the operators report on SAFETY in air and ammonia plants

Second section of CEP's exclusive report of the actual transcript of the recent informal round-table discussion at Salt Lake City. Readers are reminded that another session on this vital subject will be held at St. Paul in September.

CHAIRMAN WALTON: The next item on the agenda is combustible gas detectors. In our own case, we use the MSA W-11 model, calibrated for hydrogen, and it has been very satisfactory. It has been used a great deal in monitoring for leaks in the cold box, checking vessels before entering, and any suspected contamination of the atmosphere in a particular vicinity. Does anyone have any preference for, or experience with, another type of analyzer?

MASON, Dow: We have had some Johnson-Williams combustible gas detectors, both at Midland and at the Sarnia plant. They have been very satisfactory for detecting small amounts of hydrogen in the atmosphere. We also have units which operate on the intake air to the air separation plant. We are in a location where a serious type of accident in any of the hydrocarbon plants could dump a very large quantity of hydrocarbons into the air with no warning. The Johnson-Williams Analyzer is set to sound a warning signal when the concentration of combustible gas reaches 20% of the lower combustible limit on the basis of ethane. At 40% of the lower explosive limit it will shut down the whole air separation plant.

CHAIRMAN WALTON: Automatically?

MASON, Dow: Yes, this automatically trips the circuit breaker on the compressor of the air separation plant shutting it down immediately. This protects the air separation plant against the possibility of getting a combustible or explosive mixture into the compressor. We feel that this is very important and we test this detector daily. It has a switch which blocks out the relay that ordinarily shuts down the compressor. With this relay blocked, we introduce a sample of known concentration of ethane in air into the analyzer. This tests all of the equipment except the compressor shutdown relay itself. We must assume that this relay is dependable.

We are also in close proximity to a plant which could vent an appreciable quantity of butadiene into the atmosphere. Since butadiene can easily form explosive peroxides, we also have a butadiene detector on the intake air to the compressor. This detector consists of a glass tube containing some silica gel which has been treated with concentrated sulfuric acid. This gel will turn black with very small concentrations of diolefins (with four or more carbon atoms per molecule). It will show a very definite blackening within an hour with 1 p.p.m. butadiene. It is cumulative to a very high degree. This is watched closely by the operators but so far we have never had to shut the plant down because of evidence of butadiene. In fact, we usually change the tube after about a month's operation, even though it has turned black only equivalent to the amount of butadiene of 1 ppm. for one hour. This has been very satisfactory, cheap and reliable, and we think it is very worthwhile.

CHAIRMAN WALTON: Another question that was raised was the question of thermocouples in cold boxes, and I brought along examples of a thermocouple type installation which we have found most satisfactory. That is the use of a block, tack-welded to the line. We did try banded couples; couples held on with a band. They were not satisfactory because in the cooldown the rate of the shrinkage of the pipe and band were different, and in some cases you lost contact between the couple and the line and got poor readings. The welded block, slotted, with a thermocouple stuck into it and peened, seems to be quite satisfactory and we've had no maintenance problems with it. Does anyone else have anything they want to comment about on that?

ANONYMOUS: I might mention something that we think happened where we used a thermo-well like connection on the top of the pipe in the cold box and the thing got so cold that we think we refluxed some of the purged nitrogen in the cup. If it had been upside down it would have drained, but as it was right side up we think it filled up with liquid nitrogen and caused us a great deal of difficulty.

CHAIRMAN WALTON: I would like to give a progress report on gas chromatography. At the meeting in Baltimore, Mr. Chubb gave a short talk on the gas chromatograph. That has been in service with us now for about six months and has been quite satisfactory. This was developed mainly as an A.P.I. project in conjunction with the Los Angeles Air pollution problems, and Shell also did some work on it as a part of the project in the Franklin Institute. Experience in operation with it has been very good. We've had a few maintenance problems. One of them has been with some three-way plug valves in the system. Of course they have to be lubricated and after a period of time that lubricant worked its way into the system and gave some rather erratic readings. By changing those valves to Teflon plugs, which don't need lubricant, that has been eliminated.

You can get an analysis of a sample in 1 to 1½ of an hour; the peaks are easy to read.

CHAIRMAN WALTON: We use it for intermittent samples from the reboiler vaporizer and in other ways. We're using it to study plant air pollution. In the air pollution study, we evacuate a four-liter flask, and open the stopcock at the place where we want a sample of air. With the chromatograph; in an hour and three-quarters you'll find in parts per million, or fractional parts, just what is in the air at that point. It's a useful tool.

ANONYMOUS: What elements do you determine on the chromatograph in what ranges? How long can you go?

CHAIRMAN WALTON: To illustrate: in a sample from the reboiler of the air plant, the normal butane was 0.22 p.p.m., the iso-butane was 0.65, propane at 21, and ethane at 20.

SWOPE, Southern Oxygen: In a complete analysis, do you use one or more than one sweep gas? What is the sweep gas?

CHAIRMAN WALTON: A single sweep gas, helium, for the entire analysis.

SCHMIDT, G-E: Has this principle been used with the oxides of nitrogen?

CHAIRMAN WALTON: We are now

working on a column for determination of oxides of nitrogen. We feel we can do it without much difficulty.

ANONYMOUS: Is this analyzer used routinely or just on special occasions?

CHAIRMAN WALTON: Routinely. Eight hours every day, with at least one sample from a reboiler. One technician is kept busy.

SIMMS, Phillips Chemical Co., Bartlesville Okla.: Has anyone had chromatography trouble with xenon? We had occasion to hold a plant down for two or three days with a xenon peak that ran within 25 to 50 p.p.m., thinking it was iso-pentane.

Materials of construction

CHAIRMAN WALTON: We haven't. The next item is Construction Materials in Practice. There's been some question as to whether special construction of relief valves is necessary. In our plant we have relief valves of 304 and 316 stainless steel, and also bronze. These have both been satisfactory. Of course, they're not normally cold, but if they operate, they get cold in a hurry. Has anyone had problems or experiences with valves?

Another question has to do with satisfactory gasket materials for cold surfaces. For a confined gasket recess we use sheet Teflon; where not confined, Teflon-filled Flexitalic gaskets. Wire-reinforced Teflon and asbestos have been used satisfactorily. We also have used sheet packing "Belmont" gasket material for some flat-faced valves. There seems to be a number of satisfactory materials.

SIMMS WALTON SZE

Another question concerns materials used for cold lines, such as a line leaving a cold box which may become quite cold in case of a plant upset. We had one case where a carbon steel blow-down line had some subzero liquid dropped into it during a shutdown and some very extensive cracks developed. Our conclusion is that any line which may receive subzero material should be made of brass, stainless steel, or aluminum. Does anyone have this problem?

LAWRENCE, U.S.I.: We had an experience last year with our oxygen line leaving the air plant. We have oxygen exchangers. When we began to start up after a shutdown, the line blew to pieces. The line thermocouple was down around —180°F. We now have a pressure gauge on the line. We found oxygen would build up to about 40 lb. pressure, even though there was nothing between it and the vent to stop it. On startup, if liquid is in the exchangers, we found by watching the gauge carefully, we have had no more trouble with the carbon steel line, running it down to —200°F. There appears to be disagreement about standards concerning pressures at low temperatures. Is there a formula: so many pounds pressure per so many degrees below zero?

