear of not having an operable system when it is needed.

KEITH: It's very important, if you have a vaporizer which is using steam, to get your steam there first. In a couple of cases we have not gotten the steam there first, and we have just had a bunch of tubes with ice in them.

I just want to make a comment about leaks in cold boxes. Most of your leaks, of course, will occur around flanged joints or screwed joints, if you have any of them. We've built a couple of units up at the laboratory for test purposes, and therefore have not felt inclined to weld them up. And as a result, we have quite a few flanges, and we have had some leaks. What we have done, in cases where we have had flanges

which could leak, is to tape the flanges heavily and actually run tubes from the flanges to the outside of the box. Now, this is a kind of a drastic method, but if you have to it can be done, and it will give an indication if a flange is leaking. Our practice has been—and we think that it's probably the only way to avoid leaks—to weld and avoid flanges and screwed joints wherever you can.

BUDDENBERG: This comment concerns the question of leaks in cold boxes. Our particular problem was with a nitrogen wash column box, and not with a nitrogen unit. However, I believe the same method would work in either case. We had quite good success using a halogen detector. The particular instrument was General Electric's Model H-1, I believe, which is capable of detecting a leak of halogen of about an ounce per year. So if you use this method, make sure you put very small quantities of halogens in your box. By putting, first, a nitrogen atmosphere in the box, and then the halogen in with it, we were able to zone the box and find the area where the leak was with either probes or by taking the plates loose from the box. Then after you narrow it down, of course, you have to take out all the packing, and you can further find it by either increasing the halogen in the box or increasing the pressure.

KERRY: Do you use this system while the box is still cold?

BUDDENBERG: No, the box is shut down and warmed up.

W. C. TUEL - Linde Company, Tonawanda, N. Y.: A little more on the steam vaporizer: We have used steam vaporizers quite extensively for several years. There are two or three important considerations:

1. The steam should be free of oil or hydrocarbon contaminants, such as might occur if withdrawn as exhaust from reciprocating engines or chemical processes.
2. The system should be designed with a reservoir or sufficient isolation, so that liquid may be drained on an emergency basis, even if steam is unavailable at the moment.
3. Vaporizer should have thermostatic control so that liquid oxygen cannot be introduced unless the vaporizer is hot.

A steam vaporizer can be utilized very effectively and is an efficient practical means for disposing of liquid drainage from an air separation plant.

T. C. KRYZER - Standard Oil Co. (Ind.), Whiting, Ind.: When we built our plant, we considered both a blowdown pipe and an eductor. We went to the blowdown pipe because we felt that it was foolproof under all conditions. Since then, we've had a number of power failures during which there was no steam or air pressure available to operate an eductor. The air plant had to be blown down under these conditions.

Our blowdown system consists of a stainless steel tank about 6 feet high and about 3 feet in diameter. The tank is bottomless and rests on a crushed rock bed. A 3 inch brass line connects the air plant to the tank, which is a couple of hundred feet away from the air plant. We have a low concrete wall around the area, just to keep debris from blowing into it, and a Cyclone fence on the top of this wall.

To get intimate mixing of the vaporizing oxygen and the air, or to have that occur as rapidly as possible, we've installed a funnel shaped hood on the top of this tank, with steam nozzles to start circula-

tion of the air in the steam and the vaporizing oxygen, it's worked out pretty well. We used to have a system without this funnel type roof or hood over it, and we used to get a heavy ground fog during blowdown. But since we put in this type of system, it's carried up in chimney fashion, and it's dispersed quite well.

Lubrication

K. B. KNOX - St. Paul Ammonia Products, Inc., South St. Paul, Minn.: I have a question that goes back to lubrication problems, primarily on liquid oxygen pumps. We feel that primarily the reason for a failure of the seals is the lack of continuous adequate lubrication to the face of the seals. And one thought has been to convert the grease-type seal to a liquid feed which would have a reservoir with a small head on to keep the lubricant on the face of the seals. I've been a little reluctant to consider that too thoroughly because I haven't yet seen anything that says for sure that these liquid fluorolubes are thoroughly compatible with liquid oxygen, and in case the seal leaked some of this could get down into the pump casing and contact much more oxygen than if you have a grease type of seal where it's already congealed and sort of sticks up inside your pump.

G. PORTER - Dominion Foundries & Steel, Hamilton, Ont.: With the cooperation of John Crane Packing Company, we are working on a continuously-lubricated seal for our oxygen pumps. We had the same trouble with the seals on our low pressure oxygen pumps—wearing down of the metal—and we were afraid of sparking. So with their cooperation, we are working on this seal. We will put a special grease in a cylinder with 30 pounds air pressure. This seal will be continuously lubricated. We feel we'll overcome a lot of our troubles this way.

KNOX: I might comment again that we have tried that procedure of a continuous pressure feed on the grease, and that still didn't work out. I hope you have more success. The puzzling point is that actually it's not the carbon or Teflon face, it is the metal part of your seal that becomes cut into a channel or groove. That's the type of failure we have.

PORTER: We found out that where there were so many holes where the lubricant came through the carbon, we felt that it was cutting the steel, and the steel showed a prominent groove all the way around. We felt by putting less holes, countersinking the holes so the grease would get through, that we'd have better lubrication.

KNOX: Does anybody have any experience with the liquid fluorolubes in this type of seal?

E. H. CULP - Caribe Nitrogen Corp., Guanica, P. R.: You ask about compatibility of fluorolubes with oxygen - at about 675 degrees F, we managed to blow up a very nice little test rig and scatter the safety glass shields around with a fluorolube.

Locating leaks

R. L. STEVENS - Canadian Industries Ltd., Kingston, Ont.: I would like to comment on this problem of finding leaks in equipment. I believe this has been brought up at former sessions, but over the past winter we have constructed two models, one of our air separation unit and one of our scrub unit, and we have used these on several occasions to help us in putting a finger on the flange joint which might be leaking. They're

quite useful. It's surprising how many people have difficulty visualizing something from a plan. With a model you get a lot of help from people who otherwise might not have a suggestion. Of course, the models are used for other things, too, but they are helpful in locating leaks.

