

# GENERAL DISCUSSION

## Fan failures

BLACK—Monsanto: I'd like to know a little about keeping the fuel gas on in the primary in case of a fan failure. Is anyone doing this and is it considered safe? I'm assuming you shut the primary fuel off and leave the fuel gas on. We shut it off, incidentally.

WHITE—Smith-Douglass: We work by the wall temperatures and cut the fuel gas back to hold our wall temperatures.

BLACK: Do wall temperatures go up or down when you shut off the fuel gas?

WHITE: They go up.

BLACK: If they go up, doesn't this concern you?

WHITE: It does concern us, however, we cut back to hold it so it doesn't get out of hand.

BLACK: Does the fan trip?

WHITE: Sometimes.

SILVERLOCK—Cyanamid of Canada: Our primary has natural draft, so when we have any upset that requires a sudden reduction of fire, we feel much better if we can get control of the fire; that is, tell our operator to get control of it and cut back the firing. If we do lose our fire in a very great hurry, our refractory temperatures drop very drastically. Our primary concern is to get this under control, to make sure that, if you do have to go down, to bring them down under controlled firing rates, rather than just let them drop. They can drop several hundred degrees in a matter of a few minutes and we worry about the refractory. We do feel the operation is safe by this means.

STAFFORD—Farmers Chemical: I think there are two approaches you can really take on this thing. First of all, on identification of fan failure, you do want to maintain minimum fires in your primary furnace. This can be done by either pilot fires or by partial closure of your main solenoid valve. By this I mean, leave the valve open maybe an 1/8 or 1/16 of an inch during initial calibration so that you can maintain firing of your furnace with this fan failure.

## Shift catalyst removal

HANLEY—DuPont: I'm interested in the removal of the shift catalyst without any oxidation. We have talked about this a lot and I would like to get someone's opinion. Would anyone undertake to totally discharge a shift catalyst in its reduced state into the open air such as the Japanese are apparently doing?

MCAHON—Collier Carbon & Chemical: We have had a good deal of experience in unloading and reloading

shift catalyst without oxidation. The temperature of the bed is reduced by continuous nitrogen purge. The converter is then opened and the catalyst is screened to remove fines. The recovered catalyst is stored in drums under a carbon dioxide atmosphere until reloading is accomplished. We have experienced no difficulty with this procedure.

## Air intake position

SIMMS—Phillips Petroleum: At the San Juan meeting we precipitated a lot of warnings regarding a nitric acid plant in the same plant yard with an air separation plant, with the acid plant stacks being some 300 to 400 ft. from the air intake. Some people even went so far as to say they wouldn't build such a plant. We couldn't back up then. We built it. We can in a minute or so tell you what we're not finding. Maybe you'll warn us again that we ought to do something.

MCCANNE—Phillips Petroleum: Another company has a nitric acid plant about a mile from our ammonia plant in Kennewick, Wash., which has operated for three or four years. They do not have a catalytic combustor on their unit. Just in the last year we have put in a small nitric acid plant, 20 ton/day, about 300 ft. from our air intake on our air plant. This plant does not have a catalytic combustor either. We think that we probably had just about as much NO and NO<sub>2</sub> contamination from the more remote plant as we've had from our adjacent plant. We have monitored regularly, using the Griess-Ilsovay method for NO<sub>2</sub> in our air plant, and the maximum amount that we have found in the air to the air intake and in the oxygen of the air plant is about 1/10 ppm NO<sub>2</sub>.

We have not made any attempt so far to distinguish between the presence of NO and NO<sub>2</sub>.

On the nitric acid plant that we have in our yard we have installed an alternate stack. One stack is right on top of the absorber; that's the stack that's 300 ft. from the air intake. It is south and a little east of our air intake. The alternate stack is about 700 or 800 ft. north of our air intake, and we use a manual switching operation by the operators, depending upon wind direction to keep any stack fumes away from the air intake. This has worked very well for us most of the time. Sometimes we have light variable winds which permit some brown fumes close to the air intake. However, as I said, we have not gotten NO<sub>2</sub> in the air plant in any greater concentration than a 1/10 ppm. The air to the air plant goes through the two series caustic scrubbers for carbon dioxide removal. The NO<sub>2</sub> is probably scrubbed out completely here; the only thing that would pass on into the air plant, we think, is NO, which we would then pick up by our analysis as NO<sub>2</sub>.

