

*The industry speaks on . . .*

# Safely operating that low temperature plant

ANOTHER HARDHITTING, shirtsleeves report on safety in operating air and ammonia plants: A subject of vital interest to chemical engineers, by chemical engineers as they speak out at their annual Q. and A. session. This meeting took place at A.I.Ch.E.'s St. Paul, Minn. national gathering, where participants dug deep to find the answers.

## *Air intake impurities*

Air separation plant problems begin with impurities in the raw materials.

**NORTON WALTON—Atlantic Refining Co., Philadelphia:** Air intake, of course, is where the problem usually starts on air separation plants. Its importance will vary considerably with each individual plant, depending on the location of the plant, its surroundings, and what other plants are nearby.

There are two, or perhaps three, methods for removal of hydrocarbons; one is removal from the air intake itself by a device such as the MSA Catalytic Filter which removes them by oxidation; another is removal from the plant by blowdown from the low pressure column, reboiler, or vaporizer; the third is removal by design features at the entrance of the air separation column.

**D. L. STOCKBRIDGE—Southern Nitrogen Co., Savannah:** We have a nitric acid plant where we have trouble with particulate matter getting into the air compressor. I was wondering if anyone here had American Air Filters or would

care to comment on the success of this type filter.

**P. T. MARTIN—Spencer Chemical Co., Kansas City:** We have American Air Filters on the suction to our nitric acid air compressors and our main air plant air compressors. These filters have been in operation approximately six years and our experience has been very good with them.

**G. R. WALTON, JR.—Rohm & Haas, Pasadena, Texas:** The development of the MSA Catalytic Filter has been of particular importance to Rohm & Haas because of the inherent dangers associated with an acetylene plant located near the air plant at Houston. Generally, the use of a Hopcolite-type filter must be reserved for an essentially oil-free, but relatively clean air stream. At the Houston plant, compressed air at 90 lb. gauge pressure leaves the compressor discharge at 350°F. The compressors are centrifugals, with the usual seals which

prevent oil contamination. The outlet air temperature is controlled at 350°F by controlling the interstage cooling temperature. The air is passed through the filter, then chilled in water contact coolers prior to entering the cold box equipment. We believe that at this high temperature level, essentially all butene, acetylene, and propylene are oxidized in the filter. It appears that about 80% of the ethylene is oxidized, as well as lesser quantities of butane and propane. Methane is not affected.

Concerning catalyst activity, samples taken after approximately 14 months service show the activity to be decreased by about 10%. That is, the equivalent percentage of acetylene oxidized requires temperatures 30 to 50°F higher with the used catalyst as compared with an unused sample. The principle problem associated with the filter has been a slow but gradual increase in pressure-drop across the individual cartridges. After

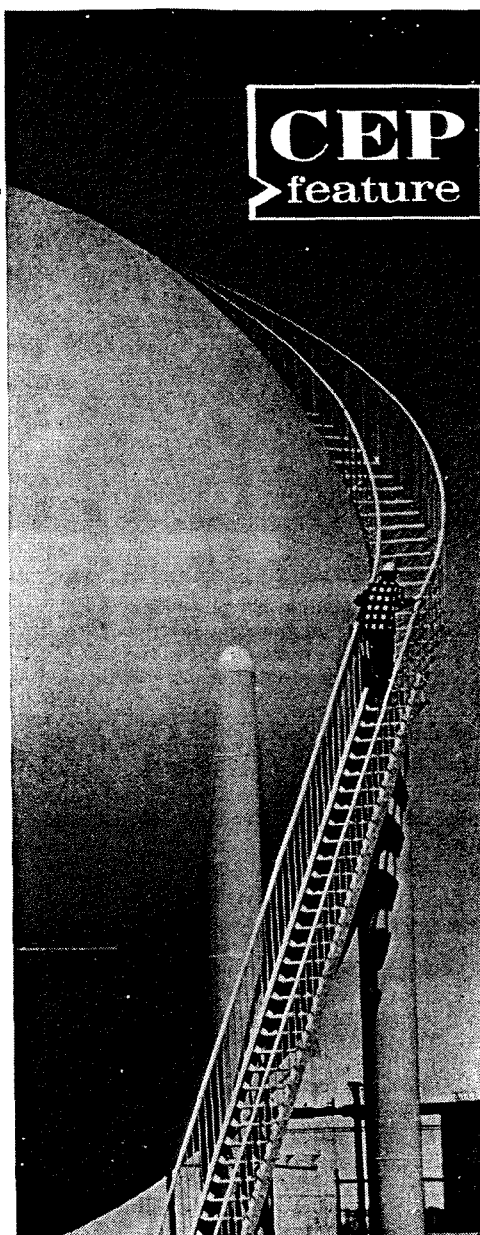


Photo courtesy Citiles Service Co.

less than one year's operation, the pressure-drop increased from the design pressure of  $\frac{3}{4}$  lb. to 10 lb., at which time the pressure-drop abruptly decreased to 6 lb. This was later found to be a result of the collapse of several of the catalyst containers, which allowed bypassing. In January, the filter was examined and found to be very rusty, the glass cloth prefilter being clogged with iron oxide. New prefilters were then installed, but soon after startup the pressure-drop increased again. By August it was sufficient to cause container collapse.

This time several improvements were made, including: metallizing the filter tank with an aluminum coating, increasing the catalyst blanket of the prefilter area, strengthening the catalyst container, and galvanizing some of the feed air piping. In future installations, we would recommend painting or galvanizing all air feed piping in high humidity plant locations. Especially important is the hot piping between the compressors and the filter tank. Finally, a bypass should always be provided around the filter tank to allow servicing, when necessary, without disrupting plant operations. In conclusion, we are quite pleased with the oxidation efficiency of the MSA catalytic filter, and now believe we have the pressure-drop problem under control.

**P. A. CHUBB—Atlantic Refining Co., Philadelphia:** We had approximately a three-month test on the MSA filter. It was operating between 375 and 425°F. The inlet propane contamination through the filter, ranged from 1 ppb to 0.2 ppm. The acetylene contamination was essentially in the same range, maybe even a little lower. At these low ranges we got good removal of acetylene. We got essentially no removal of propane. Other components such as butane and ethane were removed to varying degrees.

**R. E. BUTIKOFER—Standard Oil Co., (Ind.), Whiting:** In the Calumet region sulphur dioxide and iron oxide are found in the atmosphere. These materials deposit in the compressor as iron sulphate which is extremely corrosive. I was wondering if some of you who have centrifugal air compressors have experienced this kind of problem?

**J. A. LAWRENCE—U. S. Industrial Chemicals, Tuscola, Ill.:** We have been picking up SO<sub>2</sub> and SO<sub>3</sub> for five years and we have completely plugged-up our centrifugal several times. In fact, this year we're going to replace our suction line with stainless steel. We have also ordered from Brown Boveri, the manufacturers of our compressors, stainless steel diffusers in the compressor, and stainless steel rotors. We have installed a Roll-o-matic filter with paper back-up filters and we pick up dust on the order of several pounds a day; which means our suction line is gradually decreasing.

**BUTIKOFER—Standard Oil:** We have aluminum dryers in our air preparation section prior to the air plant. The aluminum began to disintegrate and carried over into the primary exchangers on our air separation cold box. We had some

**W. A. Mason—**  
Chairman of  
Subcommittee on  
Safety in Low  
Temperature Pro-  
cessing Plants.



peculiar pressure-drop buildups in the exchangers, and we began to realize something was wrong. We shut down and found that the tray exchangers were pretty well plugged with aluminum. We are going to go now to a molecular sieve, silica gel type of drying and try that out.

**D. C. LAMOND—Canadian Industries, Ltd., Kingston, Ont.:** We also have activated alumina dryers. Our dust filter following these is a wool-felt filter—it's the star shape type of filter. We had a strange occurrence with this wool-felt. We had a fire in the filter which destroyed not only the wool-felt, but which ignited the steel support. Our air is at 600 lb. We are not quite sure what happened. The dryers had just been changed. We were in the middle of an upset in the plant and the change of dryers was hurried without too much precooling. We felt that the very dry air might have gone into this wool-felt at around 183°C, and that the fire might have been caused by static electricity. We have since grounded the filter and we have taken proper precaution that our air is not higher than 50°C when introduced

in the filters. The filter itself appears to be quite efficient. We have had an opportunity to examine our primary air-oxygen exchanger recently and it was quite clean on the air side.

**WALTON—Atlantic Refining:** We started off with F1 alumina and had some difficulty with powdering and with carryover into the reversing exchangers. We subsequently changed to H151 alumina and that has substantially stopped the dusting problem. Our felt suppliers says that 250°F is the maximum temperature that felt will stand, so I think that may be the reason for the fire in the C.I.L. plant. But the H151 is certainly more resistant to dusting than F1 is and has been quite satisfactory.

**L. B. HENDERSON—Dow Chemical Co., Midland, Mich.:** We have an oil-bath filter which removes all dust from the compressor intake and have experienced troubles with dust in the compressor. We have had a dust problem downstream from our dryer. Desiccant dust from the dryer carried through to the expansion turbine caused erosion of the nozzle ring and housing. A Dollinger felt-cartridge filter was installed in the dryer discharge line which has eliminated the problem. Approximately a pint of dust per day is collected by this filter.

**T. H. DAVENPORT—Ketona Chemical Corp., Tarrant, Ala.:** I would like to substantiate Mr. Walton's theory. We changed from F1 to H151 and we have a glass cloth filter downstream of the desiccant and apparently get very little carry over from the H151.

## Compressors and dampeners

Damage and fatigue-inducing vibration in compressors are produced by two primary forces: mechanical and acoustic.

**G. DAMEWOOD—Southwest Research Institute, San Antonio:** For the past four years the Industrial Application Section of the Southwest Research Institute has been engaged in a wide variety of gas industry research problems. One of the programs has been concerned with the problem of pulsation and vibration in reciprocating compressors and associated piping. It is difficult to assess the damage which vibration annually causes throughout the nation. We all know that vibration causes fatigue in mechanical components and, often, failure. Such failure, especially when associated with high pressure gases, can be disastrous.

Even harder to assess is the effect of vibration on the nerves of operating per-

sonnel. Probably this last item alone is sufficient justification for vibration control. The problem of establishing an acceptable vibration level is extremely simple, philosophically. You merely reduce the amplitude of vibration until acceptable stress levels are exhibited. Technically, however, the answer to this question is almost impossible, since an absolute measure of fatigue life and of absolute stress levels is not available. There are a variety of techniques and equipment applicable to the measurement of vibration. In general these involve the use of an accelerometer and associated indicating equipment. The most useful measure of vibration is by determining the amplitude of vibration as

a function of frequency, or the so-called "frequency analysis" of vibration.

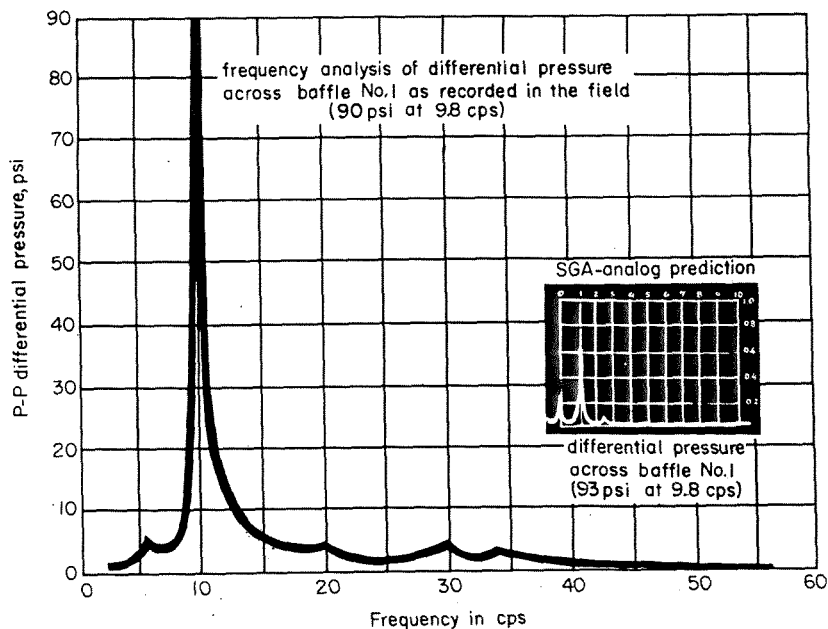
There are two primary forces which produce vibration in compressors and associated piping. These forces are mechanical and acoustic, or pulsating vibration. Of these two driving forces, pulsation is usually the major offender, particularly at the higher frequencies. Therefore, to control vibration in compressors or piping there are two possible alternates. One of these concerns altering the mechanical response of a system. This would tend to merely shift the resonant peaks to a new location or to a different frequency. In some instances this can, therefore, be a solution. If one considers changing the actual frequency of a purchased compressor cylinder however, one immediately runs up against an impossibility. At best this frequency can be moved only a few cycles per minute, not enough, in general, to be a solution to a vibration problem.

The response of the system can be altered in one other way. This involves the proper use of mechanical damping. The addition of damping to the system merely allows the system to withstand greater forces at any given frequency. The next alternate involves reducing the driving forces imposed on the system. Since pulsation is one of the major forces involved, pulsation control is a very useful and practical tool for controlling vibration.

The solution of the complete pulsation problem is complex when one considers optimizing the following parameters: compressor efficiency, pulsation control, vibration control, installation cost, operating cost, and metering accuracy. Many attempts have been made to develop adequate analytical procedures for controlling pulsation. However, even the most advanced methods known today are highly inadequate. Attempts have also been made to use general-purpose computers to solve this problem. The latest attempt at its solution was performed at the Princeton Computation Center. The work published to date indicates a realistic approach to the problem but one which, at best, can be described as naive in its present state.

Analog computers can furnish a quick, efficient, and accurate method for solution of those problems in which mathematical analysis is difficult or impossible. Electrical circuits are usually chosen as a basis for such analogs because of the wide variety of components available and because of the relative ease with which electrical measurements can be made. An electrical analog of an acoustical system is possible since there is a direct correspondence between the flow of gas, the acoustical system, and the flow of electricity in an electrical network.

From a comparison of the equations governing the behavior of both systems, it can be shown that the two systems are analogous. There are seven different basic analogies which may be used in the solution of the pulsation problem. The so-called classical analogy, is however, the most practical, and is the anal-



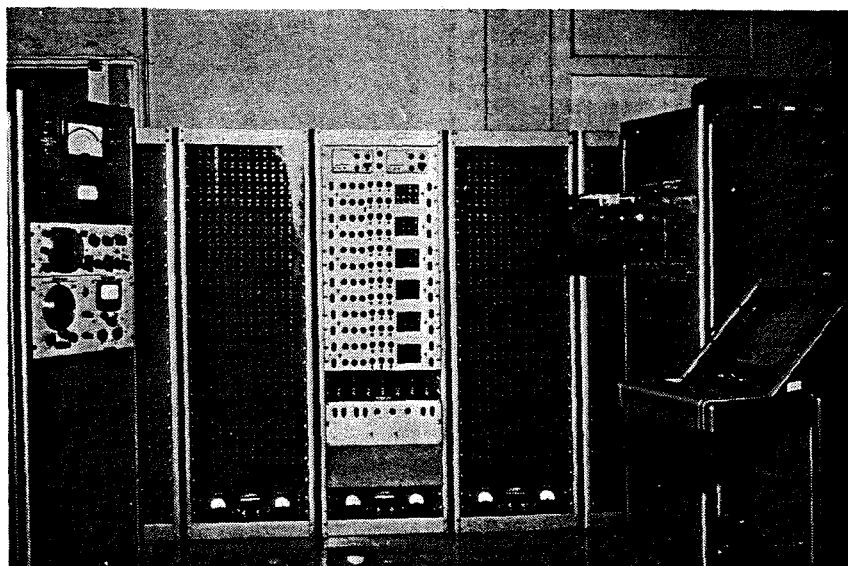
Analog computers can be used to simulate actual field conditions in compressor and piping studies. Photo courtesy Southwest Research Institute.

ogy chosen for the SGA analog. The analogies used are pressure, represented by voltage, and mass flow, by electric current.