J. H. CONKLIN - Du Pont Co., Inc., Gibbstown, N. J.: We, too, use rather accurately constructed scale models of our cold equipment, and find them very useful for maintenance work, particularly when we're tunneling. It's very nice as you're digging to watch the model and identify lines as you come across them. Also, on this halide test detector, we have found it a beautifully simple and sensitive arrangement for attempting to pinpoint leaks. I want to make one point of caution: It works fine the first time; subsequently, you have residual halides in your rock wool or whatever you have as insulation within the boxes, and it's amazing how this residual halide migrates about. So the second time you're forced to a little higher halide level in order to overcome the background concentration. After about two times around the cycle, you have to devise something else, because even when you have put in new insulation, in a month or two it likewise will give you a very positive test for halides, and it's amazing how this will migrate when you don't want it to, and how it'll stay in one place when you do want it to move about.

H. F. FUNK - Linde A.G., Toronto, Canada: I would like to comment on the subject to leaks. It is always rather difficult to find the exact spot where the leak occurs, especially if the box is fully insulated. If, however, the design of the coldbox incorporates a double wall insulation, the problem of finding leaks is most conveniently solved, since you have access to the interior of the box through a door. It means you warm up the interior after a shutdown and then walk into the box to fix the leak. After that you start up again without having to remove any wool or insulating material. The removal of rockwool can be quite cumbersome. While you are working your way into the box gradually when taking out the wool you also have to provide a dry storage space for the removed material.

E. V. SVOBODA - Dow Chemical Co., Plaquemine, La.: I hear all this conversation regarding the cold box inspection or probing; I was wondering, would it be advisable on initial installations, or new installations, to install numerous pipes or small probes throughout the box so that you could take samples from different areas in order to assist you in future leak detection?

W. I. WALKER - Cyanamid of Canada Ltd., Hamilton, Ont.: We have a nitrogen wash box where just such a procedure has been followed, and we have 16-24 zone boxes, which consist of small wire baskets suspended in the insulation with quarter inch stainless tubing. These have proved very adequate in detecting leaks, provided you can keep them from plugging. We find that we're bedeviled with water vapor leaking into them and eventually plugging the zone box tubes leading out. Now, the solution to this is evidently to use a larger tube, or use the steam jacketed tube. The steam jacketed tube would probably only have steam on it during the time when you were using the zone box. We combine this with gas analysis on a chromatograph to spot the leaks in the box, and as I say, it has proved very adequate for detecting leaks.

HIMMELBERGER: Perhaps too much has already been mentioned on probes, but a very good solution is to put

numerous pipe caps on the wall of the cold box—perhaps 1-1/2 or 2 in. in size—so that a small diameter probe on the order of 3/8 inch—can be inserted, and directed most anywhere into the insulation. The location of the openings should be selected strategically with distribution of equipment inside the box in mind. This is done more frequently on hydrogen boxes than it is on air boxes but it's a workable method of getting a probe into a box and getting it to a number of different locations.

KERRY: Would you make a statement about this explosi-meter shutdown device you have on your air compressors?

W. A. MASON - Dow Chemical: It is a Johnson-Williams type unit that samples the air intake to the compressor continuously. It is designed so that it will sound an alarm when the concentration of the hydrocarbons in the intake to the compressor reaches 20% of the lower explosive limit. I believe that's based on methane. If the concentration reaches 40% of the lower explosive limit the unit will automatically shut the compressor down. This of course, shuts the whole plant down. This unit has never shut our plant down, but we have had indications on some occasions where the concentration of combustibles has gone high enough to show us some evidence of the combustibles in the intake. This equipment is designed primarily to shut the plant down if anything should happen in the immediate neighborhood to spill a large quantity of combustible mixture into the air.

We also have an infra-red analyzer which operates in a much lower range and gives us signals of any combustible materials on the intake air that come in at lower concentrations.

Continuous bleed

HEPP: Just after our original start-up we ruptured the line and had a serious fire, at the point where the nitrogen and hydrogen joined to make syn gas. This was caused by an upset in the low pressure tower due to something blocking the reflux valve on the low pressure tower. This has happened to us at least three times. We don't have any flow indication on the reflux, so the first thing you know, the plant goes off test on the order of 1 to 2% oxygen in a matter of less than a minute. It has been our practice to use the deoxo unit as a cleanup device only, not as a safety device, adding one or two hundred parts per million of hydrogen, equivalent to oxygen.

So what we've done now is add a continuous hydrogen bleed that will take care of 2% of oxygen, and then have a temperature recorder and temperature alarms on the outlet of the deoxo. We shutdown the nitrogen stream any time this temperature reaches 125 degrees F. which is equivalent roughly to four-tenths percent oxygen. Within the last year I've seen the concentration—the temperature—go to 125 degrees F in a matter of 20 seconds or so. But by having this large amount of bleed stream in there, you've got about a half to a minute to shut yourself down before it breaks through the deoxo, and it'll go right on up to 5-6 hundred degrees without any warning. That's a shutdown limit I've never heard anyone else discuss.

G. R. WALTON, JR. - Rohm & Haas Co., Pasadena, Texas: In our particular plant we have had a similar problem; however, our low pressure column does not get upset as rapidly as yours, and normally, to get it upset we have to lose reflux pressure. We put a back pressure regulating or shutdown valve on the nitrogen

stream feeding the deoxo unit which actuates any time we lose nitrogen pressure. Now, if the reflux nitrogen pressure surges, the deoxo unit is shut off automatically.

HEPP: The difficulty with our plant is that we have no indication of reflux at all, and examining the plant afterwards you can see where you've been running without reflux for perhaps a half hour, and by that time you've utilized up all the reserve you have, and it goes off in quite a hurry.

HART: We have a setup quite similar to what you're referring to, and we burn out perhaps a half a percent oxygen thru a deoxo catalyst. We have a temperature variation shutdown on the feed gas to this deoxo. If the deoxo discharge temperature varies over 50 degrees from the set point it shuts the plant down.

HEPP: I might add to this time standpoint—we studied the time constant on this deoxo and find that the heat capacity of the deoxo gives you about a 10 to 15 minute delay. If you cut in with a half a percent oxygen it's 15 minutes later before the temperature in the outlet goes up, because of the progressive wave through the bed and the building up of the heat in the bed itself. We've overcome this by putting a thermo-couple about 18 inches under the top of the bed that gives us an answer about 2 minutes after we get into trouble. This gives an additional 8 to 10 minutes to correct the trouble or to shut down before it actually will break through the deoxo.

KNOX: I think in regard to the last trouble there, you should get back to the source of it, which is your reflux control. We analyze both our refluxes—what we call pure and impure—on the basis of sometimes every hour or two hours schedule, and keep that oxygen concentration in the reflux as near constant as possible. It would run probably one and a half percent in our impure reflux and essentially pure on the line flowing to the top of the tower. If you do that, I'm sure that your product coming off the tower will be satisfactory at all times and you won't get into these fluctuations on the deoxo unit.