LARUE—Spencer Chemical: We have also been concerned about the hazards of oxides of nitrogen. A program was established last year to make daily checks on the air stream into the air plant. Our nitric acid plant

is located about 800 ft. from the intake of the air plant. Prior to entering the cold equipment, the air stream passes through a caustic scrubber. The analytical checks are made downstream of the scrubber, with the Griess test employed to determine the oxide content. To date the oxides have averaged about 0.003 ppm. At this level we feel the NO<sub>2</sub> is not a hazard nor a problem, and that the caustic scrubber provides ample protection for the air plant.

## Air pollution requirements

MCMAHON: We have an acid plant also in the same area with our ammonia facility. The plants are approximately 500 yards apart. We are using decomposing facilities on the tail gas from the acid plant because of the stringent air pollution requirements in the Los Angeles area.

We are probably down in the range about 200 ppm total oxides of nitrogen in the gas. Because of the combination of the performance of the decomposer and the distance from the air plant intakes we have no indication whatsoever of oxides of nitrogen in the air plant. We would be interested in learning just what levels of oxides of nitrogen other operators are experiencing in their tail gas.

SIMMS: Do you decompose to nitrogen, or just decolorize to NO?

MCMAHON: To nitrogen; analysis of our tail gas indicates our oxide of nitrogen content to be less than 200 ppm. We believe we can do considerably better than this by modifying the design of the decomposer vessel.

WARREN—DuPont: I had a question on the catalytic oxidation unit that you use to remove the nitrogen oxides completely. I'd be interested in the method.

MCMAHON: We believe that we have an excellent process for decomposing the oxides of nitrogen in the tail gas from a nitric acid plant. I am not at liberty to discuss this in detail at this time. For those of you who are interested in the details, I suggest you contact the Collier Development Department in Los Angeles.

## Hydrocarbon analyzers

WARREN: I would be interested in hearing about anyone's experience with the use of hydrocarbon analyzers for reformer or shift converter gases, where you're analyzing for hydrogen, carbon monoxide, carbon dioxide, methane, and water. We're having quite a bit of difficulty with an on-stream analyzer that's been in use for roughly nine months. I won't go through all the difficulties we've had, but we still don't have the problem unraveled. Maybe somebody has some experience here.

WALTON—SunOlin: We have Greenbriar chromatographs which analyze these streams. I would say they've been relatively satisfactory. They require maintenance as would any other analyzer or instrument. However, the operators have confidence in them. The answers that they give you normally are good ones.

PAULES—DuPont: You are measuring water I presume with this instrument, is that right? Is this a prime control instrument? I mean, does your operator use this to actually control the reformer, or just as an information source?

WALTON: The water analysis is not of much importance to us; carbon monoxide, carbon dioxide, and meth-

ane are the ones which we use for control purposes. The chromatograph itself doesn't control, but the operators control, depending on what the chromatograph tells them. For instance, we vary the amount of carbon monoxide and carbon dioxide we make by how much we bypass the shift converter, and this is used for that purpose. The methane content also tells us whether we should increase or decrease the oxygen to the secondary reformer. Yes, we feel that water analysis is O.K.

## Corrosion failures in reformers

ELLIS—DuPont: We have type 304 stainless steel in our transfer lines or lines from our single reformer. Two years ago we took specimens from the piping and found that we'd lost about 50% of our room temperature ductility. On our next shutdown we're going to take additional samples and test them with a Charpy V-notch impact test.

We don't know what we're going to get this time but has anybody else had any experience with this type of activity and, if so, has he established a minimum limit for impact at room temperature?