A system analog, unlike a computer, does not compute the most desirable piping system. It does, however, permit the analysis of the system in the laboratory. This analysis is exactly like performing a field test. Measurements can be made of piping response, steady and dynamic pressures, and mass flows in piping and the compressor card may be immediately observed under controlled operating conditions.

The SGA compressor station analog facility has been used in the design of over 250 compressor stations. Approximately 60% of these installations were

studied prior to construction. The remaining 40% represented compressor stations in operation which had some undesirable characteristic such as excessive piping vibration, poor cylinder efficiency, gas metering problems, or the like. The problems studied represent the majority of compressor types found in the industry, including both single- and multi-stage installations. In addition to natural gas compressor stations, an increasing number of chemical plant problems are being studied. The use of available information and experience on the mechanical response of systems, together with the use of the SGA compressor station analog, have solved a variety of piping problems. It is hoped that current research on the mechanical system will



Southwest Research's analog computer installation has been used in design of over 250 pipeline compressor stations.

## Symposium on Safety in Low Temperature Processing Plants

**W. A. Mason**, Chairman  
The Dow Chemical Co.

**G. U. Weigers**, Asst. Chairman  
American Cyanamid Co.

**John Clapperton**  
Columbia Southern Chemical Corp.

**G. S. Cochrane**  
Sun Oil Co.

**E. H. Culp**  
W. R. Grace & Co.

**Frank Himmelberger**  
Air Products, Inc.

**Frank Kerry**  
American Air Liquide, Inc.

**G. E. King**  
Sohio Petroleum Co.

**H. E. Maune**  
Mississippi River Chemical Co.

**G. J. Odom**  
Chemetron Corp.

**R. W. Rotzler**  
Monsanto Chemical Co.

**N. H. Walton**  
Atlantic Refining Co.

**D. A. White**  
Smith-Douglas Co., Inc.

The formation of a subcommittee on Safety in air and ammonia plants was suggested more or less casually after the Salt Lake City National A.I.Ch.E. Meeting, September, 1959. It was the opinion of The A.I.Ch.E. Program committee that some attempt should be made to perpetuate the work started by these symposia on safety.

Under the impetus of Nort Walton a representative group comprised of those who had attended and had contributed to previous sessions on the subject were invited to join the subcommittee. Fourteen responded, but subsequent pressure of work forced one to drop out.

The group was formed under the Program committee of the Institute to act in a guidance capacity and to supply leadership for Safety symposia at National meetings. However, consideration is not necessarily limited to air and ammonia plants. Some other areas of possible interest include liaison with the Compressed Gas Association and the preparation of a Standards book of safety procedures in low-temperature plants.

An outgrowth of these symposia has been the published follow-up of these lively question-and-answer sessions in *Chemical Engineering Progress* and subsequent reprinting under one cover of articles pertinent to the subject area.

finally make the problem of compressor piping completely predictable, efficient, and trouble free.

**QUESTION**—Could you give us some idea of the time required and cost of an investigation?

**DAMEWOOD**—Southwest Research: Usually we like to spend approximately one week on a single-stage problem, and between one and two weeks on a multi-stage one. We have got the process down to the point where we're talking about something on the order of \$2000 per station design.

**R. F. BOLLEN**—Dow Chemical of Canada, Ltd., Sarnia, Ont.: We haven't encountered any serious vibration problems in our plant. We feel that this has largely been due to the patented dampeners which have been installed on the suction and discharge of every compressor. However, I would like to describe the operation of one particular pulsation dampener. This dampener was on the discharge of a four-stage nitrogen compressor, operating at 3000 lb./sq. in. Shortly after we began operation we found that a very high pressure-drop was developing across the nitrogen system. By surveying the pipe lines and the equipment in between, the search was narrowed down to the pulsation dampener. We watched it very closely and the pressure-drop increased steadily over a period of two or three months. The pressure-drop then suddenly started to build up very rapidly. At this point we promptly shut down and looked into the pulsation dampener. The entire internals were very badly caked with hard carbon.

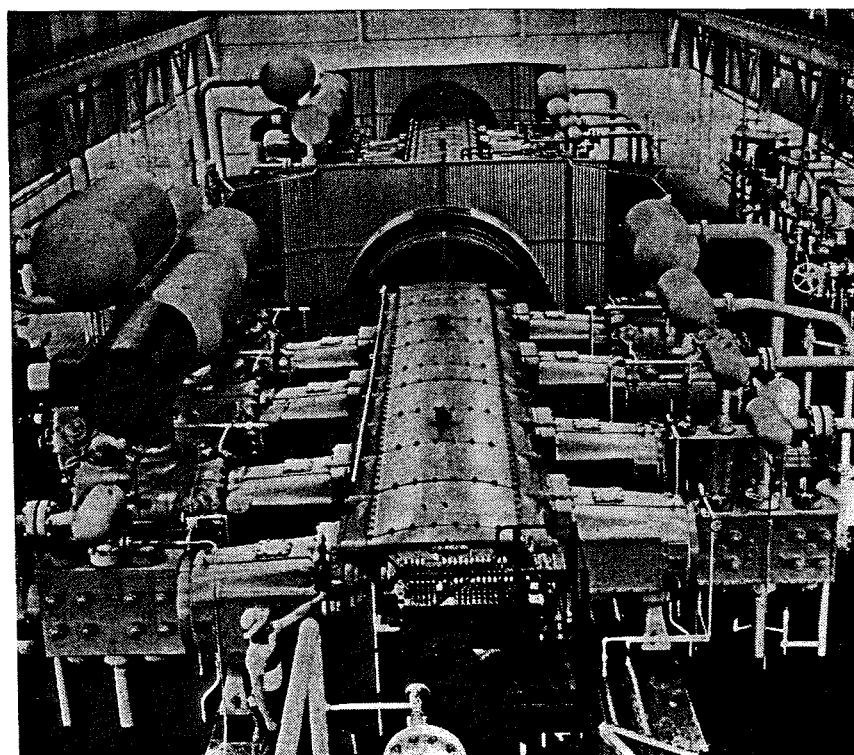


Damewood



N. H. Walton

We had to sandblast the internals and in some cases drill into hairpin bends and install plugs so that the carbon could be cleaned out. We also found that the discharge valves of the compressor were very badly carbonized. At this point we went back to the compressor manufacturer and also to our lubricant supplier and advised them of our problem. Their answer was that our problem was probably due to excessive lubrication. We cut back to the lubrication rates recommended by both the compressor people and the oil supplier but in about three months we ran into the same problem again. We cleaned out the vessel again and at this time we also made up a spool piece to be installed in place of the pulsation dampener while it was being cleaned. We operated for several weeks with the spool piece in place and noticed that even without the pulsation dampener the vibration of the pipe was no worse than it had been with the dampener installed. It just points out that in designing to reduce vibrations, it is possible to go just a little bit too far, and by introducing unnecessary equipment, you



Reliable compressor operation with minimum vibration is vital to proper plant operation. Photo courtesy Cooper-Bessemer Corp.

can very often run yourself into other problems. We have now removed some of the internals of this particular pulsation dampener so that it acts simply as a surge vessel. This has overcome most of our carbonizing problem.

**WALTON—Atlantic Refining:** We felt that the problem of pressure-drop in our nitrogen wash system was due to oil vapor getting past our oil filters and ending up in the -300°F exchangers and gradually blocking them up. We had the idea of using radioactive lubricating oil in our nitrogen compressors to try to confirm this, and to find out just where the oil did land. We have a Peerless filter, the first point where oil is removed downstream from the compressors and, sure enough, radioactivity showed up there. The next place we looked for it was downstream of the activated alumina oil filter. But we didn't find it there. So the test results were quite puzzling.

Since then, of course, we have found that our oil removal problem has been largely solved by the use of the felt filter and that our problem now is water released when a fresh charge of alumina is placed in an oil filter. The answer seems to be drying the alumina at 350 degrees, or so, for about 4 hr. and having the felt in a separate vessel so it will not burn during this period. On another subject, we had a rod failure in a synthesis compressor since our last meeting. It broke clean, directly across the diameter. There seems to be a consensus among the examining metallurgists that the difficulty was due to the fact that the grain structure was not as fine as it should have been. This grain structure coarseness had shown up in the Reflectoscope examination of the rod at one of the regular intervals in service when we check rods. As a result of this failure and considerable discussions with our compressor manufacturer, we have decided to go to a better rod

material in which grain size in the "working-up" of the rod from the original piece of steel receives better control. The new material is 4140. On piston rings, our thoughts at the moment are that we like carbon-asbestos Bakelite rings, where the discharge temperatures are below 335 degrees; and where they're above that, bronze rings. Comparing the projected ring life and liner life seems to us at the moment to be the best thing and also the safest thing, because where you have ring failures with carbon-asbestos Bakelite, you don't wreck your liners as you do with any type of metallic ring. We have also tried something in the last six months with which we're quite happy, and that is asbestos-carbon Bakelite valve discs in the K-type valve (disc valves). Whereas we have had fatigue failures about every three weeks with steel valve discs, we now have gone as much as eight months life with these valve discs.

## Hydrocarbon adsorbers

Practical experience proves the value of silica gel for removing undesirable hydrocarbons from the process stream.

**FRANK HIMMELBERGER** — Air Products, Inc., Allentown, Pa.: Adsorbent purifiers using silica gel made their appearance in air separation equipment about 20 years ago. Their sizing has generally been based on the gel's capacity for acetylene, with some adjustment for other impurities which may also be adsorbed. Their effectiveness has most frequently been measured in terms of acetylene removal. For example, near Cleveland, Ohio in 1945, adsorbers were added in the crude oxygen stream of two existing plants where acetylene concentrations averaged .7 and 1.0 cu.cm./l. It would come out about 0.9 ppm in one plant and about 1.25 ppm in the other. These numbers were the average for several months prior to installation of the adsorbers. After the adsorbers were added, the average dropped to less than 1% of the original value on analysis. Practical experience such as this has left little doubt as to the utility of the silica gel for acetylene removal. A more complete discussion of adsorptive purification appears in a paper by McKinley and Hsu in CEP 56, p. 80 (Feb., 1960).

Here are some safety rules which should be kept in mind when operating silica gel adsorbers:

1. Stop reactivation on hydrocarbon adsorbers immediately, if the plant is

down or if the purity of the reactivating nitrogen is in danger of falling below 90%.

2. Periodically, check the thermostat setting and any flow safety device on the heater unit for proper operation. (One of the most common accidents with regeneration systems is burning out the heating element when there is no flow in the system and the thermostat is not operating properly.)

3. Use the full cycle time allowed for reactivation and cooling the adsorber. Make valve changes as slowly as possible. This is very important if you wish to minimize dusting of the silica gel. (Incidentally, getting back to another question that was mentioned earlier, in our experience we've gone through the cycle from silica gel

to F1 alumina, to H151 alumina in dryers; we feel that the H151 is by far the better one. However, since then, some of the silica gel people have come out with new gels with apparently much greater resistance to fracturing. We've not yet tried these in dryers. We have used them in other applications as oil filtering media and find them to be a distinct advantage.)

4. Check a sample of the gel periodically for discoloration. We find that color is a very good indication of the degree of activity of the bed. A very dark colored gel generally will not have the capacity that an orange, tan, or white gel will have; assuming that we start out with white gels.

5. Use the discharge pressure of the reactivation blower to detect powdering or dusting of the gel. (This is just a simple means of determining whether or not pressure-drop is building up on the bed due to dusting.)

6. Do not lubricate valves with hydrocarbon or graphite compounds. (Surprisingly enough, some accidents have occurred in crude oxygen streams where lubricated valves were used.)

7. Keep the valve packing tight and replace when necessary with dry, degreased Teflon-coated asbestos. (Use a nonflammable material and minimize leaks through the valve stems, because hazardous conditions can exist where leakage occurs.)

8. Shorten the operating cycle of the adsorbers as much as possible during periods when contamination of the inlet air is possible from outside sources.

**R. L. SHANER**—Linde Co., Tonawanda, N. Y.: We use gel extensively in our plants. We have run as long as seven



Himmelberger



Shaner



years without having to replace any gel whatsoever. This, of course, depends entirely on the cycle that you use. It also depends on whether it is being used in a gas phase of a liquid phase adsorber. Our cycle incorporates both. The gas phase adsorbers have extremely high efficiency. The active portion of the bed, the length of the bed that is actually doing the work during the processing time, is one of the important factors contributing to the efficiency of the adsorbers. In the gas phase adsorbers the active portion is extremely short, and as

a result the gas phase adsorbers do an excellent job of removing carbon dioxide, acetylene, and other hydrocarbons. In the liquid phase adsorbers the active zone is much longer and, generally, the beds are insufficiently long to completely remove all of the adsorbate as the liquid stream passes through the bed.

**W. A. MASON—Dow Chemical Co., Midland, Mich.:** I reported in Baltimore that we, at Dow, had originally planned to change the gel in our liquid phase hydrocarbon adsorbers on a three-year schedule. On the first change we found

that the first four or five inches of the gel bed were very badly discolored, while the rest of the bed was still quite white. Based on that and on an analysis of the hydrocarbons that were causing these discolorations, we've now switched to a two-year cycle and at present we are continuing to change our gel completely every two years, not because we find that the gel has lost its adsorptive capacity but rather because we feel that this discolored gel contains hydrocarbons which might be an undesirable fuel source within the plant.

## Reboilers and vaporizers

Acetylene is the most critical hydrocarbon constituent of low temperature oxygen plants. Its concentration should be limited to 1 ppm.

**J. T. HUGILL—L'Air Liquide, Montreal:** What level should be allowed in the main vaporizer in regard to concentrations of acetylene and hydrocarbons? The problem is a little complicated because of the two distinct types of oxygen plants: One, where you have a low-pressure plant taking off gas from your low pressure column or through your auxiliary vaporizer; the other, where you're taking liquid off your main vaporizer and pumping it out under pressure. In each case I think the contamination limitations can be varied or relaxed. Some plants use a maximum allowable acetylene of 1 ppm, at which point they must carry out excessive purging. At 2 ppm, they must shut down. This is for acetylene. It's been suggested that if you can analyze specifically for ethylene, you can allow your concentration to rise to 300 ppm before you need to shut your plant down. At 150 ppm, you must carry out double your normal purging. Methane can be allowed to go to 1000 ppm. Again, this was not a unanimous or even a majority opinion at the last two meetings.