Recording analyzer

WEIGERS: We have a deoxo unit—actually, our concern, as I imagine yours is, is for the ammonia plant in case the oxygen concentration of the nitrogen goes high. But as far as controlling our nitrogen purity, we have, first of all, a recording analyzer with an alarm set point on it, which rings an alarm when the oxygen content of the nitrogen goes beyond a preset limit, and then we have a second alarm point which trips the nitrogen out of the header. Our situation may be a little different in that we're running multiple oxygen plants in parallel. We find that this is a very useful safeguard, particularly as one group of operators are covering more than one plant and are ranging up and down a fairly long control room.

As far as controlling reflux purities are concerned, we found it very useful to put an indicating instrument on our reflux purities to cut down on the amount of attention time of the operators and aid them in troubleshooting the plant and keeping it in line, spotting troubles before they get to the point where they start affecting other units that use our oxygen and nitrogen.

HEPP: Perhaps the value of my comments are that we could use these deoxos as an additional safety device.

The inclusion of sufficient hydrogen to burn a couple percent oxygen, which these units are designed to do—they're designed to do 3%—plus a temperature recorder at the outlet, can add perhaps belt and suspenders to an operation where you can have a bad explosion if the analyzers fail.

J. A. LAWRENCE - U.S. Industrial Chemicals Co., Tuscola, Ill.: In our plant we had a Beckman oxygen analyzer and we set it at 200 ppm, and it's an extremely reliable analyzer. We still check it with phosphorus about every half hour just to be sure, but it runs day in and day out, and we standardize it every so many days—normally, about once a week—and we have had very few problems.

Deriming schedule

J. A. GLASS - Monsanto Chemical Co., Texas City: We are quite interested in deriming schedules ourselves. The last run of our plant was for 18 months. During this run, we saw nothing unusual in the analyses of our reboiler liquid, and we have checked our rich liquid filter for its efficiency. We still find that it is in the 99% efficiency range. We had no technical knowledge as a basis for shutting down at this time. We are extremely interested in extending our runs to even longer periods, perhaps as long as two years. We are wondering how much the usual shutdown is for suspicion about things you do not know rather than for any other reason. I wonder how many other people shut down because of lack of knowledge rather than on the basis of things they have found by analysis?

LAWRENCE: We probably all, every year when it comes time to derime, have a little bit of fight with the people that want the production. I would like to go on record for myself anyway and say that until we know a lot more about these—both the hydrogen box and the air box—that this group stay on record as saying you should derime every year. We just don't know enough to say, maybe seven pounds is safe and ten pounds isn't. In our present state of knowledge, I can't agree that we can push it up to a year and a half or 15 months.

G. T. WRIGHT - Dominion Foundries & Steel, Hamilton, Ont.: Roughly a year ago, we were in the same position that you are now. We saw no reason to derime. Our pressure drops were fine. We had an examination of our plant by an outside man; he joined with me in saying that the plant was quite safe to operate—and about a week later it blew up. Now, we strongly recommend that a year is the maximum that you should go. We have recently run tests on the buildup in our vaporizer, and even in the plant that has a catalytic filter and 100% liquid product purge, there is still some small buildup in the vaporizer, and the only way we know to get it out is to derime and warm it up.

KRYZER: We have an auxiliary vaporizer, and we derime it a lot oftener than once every six months; we derime that once a month. It's a routine thing; it takes the operators about four hours to derime it, so it's no disability. And that's our schedule for the auxiliary vaporizer.

KERRY: I think we should sort of separate the low temperature plants into different categories. For example, let's consider first air separation plants by themselves. It's very difficult to generalize when a turndown should occur. If the air separation plant is in a fairly heavily contaminated area such as a refin-

ery atmosphere or a chemically polluted atmosphere, 12 months, is a pretty fair average time to take a plant down and derime it. On the other hand, if the air separation plant is in a fairly clean atmosphere, there's no reason why you shouldn't go up to 18 months. The second category, or nitrogen wash unit, is different altogether.

I'd like to point out to you one thing: oxides of nitrogen play a very, very serious role in nitrogen wash units. In coke oven gas plants in Europe they schedule a plant shutdown by integrating the amount of NO that goes into the plant. Some years ago, the amount of NO that was permissible over a period of time was about 5 kilograms. Then the plant would be shutdown and the front exchangers washed out with caustic solution. Since then, they've dropped that down to about one, because of an accident that occurred.

KEITH: Basically, there is no reason, if you are working with a strictly low pressure, centrifugal compressor type of plant, which is producing nothing but gas, that this plant, with good housekeeping, could run 36 to maybe 48 months with no shutdown. Anytime you have a plant where you're using centrifugal machinery in combination with reciprocating or lubricated, or lubricated alone, where you are running the risk of putting lubricant into the plant—and there is no way to guarantee when you're using an oil lubricated machine that you're not going to get some in there—then this is completely different.

I think it depends largely on the individual situation for each operator, and the type of plant he's got, and the conditions it's operating under. To generalize at 12 months, I think, is in many cases expensive, both in terms of time, manpower and loss of production.

Inspections

WEIGERS: How frequently do you tear down your expansion turbines for inspection? We found that it looks like a paying proposition to tear them down once a year, to check for parts which have worn to the point where they could give us some trouble during the subsequent year's operation. I'm talking now of centrifugal or axial flow expansion turbines, rather than reciprocating machines?

R. ROSENBERG - Monsanto Chemical Co., Texas City: We do not tear down our expansion turbines for inspection unless we have noted signs of faulty operation such as an excessive increase in vibration. At times we take advantage of a plant shutdown to make some checks. We have operated as long as 18 months between inspections.

J. B. ANDRIES - Spencer Chemical Co., Vicksburg, Miss.: We have no inspection program as such. We have run as long as 18 months without going into an expander. If a drop in amperage indicates that there is something wrong, why then we'll go into it. But we don't have inspection as such.

WALTON: At Rohm & Haas we have one outside man do all the oiling and greasing, while another does all the sampling and valve manipulating on the oxygen unit itself. Thus, we try to keep contamination tendencies at a minimum by separating the functions.

Oil contamination

HIMMELBERGER: Let's consider inspection procedures to prevent oil contamination in air plants.