CHAIRMAN WALTON: That's a good question.

GRUNBERG, L'Air Liquide: About twelve years ago, when many large low temperature units were designed on this continent, European experience was often followed. At that time plain steel was being used down to —350°F without any trouble. Today, no one would take the risk, even in Europe, of building new plants with plain steel. The availability of stainless steel and other nickel alloys at a reasonable cost has helped in this respect. The first step was to use stainless vessels and piping operating normally at low temperatures. Stainless steel vessels and piping have been designed under the ASME Code which had to be applied everywhere in the plant. Such construction permits good welds and eliminates flange and gasket problems. With these new designs, units start in a few days without leaks. Previous units required weeks.

SZE, Hydrocarbon Research, Inc., New York, N. Y.: We use welded stainless steel and aluminum equipment and lines in cold boxes. What Walton has said about the Atlantic plant is a description of what we do.

FUNK, German Linde: Carbon steel should not be used below —40°F. To prevent liquefied gas entering carbon steel drain lines, install a separator and use the carbon lines for the gas. If you go down to —280°F, we would suggest using either copper, stainless steel, or aluminum.

GRUNBERG: L'Air Liquide: Stainless steel is a relatively expensive material. Some designers use 9% nickel steel, at low temperatures. The trouble up to now with 9% nickel steel, has been a recommended heat treatment after welding, something not usually possible after equipment manufacture. The present studies are to establish the lowest temperature at which this alloy could be used *without* annealing operations. It is hoped that in the future this less expensive material will find broader uses in low temperature engineering.

CHAIRMAN WALTON: Another item for discussion is oxygen piping systems: materials, design features, cleanliness, and standards of maximum linear velocity.

SWOPE, Southern Oxygen: In the smaller oxygen plants most of our problems are in filling cylinders, rather than in making nitrogen and other chemicals. We used a Kinney pump for evacuating both oxygen and nitrogen cylinders. The pump was lubricated with tri-cresyl phosphate. It worked fine on oxygen. We were evacuating cylinders for about two months. Then we put the nitrogen operation on stream, and evacuated a group of cylinders without event. As soon as we switched back to oxygen we had a violent explosion. The explosion did not occur in the pipeline or in the pump, but in the open air. This we could not explain at the time, but felt it had been caused by a static discharge, because the pump discharge happened to be near another pipeline. We grounded and bonded the two together, thinking that would eliminate the explosion cause. About a month later the same thing occurred when we again had been evacuating nitrogen cylinders and switched back to oxygen. Apparently we can evacuate oxygen cylinders continuously and have no trouble with tri-cresyl phosphate. Neither does it explode in continuous nitrogen usage, but apparently switching one to the other creates a hazard.

Both gases are pumped from the liquid phase by pumps packed with graphite rings. In spite of excellent filters in the high pressure lines, some of this graphite powder tends to go through the lines and may possibly be acting as a catalyst. For instance, we know you can't switch a liquid pump from liquid nitrogen to liquid oxygen without running into potential trouble. We also know that graphite becomes activated when pumping an inert gas such as argon. Graphite dust trapped in the filter of an argon pump will flame when exposed to air. Similar reactions have been noted when cleaning the filters of liquid nitrogen pumps. The point is, the same graphite packing could have been originally used in a liquid oxygen pump without displaying this pyrophoric characteristic.

MASON, Dow: We had trouble with packing in a liquid argon pump. The pump was leaking enough argon to form a plume of liquid argon fog. Sparkling at the edge of the plume resembled Fourth of July sparklers. We noted the similarity of this to difficulty with carbon brushes in electrical generators on airplanes operating at high altitudes. Molybdenum disulfide was suggested as a lubricant instead of graphite since graphite is actually abrasive in the absence of oil vapor or water vapor. Molybdenum disulfide powder was used in some packing that had previously contained graphite, and it worked better than any previously used. It is now standard prac-

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tice to use MoS_2 as a lubricant instead of graphite in our argon, oxygen, and nitrogen pumps.

SWOPE, Southern Oxygen: I wasn't inferring that tri-cresyl phosphate is necessarily a lubricant for oxygen. I'd be the last to recommend it for that purpose, we used it for evacuation only. For oxygen compression you must use other things. We use soap water for gas compressors. Some people are using dry compressors (I believe) with graphite rings. But going back to argon for a moment, we are currently packing our pumps with a mixture high in Teflon, with good results.

HIMMELBERGER, Air Products: On our high pressure reciprocating liquid pumps we're using a Moflon packing (an MoS_2 and Teflon mixture) that has proven satisfactory, providing longer packing life, and curbing the graphite problem. Long ago, when graphite and asbestos packing was commonly used, we operated a small model oxygen generator in which the pump could be used for both oxygen and nitrogen. On some occasions, immediately after the pump was converted from nitrogen to oxygen service, explosions sufficient to damage the pump occurred. Repacking the pump during conversion to oxygen from nitrogen eliminated the problem. Recently, we were consulted on an incident where graphite from a nitrogen pump packing glowed when exposed to air. It is common to see tiny sparks in the blow-by of asbestos and graphite packed argon and nitrogen pumps. Analysis of graphite from one of these pumps in service for a long time, has shown surface areas 2 to 3 times that of fresh graphite used in graphite packing. This finely divided high-surface-area graphite is, of course, very active.

With conversion of compressors from hydrocarbon to synthetic oils in mind, we requested one of our suppliers to obtain information on the effect of carbon, or other forms of dirt, on the flash point of synthetic lubricants (including tri-cresyl phosphate). Their tests showed the flash point would be reduced when the oil became dirty.

CHAIRMAN WALTON: It sounds like graphite is to be avoided.

PUTMAN, Superior Air Products: Cases have been reported where water and soap-lubricated oxygen compressors have had serious fires in the valves when switched from oxygen to nitrogen and then back to oxygen. It may be due to the partial decomposition of the soap, or overuse of soap under these conditions, so that when oxygen contacts it a fire is likely. Within the past year we have made a few close-tolerance pumps with no packing for oxygen and nitrogen use. After taking the oxygen pumps out of service to check the tolerances, we found some carbon-like residues. This was not found after pumping with nitrogen, an indication, perhaps, that partial decomposition of whatever hydrocarbons were in the oxygen, had taken place.

MARTIN, Spencer Chemical Co., Kansas City, Mo.: Speaking of air compressors for a moment, last year we switched from mineral lubricating oil to a tri-cresyl phosphate lubricant — Pydraul — because we had several fires and explosions in the air compressor discharge system. After switching to Pydraul, we had no more fires or explosions. This lubricant will burn, but we're convinced it's better in this service than hydrocarbon oil.

Shutdowns

CHAIRMAN WALTON: The next topic is shutdowns.

CULP, Grace Chemical Co., Memphis, Tenn.: It appears that we are in the unique position of having a clean gas feed to our air plant. We normally feed less than 10 p.p.m. hydrocarbons in the air stream; have never found any acetylene nor more than 5 p.p.m. methane. Therefore, we have never considered the problem of how long we can hold liquid oxygen, or liquids, in the air plant. We have held ours during every power failure—the maximum time being 10½ hr. We did not analyze the liquids at the time . . . I wish we had. However, with one exception, we have never found any

MARTIN SHANER PERLEY

great hydrocarbons concentration in the air plant. The exception was 5000 p.p.m. methane. The methane was picked up through a test tank, or an unloader tank, of a multigas compressor. There was no baffle in the design, the compressor was down, and the unloaders were open between the air side and the methane side of the tank. Methane was picked up from the test tank to a running compressor. There are now baffles in that tank, and the air suction has been relocated to get it completely away from the methane reducing station.