WALTON: We took a piece of 347 transfer line out a year ago and got Charpy V-notches on parent metal, on a portion of a butt weld, and a portion of a shop weld. The field butt weld had a Charpy value of about 1 lb. The Charpy values on the other specimens were between 10 and 20. The tensile strengths were better than when they were new. Our metallurgist consultant says that this structure is all right as long as you don't shock it. Actually you're in better shape in operation now than you were before, and as long as you don't give it a bad shock, you're all right. This time we're going to take out a tube which is Incoloy; the pigtail which is 347; one of the weldolets; the weldolet between the tube and the pigtail is 304 ELC; the weldolet between the pigtail and the header is 347; the header is 347; and the cap at the end of the header is cast of 347; we're going to get metallurgical tests on individual pieces of these separate alloys, including the welds between them, and I'll report them at the next meeting.

As Mr. Ellis said, I'd like to know if anybody has felt, that at some definite Charpy value, it is unsafe to operate a thing like this.

## Room temperature testing

JONES—Canadian Industries, Ltd.: Aging and loss of ductility is, of course, perfectly normal under these circumstances, and I'm wondering how much useful information you will get from room temperature testing. The probability is that the material is a good deal better at operating temperature than it appears to be at room temperature. Quite frequently one can get situations in which some measure of sigma phase or other aging phenomena do give you a high order of embrittlement at room temperature, but is, by no means, as serious at elevated temperatures.

Now this means, of course, that in start-up, the line is in a delicate condition, and it could fracture before it got hot, or it could break during the cool-down cycle when contraction stresses would add additional strains. I don't know where the safety hazard is highest. Is the risk highest when you're on the line or when you're starting up or shutting down? Perhaps it really doesn't matter very much when it breaks. Perhaps the room temperature tests do represent the most critical situation and one should take notice of them.

It has been suggested that some of the loss of properties may be due to nitrogen pickup from the air

side of the pipe, the transfer line, and that it is not necessarily entirely a function of the contact with the gas stream. Simple exposure to temperature in the 1,400 to 1,500°F region may be the major factor, with progressive pickup of nitrogen from the atmosphere compounding the problem. It will be interesting to have a look at microspecimens or to know if anyone has examined pipe for metallurgical change from the outside in as well as from the inside out.

## Type 304 transfer piping

**KUENZLY**—Shell Chemical: This is to further report on our Ventura plant failure on the 304 transfer piping which was reported on at the San Juan meeting. We, of course, replaced the damaged pipe but had to use replacement 304 again; it was the only thing we could get. At our last shutdown we replaced with Incoloy 800 and left the 304 which was relatively new in place. Tests showed that the pipe had lost hot ductility due to carburization. On coming down during our shutdown to replace the remainder of the pipe, one of the pigtailed, which was 304, cracked at a weld. I think we changed it just about at the right time. I guess we're the oldest pressure reforming plant there is, although it's a relatively low pressure plant now, going in at about 100 lb./sq.in.

We also took out a tube that showed metal dusting on the inside, which I'm not familiar with at all. Apparently there is some oxide inclusions in it, and the tube appeared to have been overheated at some time, but we don't have a good record of how it happened or when it happened.

## Charpy V-notch test results

**REYNOLDS**—Standard Oil Co. of California: I have a report with me, a report of an investigation made by our materials laboratory, on our transfer piping which is 304, and has been in service, or had at that time, for about 7 years. These were Charpy V-notch tests taken on the round seam, on the long seam, and on the plate. In addition to cutting out specimens, we took out a 4 or 5 ft. section of the line just for testing. We don't know what's safe, but here is the range of the figures we got: On the round seam—this is 12 in. piping—I think the lowest result was 12 ft.-lb. On the long seam the lowest I believe was 10. These were at 70°.

In addition, on the section that was removed from the line, the weld, as removed, again tested 10. The weld, as removed, and tested at 1,300°, was 46. When annealed at 1,950° and tested at 70°, it was 76. The comparable figures on the plate were 16, as removed, taken at 70°; 41 as removed taken at 1,400°; and 153, after annealing at 1,950° and tested at 70°. In our case, no carburization was found.