There are several points that are very simple, and yet should be brought in mind as a part of the supervisor's responsibility in reviewing the operation of his plant and the performance of his operators. Point number one is the compressor. On the compressor, establish and control lube rates. Fix the number of drops per minute to each cylinder and make sure that that rate is maintained. Usually, the compressor manufacturer will recommend a rate; we find it wise to try to cut down on that a little bit—the compressor manufacturer is worried only about his machine, and we're worried about the machine and the air plants. We find that we can generally cut down just slightly on the recommended rates. Of course, during the period of establishing the minimum lube rate, careful observation of the machine is maintained to assure that no excessive wear is occurring.

The second point is to maintain oil inventories on the machine. Keep a log of the amount of oil that's added. Once a rate is established, keep a log of the amount of oil that's added, so that somebody does not unintentionally deviate from the prescribed lube rate.

Third, control the temperatures to lessen oil carryover. Traps function better if the temperature at the discharge is kept low; hence, it's a good point to keep the temperature of the machine down to the lowest possible level. Of course, this also helps in reducing the possibility of flash fires with mineral oil lubricated machines.

We've found a couple of places where plants were contaminated or dessicant bed life of the driver shortened appreciably because the operators were either not blowing down the dessicant traps frequently enough or they were just going through the motions of blowing down a trap and not actually blowing it down. It's a good point to observe your operators at the time when they blow down traps. It is a simple way of avoiding a lot of trouble.

With air dryers, use the recommended cycle, be very careful about extending the cycle. Second, use the recommended reactivation temperatures. If a synthetic lubricant is used, the reactivation temperature should be considerably higher than on a dryer following a mineral oil lubricated machine. For the phosphate esters, I would recommend about 350 degrees as a minimum reactivation temperature.

Most dessicant beds are followed by dust filters. These are excellent places to look for oil. A little dampening of the filter will indicate the excessive oil breaking through the dryers. If your filter is dry, do not lean back and say I have no oil in my plant; we've found that oil will go through the dust filters even though the filters tend to be fairly dry. However, under these circumstances, the amount of oil going into the plant should not cause any trouble in a relatively short period of time.

Another good check for the pressure of oil in dryers is to follow the dew point of the effluent air. If water begins to break through, one of the reasons may be that the dessicant bed is contaminated with oil. Examine the dessicant and change it if necessary. Color is a very good indicator. With the usual risk attendant to generalizing, I would say that the darkening of color on the bed of a silica gel absorber is a good indicator of absorptivity. We find that before an appreciable adsorption capacity is lost, the gel must darken very much. Both alumina and silica gel can be rather dark and still have a fairly high capacity for adsorption.

We also find that F-1 alumina is a better oil remover in a driver bed than is H-151 alumina. This has been more evident in small bottles than in large ones. It has been more evident in older plants (where relatively lower reactivation temperatures are employed) than in newer ones. If you have switched from

F-1 to H-151, only to have an oil problem some months later, try using a layer of F-1 in the dessicant bed.

At the heat exchangers, we can detect trouble by observing the defrost gas. There may often be a smell of oil in the heat exchanger defrost, but the presence of liquid oil connotes an abnormal carryover and suggests that operation of units ahead of the exchangers be examined carefully.

Faulty defrost procedures permit oil to penetrate abnormally deep into the plant. If there is oil in an exchanger when warmed, it will drain to the bottom. Most air plant piping is designed such that that oil will get down into the defrost header, beyond the point where the feed is made to the air line going into the body of the plant, but through either a change in piping or faulty defrost procedure, it may be possible to blow oil beyond the exchanger during defrost or on start-up after defrost. It's a good idea to analyze defrost procedures and the exchanger piping to ascertain that potential deposits in the exchanger are properly removed at defrost.

On expanders (talking now of centrifugal expanders) newer designs use a seal air system. Protection is guaranteed by alarms or shut-down devices which operate if a fault occurs in the seal air system. It's always wise to verify periodically that all safety devices such as these are working.

Oil leakage

The most frequent oil leakage around an expander does not occur in the process stream, but in the oil lubricating system of the expander—the small piping used to carry oil from the reservoir to the expander is sometimes the culprit. To minimize the problem, later designs isolate the expander from the cold box. If any leakage occurs, there's an open space between the boxes where oil can be observed. Spillage or leakage of oil in the vicinity of cold boxes must be avoided, for seepage through cracks in foundations has occurred.

When maintenance requirements afford the opportunity, inspect piping and vessels. There is always the possibility of traces of oil carrying through a plant.

If you're interested in tracking down oil and the path of oil through your plant, an ultra-violet light will indicate where the oil might collect. Good places to look are pockets of reduced flow, especially after a sub-cooling device. I can't define the solubility of oils in liquid oxygen exactly, but it is very, very low—probably in the parts per billion range. However, one thing we can be sure of is that the solubility decreases as the temperature decreases. We can reach this conclusion from solubility data on other materials.

Hence, after a sub-cooling device, and especially at wide places in a line after a sub-cooler. Oil that's been carried in solution near its limit of solubility will precipitate and collect on the walls. It's a good place to look for traces of oil. The ultra-violet light is too sensitive in detection of oil to dictate a hazardous condition per se. For example, it's conceivable that the cleaning operation, in installing a certain part, although adequate by conventional standards, quality control technique comparable to the ultra-violet light. But positive fluorescence does suggest that it's time to look at more places and to determine the extent of an oil problem.

Finally, an important part of an oil contaminant control program is a periodic plant washout. We have run a lot of plant washouts over the history of operation of plants—everyone has. My personal opin-

ion is that a washout is extremely desirable after the first year of operation. The frequency thereafter is determined by the amount of oil found in each washout. The presence of oil in a plant is not only a function of time; it's a function of the type of operation, and if somebody is being careless about blowing down traps, the frequency required for an exchanger washout is going to be far greater than if the traps are blown down properly. This sort of variable determines how often a plant must be washed out.

Alumina replacement

ANONYMOUS: We are using two layers of F-1 alumina, one on top 12 inches high, and one on the bottom. I would like to know if in the event we can detect oil on the air dryer, if it is necessary to replace the complete batch, or just replace the top section only?

HIMMELBERGER: I'd rather not give a generalized answer on that, but I think in most cases the top section would be sufficient.

HEPP: I just want to back up Frank's last recommendation with some actual data. During the first year of operation on our solvent wash we removed 14 pounds of oil, during the second year we removed a pound and a half. And it was on the basis of this that we went to the two year solvent wash.