There has been much discussion on the problem of how long to leave the liquids

in the plants after you shut down, assuming that you're having only a temporary shutdown of anywhere from one hour to 24 or 48 hours. We think that there is no time limit, within reason, on this particular question provided that careful and accurate analyses are carried out during the period in which you are in doubt. If the contamination limits reach your normal safety figures, then you must purge all your liquids before you start up. If, however, things appear to be reasonably normal and stay that way, then you can safely start up without any trouble. There are a lot of cases in which plants have been down for 24 or 48 hours and have been started up without purging off the liquids, assuming that there wasn't much liquid left during that period. Other plants set a definite time limit of one or two or three hours, at which point everything must be dumped, regardless of what the concentration is. With regard to purging during operations in a normal low pressure type plant, where you are taking your oxygen off in the gas phase from an auxiliary vaporizer and oxygen separator and compressing it, we feel that a continuous purge on the separator is necessary regardless of the concentration of hydrocarbons. The purge is set up to be a relatively small percentage of total product. It does not necessarily affect the output of a plant seriously.

**V. M. YOUNG—Naval Air Station, Alameda, Calif.:** We first became concerned with pilot and air crew safety from trace constituents in liquid oxygen for breathing, after receiving pilot complaints of odors in their oxygen. As it was necessary to procure liquid samples from aircraft liquid oxygen systems,

transfer carts, and storage tanks, as well as manufacturing plants, a method of sampling was needed which would provide:

1. A representative sample
2. Safe use by untrained personnel
3. A minimum of required liquid
4. Shipment according to ICC regulations
5. A way to clean easily and thoroughly

Early in our work it was discovered that the analysis of a gaseous sample did not represent the liquid from which it came unless all the liquid was evaporated. The trace constituents, in such a case, remain in the liquid. It was therefore mandatory that a unit quantity of liquid oxygen be completely evaporated in a container, rather than using gas from the top of the liquid.

Various types of samplers were encountered in which a quantity of liquid was captured in a container and evaporated. However, the valving was more complex than desired, and further difficulties were experienced with leaks in valves and fittings.

The sampler found best suited for use with liquid oxygen is shown opposite. It consists of a 295-cu.in. gaseous oxygen bottle modified to capture a liquid oxygen sample—a stainless steel tubular cap was welded to the nipple assembly. The sample cup has three 1/16-in. holes drilled in it, Section A-A, which control the size of the oxygen sample such that about 160 ml of liquid is collected during sampling.

The sample itself is introduced into the sample cup as shown in Detail B. The separator shown allows gaseous oxygen to be vented during sampling so that the flow of liquid can be controlled



Hugill



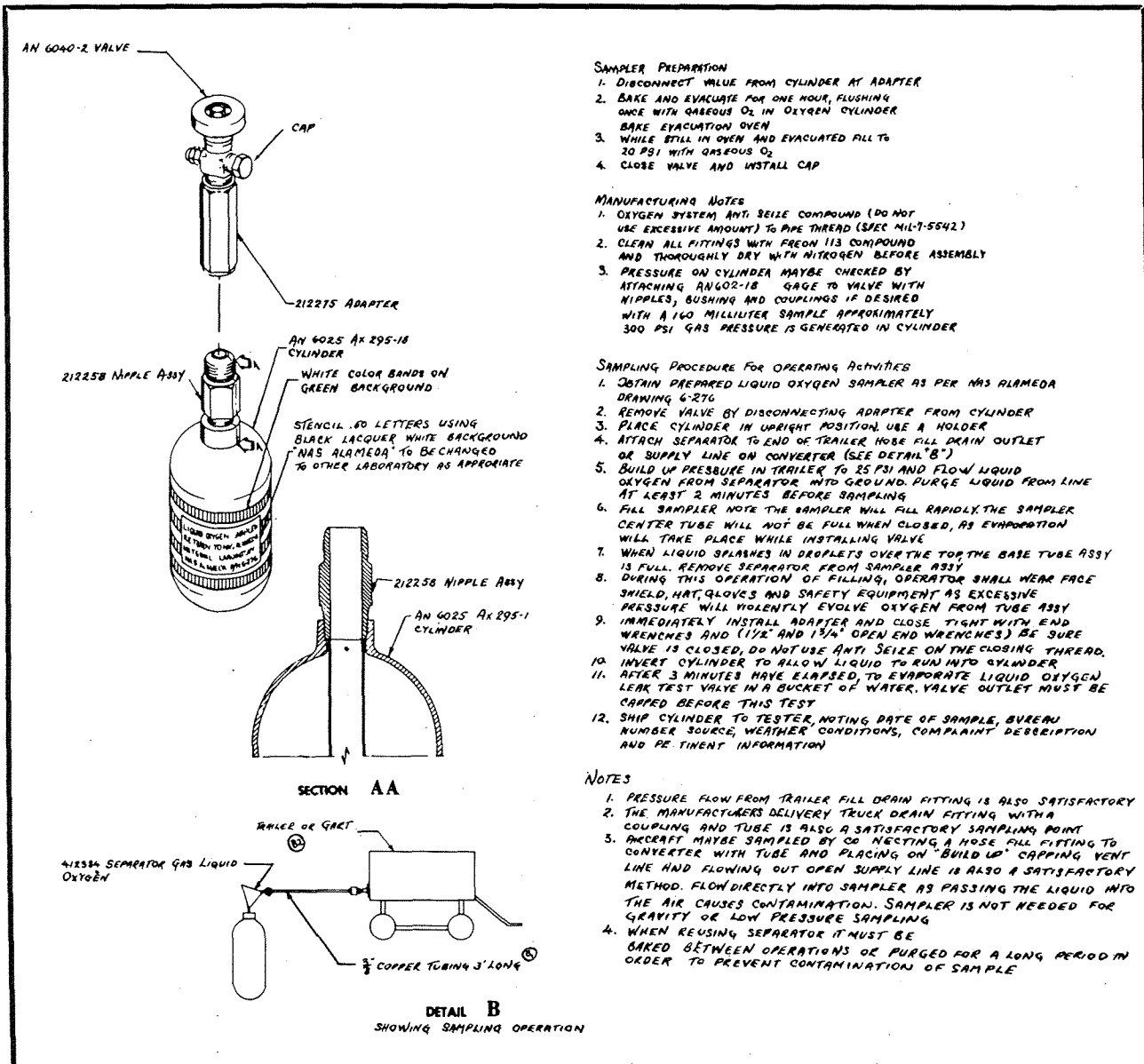
Young



Stockbridge



Lamond



Details on sampler preparation. Courtesy U. S. Navy Dept.

to a steady stream. After the cup is filled, the valve assembly is attached to the sample container and tightened securely. As the liquid evaporates it is collected in the main chamber of the oxygen bottle and the sample is then ready for shipment.

Detailed sampler preparation, manufacturing notes, and procedure are included above. Copies are available to anyone desiring a copy from Materials Laboratory of NAS, Alameda, Calif.

**BOLLEN—Dow of Canada:** We have had our air plant in operation now for approximately four years and until recently acetylene has not been a problem. We analyze on a routine basis and have never found anything that amounted to more than a fraction of a part per million. About two months ago, shortly after a new plant which is fairly close to our plant came on stream, we picked up acetylene for the first time. We im-

mediately started checking analyses. We increased the purging as much as possible and waited for the down-drop in acetylene content. It didn't come about. Instead, it went up over one part per million. As we were already purging as much as we could, all we could do was to continue taking samples and analyzing. Eventually the acetylene content went to a high of 2.3 ppm. Our shutdown limit at that time was set at 3 ppm. Since the wind was coming from the direction of the new plant, we went and checked over this plant, trying to find the source of acetylene. We could find nothing leaking there. However, they did have an acetylene system where a number of cylinders of acetylene were tied into a common header with a safety valve attached to it. After checking the system over, we connected the vent from the safety, which normally vents to atmosphere, to an absorption train for analysis

and we did pick up a trace of acetylene that was leaking through the safety valve. It was the only source of acetylene we could find but apparently it was enough to give us a problem.

**C. P. ANDERSEN—Linde:** I'd like to comment on holding time of liquids in the vaporizers. We use a recirculation system which continuously recirculates oxygen liquid through a silica gel adsorber to remove any dangerous contaminants during normal operation. With this system we keep the acetylene and dangerous hydrocarbons to a very small quantity. Acetylene concentration has always been below the detectable limit. In this way we see no danger in holding liquid for extended periods of time during shutdown. We've held it for at least a week in some cases. In some cases, we actually add liquid oxygen to the main column for extended shutdown to prevent the liquid from boiling dry. One

other comment on extended shutdowns is pertinent in regard to the gas phase silica gel adsorbers. If you have no flow through these adsorbers the CO<sub>2</sub> and hydrocarbons deposited at the inlet will migrate through the adsorber until an equal loading exists throughout the entire bed. Therefore, if you start up your plant with a silica gel adsorber that has been down for an extended period of time, you may drive CO<sub>2</sub> or hydrocarbons through the adsorber into the columns. The main requirement we have for down time is with regard to the silica gel adsorbers; namely, have a clean

adsorber ready to go on line when you restart your plant.

**R. K. SIMMS—Phillips Chemical Co., Bartlesville, Okla.:** We have found nitrogen oxides in our air plant. We don't know where they are coming from. We're interested in knowing if any of the rest of you have found them and if you did find them, how did you look for them and how often?

**G. S. COCHRANE—Sun Oil Co., Philadelphia:** We have found nitrogen oxides in our liquid oxygen also. I think the highest concentration was N<sub>2</sub>O. We analyze for it by concentrating the contami-

nants in the liquid oxygen and then analyzing the concentrated contaminants with a mass spectrometer. We have also found NO and NO<sub>2</sub> but in much lower concentrations. We feel that the N<sub>2</sub>O is inert and is not dangerous. It is a normal constituent of air.

**R. W. ROTZLER—Monsanto Chemical Co., Texas City:** We also have found N<sub>2</sub>O in our cold system, originally, I think, in regeneration of the silica gel filter bed and subsequently in our re-boiler. We found it by analyzing samples with a mass spectrometer and with a 10-meter dispersive infrared instrument.

## Construction practices

Strength of materials is the prime consideration of the plant designer. Thermal properties, and fracture and corrosion resistance are key factors.

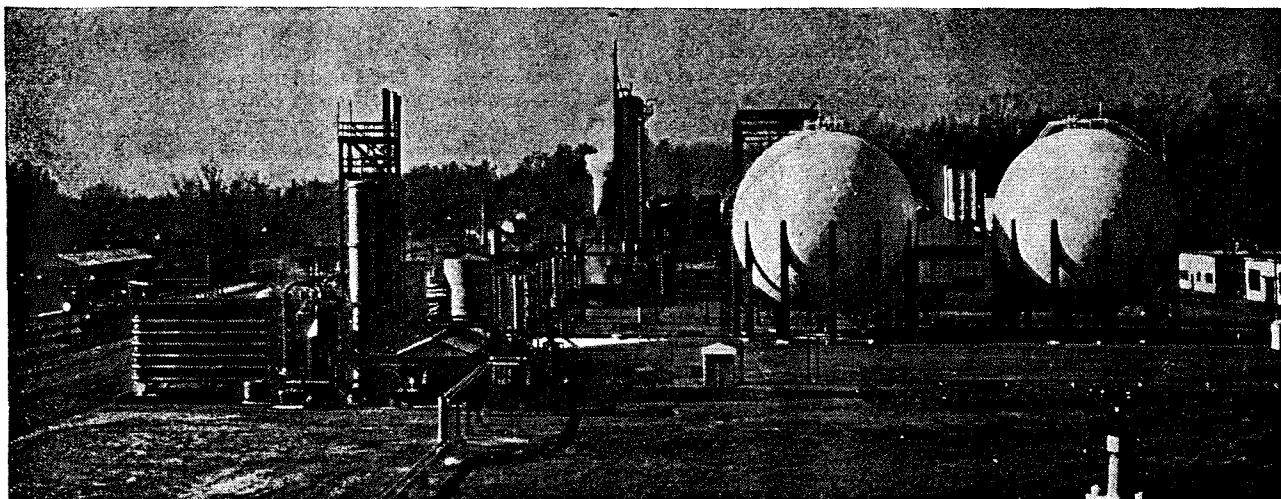
**W. S. MOUNCE—International Nickel Co., New York:** On the materials of construction and methods of construction from a safety and operating standpoint, designers of the equipment must make the basic decisions and apply materials properly. Any necessary maintenance or repair work must be done without disturbing the properties of the material in the original construction; assuming it has been properly chosen and is behaving properly in the first place. The quickest way to cover a lot of territory in little time would be to review briefly the common materials of construction, the reasons for their use, and some limitations from a safety standpoint.

Strength is a prime consideration of the plant designer. Thermal properties,

and fabricating characteristics are important. Resistance to brittle fracture is a consideration. Copper, an early and still important material, has low design stresses and good thermal characteristics, but joints must be made either mechanically, or by soldering or brazing. In large structures each method introduces problems and opportunities for leaks and difficulty in operation. Bronze gives a slightly higher design stress and the copper-nickel alloys ranging from 10% to 30% nickel show substantial gains in design stress. These copper nickels are now produced in weldable grades and welding rods are available so that you can consider welded joints. Monel has applications, not so much in air separation plants, but in some other liquefied gas

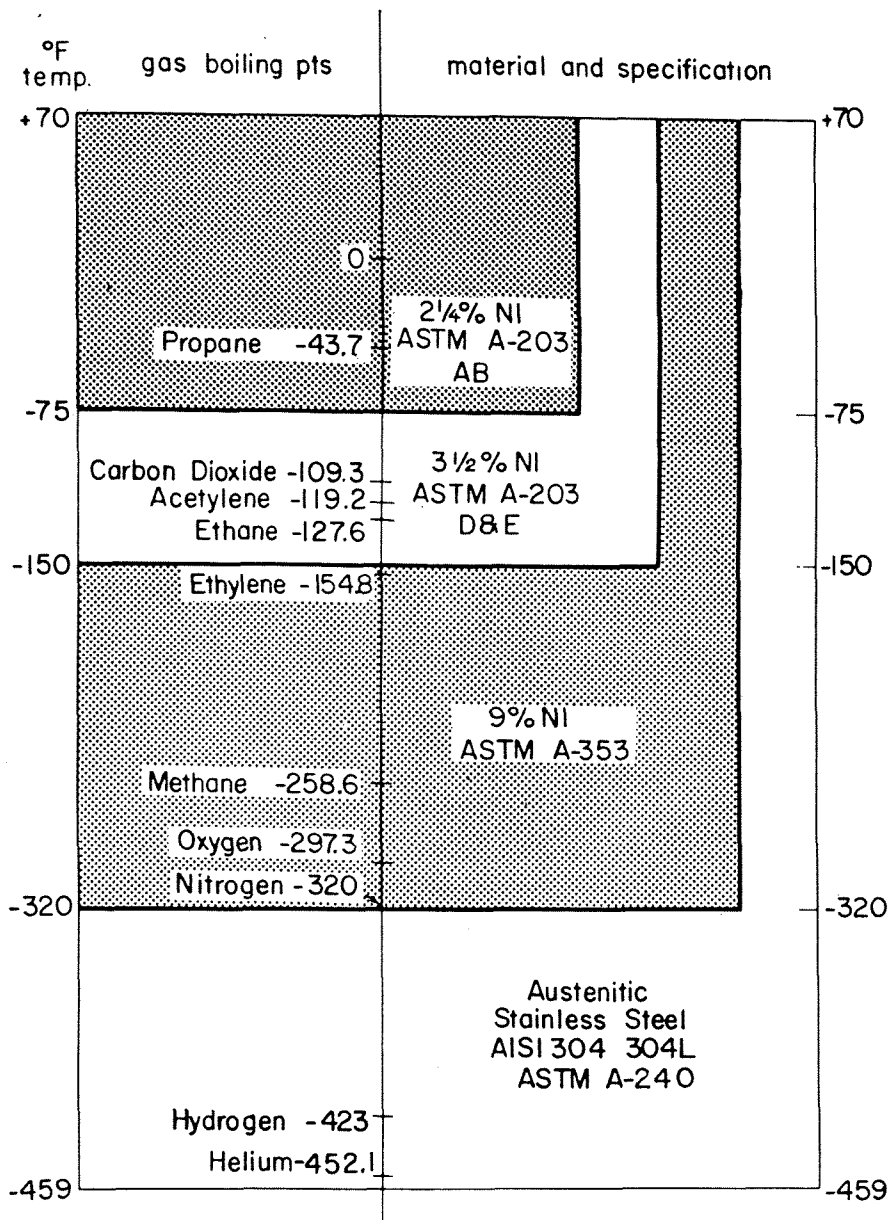
plants where corrosion problems are involved, specifically fluorine. Aluminum has come in strongly recently, in air plants. Relatively pure aluminum has a low design stress but the newer alloys, which are solid-solution hardened, basically, the magnesium manganese alloys, have good design strength. Considered on a strength-weight-cost basis, they show good economy. The main problem associated with the aluminum alloys are their welding characteristics. Aluminum alloys offer problems from a corrosion standpoint in specific instances, and finely-divided metal may get into the system through repair procedures or original assembly and cause an explosion.