For several years, we disposed of our liquid oxygen during shutdowns in a very slow, nerve-wracking manner. We poured it into a copper defrost header and evaporated it with a steam hose. To get all the liquid out took from 20 to 24 hrs. Generally, the operator got impatient towards the end and poured the remainder on the ground. That was just a little too nerve-wracking, so we tried to develop a better system. We tied in a two-inch line from the air heater to the bottom of the defrost stack and up into an elbow. We have a throttling valve in the air line, and a pressure gauge downstream of the throttling valve. The first ten feet of this stack are stainless steel; the rest of the 53-ft. elevation is carbon steel. At the bottom of the carbon steel section, a thermobulb was installed with an extension gauge down to the ground operating level. We maintain a minimum temperature at that point of -20°F. This minimum was selected for carbon steel handling of liquid on the basis of a metals testing laboratory study on various steels at low temperatures. Carbon steel impact resistance is still good at -20°F, whereas it drops off sharply at about -50°F.

We were fortunate in having about 2% excess air compression capacity at our plant. The 2% excess is used to dispose of small amounts of liquid oxygen from the hydrocarbon adsorbers and from the derime of oxygen pumps. During total shutdowns we use up to one full compressor, or ⅓ of our compression capacity, on this disposal unit. We bring the air in through the heater at about 200°F and drop it across the throttling valve in the orifice. It drops roughly 400 lb. here, and drops approximately 180°F going into the stack, picking up the liquid oxygen being throttled into the defroster header and throwing it out the stack. The unit has worked well on intermittent service, and on total shutdowns. We never had a stack concentration above 40%, maintaining -20°F. The unit handles six tons of oxygen per hour using air at 30,000 cu. ft/hr. The gooseneck at the top was considered our biggest problem as it would throw this 40% oxygen gas to the ground level. We have run many tests on the ground level and never found it to be in excess of 25%.

During our few shutdowns we had extensive repairs in our air plant. It is packed with rock wool which (theoretically) fills all the voids in the cold box. By use of hot air purges in the rock wool, we tried to get a reasonable gas concentration for a person to enter the area to remove the rock wool. In a 10-cu. ft. section, we purged as much as 20 hr. and got analyses ranging from 10% to 75% oxygen with a sample probe. We feel it is unsuccessful to use probes in purging rock wool. Channeling is almost imminent. Therefore, we use a high volume blower of the Coppus variety—one or more, depending on the area—to keep the atmosphere at a reasonable level directly at the point of working. We consider 18-25% to be the safe limits of this atmosphere for a human being to work in; 17% appears to be the minimum safe working level. If we get into 18% we run several analyses, and get a little nervous. For extremely short intervals, we have worked in slightly over 25%, but back out if it lasts as long as 15 minutes.

We are not completely satisfied with using dilution of oxygen-rich gases, but it's the best to date. We would like something better. In the air plant derime, we use the system outlined in liquid disposal. We let it continue unil we have diluted the atmosphere in the air plant itself. For other intermittent services where dilution cannot successfully be used, we try to vent on a stainless steel stack at an elevation of twenty feet, or better, through a vertical riser discharging at the top. This brings out the problem: how to keep the stack clean. We stole an idea from the tractor, put a balanced vent cap on top, and found it

successful in keeping dirt, flying debris, etc., out of the stack and reducing the resultant explosions. The continuous purging, or the purging associated with operation of the air plant, is, by design in our plant, blended with the impure nitrogen before it is discharged to the atmosphere. The oxygen vented, except during startups of the air plant, seldom exceeds 1-2% of plant capacity.

Our people have not standardized on metal inspections. We would like to inspect the insides of our towers, but to do so we must cut holes in them. We are not happy with this prospect, and would like to hear what solutions are available.

SHANER, Linde Co., Tonawanda, N. Y.: Safe holding-time, in some of our plants, is about one week. This depends on the liquid condition at the time the plant is shut down. It also depends upon whether there is enough liquid to hold, and on the initial amount of contaminants in the liquid. We maintain clean liquid in the main condenser at all times, even when the plant is shut down.

CHAIRMAN WALTON: At Baltimore, people suggested as little as 15 minutes and up to 36 hours. Now Mr. Shaner mentions a week, so there's a great deal of difference here, but of course, it depends on how clean your liquid is.

SWOPE, Southern Oxygen: I can verify Mr. Shaner's statement. It's not unusual in the oxygen industry to hold liquid in columns for some period of time. As he pointed out, you generally have a very clean liquid to begin with. But it might not be recognized (and could be a source of trouble) that the liquid quality changes as it is held. When you first shut down, a quantity of reflux nitrogen from above will drop down and dilute the oxygen. But as the liquid is held over a period of time the nitrogen will gradually boil away, leaving fairly pure oxygen in the condenser or holding point. If oil-lubricated equipment is connected to the piping of the waste nitrogen line a potential hazard will develop during long periods of shutdown. Gases passing through the nitrogen line will become rich in oxygen, and may cause an explosion or fire in the oil-lubricated equipment. We had such an incident following a long shutdown.

LAWRENCE, U.S.I.: You fellows scare me when you talk about purging this liquid. We've kept it for as long as five weeks at one time. All the nitrogen drops into the liquid in the tower bottom, and as long as the liquid level is higher when down than it was before, and if you know the test when you went down, and run a test when you are down, and it still shows good or even better (it normally shows better when you shut down) I fail to see the danger, I mean, you have a better situation after a shutdown—to let it sit.

CHAIRMAN WALTON: We surely have a divergence of opinion. Of course, the longer it sits, the more it's going to evaporate; the more things are going to concentrate in it. It depends on what you start with.

SHANER, Linde: I think that depends on the design of the plant itself. The point is to provide for maintaining a clean liquid, whether the plant is in operation or not. Clean all streams of hazardous contaminants by adsorption before entering the columns.

SANDERS, Texas Co.: In holding the liquid in the column, always keep the liquid oxygen pump going and the wash through the reboiler. We have held as long as 30 hrs. without finding contaminant build-up in hourly analyzing or with infrared monitorings.

MASON, Dow: I would like to ask the proper means of disposing of liquid oxygen when a river bank is not available. Our air plant is in a congested area. We must dispose of liquid oxygen at shutdowns even when the hydrocarbons concentration in the liquid in the column is not dangerous, because these concentrations might increase as the liquid oxygen evaporates. We now dump into an outdoor, covered aluminum tank having an 18 inch vent line extending above the roof. Has anvone had an experience indicating hazards or explosion possibilities in such a tank?

CULP, Grace Chemical: We considered a covered tank with a vent stack, but, on several of our gas vents, we have had minor explosions in the lines resulting only from atmospheric dirt. The biggest hazard of a covered tank would be the explosion possibilities from dirt, or a tremendous cleanliness problem.