Materials of construction

HEPP: We've discovered an unsafe situation that other people might not be aware of. The electrical conduits leading out from our boxes carrying thermocouple wires from both hydrogen box and air box were brought into a common junction box, and this provides a unique way of transferring hydrocarbon into the air box or air into the hydrogen box. Actually, we discovered this because we developed an explosive atmosphere in this electrical box. So there is a type of construction that you might want to examine when you get back and see if perhaps inadvertently you've connected your boxes through utilities or electrical connections.

WEIGERS: I might go even further and say that even if you don't connect your hydrogen box and your oxygen box, you can very well lead to either an oxygen-rich atmosphere or a hydrogen-rich atmosphere into your control room. We checked our boxes very carefully and found that a great many conduits running out of the cold box did not have conduit seals on them, and we were very much relieved that we remembered it as painlessly and as inexpensively as we did.

Insulation

WEIGERS: We have been looking and looking, and we would like to find an insulating material that flows freely, that is powdered, that you can blow in and out of the box at will, and so far we are still using the pick and shovel excavating method and digging through the slag wool when we have to find the spot when we have to do some repair work. Has anybody here come across an insulation which can be moved readily, or has anybody here found a method of moving rock wool or slag wool easily?

CULP: With a moderate degree of success we removed quite a bit of rock wool with furnace cleaning equipment, a large fan, a centrifugal blower with bal-

loon bags for collecting the material, and we were able to remove it very, very fast. I'd say we emptied out the wool in about a tenth of the time, by taking a blower and sucking the material out through this furnace cleaning equipment. It contains a flexible hose about 6 inches in diameter. We made a couple of adapters to use it like a cotton suck, if any of you are familiar with a cotton gin—and then put a large cleaner bag on the end in a truck. We opened the back end of the bag into this large van and blew the material in there quite successfully. Getting it back into the unit was just like everybody else so as to pack it in tight enough. But it was very fast in getting out.

WEIGERS: Did you find that sucking it out in this way fluffed it up to a point where the replacement was more difficult than it usually is?

CULP: No, not a bit.

KEITH: We have been using rock wool right along, and it's installed by machine. We've found no real need to pack it in by hand. We normally pack about 10 to 12 pounds per cubic foot. We find that this can be done readily by machine once the equipment is understood. We have illuminated one sore spot, we feel, by doing this. There is a lot of trampling around that people do when they're packing it by hand into a cold box and the rupturing of drain lines, instrument lines and so forth, is avoided to a large extent. I'd like to make one more comment about using slag wool. A lot of people have complained sometimes about pockets occurring when packing by hand. These pockets can be pretty much avoided if you pack by machine. If you have any trouble with pockets, and if you have any problems with thermal circulation of gases inside the cold box, there is one thing you can do that we've found to be quite effective. That is to stratify the insulation anywhere from every two feet to every six feet, by putting in a layer of polyethylene film or other impermeable material. In some cases we've used a fireproof paper, just to keep the air from going up and down between the walls of the cold box and the cold equipment.

TURNAGE: I've seen granulated vermiculite type insulation used as high temperature insulation on a pilot-sized still where they encased the still in stovepipe and poured the insulation in the top. When a change was to be made, a stopper was pulled at the bottom and the material was collected in tubs and bags. It was extremely easy to insulate and uninsulate. Is this material used to insulate cold boxes?

FUNK: We can not say too much from our own experience, but we have checked into this. The material as such has good insulating properties and the coldbox can be filled conveniently by means of pneumatic conveyors. However, if moisture enters the box and it seems to be difficult to seal the shell of the coldbox perfectly tight, this insulating powder would freeze up, which would cause a considerable delay in removing the insulation. In case there is a leakage in the box this powder is blown away and acts like a sandblast causing erosion and even cuts on pipes. If one can prevent these side effects this material would be ideally suitable for full insulation cold boxes, unless you prefer to have a double wall insulation.

LAWRENCE: I was going to say we use vermiculite in some of our cold insulations, but not the cold box. And I would say that the most critical problem other than the freezing would be the fact that it has a terrific tendency to slide out. If you took a panel out of the bottom of the column, you might have the whole darn box slide out. If it wasn't wet, it wouldn't stick in there.

ANONYMOUS: Have any of you people used some of the other granular insulations like Perlite?

R. L. SHANER - Linde Co., Tonawanda, N. Y.: We use Perlite extensively. One reason that we have gone to Perlite is that it does do away with this problem of convection that you run into with a packed material such as rock wool. Perlite will flow around the pipes, and the equipment. Voids, if created by shifting of piping and equipment will be continually filled. Perlite is a very good insulating material, plus the advantage that you can keep the voids around the equipment to essentially nil. Another feature on insulation is the problem of keeping the insulation dry. The use of welded casings, certainly, adds tremendously to your ability to keep the insulation dry. We use pneumatic conveying means for both emptying and filling our casings. The ease with which this is done, of course, depends upon the Perlite that you use. We have done extensive work on the various types, and have come up with specifications that require it to pass both combustibility limits, moisture limits—and strength limits. As you would expect, when you transfer materials pneumatically, you're subjecting it to quite an extensive mechanical breakdown. The Perlite that we have specified must pass rather stringent mechanical tests as well. But you must maintain a good dry environment, or you do get into trouble in transferring it. It is, of course, difficult to move any insulating materials when they are wet.

Catalyst purging

WALTON: One major accident involving fatalities and several near misses have occurred in recent years when nickel-containing catalysts such as certain reforming catalysts are purged with inert gases containing trace quantities of carbon monoxide. If the purging is started when the catalyst is still hot, nickel carbonyl formation will most assuredly occur. This purge gas should never be released into the atmosphere near operating personnel unless fresh air mask protection is provided. Good ventilation is a necessity when dumping the purged catalyst as surface contamination by nickel carbonyl might have occurred.

Nickel carbonyl has been known for many years to be a bad actor. However, recent work shows its toxicity has been underestimated. In 1951 the American Conference of Governmental Industrial Hygienists set the threshold limit of nickel carbonyl at 1 ppm. Their most recent work published in February, 1960, reduces the threshold limit to 0.001 ppm. Values of more common chemicals include hydrogen cyanide at 10 ppm and phenol at 5 ppm. In fact, nothing in their published data has a greater toxicity than nickel carbonyl.

This threshold limit is defined as the greatest amount of a particular gas that can be tolerated without harming the health of the average worker if he is exposed to it 8 hours a day for a long time. A very low threshold limit of course puts a burden on analytical procedures. Normally most industrial poisons have odor or taste. This is not significant with values of 0.001 ppm. Symptoms of nickel carbonyl poisoning are very vague. The only sure test appears to be a urinalysis for nickel content about 8 hours after the exposure.