**WARREN**: Thank you for the numbers because basically they fit just about the same numbers that we have been getting in our test.

**STOCKBRIDGE**—Southern Nitrogen: Mr. Kuenzly, you said you removed a tube and found metal dusting on the inside. I wonder why you removed it; did you have some symptoms of trouble beforehand?

**KUENZLY**: As I understand it there was a slight bulge on the outside of the tube, which indicated that something was happening, so they pulled the tube for examination. The result was described as metal dusting. I don't understand the mechanics of it since I'm not a metallurgist.

## Wrought or cast headers

**STOCKBRIDGE**: I wonder if anybody would care to comment on the advisability of using wrought or cast parts in these high temperature headers? We have a header, which originally was made from 310, on which I reported three years ago, that we replaced with Incoloy. This is the large header. Now our reformer tubes are cast 310 and the smaller headers are 310 seamless 4-in. pipe. The 1 1/2-in. pigtailed are 310 seamless pipe. The weldolet, between the 4-in. collection header and the reformer end of the pigtail, is a cast piece. I don't know why it's cast. I'm thinking about replacing it with just a piece of seamless pipe, since we've had some cracks at this point. I was wondering if anybody would care to comment on this: whether you should use cast or wrought parts for this hot service?

**JONES**: I think this is largely an economic consideration. The 25-20 HK alloy castings for the furnace tubes will probably be about one-third the price or a little more than equivalent wrought material, that is, material having equivalent sound wall metal thickness. The cast sections, of course, are invariably cast using centrifugal techniques in order to insure soundness.

Castings which are not capable of being spun are sometimes regarded as being less reliable than centrifugally cast material. I would suggest that, if the section lends itself to casting, you specify the necessary assurance of weldability in your casting; I think perhaps this should be an essential part of any casting specification if you're going to weld. The casting would generally be preferred primarily on grounds of cost, it's a much more economical way of obtaining what you want.

In addition, creep properties of cast material are usually superior to those of wrought material, so that at elevated temperatures the cast form is the stronger form of the two. I'm wondering, with particular respect to transfer lines, if we're not approaching the stage where increased pressure, temperature, and size dictate a change in design approach. The water-cooled refractory-lined mild steel line, with an alloy internal shrouding, seems the most feasible solution as plant sizes go up, and this should take most of the guess work out of this situation. I don't know at what size of line this becomes the attractive and economical choice, but perhaps this is the safe direction in the future.

## MEA corrosion

**LAWRENCE**—Central Nitrogen: In the literature on CO<sub>2</sub> corrosion in which failure usually can give you gas in some pretty dangerous places, there has been quite a divergence of opinion in the past couple of years. Some of the companies in the audience here who make MEA have changed their position on what temperature is too hot for solutions of MEA between 15% and 22%.

I remember—it wasn't too long ago—that temperatures much above 300°F were considered corrosive and now we don't seem to worry at 350° and 360°F. That's the opinion I get from the technical representatives from the three or four leading producers. Has anyone in the audience done a lot of studying on MEA corrosion that would care to answer that question? Is 350°F too hot?

**WALTON**: Here's a little actual experience. We had three reboilers on our MEA stripper. Two of them have, on the hot side, a hydrogen syn gas stream that runs about 315°. The tubes are cupronickel. They've lost about 20% of their wall thickness in three years.

The third reboiler is a new one which was added about a year and a half ago. That has 355° hydrogen stream heating it. There was quite a bit of concern about this, so we used 316 tubes. One tube failed three weeks ago. When we opened it, we found that a third of the wall thickness was gone on the MEA side of the hotter tubes graduating down to less on the colder tubes. All of the tubes at the top and bottom tube sheets, where you could look into them, were heavily etched.