COCHRANE, Sun Oil: We get the liquid oxygen out of the plant as quickly as possible during a shutdown, especially if the shutdown is caused by a high concentration of hydrocarbons in the oxygen. In an oil refinery we cannot use the French drain type of disposal. We have a remotely located tank into which we dump the oxygen. We have never found any problem in this type of arrangement. Almost all the oxygen vaporizes in the line going to the tank at high velocity,

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where we do not have any problem of hydrocarbon deposition. A heater is not required in the tank itself. All the oxygen is vaporized within, say, two hours after the plant has stopped.

CHAIRMAN WALTON: How far is that from the nearest operating unit or storage tank?

COCHRANE, Sun Oil: About 100 ft.

WEIGERS, Cyanamid: We also have covered aluminum tanks. Open drain pits were used in our area for some time, but in Louisiana the ground pitch is minimal, and oil can float some distance during a rain storm. We devised a simple, effective vaporizer consisting of a stainless steel box with a 12 in. diam. stainless vent stack. It contains a flat plate heated from below by steam. The liquid oxygen draining out of the plant falls onto this heated plate. This vaporizer can take care of any normal purge rates. We find no evidence of oxygen enrichment around the stack which ends 12 ft. above ground. The oxygen drain tanks have been in service for five years. We open them once a year to check accumulated dirt. Up to now the only thing found was a silicate, which was probably due to dust blowing around the neighborhood.

* SAFETY ROUNDTABLE

CHAIRMAN WALTON: If you have a rapid drop-out, do you use this box too?

WEIGERS, Cyanamid: No. If we have to purge liquid rapidly we use the tank. The vaporizers handle more than 5 gal./min., and if we are in trouble, we like to get rid of it faster than that. We don't permit liquid to accumulate in this vaporizer.

BOLLEN, Dow (Canada): We were using a stainless steel tank located externally but adjacent to the air separation plant. The continuous oxygen purge was dropped into this tank and vaporized by a steam injector. The tank was vented to a 40 ft. stack running up along the air plant. However, the quantity of purge oxygen was too much for the steam vaporizer to handle with a resulting liquid level build-up in the tank and stack. This presented a hazard, in that we could have been concentrating hydrocarbons that might have been present in the liquid oxygen in the tank, and, therefore, a source of explosion next to the cold box. We have since discarded the tank and run copper lines from each of the purges to a cascade cooling pond about 80 ft. from the cold box. The pond water is about 15 in. deep, maintained by a weir. The oxygen lines discharge below the water surface, and the oxygen is vaporized by heat exchange with the large body of water. Since water flow from the cooling coils is continuous, the water in the pond is not cooled sufficiently to freeze.

CHAIRMAN WALTON: About a year and a half ago we had a shutdown where we emptied the cold box of rock wool, and the metal inspection people checked over every vessel and line. They reported there was no indication of pitting in any location. The thickness readings they got were equal to, or better than, the readings they took when the plant was installed. Since that was after three years service, they felt that we can go for another five years. If there are any indications then, they will insist that we cut open a manhead and go into one or more of the vessels to look. Does anyone else have different practices?

WEIGERS, Cyanamid: Our plant has

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internal copper piping, and we operate in an area where the plant's central refrigeration system is also located. For the last year we have operated with a continuous trace of ammonia present in the intake air. When we shut the plant down for a scheduled derime, we ran the customary pressure tests to determine whether or not we had leakages and discovered a slight leakage beneath one of the regenerators in a small (98%) copper one-inch drainline, which was very brittle, paper-thin, and could be crushed in your hand. We sent a section to our metallurgical department to determine what happened. It looked like ammonia might have gotten down there during derime. We knew from temperature checks made during the derime that we had 40 or 50 lbs. of solid ammonia in our regenerators. We found that this line had failed in the same manner under each one of our regenerators. We have no idea why. I wonder whether anybody else has experienced a condition where copper turns brittle, possibly in the presence of ammonia.

CHAIRMAN WALTON: One of the questions still unanswered concerns velocities in oxygen piping. Someone mentioned 23 ft./sec. as European practice and he felt this to be a good maximum velocity.

Fires

CHAIRMAN WALTON: The last item on today's agenda is the Description and Analysis of Air Plant Fires. R. L. Shaner of the Linde Division of Union Carbide will discuss the recent Texas City fire.

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SHANER, Linde: The March 30th Texas City oxygen plant explosion has been under intensive investigation. It has not been possible to reach definite answers to all that took place because of the extensive damage and lack of first-hand stories. However, some conclusions have been reached.

It is certain that although the explosion occurred in the oxygen plant building, it was not in the oxygen production equipment. Such equipment sustained only external damage due to flying debris, and has since been returned to production.

Evaluation of collected evidence indicates that the explosion resulted from ignition of combustible waste material, together with a high oxygen concentration in a covered trench.

Reconstruction of events before the accident shows that operators were draining liquid oxygen from one of two columns preparatory to thawing it out for routine maintenance and inspection. This liquid was being drained into a disposal pit 135 ft. away through piping.

Phone contact with the operators about 3 min. before the accident indicated the operation was proceeding satisfactorily, although it was stated that the draining rate might have to be reduced. The operators had been provided with a schedule, and appeared to have been following this in correct sequence. After the accident, all the valves were found in proper operating positions.

The explosion centered in a covered floor trench carrying a 24-in. air line at about 80 lb./sq. in. gauge. The line used to drain high purity liquid oxygen from the column was also carried through a part of this trench out of the building to the disposal pit. However, the explosion center was in a portion of the trench occupied only by the air line (and a water line), about 20 ft. from the point where the liquid oxygen drain line entered the trench.

Metallurgical studies of fragments of the air line showed low temperature failure (below −60°F); indication that liquid oxygen entered the trench. We are forced to conclude there was a mechanical failure in the high purity liquid oxygen drain line, which let liquid into the trench. After the explosion, a break was found at one point in the drain line, and a damaged flange at another point, but whether these were "cause" or "effect" is undetermined.

The amount of contaminating combustible material in the trench before the accident is not known. A sample from the trench bottom after the accident showed 1.7% organic material dispersed on what was probably a mixture of powdered insulation and floor sweeping compound.

The ignition source is a matter of conjecture. It may have been low temperature failure of the air line, or handling of a trench cover plate by an operator sensing trouble. *The important point is that intimate contact of combustible material with a high concentration of oxygen had been inadvertently created.*

CHAIRMAN WALTON: The oxygen drain line was of what material?

SHANER, Linde: Aluminum.

KNAPP, American Messer: Has any estimate been made of the quantity of combustible materials present to create this effect?

SHANER, Linde: From the extent of damage it was calculated there would have been required about 20 lb. of liquid oil, or other combustible material in the explosion area.

CHAIRMAN WALTON: There was an explosion and fire at National Cylinder Gas in Conshohoeken, Pa. next to the Alan Wood Steel Co. The gas plant supplied liquid oxygen across the fence to the steel plant and the difficulty started when a back pressure (diaphragm-type) regulator in the oxygen line caught fire. The reasons have not been established. There was no explosion or malfunctioning of the air plant equipment itself. Does anyone have other incidents to report?

PERLEY, Canadian Industries Ltd., Montreal, Quebec, Canada: A year and a half ago we had a fire in a stainless steel, five-stage, high pressure oxygen pump with bronze impellers. The sustained combustion (stainless steel is not supposed to burn in oxygen) completely "gutted" the pump and destroyed the casings of two stages. We could not determine the cause. Our plant is in an agricultural area. We have never found trace acetylene in the oxygen, and we have exceedingly low total hydrocarbons.