The important point is to avoid any contact of hot, activated nickel catalysts with purge gases containing carbon monoxide, even in trace quantities. If it cannot be avoided, then accept the fact that nickel carbonyl formation can occur and insure that all personnel likely to be contaminated are adequately protected by fresh air masks.

D. A. WHITE - Smith-Douglass Co., Houston: Were you able to find out the temperatures for formation of nickel carbonyl?

WALTON: At the normal operating temperatures of reformers nickel carbonyl is decomposed quite readily, while there appears to be no formation at ambient temperature. The danger occurs during the cooling down or heating up cycle.

WHITE: The danger is because most of us do, and always have, followed the practice of using some sort of inert gas while we are dumping the catalyst hot to save time, and it is a real hazard.

WALTON: Nickel carbonyl deterioration is not as rapid as one would suspect at high temperatures. There have been cases where a solvent containing traces of nickel carbonyl was actually burning with the resultant smoke being quite toxic in nickel carbonyl content. Further, the compound is relatively stable in trace quantities at room temperatures.

W. A. MASON - Dow Chemical Co., Midland, Mich.: Is this toxicity peculiar to nickel carbonyl only, or are there some other metal carbonyls of the same toxicity or the same order of magnitude?

WALTON: Metal carbonyls are noted for their toxicity. Iron carbonyl as you know can be found in methanol synthesis loops, and it is to be avoided. However, the spotlight in recent years has been on nickel carbonyl.

MASON: Do you have any quantitative data for this toxicity?

WALTON, Rohm & Haas: We do on nickel carbonyl. It has been well publicized and I refer those of you interested in toxicity of gases to the recent publication, Occupational Hazards, February 1960 issue. This is the major industrial health publication that lists the latest work on toxicity of all common gases.

A. N. HOLCOMBE - Shell Chemical Co., Ventura, Calif.: I am thinking about some work we did quite a long time ago now, but as I remember, nickel carbonyl decomposes pretty nearly quantitatively at 300 degrees.

Hot spot

KNOX: We had a hot spot develop in the wall of the generator in the area of the drip flange, which is just about opposite to the bottom layers of the refractory. We shut the generator down, depressured, and went out to check the wall temperatures. In one spot we found temperatures between 10 and 11 hundred degrees.

The source of this high temperature was finally pinned down to the fact that the steel support plate that forms the floor of the combustion chamber, had cracked in the seal weld between it and the wall of the generator proper. This has happened on two of our generators. The repair was to install an angle inside the circumference of the wall, in such a manner that it had some flexibility for expansion, welding one leg of the angle to the generator wall or shell and the other leg to the bottom of the combustion chamber. This temperature that occurred on the wall did not register on the Kidde elements because the Kidde element was too high, and actually, the hot spot was below and in between one of the loops. As an additional safety precaution, we installed additional

Kidde elements around the circumference below the normally installed elements and down almost to the top section of the quench chamber.

Our design has the quench chamber as an integral part of the generator body. I think the addition of Kidde elements down in this area might be a safety factor that some of you people might want to consider. We inspect the chambers in detail on a routine basis at least once a year. If there is some other reason to shut down a generator for just a few hours, it's relatively easy to cool the quench chamber to a point where you can make a fairly good inspection, even though the combustion chamber is too hot to look at. Intermediate inspections are accomplished in this fashion.

WALTON: Our Kidde elements are normally placed about nine inches apart. How close are your elements now that you have revised the system?

KNOX: On the new detector strip that we put in, the elements are about four inches apart.

Referring to the quench ring, we did have the same problem and our cure for that was to change it entirely to stainless steel. Since then we have had no further trouble.

ANDRIES: We have changed the design also. We closed the aperture around the ring which seems to help considerably. I think one of the main troubles is whenever it gets too hot, there is a possibility of overheat in your outlet lining. In that respect we are concerned now.

WALTON: Did you change metal or design?

ANDRIES: We only changed design. Metal was not changed at all.

Check valves

WEIGERS: We have two parallel MEA circulating pumps on our system and as is customary, we rely on check valves to prevent reverse rotation. We had been inspecting these check valves about every two years. About two months ago, one of these pumps tripped out—and the check valve had corroded on the pin, just enough so that it would not seal properly.

The end result was that the pump ran backwards to overspeed, the fan cooling the motor shattered, and the pump froze solid. Fortunately, the casing of the pump held. There was no injury, in fact, not even a leakage, but it certainly made us stop and wonder what could have happened with the pump overspeeding to the point where an aluminum fan disintegrated, and we for one, have changed our inspection system on these check valves to once every six months to make sure that within reasonable limits they are operable.

D. L. STOCKBRIDGE, JR. - Southern Nitrogen Co., Savannah, Ga.: What type of check valve was it?

WEIGERS: It was a swing check valve.

STOCKBRIDGE: We had the same thing on our hot potassium carbonate system—same experience except we had it twice. Luckily no one was injured, but we lost some pretty valuable motors. Since then we've installed a different type check. We use a Williams Hager spring loaded check valve, which we have had a chance to observe in operation for two years. It has not shown any wear or malfunction. The only time we had trouble with it was when a piece of metal got under

the seat and, of course, no valve can close in that condition. We also installed a device on our motor so that it cannot run backwards on the pumps. We did this on the outboard end of the shaft by installing a short shaft with an anti-reverse device attached to it.

N. H. WALTON - Atlantic Refining Co., Philadelphia, Pa.:* We had a similar incident where we had a pump driven by a 100 hp explosion proof motor, and after a power failure, the check valve didn't close. The pump and motor ran backwards and the motor exploded into a good many pieces. Several persons were injured badly. This was a modern General Electric explosion proof motor. This is a real problem.

A. G. EICKMEYER - Process Consultant, Prairie Village, Kansas: Regarding the corrosion problem, I've had experience with MEA plants, having designed quite a few in the years past. We have always considered 300 F. too high a skin temperature for reboilers, even when using stainless. As a general rule, the policy was to keep the skin temperature as low as practical by using low pressure steam for regeneration. I believe Stanolind (now Pan American Petroleum) gave a paper on this subject in Chemical Engineering Progress (48, 333-1952). They found that reboiler tube corrosion was quite serious at 300 degrees or higher. As a usual limitation, we try to hold our designs down below, around 280 degrees F. I don't mean to say that this is necessarily a limit, but it's better down around there.

ANONYMOUS: This is a problem that you would have if you get off gas from another plant where you have no control over the source. Does anyone have a system where you have a long feed line, and if you do, do you have a shut-off valve?