We are going to retube this reboiler next week with Monel. It originally went in service January a year ago. This is a vertical thermosyphon reboiler and on the tube side you have liquid MEA coming in the bottom and vaporizing as it goes up through the tubes. On the shell side you have hydrogen, saturated with water, and containing carbon dioxide. I don't know what's going on in the shell side. When we get to retube it and I look at the tubes I'll know. (Later examination showed no corrosion on the shell side.) The pressure at the bottom of the column is about 5 lb., that's about 240°.

STAFFORD: We had the same problem that you've pointed out. Ours were 304 ELC, and we finally decided that we were stripping in the reboiler. I think this is the one condition that cuts your tubes out faster than temperature itself.

## Stripping column

WARREN: We had some experience with MEA corrosion, not in the reboiler, but in the carbon steel stripping column. We lost most of the risers and caps in the bottom 14 plates of the column. The plates were thinned particularly in the areas of high velocity and the column walls were corroded adjacent to the plates. The following changes were made over about a period of one year:

- (1) We installed a system for purging roughly 1% of the lean MEA solution.
- (2) We reduced the pressure in the regenerator from 25 lb./sq. in. to 15 lb./sq. in., which, of course, was accompanied by a corresponding temperature reduction.
- (3) We add a metal carbonate to the lean MEA.
- (4) We monitor the rich MEA for MEA carbonate and avoid overloading by making adjustments in circulation rate, regeneration rate, and upstream carbon dioxide removal.

We also ran into foaming problems for a while which we thought were associated with corrosion. We looked at our MEA quality and couldn't find anything wrong with it. We tried two different suppliers. They assured us that MEA by itself doesn't degrade. We're convinced now that degradation does occur because the purge system really helps and the sludge purged from the still is pretty good evidence of the degradation.

PFLASTERER—U. S. Steel: We've noticed some of the same trouble in our regenerator for the MEA. We've lost quite a few trays. In analyzing some of the MEA solution that resulted, it seemed as though there was quite a pickup of sulfur, which could have come from some of the sour natural gas we were handling at the time. (We have since added sodium metavanadate to reduce or eliminate corrosion in this system.)

WARREN: In our case, we did not have any sulfur present in the gas because we remove the sulfur compounds from the natural gas by activated carbon beds. In addition, sulfur analysis of the MEA solution showed no sulfur present.

## Purifier effectiveness

MCMAHON: Your comment about the sludge that you're removing from the purifier interests me because we were attempting to establish the effectiveness of our purification unit. We are operating with purifier temperatures around 325°, and did not suspect that we would be suffering thermal decomposition of the MEA. Some laboratory work indicates degradation is occurring even at this temperature because of skin effects. We are wondering just how successful the purification is and whether or not some of the sludge that we are throwing away is being formed in the purifier even at these relatively low temperatures.

WARREN: Sludge removal is about every 6 to 8 weeks.

REYNOLDS: During the past few months I've just about convinced myself that the purifier or reclainer doesn't do us much good. I had to shut it down because, when I pulled the bundle out on shutdown to clean it up, it was choked up so badly that you couldn't even clean it. It took several weeks to get the tubes, and our corrosion rates stayed about the same. We measure our corrosion continuously by specimen, that is, keep a specimen in all the time and change it once a week.

Our corrosion rates, as measured at the reboiler outlet, in the L, run about from 50 to 100 mils, which we consider is pretty good. Now it sounds kind of horrible, but I've heard some much worse figures, like 200 or 300. One other thing, in the early days of the plant, before I saw it, we gave up on trays, mainly because we got caught short on a shutdown. We didn't realize how bad they were, and frantically started making some homemade Raschig rings, using 3-in. x 3-in. Schedule 40 pipe, that have given us very good service. I noticed on the last shutdown, that the rings that are visible at the bottom are getting very thin. Maybe we're getting rid of some of our corrosion, or corrosion products, right there, and protecting some of the rest of the system. We have no troubles in the rest of the system as far as corrosion goes. Schedule 40, 3-in. pipe will run quite a while at a fairly high corrosion rate, as long as you don't have to hold any product in it.

ELLIS: I worked with John on this problem, and our shell is in terrible shape from the midpoint up.