Ammonia Plant Safety

CHAIRMAN WALTON: The first topic, Hydrogen Purification will be introduced by Gordon Weigers of American Cyanamid, New Orleans.

WEIGERS, Cyanamid: Some of the problems we faced and some solutions. The first is relief-valve fires—their prevention and control. Relief valves are not supposed to lift in a smooth operation, but we know that safety valves do lift, and that with the low energy required to ignite hydrogen, safety valve fires do occur. As long as the safety valve vent stack is in open air, these fires are not really a problem. By providing a means of injecting nitrogen into the valve stack, we can snuff out the fires.

Another problem is encountered during nitrogen wash unit startup. Large quantities of hydrogen-rich gas are vented and occasionally these vents ignite. We adopted a safe, simple solution. Dual vents are provided with means to inject nitrogen into either one. If one vent ignites, we switch to the other one, and blanket the culprit wih nitrogen.

Another problem concerns hydrogen leaks inside the cold box, which creates a hydrogen-rich atmosphere. In the New Orleans area we average at least one summertime thunderstorm per day. We equipped our cold box with a steam snuffing system, and as a normal safety precaution, we turn on the steam to blanket the roof of the cold box whenever thunderstorms are imminent. We have been able to prevent fires along the seams of the cold box this way.

The problem of retention of low boiling point liquids for hydrogen purification units has again been placed on the agenda. In a nitrogen wash box the retention of liquids does not present the same problem as in an air separation plant. In this box you normally find hydrocarbons that would make an oxygen-plant operator's hair stand on end. The only problem in retaining these low boiling liquids (mainly nitrogen and CO) is to prevent the migration of solids deeper into the cold box while it is shut down. When forced down for any reason, we simply valve the box so that gases boiling off the liquid nitrogen pass back out of the box through the same circuits the incoming raw gas uses. This way the solids deposited in the cold box are

retained in areas where they don't cause problems. The rate of heat leak determines how long the liquid can be maintained; 24 hours is possible. If the shutdown time is longer we start losing our heat levels and then most of the liquid is gone. The deposited solids sublime and migrate deeper into the cold box, redepositing themselves in areas where you can't get rid of them. If the shutdown is so long that all the liquid inventory would evaporate, we have to derime the entire box if we intend to restart without excessive pressure drops in places where we are unable to cope with them.

Additional topics on this agenda are: the prevention of leaks; the detection of leaks; and once detected, how to repair them.

Unfortunately, it is difficult to build and operate a cold box that doesn't spring an internal leak sooner or later. A cold box has to be maintained under positive pressure and if the box is allowed to breathe, even a minor leak could result in a catastrophe. If the interior atmosphere of a box is kept free of oxygen, even major leaks can be handled safely. A major leak (large enough to interfere with the process) usually heralds itself by the appearance of ice spots somewhere outside the walls. The site of the spot is often enough to locate the leak. Unfortunately, it's not always so simple. We find it helpful to monitor the nitrogen we use to maintain a positive pressure in the box. Numerous sample points, judiciously placed throughout a cold box, help in spotting a leak and pinpointing its location. In one cold box we even provide each flange and instrument connection with its own monitoring, or sniffing connection. But even without such an elaborate system, careful analysis can pinpoint the location of a leak in 90% of the cases. We make routine explosimeter tests of our purge gas. It's important that the operators know the proper procedure when using an explosimeter in this particular service. The sampling gas is free of oxygen and the *first* deflection of the explosimeter needle is significant. As the sample gas is pumped through the meter, the oxygen present in the meter is displaced and the meter gradually drifts back to zero. An operator not familiar with this phenomenon could make a zero explosion-reading on a pure methane sample! Once a combustible material is found in the cold box, we run a complete gas analysis by mass spectroscopy or a gas chromatograph. Knowing the normal composition of various process streams and the composition of our purge gas, we can usually spot the leakage source even when there are two and three simultaneous leaks. With this sort of monitoring system, it should be possible to know just where to dig into the slag wool to take care of the leaks.

The most important factor in leak prevention is careful maintenance. We have tried torque wrenches when taking up on flanges, and have worked without them, without any definite conclusion. We have adopted the policy of tightening major flanges once, cooling down the cold box without replacing the insulation, warming up the cold box, and tightening the flange once more. This is effective in getting tight closure on large flanges.

Instrument connections seem to be a major fault in internal leaks. Leaks can be reduced by supporting instrument lines on rigid supports. When installing instrument lines, extreme care must be used to provide proper expansion loops. A number of gasketing materials have been tried, including Flexitalic gaskets with Teflon or asbestos lining, or Teflon gaskets. We had good results with Garlock 900.

The problem of readying a cold box for maintenance: Most nitrogen wash plants are equipped with sparger pipe systems under the slag wool, which permit the nitrogen purging of the slag wool. Our box is so equipped and whenever we derime it in preparation for maintenance, we pass nitrogen through the process vessels, the piping, and through the slag wool. In this manner, most of the lighter hydrocarbons are displaced from the slag wool with little difficulty. However, on opening the cold box, we still find a positive explosion reading just about anywhere along the exposed face of the slag wool. We've probed to see whether this condition was general, and found to our surprise that this densely packed wool hinders diffusion of air through the mass. Explosive mixtures exist mainly along the face of the exposed wool. The hydrocarbons persist, but oxygen diffusion to create an explosive atmosphere is restricted. Despite this narrow band of explosive atmosphere, we do not permit hot work. Cold work is no problem, if maintenance people have adequate ventilation or air masks. We have soldered inside the cold box under these conditions, after the slag wool had been cleared from the work area and the area blanketed with asbestos; but we heated the soldering iron in a safe area away from the box, and then brought the hot iron inside. There is no safe way of doing hot work inside the cold box unless the slag wool is completely removed—a major undertaking. An alternate solution is to pass nitrogen through the slag wool to eliminate oxygen, but this presents serious problems in protecting maintenance men. They must work in masks, which appreciably slows maintenance work. On those occasions where we did hot work, we removed the piping sections to be worked on, to a safe area, did the work, and reinstalled them. The problem of flame propagation through slag wool enters this picture. Experimental work along this line will be discussed later.

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MASON, Dow: Many years ago we had several fires on outdoor vent lines from purge valves and safety valves at Midland. These fires were more frequent during static electric conditions, during thunderstorms, or when thunderstorms were impending. We suspected that static discharges were igniting the mixture and, on this basis, installed fiber tubes in the tees on the top of our purge lines. This reduced fires and worked well, until the fiber wetted and unwrapped in layers, ruining the insulating qualities of the fiber tubes. We then used Saran. The fires have not been completely eliminated. We still have steam snuffing connections in these places and we start a stream of steam into the line whenever the static conditions exist.

FUNK, German Linde: On the subject of rock wool as a flame-propagation deterrent, I would like to read a note by Dr. Karwat. For testing, we chose a container of about 7 cu. ft., filled with rock wool, and then displaced the air with a mixture of 2 volume-parts of hydrogen and 1 volume-part of oxygen. We left a 1-liter space in the middle of this box to ignite this explosive mixture with an electric spark. We discovered that the explosion occurred only in the void space. The explosive gas mixture was still in the wool, practically untouched. So we concluded that slag wool is the best agent to limit, or to block explosions.