Cleanliness requirements in the missile fuel systems are very strict; the corrosion products that may form with aluminum and a steel which is not essentially corrosion resistant impose limitations for such service. Stainless steel, extra low-carbon grade, gives a very desirable design stress and is particularly corrosion resistant. It is weldable, and is increasingly considered for some applications filled previously by copper and aluminum. The cleanliness requirements for missile fuels are now being met in the handling and storage end of the systems, with stainless. Stainless' low thermal con-



In plant construction, equipment designers must make basic decisions and use materials properly. Photo Spencer Chem. Co.





Temperature range in which steels are used for low temperature processing equipment.

ductivity may be a disadvantage in many applications, though in some places it is not. Stainless is expensive, for though it does have a higher strength, it is heavier. Sometimes the price is high because you buy metal by the pound. ASTM A-353 is 9% nickel steel, a ferritic steel as compared to the austenitic steel 304. It is cheaper than stainless, and

has a higher strength. The steel is readily fabricated and welded and work is now going on to develop a better and stronger weld rod so that even larger stress allowances can be used. The material does not have the corrosion resistance of stain-

Table 1. ASME boiler & pressure vessel allowable design stresses

Copper-plate	6,700 psi
Copper-tubing	6,000
Muntz Metal-plate	12,500
Cupro-nickels -90-10	10,000
Cupro-nickels -80-20	10,700
Cupro-nickels -70-30	12,000
Monel-annealed	17,500
Monel stress relieved	21,200
Aluminum-3003-0	3,350
Aluminum alloy-5456-0	10,500
Stainless steel-304	18,750
9% Nickel steel-353A	22,500
9% Nickel steel-353B	23,750



Mounce



Davenport



Morain



Putman

less steel. Thermal expansion is low compared with stainless steel, aluminum, and copper. The pressure vessel code now requires that welded 9% nickel steel vessels be stress relieved after welding. However, our work indicates that the low temperature impact requirements can be met in the as-welded condition, and a case will be presented to the ASME Code Committee for consideration. Generally, the ferritic steels or the lower alloy steels may be subject to fracture in a brittle manner under certain temperature and loading conditions.

The ASME code and the ASTM specifications have established a system which indicates the temperatures at which these materials are resistant to brittle fracture. We know of no instance where a material conforming fully to the code and to the specifications has failed in a brittle manner in service. In the stainless steels the 304L grade is preferred because it can be welded without danger of carbide precipitation, which might harm the corrosion resistance of the material, or the danger of excessive development of ferrite, which might affect its low temperature toughness. Appropriate rods and practices are well spelled out for most of these materials by the American Welding Soc., the ASME codes, and the ASTM Specs.

**LAWRENCE—U.S.I. Chemical:** You left two questions in my mind, one was if aluminum corrosion products end up in the main vaporizer will they cause an explosion? Most of our air separation plants have aluminum exchangers, I believe.

**MOUNCE—International Nickel:** The only instance that I know of was in the storage and handling facility not in the main oxygen plant. This was where an explosion and fire occurred in transferring liquid oxygen from a storage tank to a tank truck which was to take it to a launching pad. They investigated the cause, and as far as they could determine, the repair to the aluminum pipe might have left either flux or powdered metal in the line, and this became heated and burned.

**LAWRENCE—U.S.I.:** You mean it reacted with the liquid oxygen?

**MOUNCE — International Nickel:** There was an external source of heat somewhere that heated it up to the point where it actually caught fire.

**LAWRENCE—U.S.I.:** The other question was on 9% nickel. Is it not used because of the depreciation, otherwise it

would be a good metal for low temperature plants?

**MOUNCE—International Nickel:** It is being used now. The restricted availability of nickel from 1950 up to about a year ago is the reason why it wasn't used more widely.

**LAMOND—Canadian Industries:** I wonder if any of the gentlemen here have any idea on tightening of liquid oxygen flanges. We have a problem, especially in the high pressure lines. It seems that no matter how hard we tighten them to effect a leak-tight joint at ambient temperature, the joint may start leaking again when the line is cold. Our only answer to this is to retighten the joints at operating temperature. The system is depressured and a heavy nitrogen purge is provided to keep the oxygen concentration at 21% or below.

**ODOM—Chemetron Corp., Searsport, Me.:** In cases of leaking flanges we have found that doubling the number of bolts helps. In other words, in a four-hole flange drill out and put in eight bolts. It helps distinctly out of proportion to the number of holes. We also have abandoned Teflon for cold box use. We find that Teflon has a flowing coefficient even at low temperatures and it becomes brittle at the temperatures encountered.

We're using Darcoid, an asbestos-type gasket with somewhat better success. Some time ago, we picked up, I think at one of these meetings, the hint that many people soak their asbestos gaskets in wax or petroleum wax. This seems to help. But we have found that we are unable to prevent the mechanics from oversoaking them. They get too much wax in and while it appears solid when it's cold, the wax squeezes out when the flange is tightened. In self-defense we have discontinued that practice; but doubling the bolt holes in the flange will certainly help tremendously in making these joints tight.

**MARTIN—Spencer:** This may sound a little ridiculous but I offer it in perfect seriousness. Maybe you can eliminate the flange joint. I think a lot of us lean over backwards to get joints in where we could just as well use a welded joint.

**SHANER—Linde:** We would consider the tightening of flanges while liquid is in the line an extremely dangerous and hazardous operation. As a precautionary measure, we do not perform any maintenance function on the lines while liquid oxygen is in the lines.

**R. L. SWOPE—Southern Oxygen Co., Washington, D. C.:** I know the gentlemen from Chemetron stated that they were getting away from Teflon. But we have found that where we have troublesome joints, the Teflon is the one sure cure for them, just to reverse the theory. One of the most recent things that we have found to be very helpful on a particularly troublesome joint, namely a flare-type connection, is Teflon 30; one of the dispersants of powdered Teflon, in a liquid carrier. There is, in this material,



Rogers



Swope

a wetting agent which may not be completely safe in oxygen. We have run tests attempting to fire it under oxygen conditions and if it's permitted to dry thoroughly before oxygen is admitted to the lines we have found that there is no difficulty. One of the interesting applications of this particular liquid Teflon was on a leaking joint which was equipped with a solid Teflon ring gasket. This was in a joint between two halves of a solenoid valve. We coated the solid Teflon gasket with liquid Teflon as we put it back in the valve and tightened the valve body up. We had no further trouble from that source.

**ODOM—Chemetron:** Just to make this thing fully ridiculous, we have departed from the custom of using so many welded or brazed joints and are putting in more flanges. Such problems in the air plant are illustrated by one recently where one of the soldered joints suddenly popped open about 1¼ in. Obviously the joint wasn't constructed properly in the beginning, otherwise there wouldn't have been such a strain.

We also found that this joint had been brazed with ordinary 50-50 solder instead of silver solder. We then deliberately broke a lot of 50-50 solder joints and resoldered them with silver solder and have had no further trouble. This job was around the hydrocarbon absorber

manifold valving section. We had to break several joints before we got back to a place where the flanged joints were available, permitting the lining-up of the whole assembly without strains. The lack of enough flanged joints resulted in considerable delay.

**DAVENPORT—Ketona:** We've had considerable difficulty with stem packing on our valves. It consistently leaks on us. We tightened it down to the point where we stopped the leak and the valve became inoperable. I wonder if I can get any comments on this?

**W. A. MORAIN—Cooper Bessemer Corp., Mt. Vernon, Ohio:** We found that braided Teflon is a very good packing for valves on expander engines and in quite a few cases have experienced no trouble whatsoever.

**ODOM—Chemetron:** We tried a little dodge based upon the Graphlon packing we buy from Air Products for our liquid oxygen pumps. We tried it out on the shaft of a valve which isn't moved often. We put in a couple of layers of solid Teflon sheet first, and then filled the packing box with Graphlon. Then a sheet of Teflon was put on top, good and tight. A pretty good, tight joint that will last a long while was obtained.

**GORDON WEIGERS—American Cyanamid Co., New Orleans:** We came up with what we think is a fairly simple solution. Packing-wise we use braided asbestos and paraffin, and we find that if the operators just steam the valves, the valve bonnets, so that they are warm before they are operated, we get no leakage.

**L. E. PUTMAN—Superior Air Products, Newark, N. J.:** In connection with using graphite in a valve stem packing, you can set up an electrolytic corrosion problem, particularly if moisture diffuses inward over a period of time.

## Instrumentation application

Changes in atmospheric conditions rather than operating techniques cause changes in the product stream.

**SWOPE—Southern Oxygen:** Approximately a year ago, the Navy Department, Bureau of Aeronautics, placed certain very low limits on the permissible amounts of specific hydrocarbons and other contaminants which would be considered acceptable in liquid oxygen. Of principal interest to them was methane, which they originally limited to 5 ppm. (This has since been revised to 25 ppm, and is still in controversy.)

Although our liquid was normally ac-

ceptable, several cases of contamination occurred during periods when the atmosphere was approaching a "smog" condition. According to Navy tests, the methane content of the liquid was reported to be as high as 54 ppm on one occasion, and may well have exceeded this value on others. Other contaminants such as CO, CO<sub>2</sub>, acetylene, and oxides of nitrogen were reported as remaining within the acceptable limits.

When the Navy originally established

the limits on methane and other contaminants, they set up their own facilities for testing liquid oxygen at key points. Acceptance was based on their tests at the time of delivery or upon qualification tests made at the producing plant subject to acceptance tests at the point of delivery.

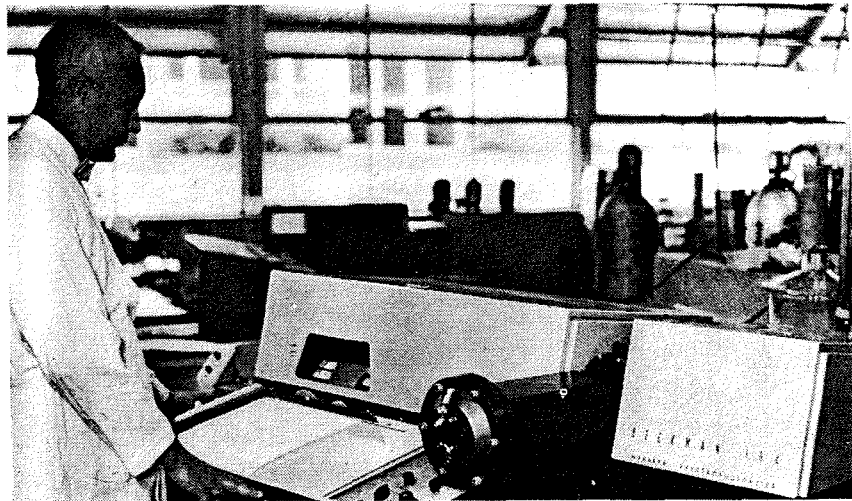
This was fine from their standpoint, but left the supplier in the uncomfortable position of not knowing, in advance of delivery, whether or not his liquid would be accepted. The Navy's original belief was that a plant capable of producing methane-free liquid oxygen on one occasion would always produce methane-free liquid. The fallacy of this theory became apparent almost immediately when it was observed that changes in atmospheric conditions, rather than operating techniques, were responsible for changes in the product stream. The necessity of testing individual shipments became apparent. It appeared that infrared spectrophotometry held the only solution to the problem of analysis. We, therefore, purchased a Beckman IR4 instrument with a 10-meter cell. This is an extremely sensitive and flexible instrument and requires a great deal of experience to operate.

Analyses are now made on all shipments prior to delivery. When it is not being used for the analysis of a specific sample, the instrument is constantly monitoring the methane content of our product. In the event of a methane increase to a predetermined limit, our operators divert the production to a disposal point until the condition clears up, thus avoiding contamination of our storage and transport vessels.

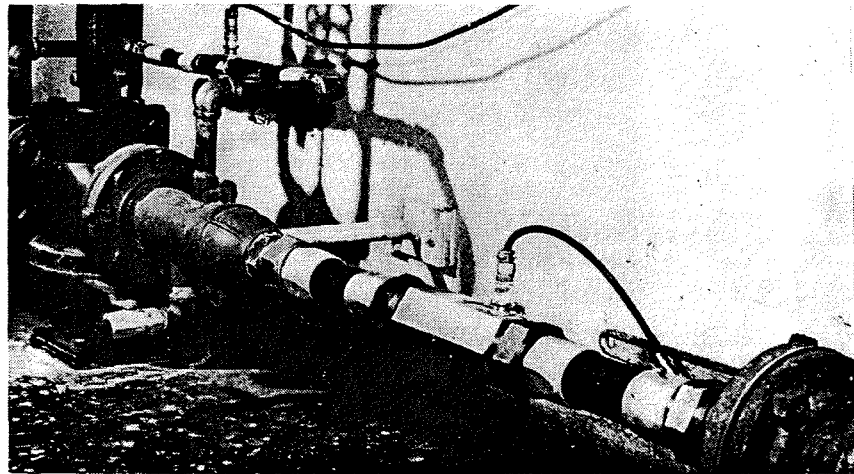
We anticipate that the instrument will be of greatest value to us in helping to correct the methane condition, but it is still too early to report much progress in that direction. Using the IR4, we have learned that the primary source of methane is the atmosphere—there being little or no increase traceable to the breakdown of lubricants. We also find that nearly all of the methane present in the air will finally appear in the liquid oxygen. We have also found that the concentration can be reduced, but only slightly, through the use of adsorbents and molecular sieves located in the liquid oxygen stream. Our current thinking is that methane can probably be more easily eliminated from the high pressure air feed.

**L. MALEY—Mine Safety Appliances Co., Pittsburgh:** We have built several analyzers, liquid oxygen vaporizers, and continuous analyzers for acetylene in liquid oxygen and have installed them in several plants. Quite frankly, we are experiencing difficulty with them in getting the volume of sample required to obtain a good analysis of acetylene in the liquid oxygen.