KRYZER: We get off gas from two major refineries. One line runs about a mile, the other probably about two miles. We have a motor operated shut-off valve in each line. Each of these valves can be operated from the central control room. In case of a line rupture or any upset, we can shut off the flow of gas from either refinery from the main control room.

ANONYMOUS: Can it be set up at the consuming end as well as the generating end?

KRYZER: It's shut off from the ammonia plant, from the consuming end. In fact these are two locations for shut-off. One at the valve itself, and then one in the main control room.

R. W. E. GUELZON: Commercial Solvents: We have cupro-nickel reboiler tubes and we have set a maximum limit of 300 degrees on a heating medium. Our heating medium is low pressure steam, but it has quite a bit of super heat in it. We have two units, one that has operated about 12 years without any trouble, and the other, a new unit, that we inadvertently allowed to run at over 300 degrees and lost two sets of reboiler tubes.

Nitrogen wash

CULP: Why does anyone solvent-wash their nitrogen wash column?

ANDRIES: We solvent-washed our column because we found oil in the top trays. It evidently gets through from our compressor system.

*Now with Sun Olin Chemical Co.

CULP: How did you find this oil? Was it just a routine investigation or did you have a pressure drop?

ANDRIES: We had pressure drop, and then inspected the trays.

WALTON (N. H.): We washed our nitrogen system with hexane. This was because we had pressure drop from the exchangers prior to the nitrogen wash column. We analyzed the hexane afterwards to find out how much oil we took out. It only amounted to something like three quarts but this was enough to cause serious pressure drop problems. We have since found ways and means of improving the oil removal from the nitrogen compressor discharge by use of felt filters and this problem has not recurred.

KERRY: We found that the most effective way of handling oil from compressors is to use activated alumina. First of all, get the temperature down to plus 40 degrees. We use approximately 100 lbs. of alumina with a million cu. ft. per day of either air or feed gas. We generally have two cartridges, one in operations, the other one as a standby. About 3 months or 6 months, we switch over and the contents are dumped.

HEPP: On this question of purging hydrogen boxes, I'd like to call your attention to results of the committee's national survey. This will give some people perhaps an idea of how much purge is necessary or at least, has been found by 50% of the industry to be satisfactory. That is purge equivalent to a 4-hour turnover assuming that your box is an empty box. The Committee is quite alarmed at the large number of people who are not testing for oxygen, either at all or on a routine schedule—47%, and only 29% of everyone who has hydrogen boxes sets any kind of a limit on oxygen. I think this is an area that we ought to all look at very closely.

Leakage

WEIGERS: We have leaks on our primary condenser flanges and we weld them up at the first opportunity. Sometimes they actually stop leaking before we shut down, but we have often debated whether it is safe to run with a primary condenser flange leaking. Is there anybody here who makes it a practice to shut down immediately when you do get a leak in your synthesis lube?

WALTON (N. H.): The only place that we tolerate a leak for any length of time would be at the top head of the converter where the heater flange is, or where one of the thermo-couple lines comes through. We have tolerated a small leak there because it's way up in the air, and there seems to be very little possibility of having an explosive situation created, but at no other place in the plant would we tolerate one.

H. A. SOMMERS: Pennsalt Chemicals Corp., Philadelphia, Pa.: We had a similar experience to Mr. Walton's concerning leakages in the heads of converters. It happens that our converter at Wyandotte is leaking at the present time, and has been for the last several months. It's a relatively minor leak, and as has been pointed out, it's way up in the air and in a place where if it should catch fire, it would not make any particular difference. Probably the reason why we let it leak is because it's so darn much trouble to stop it—it means taking the pressure off, of course, and taking the head off and a lot of lost production. I think it can be said that most people do not tolerate

leaks in the rest of the system, because they are usually in places where they just cannot stand to have a possible fire.

Condensers

W. M. LOWMAN - Du Pont Co., Belle, W. Va.: We have quite a lot of experience with condensers, hairpin type condensers, high pressure tubing. We have no trouble with leaks or welded tubing. The manifold fits to the unit with a male-female joint on it. It operates at 10,000 pounds, and the condensers are changed approximately every two years and hydrostatic tested just to observe the outside shell and make sure there's no pitting. On leaks, we get them like everybody else. Depending on the type of closure—most of ours are four bolt flanges—we lower the pressure to about five eighths of the operating pressure, maintaining heat in the converter and making a little production and pull up on them if the leak is not too serious. Otherwise, we shut down.

LAWRENCE: We actually build a guard over our hairpins and we tighten them tighter than the normal torque specified and they still leak slightly, but we feel if any of them come loose, this guard will catch it and not allow a major gas leak. I don't know if this is new or not.

WEIGERS: We may have a unique construction situation, but all the safety valves in the synthesis section are piped into one stack, which runs up the side of the steel work for the crane over the synthesis converter. The thing that has always worried us is how do we get men up onto that synthesis crane for maintenance or inspection while we are running the plant?

HEPP: It sounds like you have exactly the same setup that we do. We were concerned, and what we did was to build another stack attached to the cooling tower about 300 feet away, and if we have extensive maintenance we use the alternate stack.

FETZER: Do I understand you have a number of your relief valves manifolded into one stack?

WEIGERS: That is right, sir.

FETZER: What do you do when you're changing your relief valve? Do you shut down?

WEIGERS: We have the relief valves set up with selector valves—dual relief valves on a three-way selector valve.

FETZER: There's a danger that while you are working on one and you blow a relief valve you could get back flow on one of the mechanics.

WEIGERS: True. What we do if we change one is to put a blind flange in on the downstream of the relief valve. The stack is an immense thing, so that there is no danger of pressure building up in it.

Dumping catalyst

A. NIELSEN - Haldor Topsoe, Hellerup, Denmark: I am sure there are several here who have much more practical experience with dumping ammonia catalyst than I have, but I might try to summarize my own experience and what I have been told by friends. There are several different ways when you want to remove

synthesis catalysts which would provide a safe way for it. One of them is based on stabilizing the catalyst by giving it a slight skin oxidation. You can also use other ways of pacifying it, and at least in certain plants, it can certainly be taken out in a safe way without doing anything to it. But I think that depends very much on local conditions.

I would like to say also, that a lot of repair work can be done on converter baskets without dumping the catalyst when it's kept in a nitrogen blanket.