In the slag wool packing of gas separation units we usually find a mixture of flammable gases, nitrogen, and some air, since a cold box cannot be built so tightly as to prevent air from entering through leaks in the shell after weeks, or months. Several thousand cu. ft. of air may penetrate the box from the top and leave through lower sections. If the shell is opened for maintenance, and slag wool removed to allow access for repairs, there would be a void space in which the gas-air mixture might ignite and explode. The heat would force the gas to leave the wool and to burn on the surface.

To extinguish flames with water would only promote the drainage of gas out of the wool. Therefore, before opening we suggest the box be purged with nitrogen, using a quantity five times the volume of the box. Later, the nitrogen can be displaced by air to allow the operators to remove the insulation.

MARTIN, Spencer Chemical: We consider relief-valve vent fires with a certain amount of favor. They have shown leaks we didn't know we had. When we started up we looked like the Fourth of July. We continue to fight leaks in a nitrogen wash cold box. We had a worse-

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than-average problem for a couple of years until we found two leaks in the (Trane type) switch exchangers. The leaks were in the external walls. Not knowing their cause, we'd been looking almost entirely at flanges. One more thing happened to us on two occasions. After purging the nitrogen-wash cold box with nitrogen, to what we considered a safe point, our operators descended into the cold box without masks. There was no oxygen and they had to be rescued.

KELM, Grace Chemical, Memphis, Tenn.: We had a five-foot void above the insulation level in the top of the cold box. To fill the box to prevent an explosive mixture, we purged with nitrogen until we had about 2% hydrogen concentration in the top of the box. Within half an hour after the explosion door at the top of the box was opened, there was a slight explosion, probably not severe enough to have lifted the door. At that time three nitrogen hoses were blowing into the top of the box.

It was a cloudy day, however, there was no lightning or apparent static condition. We were using ungrounded rubber hoses, but oscilloscope tests later did not show any static pick-up through the hoses. We still don't know just what did happen. The fire was snuffed very easily. The operator closed the explosion door and packed insulation around it, preventing more oxygen from entering the box.

Since then, whenever the box is opened, an analysis of the atmosphere for oxygen, hydrogen, and nitrogen is made immediately, and periodically.

BOLLEN, Dow (Canada): We have also done some work with flame propagation through rock wool. We made 22 duplicate tests in mixtures of hydrogen-air, ethylene-air, and hydrogen-oxygen-nitrogen, at concentrations corresponding to the highest flame velocities of these mixtures. Neither the ethylene-air nor the hydrogen-air mixtures produced flame capable of propagating through rock wool insulation at a depth of 4 to 10 in., and a bulk density of 6.9 to 15.3 lb./cu. ft. Flame propagation through rock wool was possible only with hydrogen-oxygen-nitrogen mixtures containing much higher oxygen concentrations than are present in air. The following conditions appear necessary for flame propagation: with 50% H_2, 37.5% O_2 and 12.5% N_2 the resulting flame propagated only through rock wool of a bulk density 9.48 lb./cu. ft. or less, or a thickness of 4 to 10 inches; with 50% H_2, 40% O_2 and 10% N_2, or any mixture with a higher oxygen to oxygen-plus-nitrogen ratio, the resulting flame propagated through rock wool insulation at a bulk density of 15 lb./cu. ft. or less, and a thickness of 4 to 10 inches.

CHAIRMAN WALTON: In some preliminary work we found hydrogen-air mixtures corresponding to the highest flame propagation conditions did not propagate flame through rock wool, but that hydrogen-oxygen mixtures did.

MASON, Dow: This problem of propagation through rock wool ought to be taken with a grain of salt. In spite of the fact that rock wool may act as a flame retardant when packed at a certain density around pipe connections, the expansion and contraction of the equipment pushing these connections is likely to create a tunnel between the packing and pipes, which could serve as an explosion path, even if the packing around that tunnel might be a good flame retardant.

CHAIRMAN WALTON: That's true, it's almost impossible to prevent voids no matter how well the box is packed. On occasions we had our box repacked by the bidder and the results were bad. The last time we got the best people we knew, and it wasn't much better.

CLAPPERTON, Columbia - Southern Chemical Corp., New Martinsville, W. Va.: Our hydrogen comes from electrolytic chlorine cells. It is quite pure with the exception of some organic chlorides. We have operated our ammonia plant since 1955 without many problems, adsorbing the organic chlorides on activated carbon. However, this year we put mercury cells into service, and shortly had a problem we think is mercury contamination of our deoxo catalyst. We temporarily stopped using the mercury stream, but we are wondering what effect the trace amounts of mercury would have in the synthesis loop. Can mercury

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get beyond the main compressor? We considered that it would be trapped in the cooling sections around the compressor system. Since our main trouble started with deoxo-catalyst poisoning, we were not able to run long enough to determine the effects of mercury getting further into the system. Has anybody had experience along those lines?

BOLLEN, Dow (Canada): We use H_2 from both the diaphragm and the mercury-cell process. The mercury cells have been sending hydrogen to the ammonia plant since 1952. Since then we have noticed mercury in various compressor stages, but have never found it in the synthesis loop. In our first-stage intercooler we found the mercury had attacked the Admiralty brass tubes, causing embrittlement to the point where several tubes snapped off behind the tube sheet. Now the brass tubes have been replaced with stainless steel tubes, and activated carbon filters have been installed following the compressor stages to ensure the removal of the final traces of mercury.

FAHRENBRUCK, Columbia-Southern Chemical Corp., New Martinsville, W. Va.: What about discharge pressure of your compressor?

BOLLEN, Dow (Canada): Our final synthesis-gas pressure is 5,000 lb./sq. in. In the intercooler the pressure is in the order of 35-40 lb. and most of the mercury is knocked out at that stage.

CLAPPERTON, Columbia-Southern: If you have a deoxo unit, what is its location relative to the synthesis compressor?

BOLLEN, Dow (Canada): Our deoxo unit is located immediately after the charcoal towers. We combine our electrolytic hydrogen with the synthesis-gas mixture we obtain from our nitrogen-scrubbing unit, and the combined stream is passed through the deoxo unit.

CHAIRMAN WALTON: I might give you a little of our philosophy on rock wool. After our experiments, we thought that if we had a leak in the box we could feel safe in living with it and continuing operation without an immediate shutdown. We agree with Mr. Weigers that we would not do any welding or hot work inside the box with the wool in there. We found that to purge the box properly, it is necessary not only to have spargers at the bottom but also at several levels up through the box. We have about five distributor pipes or spargers at three levels in the box, and we purge with a minimum of about 20,000 cu. ft/hr. of nitrogen. Before a shutdown, where we may want to go into the box for some reason, we usually step it up to about 40,000 cu. ft/hr. We have about 27 different points where we have probes in the box and every other day each point is routinely checked by operators with an MSA hydrocarbon detector, and a Fireite oxygen indicator for the percent oxygen present at that point.

HIMMELBERGER, Air Products: Have the experimenters noticed how slowly the flame propagates through rock wool? We luckily chose to use a glass tube to run some of our experiments and were able to see the flame move through the rock wool from a void at the bottom to a void at the top of the glass tube. It appeared that it took several seconds for the flame to travel through the bed. We took motion pictures of it. The flame propagated through an 18 in. bed, 2 in. diam., in ⅝ of a second (six frames of 16 frame/sec. film). The rock wool was of relatively low density, although perhaps not much lower than you might find in some portions of a cold box. Also, the flame did not propagate through the mass of the rock wool, but definitely channeled, leaving charred trails.