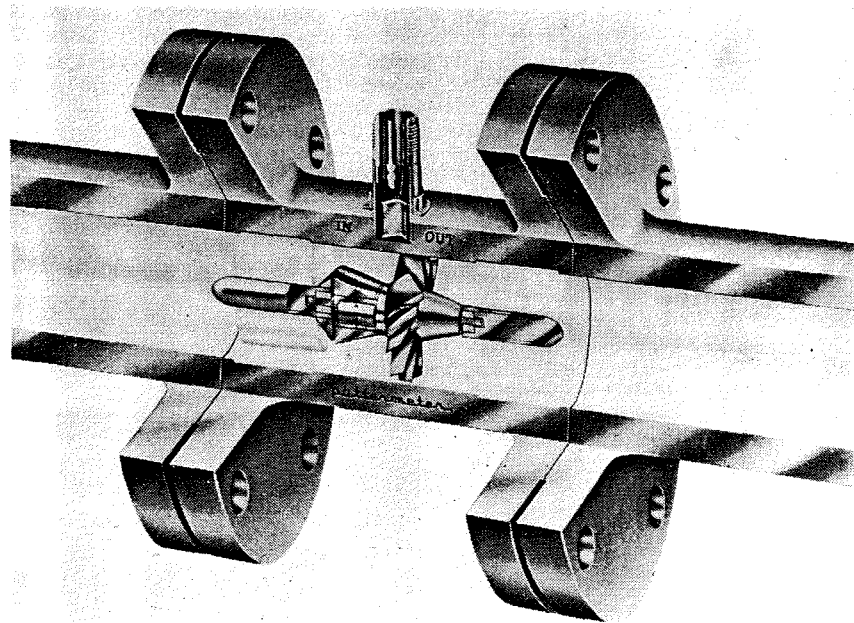
Consequently we have pulled back some of the analyzers and are continuing work to develop a continuous acetylene analyzer and vaporizer. We have found that most of our difficulties were in ma-



Infrared spectrophotometry is used as a means of analyzing product oxygen for methane content. Photo courtesy Beckman instruments.



Turbine meters are finding use in liquid oxygen installations. Photo courtesy Fischer & Porter.



Cutaway view shows principle of turbine meter operation. Photo Bowser, Inc.

terials of construction and design. I would like to ask you people here what your reaction would be to an analyzer that would give a reading once every 30 minutes, or once every hour, automatically. The vaporizers that we originally set up were designed to operate on a 6-minute cycle; 3 minutes on one chamber and 3 minutes on another chamber. What speed or time requirements would you set down for the analysis of acetylene in liquid oxygen?

**LAWRENCE—U. S. I.:** Our feeling at Tuscola is that an analysis every half hour or hour would be better than present practice.

**P. O. McELROY—Wyandotte Chemicals Corp., Geismar, La.:** Detection of acetylene in our liquid oxygen has always given us a problem because of the apparent low concentrations. On a go or no-go basis, we have adopted the NBS method described in *Analytical Chemistry*, Jan., 1959. In essence, the method is: 2.5 l. liquid oxygen are passed



Maley

McElroy

through a 10-mm tube containing 3 in. of 3x8-mesh silica gel, the tube is flushed with pure nitrogen until room temperature is reached, a few ml of recommended indicator are sprayed on the gel; a pink or red tinting of gel indicates acetylene present. Negative test indicates less than 1 ppb acetylene.

**BUTIKOFER—Standard Oil:** I want to ask a question about the turbine flow meters. Can you give us a more detailed description of what you are using?

**HIMMELBERGER—Air Products:** We

use turbine meters in streams with diameters on the order of 1½ to 2 in. Bearing maintenance problems in smaller lines have suggested that bearing friction will require some consideration with regard to safety. We found that a bypass located close to the meters, permitting slower cool-down has reduced bearing problems. A fire in a system at Cape Canaveral was probably caused by a turbine meter, designed for liquid flow, being used in a precooling service, where gaseous flow at high velocities passed through the meter in a reverse direction. However, I think the turbine meter is perfectly satisfactory for liquid oxygen service, if a little judgment is used in its installation and use.

**K. A. ROGERS—Liquid Carbonic, Chicago:** We've been testing turbine type meters (Fisher & Porter) for about three years and found them, in general, much more satisfactory than positive displacement. We found them the next best thing to weighing the trucks.

## Repairs and shutdowns

Purging rock wool with nitrogen on shutdown is not the complete answer to making the rock wool safe. Pockets may remain.

**COCHRANE—Sun Oil:** I would like to discuss briefly the methods of purging the cold box before repairs are made, and the method which Sun Oil used to make repairs in its hydrogen purification cold box under a complete blanket of nitrogen. There are three requirements which must be met to have a detonation, or an explosion. Fuel must be present, an oxidant must be present, and there must be a source of ignition. In digging into a cavity in the insulation of a hydrogen-purification cold box, it is possible that these three conditions may be met unless special safety precautions are taken. Fuel will almost certainly be present. Even if the hydrogen box is purged before it is opened, small pockets of high hydrogen concentration will remain. Because of the channeling of the purge gas through the rock wool, these pockets are almost impossible to eliminate.

The possibility of oxygen from the atmosphere getting into the cavity, either while the rock wool is being removed or during the repairs, is also very likely. Even with purge hoses in the cavity and a tarpaulin over the opening it is difficult,

if not impossible, to keep the oxygen content at a safe level. We have never succeeded in keeping the oxygen content below 17%. Finally, there must be a source of ignition. This is the most difficult requirement to eliminate, since there are so many possible sources. In preparing to do maintenance work inside our hydrogen purification cold box, we decided that the easiest, and most reliable, method of preventing detonation was to eliminate the presence of oxygen.

For about a year, the routine analyses we made in our hydrogen box atmosphere showed a high-hydrogen concentration in one portion of the cold box. Since the

concentration was localized, it indicated a small leak. However, one day a large frost spot developed on the side of the cold box, indicating that the leak had suddenly gotten worse. The exchanger nearest the frost spot was taken out of service, and consequently the frost spot disappeared. We continued to run the plant at reduced capacity, using only the remaining exchangers. A hole was cut in the side of the cold box, and the insulation was removed in the presence of nitrogen from purge hoses. The minimum oxygen concentration which we were able to maintain in the cavity was 17%.

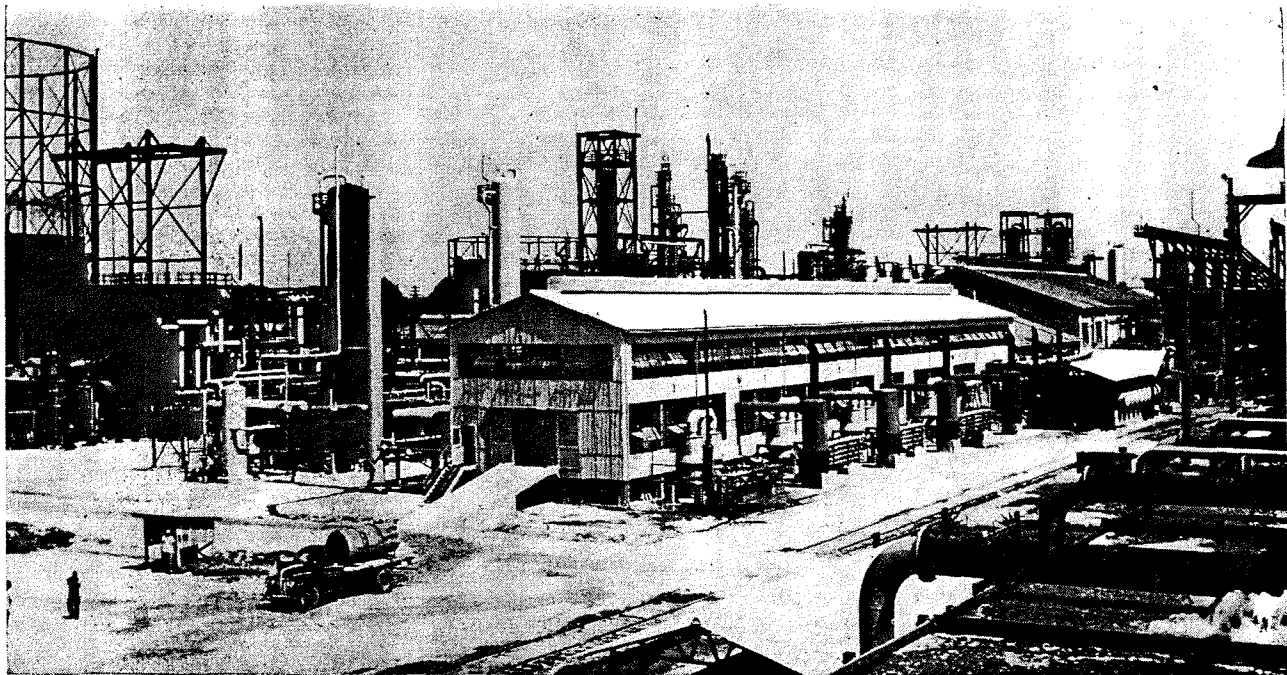
The 3 in.-copper pipe in which the leak developed normally contains a 95%-hydrogen stream, at about 350-pounds pressure, and -100 to -130°F. Off this pipe is a 1-in. stainless steel pipe running to a safety valve located outside the cold box. A small pin hole developed in the 1 in.-stainless steel pipe allowing the 350-pound hydrogen to leak out, impinging on the 3-in. copper pipe. This had apparently been going on for about a year; the leaking hydrogen churned up the rock wool in the vicinity of the large copper pipe, grinding the surface. Eventually the copper pipe became so thin that it ruptured. It was only then that we noticed the large frost spot on the outside of the cold box.

Our maintenance people decided not to replace the damaged pipe, but to design a Tee-shaped clamp which would completely enclose the area of the leak. While one of the workmen was removing additional insulation to make some measurements, he saw small glowing particles in the rock wool he was removing. Until a decision could be reached on how to proceed with the repair, the rock wool insulation was replaced in the



Cochrane

Weigers



Many advances have been made in air separation plant technology, but common sense must still be used in repairs and shutdowns. Photo courtesy Commercial Solvents Corp.

cavity, a tarpaulin was placed over it, and a nitrogen purge hose was placed behind the tarpaulin.

The presence of the glowing particles was very puzzling. It was found that when a nitrogen stream was directed at the particles, the glowing stopped. However, when the nitrogen stream was removed, the glowing resumed. This indicated that oxygen was necessary for the glowing to occur. The rock wool in the area of the leak had been in a reducing atmosphere for about a year, subjected to temperatures ranging from  $-130^{\circ}\text{F}$  during normal operation, to about  $+100^{\circ}\text{F}$  during the twice-weekly defrosts. During this period some of the iron inherent in rock wool may have been reduced to a pyrophoric state. When the insulation was exposed to atmospheric oxygen as the insulation was removed, the pyrophoric iron glowed.

This is merely a theory which we were not able to substantiate in the laboratory. Some of our people thought that certain particles in the rock wool were heated to red heat by catalyzing an exothermic oxidation reaction. This also could not be substantiated in the laboratory. Efforts were made to produce pyrophoric iron in insulation in the laboratory, but with no success. Rock wool from the hydrogen cold box was placed in a hydrogen atmosphere at about  $850$  to  $900^{\circ}\text{F}$ . After purging, the rock wool was exposed to oxygen, but no glowing occurred.

Because of the presence of glowing particles it was imperative that the repairs be made under a complete blanket of nitrogen, with the hydrogen box shut down. To insure an adequate nitrogen blanket a special enclosure was constructed around the hole. The enclosure was made as gas-tight as possible. A 6-in. hose carried purge nitrogen into the en-

closure. Sample lines from three points inside the enclosure were run outside so the atmosphere could be tested frequently for oxygen content. The oxygen content was kept below  $1\%$  inside the enclosure, requiring the workmen in the enclosure to wear fresh-air masks. During the repairs no glowing particles were observed, even when insulation was removed from the enclosure. The leak was successfully repaired and the unit was put back in operation.

**LAWRENCE—U. S. I.:** I have two contradictory questions. The first is: Did he consider the possibility that the copper that he sloughed off in fine particles could have oxidized to copper oxide or copper carbonate? The second is: Forgetting about the copper—was the insulation higher in iron—maybe this is a general question—is there any color specification on the insulation? I ask that question because we're thinking of changing insulation, and the insulation we contemplate is higher in iron, and is also a little darker colored. But, otherwise, on hydrocarbons and K-value it conforms with what we've been using.

**COCHRANE—Sun Oil:** I don't know what the iron content of our insulation is. I do know that all rock wool does have

iron in it. I don't know if ours is higher or lower than what would be considered average. On the other question about the copper—we had not considered that these particles could have been copper, but this might be a possible explanation.

**WEIGERS—American Cyanamid:** In an analysis we made—an emission spectrograph of the insulation in the vicinity of our cavity—the iron content was  $0.55\%$ . I don't know if that's high or low, or in-between.

**HIMMELBERGER—Air Products:** The Kirk-Othmer Chemical Engineering Encyclopedia, Vol. 9, p. 122, gives analyses of typical rock wools. Rock wool from Pennsylvania blast furnaces differs from that from Ohio blast furnaces; but all of them contain metallic material such as iron oxide and magnesium oxide which may run well above  $0.5\%$ .

Another comment was made about the oil content in rock wool. The manufacturers prefer to add some oil to minimize the dusting in manufacture. Rock wool in the U. S. generally runs below  $0.3\%$  oil. Experimental tests have been run to determine whether quantities of oil, on the order of  $0.3$  to  $0.5\%$ , could be explosive, without allowing for any leaching or any change in content due to temperature change, or temperature cycling. About  $4\%$  oil was needed in rock wool for an explosion to occur in contact with liquid oxygen.

**MASON—Dow:** I wonder if an analogy might be drawn between the wearing away of copper under an extremely reducing atmosphere and the wearing away of carbon packing in argon or nitrogen pumps under low-oxygen concentration; where you get, apparently, unsatisfied bonds of the molecules. This might have



Lawrence

Nielsen



made this copper pyrophoric from that standpoint.

**ANDERS NIELSEN—Haldor Topsoe, Denmark:** When you tried to reproduce the events in the laboratory you reduced the rock wool at 800 to 900°F. What I had in mind to say was about the same as Mr. Mason only in this case with the iron. I don't know whether it's possible to reduce at the temperatures you have in the cold box. But, if it is possible, it certainly would be a completely different type of iron, and probably extremely pyrophoric. At 800 to 900°F, pure iron would have enough mobility to form fairly large crystals.

**COCHRANE—Sun Oil:** Are you saying that it was not a fair test—that it is not comparable to try to speed up the process in the laboratory by going to higher temperatures? If the reduction took place in the period of a year at a much lower temperature, say, around 100 or 150°F, which we had in that vicinity during the defrost, this would give us an entirely different and more pyrophoric iron?

**NIELSEN—Topsoe:** Yes, that's right. I don't know whether it's possible, but if it is, it would give a different iron. This could very well have been pyrophoric iron.

**BUTIKOFER—Standard Oil:** During a recent strike the Calumet plant was down for about 21 days. The nitrogen wash box vessels were warmed to about 150°F and thoroughly purged with nitrogen. While the box stood idle the equipment inside the box cooled to -100°F by virtue of the refrigeration stored in the insulation. The atmosphere inside the box became flammable, and had a rather high hydrogen concentration. Nitrogen was obtained to purge the box and the interior of the box was checked three times a day for hydrocarbons.