In all events the converter has to be cooled completely down and to be purged for hydrogen and ammonia. I think it is preferable to carry out the stabilization in nitrogen, and it is, of course, considerably easier to do it in a plant where there is an air fractionation unit so that any amount of pure nitrogen is available. In that case, I think the best thing is to go once through the converter with a fairly large amount of nitrogen and add air to make up the desired concentration of oxygen, which in the beginning should be fairly low, a few hundred ppm of oxygen—maybe up to 1000.

Then, with the thermo-couples available, follow the temperatures in the converter. These should not be allowed to exceed 200 Fahrenheit, 70-90 Centigrade, if possible. You will not gain time by taking higher oxygen concentrations and allowing temperatures to go higher. The only thing you obtain is that more oxygen is taken up by the catalyst, and you will still have to use at least the same period of time.

If a zone of the catalyst gets too warm, all oxygen may be taken up in that zone and the following catalyst may not become stabilized at all. Therefore, if temperatures tend to become too high the oxygen concentration in the nitrogen should be decreased or the air supply cut out completely for a period.

Before the basket is taken out, oxygen concentration should be brought up to a higher level. When the temperature starts to fall down at the low level of oxygen, the oxygen concentration should be brought up first to 2000 ppm, and when temperatures drop again, higher. To complete the stabilization it may be desirable to increase the oxygen concentration to a couple of per cent, and when even with this high concentration there is no heat produced, the procedure has been completed. I think it will generally take 20-30 hours to stabilize a batch of catalyst. That, of course, is a long period of time.

If there is not a nitrogen source available in the plant, the look should be filled probably to some fairly low pressure like 50 to 100 psig with nitrogen from tanks and circulation should be applied and air added upstream of the ammonia converter. In that case you would have to keep a very close analytical check on the amount of oxygen built up, and on the whole be even more careful than in once-through.

Another procedure which has been used is to wet the catalyst with water. It has been done while the basket was still in the high pressure shell; it has been done after lifting the basket out of the shell. In both cases cooling completely down and purging with nitrogen has been carried out before admitting water. The catalyst has a lot of alkali in it, and if this watering is done in the high pressure shell, the shell should be washed very well afterwards, particularly the converter outlet line so that alkali corrosion is not started in this line. The risk is greatest for carbon steel. When watering the catalyst in the basket a little hydrogen may be released and accumulate in empty spaces in the basket.

In many cases when the basket is to be cooled down and purged with nitrogen and when it is intended to remove the basket without stabilizing the catalyst it might be worth while to work out some method of put-

ting nitrogen on the basket while lifting it out. It could be hoisted out and maybe somebody would just put in another basket and have oxygen diffuse in slowly to stabilize the spent catalyst. In some cases the active catalyst might be dropped out on the ground if it is done in a place where you do not have explosive gas and where it will not drop down on structural elements. If it should heat up it could be sprayed with water as it came out. This depends upon how much time would be needed to get the catalyst out.

One small thing to add is that you should probably put water on it at intervals and never allow it to get so warm that you do not dare to put water on it from fear of making hydrogen by the iron-steam reaction.

CONKLIN: I would like to add that Dr. Nielsen really knows of what he is speaking. Recently, we had the unhappy occasion of having to dump some of his catalyst which was very new and extremely active. We had to make extensive repairs to the cartridge, which made it necessary to get the catalyst out of our way. Thus, with this extremely active catalyst our problem was how do we tame this beast and get rid of it. We followed Dr. Nielsen's recommendations rather closely, although we did depart a little from some of the limitations that he has just given us.

We used the once through method as he recommended. We figured that we would use nitrogen at about the same space velocity that we had used, or intended to use, when we reduced the new charge. Then we added air to this incoming nitrogen and maintained an O₂ content between 500 and 1000 ppm and, of course, kept close tabs on the temperature rise in the bed. We had a maximum temperature limitation of 300 degrees Centigrade. At this 500 to 1000 ppm of oxygen we did from time to time have to back off on our addition of air and wait for the temperature to come down again. But toward the end, as temperatures began to sag and did not respond with small additions of air, we increased the air flow to give an oxygen content of about 3% in the nitrogen. The final stage was a cooling blow with 3 1/2% oxygen in the nitrogen. We then dumped the catalyst, and as Dr. Nielsen had mentioned, we had planned, or we intended, to spread water as it was dumped, fearing that there may have been some channeling and that unreduced portions would come out on us.

Hurricane Donna solved that for us. We got to the dumping period just at the time that the hurricane passed through the area, so it was well wetted. But of the 23,000 pounds of catalyst that we did dump, there were portions in it that had not been reduced, and they were quietly steaming away two days later as we continued to keep water on it. It took about two days for this pile of partially killed catalyst to cool sufficiently so that it would no longer steam.

KRYZER: I wanted to mention we have been following this type of practice for about three or four years now, and we have never had any real difficulty with it. Incidentally, we do this exterior of the converter. We pull the cartridge out of the converter, put in the rack, and do the oxidation exterior of the converter. It saves time in changing cartridges. We start out with nitrogen and then add the air. We have a rotometers in each line, so we have developed over a period of time, charts which we go by.

It takes us about five days to oxidize the spent catalyst. We end up eventually with all air and the nitrogen shut off. Our maximum temperature is 350 degrees, and we have four thermocouples in the bed, and we follow the temperature on the way up. The catalyst starts warming at the bottom of the cartridge

and soon the top section warms. When the top section has heated and then drops off, which indicates the oxidation is completed, we start increasing the air and cutting back on the nitrogen. The entire cartridge soon begins to cool down. We finally end up with air. We have never had any difficulty in dumping or with catalyst that was hot after dumping. However, we do keep water hoses handy when we dump, but we've never had to use them.

Shipping and storage

HEPP: I might just relate to you our thinking in the matter of ammonia hose. Our procedure used to be to test new hose at 700 pounds hydrostatic and then to run a hydrostatic test every three months at 350 pounds, and continue to use until it either failed under

test or failed during usage. We thought that was a pretty good system. Actually, in a period of about four years, we have had something like 12 failures, none of them serious, but pinhole leaks and so forth. We have had failures three days after a hydrostatic test. We took a look at this, and we discovered that 85% of these failures occurred between a period of 15 and 20 months. We took another look at what we were paying for hose—we were getting an average life of 15 months out of it—and what we were paying for manpower to hydrostatically test these hoses every three months. We came up with the very startling conclusion that we could pay the exact same dollars per year by eliminating all hydrostatic testing and discarding the hoses every six months. And, at the same time, statistically eliminate all failures, because we had never had a failure in less than six months.