BOLLEN, Dow (Canada): I can't answer your statement about speed because our tests were carried out in an enclosed tube, and I didn't carry out the experiments. Concerning hot work in cold boxes, we had a bad methane leak develop in our first nitrogen-scrubbing unit; the leakage dripping down the foundation of the cold box caused the foundation to heave, and the whole cold box gradually lifted approximately 8 in. When we got into the cold box, we found that one of the long lines (as Mr. Walton has mentioned) with an expansion loop in it had broken open at one of the welded seams, located near the top of the cold box. We cleared out the top third of rock wool

and spread fireproof blankets on the top of the rest of the wool, gas tested carefully, and carried out repairs. At that time, we had nothing like the experience we have today. I doubt that we would undertake such a repair job in the same manner again.

CHAIRMAN WALTON: We experienced a leak in the cold box and thought that it was a flanged joint about 2 ft. from the wall of the box. We opened the box at that point and dug the wool out while continuing to operate. We thought that probably all we'd have to do was tighten the flange studs. We uncovered that flange and there wasn't any leak there. There is another joint a little bit farther on, and in digging toward that, an explosion occurred, followed by two others. They were of minor intensity, but they did blow rock wool into the eyes of the repairmen. By talking to the men at the time of the explosion, we found that no one was poking in the box with any tools. We have made it a rule not to probe in the box while we're operating. We shut down and purge to a low hydrocarbon content before entering the box.

Does anyone have gasketing problems? On threaded joints we have found, Cyl-seal to be effective. It's made by the Westchester Chemical Co. It's good for oxygen lines too, as it contains no carbon-atom material. One thing with which we're particularly blessed is a scale model of our cold box that has been used many times in helping to determine where leaks might be, and how to get at them easily. Anybody contemplating an addition, expansion, or new cold box might consider that.

de PAUW, Carbochimique: Have any of you analyzed for the chlorine content of your synthesis catalyst after installing activated carbon adsorbers?

BOLLEN, Dow (Canada): We invariably find that there has been some poisoning by the chlorine. That is not an indication that our carbon filters are inadequate. In our process, part of the electrolytic hydrogen stream does not pass through the carbon filters, so some impure gas is going to our catalyst.

de PAUW, Carbochimique: We are using activated carbon filters on our whole gas stream and although we are not using hydrogen from chlorine cells, chlorine (coming probably from a water wash in previous stages in the gas-purification system) is going through the activated carbon-hydrogen purification equipment and is accumulating slowly in the synthesis catalyst.

CHAIRMAN WALTON: What kind of catalyst life are you getting under those conditions?

de PAUW, Carbochimique: We have been conducting these experiments on a systematic basis only for the last 1½-2 years. Actually, we replaced our catalysts at the end of 1956, on a routine change, so we have had only enough experience to know that the catalyst is doing very well although the chlorine content is increasing.

BRUNI, Soc. Edison, Porto Marghera, Italy: We have a mixture of 80-85% hydrocarbon from natural-gas reforming, and 15% hydrogen from chlorine manufacture. We have found, after two years, a great quantity of chlorine in the synthesis catalyst. Our silica gel adsorbers are not sufficient. At what temperature do the activated carbon adsorbers operate in your plant?

BOLLEN, Dow (Canada): Our carbon towers are located after the compression stages. However, the gas from the compressor aftercooler knockout pot is preheated to approximately 120°F before it enters the carbon tower.

CLAPPERTON, Columbia - Southern: Our carbon adsorbers are actually on the hydrogen stream as it comes from the chlorine plant. Various analyses indicate there are 5-10 p.p.m. organic chlorides (expressed as HCl) entering these adsorbers. We operate them at a little higher than ambient temperature, and the exit chloride content probably averages about 0.1 p.p.m., sometimes less. We have found some chloride despositing on our deoxo catalyst, ahead of our main compressor in the ammonia plant. We also find traces of chloride in our ammonia product. We have not checked our synthesis catalyst, but assume that chloride is there since we do find some in the ammonia.

FAHRENBRUCK, Columbia-Southern: I might add that we have had the plant on stream 3½ years and have detected little loss of catalyst activity, so apparently the chloride isn't affecting us too much.

SANDERS, Texas Co.: We had occasion to do some hot work a few feet inside the cold box during a downtime when the box had been purged with nitrogen for a week after the unit was down, but we still detected hydrocarbons there. We lined the tunnel we made, with polyethylene sheeting and taped it with masking tape all around the lines going into the box. We turned on a blower in the tunneled area and, (with continuous gas testing) did some Heliarc welding. We and our safety and maintenance people considered it safe.

CHAIRMAN WALTON: Did you supply the area with nitrogen?

SANDERS, Texas Co.: No, we used an air blower into the area where the hot work was done, and nowhere over that whole area did we have any indication of hydrocarbons.

CHAIRMAN WALTON: Had you warmed up the box before?

SANDERS, Texas Co.: Yes.

CHAIRMAN WALTON: That's always a problem; whether you dare go in without warm-up because, on a moist day condensation in the wool will eventually build icebergs. When we completely removed the wool from our cold box a year and a half ago, there were some large icebergs in it as a result of the burrowing. I have worried about the building up of such things and their resultant strains on piping, and so on.

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So, it seems there's always a calculated risk when you go into a cold box.

LAWRENCE, U.S.I.: I had the dubious distinction of being inside the box when it caught on fire one time. We were doing some welding and had about 30,000 ft./hr. of purge on the box. We'd been purging for about two days and had taken normal precautions. We had the normal insulation dug out and had it blanketed between us and the insulation, and had a blower supplying fresh air. The nitrogen was coming out in a pretty good stream, the welder was welding merrily away. Our flame checks had been good up to that point. For some reason, we evidently had some heavy hydrocarbons at the bottom of the box that the purge apparently started picking up. Suddenly, about 6 ft. from where the gas was leaving the insulation from under the tarpaulin, it ignited. There we were sitting—the torch on, and the fire burning alongside. We turned off the torch and grabbed insulation and stuffed the hole where the purge was coming out. This stopped the fire. But we decided we would never weld in the cold box again, anywhere near the insulation.

At times we've been able to take the paneling off the box and see cracks in the edge right into a cold vessel—slightly hard on refrigeration, so we've replaced the paneling with stainless steel and sealed the box. Before that, we actually had holes in the top, so our box is full of ice. We've worried about stress on pipes and voids in the ice.

Since we've put the stainless steel paneling on, we've carefully carried out a box sealing program. This is to go over the box with sealing compound and continually seal every little exit except the roof vent. We normally run with 15,000 ft./hr. of nitrogen purge in the box and the only thing we get out the roof vents is nitrogen, plus our leaks.

CHAIRMAN WALTON: This business of sealing the box is really a problem. We've gone over our box several hundred times, and do it continually, yet there are leaks that you just can't find. Even with 40,000 cu. ft/hr. of nitrogen in the various purge lines, you can't detect any velocity in the roof vents.