As time went on the molecular weight of the hydrocarbons in the box increased. It wasn't until about the end of the 21-day period that the hydrocarbons were predominantly propane. This showed that the insulation was weathering due to the purging effect of the nitrogen. We are now concerned about how to remove the insulation from the box safely during a shutdown without going into a long purging period.

**LAWRENCE—U. S. I.:** We took all the insulation out of our box last year to do some repairs. What we did was to increase the nitrogen purge to a very high rate, and then—instead of worrying about hydrocarbons—we worried about the guys breathing. We kept the oxygen concentration down around 10%, except in big openings. Any hydrocarbons that are in there (they're heavy) seem to accumulate down on the floor level. Once you get them out you're in pretty good shape. Of course it sounds wrong to take the floor out before you work up above, but we had a lot of ice up above and it took us longer to get out. And once we removed the insulation from the bottom we didn't have any hydrocarbons to speak of.

**WALTON—Atlantic:** We removed all



Culp

Butikofer

of our rock wool from the cold box. It was a nasty job because we had a distillate leak in the cold box and the rock wool on the bottom, about a foot above the floor in some locations, was pretty well saturated. Our approach was to ventilate as much as possible and to take large panels off the side because this wool (about 12 to 18-in. thick on the bottom) was not only saturated with hydrocarbons, but was also bound together with ice. We kept the box as well ventilated as possible so that if a spark occurred there wouldn't be an enclosure to generate a lot of pressure.

Originally, our rock wool was bought on a low-bid basis and was grey and black. That was the wool which we removed this first time. In many places there were icebergs and accumulations. Later we bought Johns-Manville Spintex. It's quite white. It handles easier and doesn't cause as much difficulty when blowing it in. We also found that this material is much easier to remove than

the darker color rock wool we used in the beginning.

**ODOM—Chemetron:** Not long after we started up, we had to purge our hydrogen-purification cold box. The purging of the box took us nine days. We have had three other occasions when we wanted to purge the box but did not want to spend the necessary time. The penalty of taking such a long time to purge the box with the facilities at our command has been one of the big deterrents to getting the box in better shape. How long did it take Sun Oil to purge their box? Do you have some secret which would enable us to do it quicker?

**COCHRANE—Sun Oil:** When you talk about purging a hydrogen purification cold box, it depends to a large degree on the quantity of nitrogen that you can put into the rock wool insulation. As we are set up, we can put a fairly large quantity of nitrogen purge into our hydrogen purification cold box.

However, we feel that purging the rock wool is not the complete answer to making the rock wool safe. Pockets will remain where it is possible to have high concentrations of hydrogen or hydrocarbons, because in purging rock wool you get too much channeling. The nitrogen follows the path of least resistance up the side of the cold box and out to the atmosphere. There can be areas in the cold box which will have pockets in which the presence of oxygen could possibly form an explosive mixture.

## Hydrogen production

Gaseous hydrogen presents the greatest fire and explosion hazard of any gas because of its wide flammability limits.

**MARTIN—Spencer Chemical:** There are from 5 to (at least) 14 methods of producing hydrogen in commercial use in the world today. The number of commercial hydrogen purification systems is not as great. The type of hydrogen production system used, and other economic factors, have some effect on which purification systems are used. CO<sub>2</sub> removal is accomplished commercially by scrubbing with monoethanolamine (MEA), diethanolamine (DEA), caustic, water, or hot potassium carbonate. Final traces may be taken out by copper-liquor scrubbing, solid adsorbents such as alumina, and freezing. CO<sub>2</sub> in small quantities, can be removed by copper-

liquor solutions, liquid nitrogen scrubbing, and/or the use of a methanating converter, wherein the CO is reacted with some of the hydrogen present to form methane and water.

There are some hazards common to all of these processes. Gaseous hydrogen, because of its wide flammability limits, presents the greatest fire and explosion hazard of any gas. Carbon monoxide is a particularly dangerous material. It is flammable, has no odor, and has high toxicity. It is always present in highly lethal concentrations in any hydrogen production and purification processes which start with a hydrocarbon raw material. Most of the combinations of



hydrogen production and purification in use today, at some point, involve relatively high temperatures, compared to other chemical processing, and these require special safety precautions.

In those processes utilizing a controlled oxidation between hydrocarbons and oxygen, the reactions can become uncontrolled, resulting in severe damage. The low temperatures involved in ni-

trogen washing offer hazards of a type which are sometimes unfamiliar. In the first few months of our Vicksburg, Mississippi operation, we ruptured a 6-in. carbon steel line which released a considerable amount of hydrogen into the atmosphere, by subjecting this line to temperatures below  $-100^{\circ}\text{F}$ . We were fortunate that damage was restricted to this line and there were no injuries.



Martin

Maune

## Ammonia plant compressors

Valves and gaskets are critical; inspection and testing schedules an enigma.

**H. E. MAUNE—Armour Agricultural Chemical Co., Crystal City, Mo.:** My comments concern our particular plant at Selma, Missouri. We'll start first with the air compressors. In the past we've had some difficulty with fires. We do use synthetic lubricants. In the third stage of our air compressor which is at 650-lb. pressure, we did have some trouble in the earlier days, but we changed the valve design. We are now using circular-channel type valves with which we have no difficulty. They will stay in service under these conditions for a year or more.

Going along to another service where we did have trouble, we compress nitrogen from approximately  $1\frac{1}{2}$  lb./sq. in. ga. to 325 lb. in two stages. Our second stage discharge temperature is quite high—about  $390^{\circ}\text{F}$ . We experienced some difficulty with carbon formation in the valves. We can manage to operate nearly a year under these conditions without any

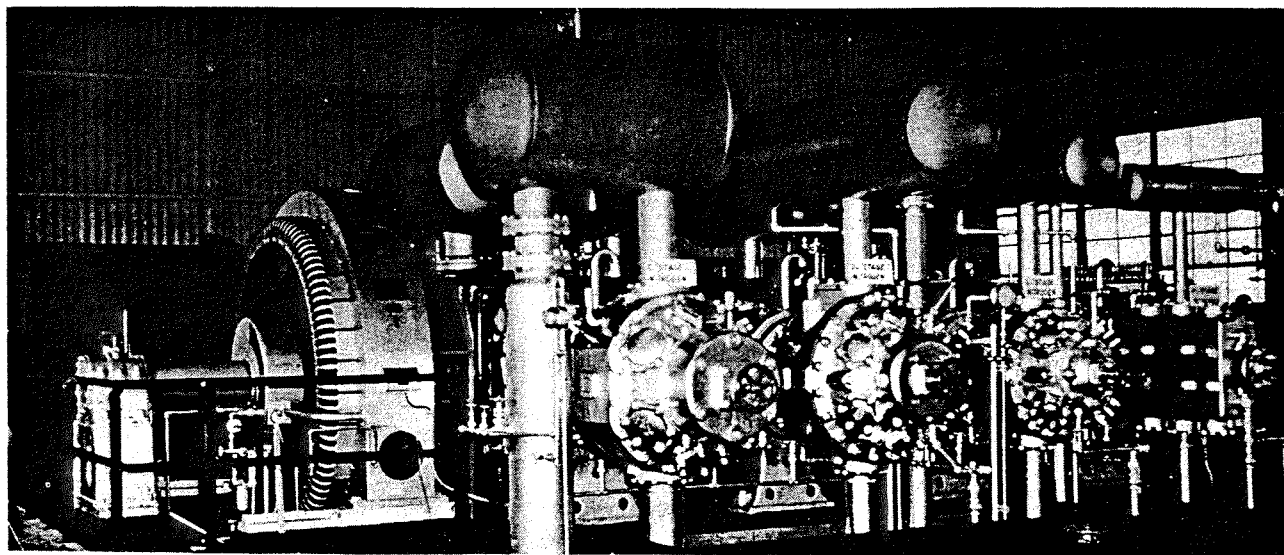
serious difficulty. However, we had an experience and didn't know that we were in trouble from carbon formation in the valves. Of course, when our air plant is not producing pure nitrogen, we must take in a little air through the nitrogen cylinders to balance out the load on the gas engine. We can't allow too much air to get through or let the discharge pressure go too high, because hydrocarbon oils are used in this particular service. While it's all right (when using nitrogen during normal operation) to take the machine down for some reason, and put the nitrogen service on air, a fire could develop. We did have a fire in the cylinder and in the pipe line. It cleaned the carbon out for us without any serious damage resulting from it.

In another service, synthesis gas compressors on our high-stage cylinder were compressing hydrogen and nitrogen from approximately 4000 to 9000 lb., in a double-acting cylinder. We experienced

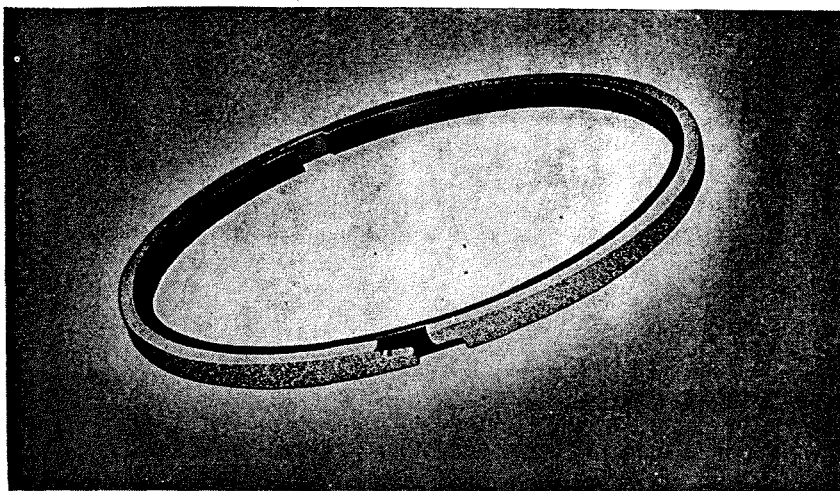
some valve difficulty in our earlier days when we had disc type valves. We changed to channel valves in this service, chrome-plated valves with circular channels. It's the best we have seen. I don't think they will ever wear out, nor break, nor do anything else; which is really what we are looking for.

We had an experience one time on this service when the valve actually came apart. The bolt that holds the seat and the guard together worked itself loose and dropped down in the cylinder. Nothing serious happened. When the piston came by it clipped the head of the bolt off and dropped it down into the discharge valve port. But, if a longer piece had been broken off, the piston would have pushed it against the head and we could have had serious damage—even the possible loss of life.

**BOLLEN—Dow Canada:** I'd like to make a comment on channel valves. When we first started our plant we had disc valves in the circulator and the rate of plate breakage was extremely high, usually resulting in a very loud clattering and pounding noise in the machine. Sometimes it sounded like the machine was just about ready to jump off its foundation. We had the compressor manufacturer investigate. We tried increasing clearances and changing springs without too much success.



Compressors are heart of both air and ammonia plants. Photo courtesy Cooper-Bessemer Corp.



Extremely low coefficient of friction of Teflon permits its use as piston ring without lubrication. Photo courtesy France Packing Co.

Eventually we tried the channel valves and since that time we have had almost no valve plate breakage. To my knowledge they are a little less efficient valve than the disc valve, but in some installations they are certainly worthwhile.

**MARTIN—Spencer:** Two incidents: The Cactus, Texas explosion and a fire that were due to a valve problem. As I recall, the seat ring broke. The suction valve dropped down to the cylinder, went out through the discharge valve, through a let-down valve into a low pressure system, and was traveling with enough speed when it came to a malleable elbow (which shouldn't have been there) it went right through the elbow. That's what triggered the explosion.

An accident that we had another time resulted in a man's arm being lost. We had a procedure for checking leaking valves which involved putting a little bit of rag on a wire and sticking it through a suction valve to determine whether the other valves were leaking. This particular compressor was a steam-driven machine. The man had followed the procedure. But then, just to make sure, he put his arm into the suction valve opening. As he did, the machine turned over and he lost his arm.

**STOCKBRIDGE—Southern Nitrogen:** I want to ask Mr. Maune about the chrome-plated discs he mentioned. First of all, what stages have you used them in, and are they channel?

**MAUNE—Armour Nitrogen:** The channel-type valves are used in the third-stage air, which is 650-lb. service. They are used in all four stages of our synthesis gas compressors. The chrome-plated channels are used in the third and fourth stages of our gas compressor. We found that they were not necessary in the two lower stages. Why, I don't know.

**FRANK HUNTER—Cooper Bessemer Corp., St. Louis:** Some points are raised here that are related to problems in another industry that I've had experience with and they're pretty basic. This

was a major oil refinery. In putting valves into a cylinder there is, of course, the problem of tightening. You can put an uneven pressure on your gaskets and cause gasket leakage. But in the refinery that I'm describing, we had some machines in service, and through carelessness, the gasketing surfaces on the valve cages had been damaged, and without refinishing them, the workmen put the cages back into the machine and put the machine back into service. Naturally, they ultimately developed leakage.

Another problem we ran into in this refinery was the reuse of some metal gaskets without annealing. A metal gasket seals with its "softness" and once you have pulled down on the gasket you have hardened it. Unless that gasket is annealed (if it is to be reused at all) it will not serve its purpose.

**H. A. SOMMERS—Pennsalt Chemicals, Philadelphia:** When we started up the Food Machinery plant at South Charleston, W. Va., some four years ago, we ran into a very unhappy experience with feather valves. The first three stages had feather valves and the last three stages had plate valves. The first stage gave us very little trouble, the second stage gave us a great deal of trouble, and the third stage probably 50% as much as the second stage. There was little trouble with the plate valves in the last three stages which handled substantially the same gas. This was serious because it limited the plant to about two-thirds of its capacity.

At first we thought that, perhaps, the first-stage separator was too small and that water was passing through to the second stage. A much larger separator was installed, but we had the same problem as before. It was finally decided to throw out the feather valves and to use plate valves. There has been no problem since. The peculiarity of the feather valve is that when it breaks, the pieces fly around through the system and can't be found easily. They cause lost time far in excess of the time

required to replace the valves themselves.

I would like to ask what procedures are followed when a valve is changed on a compressor handling, say, hydrogen and nitrogen, or hydrogen alone? My experience goes back to about 1925 in this particular plant which I refer to, Olin Mathieson at Niagara Falls. Since no nitrogen was available, we simply opened the compressor, changed the valve, and flushed out the air with hydrogen. That has been going on for some 35 years and nothing has ever happened. Still, it is fundamental that you don't permit air and hydrogen to be in the same place at the same time if it can be avoided.

**BUTIKOFER—Standard Oil:** We always purge with nitrogen before going into any of our compressors containing an inflammable gas.

**JOHN CLAPPERTON—Columbia-Southern Chemical Corp., New Martinsville, W. Va.:** We are chlorine producers. Part of our hydrogen comes from mercury-chlorine cells. Last year I brought up the problem of the poisoning of our deoxo catalyst. We've since managed to solve this problem. But about six months after we stopped putting mercury-bearing hydrogen into our ammonia unit, we had a ring failure in the sixth stage of our synthesis gas compressor. At the time we experienced the deoxo trouble, we looked into the first two stages of this compressor, expecting evidence of mercury there and found none. We also looked at the inter-cooler (or after-cooler of the first stage) which has cupro-nickel tubes, and found no evidence of mercury at that point. So, we were somewhat surprised that this great length of time after we had used mercury in our system, to find disintegration (due to mercury) of bronze rings in our sixth stage.

**SOMMERS—Pennsalt Chemicals:** There are probably more than half a dozen plants in the country using hydrogen from mercury cells, and there are a whole series of problems associated with using this hydrogen, particularly organic chloride and mercury vapor. The plant I now refer to is the one mentioned before—in Niagara Falls. It obtained its hydrogen from Castner mercury cells and there was no doubt that there was mercury in the gas. Three new primary compressors were installed but somebody forgot that there was mercury in the hydrogen. The second- and third-stage after-coolers had brass tubes and they lasted about 10 days. They were quickly changed to steel tubes.

A real problem that exists in all ammonia plants, is the problem of packings at high pressures. Pennsalt has a plant running at pressures of up to 12,000 pounds and we do not know the full answer to the high pressure packing problem. It may or may not be associated with mercury in the gas, but I think it is. We use a conventional packing with bronze rings; so-called bearing-bronze rings and the service is erratic. Sometimes they last a couple of months and other times they will last ten months

to a year. I have observed the same thing at several other ammonia plants and I'd be interested to know if anyone has really solved the packing problem at pressures in excess of 5000 lb./sq. in.

**MAUNE—Armour:** Our synthesis pressures are 9000 lb. and we have had little, or no trouble with our high-stage packing on the compressor, or on the circulator. The circulators have original packing cases and rings (for 4 years). They don't leak or get hot, so we leave them alone.

The syn-gas compressor has about three years' service, but we anticipate no difficulty there. We do have a very clean gas—nothing in it but hydrogen and nitrogen. Perhaps that's significant.

**SIMMS—Phillips Chemical:** In one of our plants where we have gas-engine driven compressors, we instituted a program last year of inspecting by Magnafixing power rods. In one stage (our low pressure compressor) we have 200 power rods and found it necessary to discard 40 of these; some of them were on the verge of failure.

**HENDERSON—Dow Chemical:** I have here a Teflon ring which has been in service for 3600 hours with no lubrication. We use this in our circulator, operating at 170 rpm, at about atmospheric temperature, so we don't have the high temperature problem. We also have some France Flur-o-Fran rings in service, and we are installing a France Teflon packing, backed with bronze rings. I have a France Flur-o-Fran history on packing and piston rings, where they've been operated in oxygen, air, and syn-gas, with up to 2 years or 11,000 hrs. service.

**MAUNE—Armour:** One other important point in safety should include the training of operating and maintenance people. We had one occasion where one operator mistook a pressure discharge line for a steam line. This didn't cause any serious trouble, but it points out the need for better training. Such an error could cause serious trouble.

**R. F. GOETTLING—Hooker Chemicals, Tacoma, Wash.:** About 5 years ago, we found leaks in two of the 12 banks of coils in our primary condenser. One coil had been serviced six months; the other for 12 months before. All coils had been hydrostatically tested to 7800 lb. six months previously. All failures occurred in the bends subject to the highest operating temperatures and most severe corrosion. Each failure consisted of splits several inches in length. The pipe continued to hold system pressure without rupturing, while the plant was prepared for repairs. The faulty coils were blanked off, and plant operated with the remaining coils.

In the process of blanking off the coil, we were surprised to find that three of the flange bolts were broken completely in two. These had been in the primary manifold flanges. A thorough examination of the samples of the pipe by the laboratory of the tubing suppliers concluded that the failure was due to stress corrosion. To remedy this situation,

we sandblasted and painted the pipe, the bends, flanges, and manifolds of the primary condenser with epoxy type paint. We flooded the coils with sprays until no dry spots occurred on the bends. A polyphosphate type of corrosion inhibitor is used in the water which circulates through a cooling tower. Coils installed in the future, of course, will be stress-relieved. The remaining coils have now been in service for five years without developing leaks. During this time, they have been hydrostatically tested once at 5200 lb. Since the condensers appeared to be a weak point in the synthesis system, we are concerned with knowing the life that can be expected from them and the methods of testing that might detect weakness before failures.

**MASON—Dow:** This stress corrosion is a problem that is peculiar to some specific materials. We had some trouble several years ago with a test piece of stainless steel pipe in a film type intercooler. There was a fine network of cracks in the short piece of pipe. Of course it was replaced immediately with steel pipe. At Dow we now use copper clad steel pipe for intercoolers and have practically eliminated any difficulties with corrosion from the outside. Of course there is no trouble with corrosion from the inside. We have some pipe in those film type coolers that has been in operation since 1937 and looks as good as the day we put it in.

**MAUNE—Armour:** That's a point that's of great interest to many of us. Just what sort of normal life can you expect from primary condensers? Ours have been in service for approximately five years now, and the only place we're getting leakage is at flanges. The various sections of these coolers are flanged into an inlet and discharge manifold, and we're thinking of cutting out all those flanges and welding.

**SOMMERS—Pennsalt Chemicals:** External corrosion can be generalized by saying that it exists wherever you have a cooler that comes in contact with water, and, particularly, if it's the type of cooler where you have a "wind and water" line. The kind of corrosion that you get in a coil where you can see it, of course, is not so bad. You take care of it when required, but when the corrosion is internal it is apt to be concentrated in places where you have a condensed liquid. The liquids that are condensed out naturally rest in the bottom of the vessel, or the pipe, and

in the course of time, cause corrosion.

In almost all ammonia plants, particularly plants that are running beyond their normal design capacity, the most hazardous place is probably in the discharge of the converter. There have been at least three examples of this in my experience at different locations, where catalyst dust blown from the converter (where you have the highest possible temperature and the highest velocity) has eroded a bend in the pipe to the point where it was a hazard. This would be a good place to look in almost any plant. This piping usually needs to be replaced after some 5 to 10 years of operation.

**ODOM—Chemetron:** We use salt-water cascade ammonia condensers. Our condensers were specially built and were unique in design at that time (1956). They are Admiralty-covered steel tubes of all-welded construction. At the time we put them in there were no available performance data. But, we've never had a moment's trouble with them, and a recent Audigauge survey disclosed no diminution of wall thickness.

**WALTON—Atlantic Refining:** An extremely important safety problem, with which the industry, to my knowledge, has not come to grips, is the question of hydrostatic testing of high pressure vessels. There's a wide difference of opinion and practice on this. Those of us with a background in the oil industry have a long tradition of hydrostatic-testing our pressure vessels at some regular intervals, so we feel quite strongly about it.

Now, hydrostatic-testing of a converter, for instance, is quite a problem, because it involves considerable shut-down time. And, yet it's also a vessel which is probably one that you'd be most concerned about if it should fail. In our case, we said originally that we would hydrostatic-test our converter after five years service. When we changed catalysts at something less than five years, we talked our inspection people into examining the vessel internally and *not* hydrostatic-testing. But, they told me, "Next time you have that thing down, we're going to hydrostatic-test it, or else!"

As I say, there is a wide difference of opinion. This is a safety device, which has been considered very important for a number of years, and yet we don't really seem to have a meeting of the minds on it in the ammonia industry.

**SOMMERS—Pennsalt Chemicals:** I think the basic reason for testing something is to find out whether it will stand the test—whether things have happened in the intervening years to make its continued operation questionable. In the early days of the ammonia industry, everyone was much concerned about whether or not he had a good pressure vessel because, in those days you didn't always get them. And then, too, you didn't know the effects of hydrogen on the embrittlement of steel and of the possible nitriding effect. By now a con-



Hunter

Clapperton

siderable backlog of information has been built up which affects the decision to test or not to test.

The first converters that I ever had anything to do with were eventually sold to the Great Western Electro Chemical Company out at Pittsburg, California, and I learned several years ago what

eventually happened to them. After being in continuous service for at least 15 years, they were cut open and found to be as good as the day they were made. I think if you can apply that experience to other converters, there's not much point in testing them.

The other components of an ammonia

plant, the collectors and oil filters and whatnot, are probably even less likely to deteriorate with age. But there is, of course, always the annoying feeling that maybe you didn't have a good vessel in the first place, and that over the years an incipient crack might become a dangerous one.

## Ammonia storage

Water is anathema in high pressure ammonia storage tanks, because of ammonia's high rate of water take up.

**SIMMS—Phillips Chemical:** In the early days of the ammonia business the specifications for storage tanks were essentially copied from the LPG business. The specifications were dictated by vapor pressure considerations. Phillips presently designs and builds high pressure ammonia storage tanks according to the 1956 ASME code, 250 pound W.P. ASME SA-212-70,000 psi steel test per code requirement.

In recent years some stress corrosion cracking has been reported by AAI in A-A storage tanks, particularly field tanks. One step in overcoming this difficulty was the recommendation by AAI that vessels of 36" diameter and larger be stress relieved or furnished with hot formed heads. Phillips has adopted this recommendation as a specification for our storage tanks.

As production facilities have been expanded the supply and demand situation required the storage of larger quantities of A-A in the off-season. Storage of A-A in the typical high pressure tanks is usually not economical. Most all producers have resorted to 1,000-ton to 2,000-ton spheres operating at 30-75 lb./sq. in. ga.

We have considered the possibility of storing A-A at atmospheric pressure. This practice appears to be coming into wider use in LPG business. It has been reported that one of the most progressive

ammonia producers is storing A-A in this manner. I am sure we would all be interested in hearing about any actual experience in this type of storage.

The desirability of storing still greater quantities of A-A in the off-season has resulted in the use of large atmospheric pressure cone roof tanks to store the ammonia in the form of aqua. Many of you have recently installed such storage. Phillips has several installations, the largest being a 323,000-barrel tank in the Texas Panhandle. I am not aware of any serious problems with this type of storage although some of us have managed to collapse a ring or bulge the roof on these tanks.

The best type of coating depends upon the type of storage and geographical location. For high pressure storage in areas where weather conditions adversely affect paints, we prefer the following: sandblast to bare metal, apply one coat of Dimetcote, followed by one or two coats of white vinyl paint.

For less severe conditions, we use an epoxy system prime coat of about 5 to 10 mils dry thickness, followed by one coat of either white or aluminum gray paint, cross sprayed. The spheres are usually insulated. We presently use foam glass coated with asphalt weather seal and painted with one coat of asphalt base aluminum paint.

For large aqua tanks, where sweating is a problem, we prefer to coat the sides of the tank about 3/4-in. thick with asphalt mastic, such as No-Korode, followed by one coat of tank white on both top and sides. Where sweating is no problem the Dimetcote and white vinyl or epoxy system may be used. The latter two are more expensive, but also more attractive than the asphalt mastic.

**L. A. SWIFT—Consolidated Mining Co., Calgary, Alberta:** We have four atmospheric pressure anhydrous ammonia

storage tanks. They're 35 feet in diameter, 27 feet high, and 500-ton nominal capacity each. We have had very little trouble with them, although, occasionally when we take one off line, we have cracked the bottom when putting it back in service. It's a tricky business, because when you put the ammonia in it drops its temperature to about -35°C. When a bottom cracks, we dry out the tank, weld a patch over the crack, and start all over again, doing it a little more slowly.

The insulation was originally 8 in. thick in 3 layers of cork, with vapor-barriers between each layer. Those vapor-barriers are probably the most important of all, because they keep moisture from infiltrating the surface of the tank. We did have a certain amount of leakage of moisture down from the top that eventually bulged the insulation off, and we had to replace it on a couple of tanks. When we replace it, we put on 5 in. of fiberglass in 3 layers. We put vapor-barriers in between each layer and it's been a very satisfactory job.

**WALTON—Atlanta Refining:** Are these carbon steel tanks?

**SWIFT—Consolidated Mining:** Yes, they're just carbon steel tanks, quarter-inch steel plate.

**R. E. REED—Girdler Construction Div., Louisville:** In view of the remarks about the tanks, I think a little historical information might be appropriate at this time. I believe that the installation that you just heard of at Consolidated Mining and Smelting was the pioneer installation of that type. There were two atmospheric storage tanks installed in the Havag Plant at Ems, Switzerland somewhat later which also operated very successfully. Those two installations were the only ones that were in existence that we could obtain information about at the time the Southern Nitrogen Plant was being built—being designed in 1955. On the basis of the successful experience



Simms

Swift



Reed

Odom



Sommers

Goettling

that those people had, we decided to take advantage of the savings available in utilizing a large-size atmospheric pressure storage tank for ammonia at the Southern Nitrogen Plant. The particularly attractive economic advantage was that there is a use for the ammonia vapor that is given off from storage and also given off as the ammonia is reduced in temperature, going into storage.

The tank is 7500 tons, nominal capacity, 110 ft. in diam., 40 ft. high, and it's a regular API flat-bottomed, cone-topped tank. The roof is designed for six inches of water pressure. The operating pressure on the tank is approximately 3 in. It has proven to be a simple matter to control the tank and maintain the pressure at 3 in. The system is airtight and there is no possibility of infiltration. The tank was filled with inert gas before the ammonia was initially put in. A special manifold system was put in to avoid the differential quick-cooling of the base of the tank during the initial start up. The tank has never been heated up since it was started about three years ago.

The tank is insulated externally with 4-in. Styrofoam insulation with an aluminum vapor barrier. The base of the tank is set upon a pad of insulating concrete, beneath which is an electrical heating coil, used to maintain the temperature beneath the tank above the freezing point. One of the principal differences between this storage tank and the ones

at Consolidated that rest upon a gravel fill, is the permanent frost beneath the Consolidated tanks.

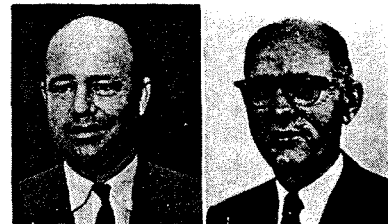
Others have used the ground heating technique since, in the large-scale storage of liquid air and liquid methane at atmospheric pressure. In both cases, heating of one type or another below the tanks has been used to avoid the possibility of heaving of the soil. In storing liquid methane or air they have actually had one tank within another to get an absolute vapor barrier. At Southern Nitrogen we relied upon aluminum foil coating to provide a vapor barrier inside the corrugated aluminum covering which is on the tank.

**WALTON—Atlantic Refining:** Sphere storage usually is built with little corrosion allowance. You have insulation over the steel and a sealing and paint system over the insulation. If the sealer on the outside of the insulation fails and water infiltration results, you can have corrosion. This could lead to a dangerous situation. This has concerned us greatly. We have not been able to keep a paint system satisfactorily on the outside of the sphere for more than 6 months at a time.

Another reason why it is a safety problem is because the paints which are usually considered satisfactory are ones which should be sprayed; and where the spheres are close to the air intake of your air plant, this becomes a problem.

We carefully tested many paints and discovered that the white coat cracks and checks very badly, exposing the seal-coat underneath. Our investigations indicated that the only way to keep a satisfactory white coat on the surface was to reinforce it with glass cloth. This is an expensive proposition, but, if necessary, one that must be done. We found that we must use a glass cloth reinforcement and a vinyl-type paint.