Gas reformer furnaces

MAUNE, Mississippi River: My experience has been with the low-pressure reformers at TVA. They were the revised design of the Chemico round-type furnace. There were four units in operation. Each furnace had 20 tubes in cross pattern with 5 tubes to each quadrant. It has always concerned reformer operators that leaks might occur in furnace tubes and flanges, or that tubes might rupture.

The temperature control was easily managed. The tube skin temperatures could be easily maintained within limits,

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if catalyst could be contained in the tube. The general design was a type 310 stainless steel tube, about 21 ft. long and 8 to 10 in. in diam. A smaller inside tube of about 2-in. diam. made an annular space in which the catalyst was placed. The bottom of the inner tube was held in place by an engaging sleeve coming up through the bottom flange. During startup several of those tubes were not engaged, so that as soon as enough pressure-drop across the catalyst bed occurred, the catalyst would sweep out of the tube and end up in the secondary reformer. Of course, this took time. The catalyst would break up, resulting in a hot furnace tube—a readily noticeable condition. However, the furnace operated under these conditions for about a week without any damage, after which the unit was taken down and proper repairs made.

To control the furnace tube temperatures in this particular installation, there were balancing valves for each set of tubes, and each tube inlet had a restrictive orifice of a size calculated to permit even gas distribution to all the tubes. The orifices were important, as demonstrated on one occasion when one of the orifices was plugged with gravel left in the piping during construction. This restricted the gas flow to the tube, resulting in a hot tube. We never experienced ruptured tubes or flange leaks which could catch fire inside the furnace. Actually, the flanges on this particular tube are not inside the furnace. The bottom flange was outside, on the bottom of the furnace and covered with a protective hat, not really in a hot zone. Also, the top flanges, which included the inlet and outlet gas from the tube, were not in the fire zone.

KENARD, Selas Corp. of America, Los Angeles, Calif.: We have supplied to Best Fertilizer a steam methane reforming furnace. This heater has no bottom flanges on the tubes. We supply a case fitting, welded on the bottom of the cast stainless tube by the tube supplier in the shop. The upper inlet end of the tube is a conventional flanged inlet, but the hot outlet (I believe the temperature is 1450°) is a cast fitting. A pigtail connection leading out of this cast fitting is welded in the field. The pigtail connection leads down to an outlet manifold header, where the outlet gases are accumulated.

This steam methane reformer furnace uses the principle of the Gradiation heater that we have successfully applied to the cracking of ethane and propane. Selas Duvadiant burners, used in this heater, are radiant burners with no flame in evidence in the firebox of the heater. The flame is contained within the burner cup. It's a pre-mix type burner with no secondary air required. Consequently, we are able to control the heat distribution to the tubes by using a multitude of these burners, in horizontal and vertical rows, giving even heat distribution through the firebox. The Best unit operates at a pressure of 120 or 130 lb. Inlet temperature to the tubes is about 700 or 750°, outlet temperature, 1450°.

SZE, Hydrocarbon Research: Has the Selas furnace been in operation for some time, and if so, have there been any tube failures?

ANONYMOUS, Selas: The only other steam methane reforming furnace we have in operation is in Germany and, unfortunately, I'm not qualified to comment on it. The Best Fertilizer unit will be in operation probably by the middle or latter part of November (1958-Ed.).

KING, Sohio: We operate a high-pressure reformer furnace and have operated for three years with no tube failures. We have some 336 S.S. 3-in. Incoloy tubes with external flanges, and inlet and outlet pigtails on each tube. The failure problem has been in the pigtail weld made in the field. We had about 30 failures in our first year of operation. The wide distribution of gases through a large number of tubes did not result in any serious fires from any of the failures. Has someone an experience with tube elongation as a result of continued operation?

WHITE, San Jacinto: We have a low-pressure unit in operation about 15 years. The tubes have stretched about 3 in.

CHAIRMAN WALTON: What was the material?

WHITE, San Jacinto: It's an old Hercules furnace, very high in nickel. When we started operating these back in '50, we weren't careful to compensate for elongation of the spring suspension of the tubes from the top. They elongated to a point where the bottom flanges started to build up tension and the tubes warped considerably before we found the trouble. By correcting the spring tension, we practically stopped all troubles.

CHAIRMAN WALTON: Did you have to replace any of the tubes because of distortion?

WHITE, San Jacinto: No. A year and a half ago one of them failed in front of one of the burners but we patched it. So far it has not leaked again.

CHAIRMAN WALTON: You repaired a crack by welding it?

WHITE, San Jacinto: We repair all our cracks by welding with stabilized 310 welding rod. A number of the original welds which have failed, we repaired right in place.

deVRY, Hercules: We guard against tubes breaking inside furnaces by having a 1-in. connection and valve on top of each tube. A steam outlet at the top of the furnace can be quickly connected to one of these valves. Should a tube rupture, there is a large evolution of gas and an impingement of the flame upon the furnace wall. The operator is warned as the temperature rises on the wall thermocouples. He then goes to the top of the furnace, connects the steam hose to the appropriate tube, and blankets the tube with steam, forcing out the flame. The steam prevents backflow of cracked gas from the other tubes of the furnace and also keeps the natural gas from coming in at the top. You can operate with a ruptured tube for some time in this manner.

On the attainment of even distribution of gas in furnace tubes, we found it wasn't too easy to valve-off certain tubes to force the gas into the other tubes. To let the distribution take its normal course, it will follow into the tubes with the least resistance. The critical thing is the grid support at the bottom of the tube on which the catalyst rests. Often this gets plugged, and one tube resistance might be ½ lb./sq. in. more than some of the other tubes, and the tube will run hot. We try to have an open grid at the bottom and have all the tube resistance in the catalyst packing, itself, by trying to obtain uniform packing. We don't just dump the catalyst in; it is lowered in a loading device and spread in the tube.

In taking a shift converter out of service, we use the relatively pure CO_2 available from our CO_2 scrubbing system and pipe it to each of our individual shift converters. We isolate the converter with respect to the gas stream, admit the CO_2, and exhaust the outlet gas to the atmosphere. That way, we can safely lower the temperature without runaway heating. This also preserves the iron-oxide catalyst in its lowest oxidation state and gives a good cooling and tempering job on the catalyst.

When we shut down our reforming furnaces we allow the steam through the tubes until the tube walls are down to about 800°F, measuring tube-wall temperatures with an optical pyrometer through ports along the furnace wall.

STOCKBRIDGE, Southern Nitrogen: In reference to this loading device, what size are the tubes?

deVRY, Hercules: 8-in. tubes, 24 ft. long. The loading device is about 7⅞ in. diam.—a close fit in the tube. It can't be used in badly warped tubes. It has a vane at the bottom tripped by the weight of the loader as it comes to rest on the catalyst in the tube.

MORRIS, Texas Eastman: Have you no orifices in the inlet of the tube? Do you just let the pressure drop of the individual tube take care of the flow through the tube?

deVRY, Hercules: We tried orifices but had little success with them.

ANONYMOUS: We think we get better distribution through our ring-type catalyst than through a solid type.

CHECKSFIELD, Air Products: What tube life has Sohio had with the Incoloy tubes at 125 lb./sq. in. pressure? There is controversy over Incoloy tubes.

KING, Sohio: We have had no tube failures nor indication of elongation during three years of operation. These tubes are 3-in. O.D. and about 40 ft. long. We have removed and replaced the catalyst, and to get distribution through the 336 tubes, we carefully weigh the amount of catalyst going into each tube.