**COCHRANE—Sun Oil:** We feel that



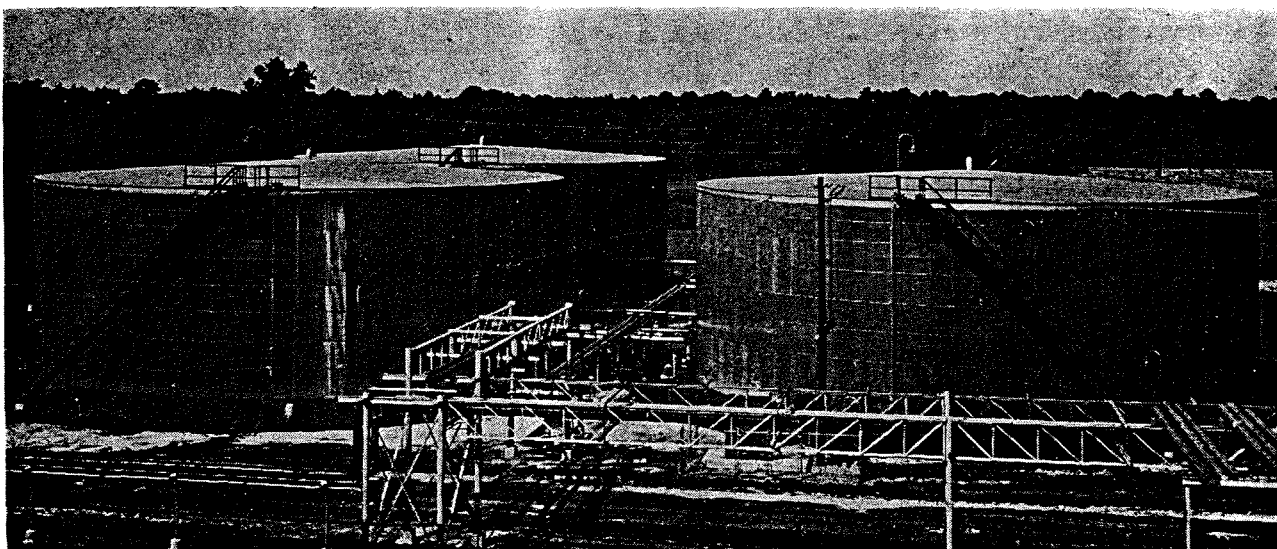
G. R. Walton

Henderson

the tank we have is definitely the safest kind of storage you can get. We have what we call bullets; horizontal tanks about 90-ft. long and about 13-ft. in diam. The bullets are covered with coarse gravel or stones which keeps the temperature controlled, even in the summertime, somewhere below 70 degrees. Operating anywhere from 100 to 135 lb. pressure, these tanks have never given us any trouble. We feel that these may be slightly more expensive than spheres, but definitely much safer.

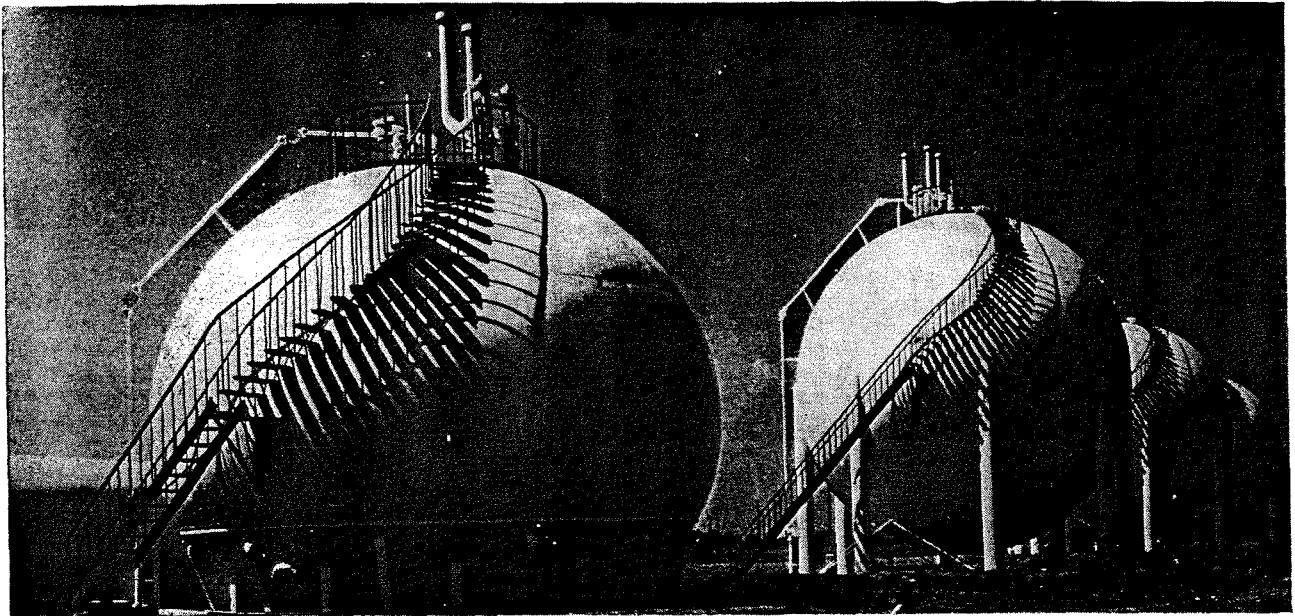
**ODOM—Chemetron:** A first magnitude safety problem came up with us when the internal level gauge became dislocated from its fastening at the bottom of one of the spheres. We have two 2000-ton spheres and the refastening of that level gauge posed quite a problem. Fortunately, someone recognized the implications of putting water in the sphere, in time, so that we didn't make this mistake. In ammonia tanks one of the principal dangers one must guard against is the terrific solubility of ammonia vapor in water and the hazard of producing a vacuum in these tanks if water is added when the tank is still full of ammonia vapor.

**L. B. HENDERSON—Dow:** On our sphere, we insulated with Styrofoam, banded on with galvanized iron bands, covered with galvanized chicken wire, over which we put Insul-mastic, and then white paint. After about 4 years, we had cracking, big bubbles of water blisters



Cone roofed tanks, as well as spheres are used for ammonia storage. Photo courtesy Chicago Bridge and Iron Co.





Field tests indicate that the only way to keep a satisfactory white coat on a tank surface is to reinforce it with glass cloth. Photo courtesy National Petro-Chemicals Corporation.

on the tank, and, eventually, a big section peeled off and fell to the ground. At that time we found that the banding and the chicken wire had rusted out and it had to be rebanded. So, what we did, was to reband with stainless steel banding, and a water-base asphalt, in which we embedded Fiberglas cloth, and then covered that with No-Korode Permaseal. Now, we are going to put on aluminum paint over that, when the No-Korode

becomes entirely sealed over, and, perhaps next year, we can tell you whether that system will do the job.

**R. W. SANDERS—Texaco:** On Mr. Walton's points about safety, I think we've missed one, that is, inspection of spheres—hydrostatic testing or pneumatic testing. And, as neophytes in this, we were just wondering what was considered good practice as to test intervals. Our tentative thoughts were hy-

drostatic at something like 4 to 5 years. Any comments we could get we would certainly appreciate.

**L. B. HENDERSON—Dow:** We follow I.C.C. regulations of retests for anhydrous ammonia tank cars. This at one and a half times its working pressure after seven years, when it was out of service for repair. We plan to continue at 10-year intervals, unless repair programs make the period shorter.

## *Materials of construction*

Compatibility studies of materials in contact are a must.

**G. E. KING—Sohio Chemical Co., Lima, Ohio:** We had a fire that could have been prevented by a quick physical inspection, particularly if someone had hung a red tag on a particular valve in which the packing needed replacement. It was on a starting heater (an externally gas-fired vessel in the synthesis area) where the packing started to leak. This should never have happened in the first place, but it did start to leak. It ignited, and then ignited the leak on the bottom of one of the synthesis converters. The heat was so intense that the packing follower holding-bolts actu-

ally melted, and extended so that the packing eventually blew out.

The second fire we had was due to a failure of a check valve in a pump discharge. We were having difficulty in circulating MEA into the CO<sub>2</sub> adsorber and not getting the proper flow. Two pumps in the service were running in parallel and the check valve in one of the pumps had lost its flapper in the discharge system. This blocked the flow of liquid. The pump was shut down without knowledge that the flapper was loose in that particular check valve. The hydrogen or synthesis gas backed down

through the pump discharge line into the pump and out through the seals and we had a fire.

A physical check is quickly and easily done and prevents subsequent failure. We have used radiological inspection and have gone to the extent of actually photographing the CO<sub>2</sub> scrubber. This is the portion of the MEA system where we had a question in our minds as to whether the trays from the bottom portion of the tower would require clean-up. Corrosion was severe at that point. We took a radiograph through a tray and got all the details—the nuts and bolts all stood out—you could tell what the liquid level was on the tray. Radiological inspection is of considerable value not only for determining whether or not a tray is there, but also because you can find out what is going on in the tower. I have the print of the hairpin bend on the aftercooler in the third stage of our synthesis gas compressors—our high pressure stage at 5000 lb. The X-ray shows a measurable loss. This metal loss is a result of the waterside corrosion.

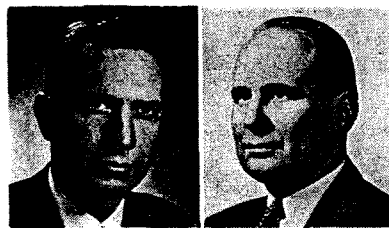
The corrosion loss on the water side



of the tube can be measured due to the precise location of the film in relation to the radium source used in the radiological equipment. One cobalt and one radium source make measurements to determine corrosion loss in preparation for equipment replacement. This jarred us because we found out that we had used up the corrosion allowance on this particular tube. Even on a physical inspection, we would not have known that we had actually lost that amount of metal from this particular tube.

**MARTIN—Spencer Chemical:** Here is a picture of a failure of a 6 in. carbon steel elbow which is located in a line between the MEA reboiler and the hot condensate drum. The line carries crude hydrogen which has a high percentage of CO<sub>2</sub>. A lot of water has been condensed out of the excess steam from the shift converter. The elbow seemed to have been eroded from the inside until a hole appeared. In this situation, the gas contained water loaded with CO<sub>2</sub>. We replaced these elbows with stainless steel and installed a backup jacket. This jacket is a second elbow section on the exterior portion with a small nipple in it. In the event that the elbow lets go, this jacket will contain most of the gas but some hydrogen will come out. A nipple in the jacket serves as an indicator.

**BUTIKOFER—Standard Oil:** There is a problem in our nitrogen wash box related to materials of construction that has bothered us for quite a while. The ex-



King

White

changers handling the ethylene in the nitrogen wash box have copper coils. The ethylene which we purchase for our cascade refrigeration system contains anywhere from 50 to about 15 ppm of acetylene. We think it is possible for the acetylene to react with the copper to form copper acetylide which can either explode by decomposition of the molecule in the absence of air, forming copper and carbon, or oxidize in the presence of air. We have tried to discuss this with other people whom we thought were experts in the field to determine whether or not we really have a problem. Since we have found no one to commit himself, we have continued to carry out special precautions to wash this equipment prior to doing any work on it. We wash it with a detergent in water solution and then dry it out before we do any mechanical work to that part of the plant. I wonder if any of you can help clarify this situation?

**BOLLEN—Dow Canada:** Referring to our nitrogen scrub plant explosion about a year and nine months ago: In open-

ing some of the exchangers that weren't too badly damaged by the explosion, but were damaged enough by the fire to warrant their inspection, we found that the tubes in one of the exchangers were perforated in regular intervals throughout their length. In reviewing this with the cold box supplier they were of the opinion that this was caused by the deposit of copper acetylide which had exploded because of the heat. They did not believe this was a possible cause of the explosion, but rather an effect.

**D. A. WHITE—Smith-Douglass Co., Inc., Houston:** It definitely will blow up. You are right in washing out the equipment. I have seen a terrific explosion with copper acetylide; especially as the NO deposits build up too. That makes a very bad combination.

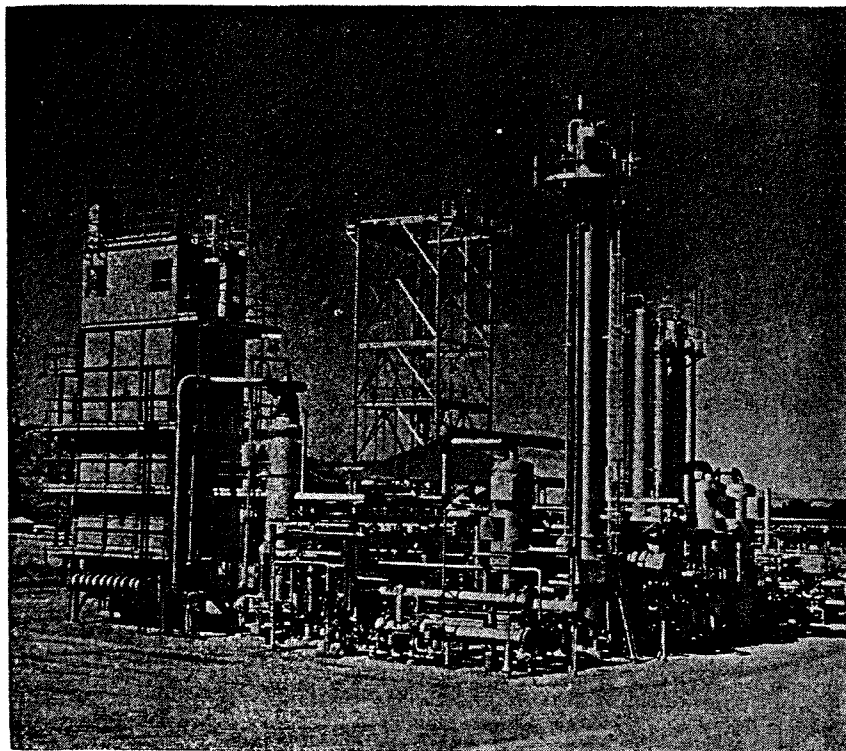
**YOUNG—NAS:** I hear more and more and more about the use of stainless steels, particularly in oxygen-hydrogen lines. I wonder if the metallurgist is still here who could comment on hydrogen embrittlement of stainless steels?

**REED—Girdler:** The only comment I could make is that, as I recall, the austenitic stainless steels are not normally subject to hydrogen embrittlement. I believe that it is confined to ferritic and, perhaps, martensitic structures.

**BUTIKOFER—Standard Oil:** We had a nitrate explosion which occurred while we were pumping down one of our large nitrate storage tanks, which contained about 90% ammonium nitrate in water solution. We used an overhung impeller pump driven by a 10 hp. motor. The tank was down to about three feet when the pump lost suction. About the same time, the impeller began to rub on the casing, generating heat. This was enough to explode the nitrate. It blew the end off the pump and shoved the shaft back into the motor. Both pump and motor were a complete loss.

It is difficult to develop a safety technique for anticipating such breakdowns because nitrate is a difficult material to instrument. However, we have established the practice of pumping out nitrate tanks with a reciprocating pump where there is a chance of losing suction.

**MASON—Dow:** There is always some possibility of inspiring air into combustible gas mixtures if the compressor intake pressure drops below atmospheric. Such inspiration of air can be prevented by the proper selection and maintenance of packings, however, an even more effective method of protection is presently being practiced. A Mercoid, or other type of pressure switch, is placed on the inlet line to a compressor and set to operate at a low, but positive, pressure. This switch is connected electrically into the motor circuit to shut the compressor down immediately when the pressure reaches dangerously near atmospheric pressure. #



Thermal stress, corrosion resistance, and strength are the prime design factors. Photo courtesy Girdler Construction Division.