Anonymous: That column is gone. We have a new column now. The new column is running very well. I'd say that first year, when we had the corrosion problem, we were in there every day measuring corrosion rates; we had sidestreams coming off of the regenerator; we had a sidestream coming off the fifth plate; we had one off the 10th and the 15th. We had more coupons than you could shake a stick at. We had a laboratory program going which was trying to develop the effect of the variables, and we were reading all of your reports and the problems you've had and trying to relate these to ours. We had these corrosion probes in there also, and they didn't work. But it's sufficient to say that this last year we felt very comfortable. In fact we went through a shutdown last time and opened up one heat exchanger. This is a pretty good indication: you pull your hot bundle and, if you have a lot of sludge up against your baffle plates, you'd better look a little closer at your regenerator, because that's probably where it's coming from.

I think last year we found very little sludge there, and also very little in the bottom of our regenerator. Of course, we have been checking pressure drop; this is a pretty good indication, and it seems to be all right.

## Regenerator replacement

PFLASTERER: Has anybody found it necessary to replace this regenerator with any material other than carbon steel?

REYNOLDS: I have been trying to get a little better material for the bundle, but it couldn't be justified on the basis of the expected life. It's an uncomfortable situation to be in, most people won't assign a dollar value to an uncomfortable situation.

HANLEY: At our Victoria hydrogen facility, which is quite small and not connected with our ammonia plant, we have a carbon steel MEA regenerator, which may soon be replaced with stainless steel. It has a large number of patches on it.

LAWRENCE: Most people, who have had corrosion, have replaced part of their stripper with stainless steel, probably by patching. On the unit we have now, before the plant was run, there was a band of stainless steel put on the feed tray. The bubble caps, of course, are stainless steel, the rest of it is carbon steel.

I might add, on inspecting ours after one year's operation, with 350° hydrogen on the reboiler, there was no corrosion anywhere in the tower. We started down through the tower and quit at the third tray down because everything looked brand new, and the reboiler MEA side, the tubes, looked very good. I expected at that temperature to find a lot worse corrosion.

I believe the construction companies are building a stainless steel skirt on the feed tray.

## Monel reboilers

RYAN—Skelly Oil: I believe if you'll check the literature you'll find that, either in your syn gas or your amine storage, trace oxygen is detrimental to your MEA. I also understand, although I'm not a metallurgist, that this trace oxygen is not compatible with Monel reboilers. I was wondering if anybody, who either has a Monel reboiler or is intending to put one in, has any background or opinions on this matter?

KUENZLY: We've had Monel reboilers in our MEA system now for 10 years and have stopped inspecting them; it was a waste of time. However, I'm pretty sure we don't have any oxygen on our syn gas.

REYNOLDS: I can corroborate the experience of Mr. Kuenzly. I know we have no oxygen in the syn gas, but we do not take special precautions to keep oxygen out of the MEA. Our Monel tubes have given us no trouble in the reboiler. We're operating at about 240 to 250° F. That's 240 to 250° MEA temperature, about 300° gas temperature.

## Carbon dioxide removal system

JONES: We have a Benfield carbonate system for carbon dioxide removal and have encountered corrosion problems, particularly in the regenerator tower. We have found that cladding with stainless steel sheet internally is an effective method of extending the life of the shell. The cladding is not liquid tight, and liquid certainly finds its way to the carbon steel shell. It appears that the oxygen supply, or whatever the critical aspect of the situation is, is so controlled that the carbon steel, once shielded, enjoys a very low corrosion rate indeed. I'm very interested in all of this discussion about MEA, and I'm wondering, since we've had

some experience with carbonate and a lot of gentlemen have experience with MEA if there are any new carbon dioxide removal techniques on the horizon which would offer a more predictable approach to this problem.

WARREN: How long have you used this Benfield process?

JONES: Our plant is a Texaco plant installed in 1956. Initially hydrogen was made by partial oxidation of residual oil; at that time we, by and large, did rather better in our carbonate system than we presently do after our change to natural gas. It appeared that the sulfide corrosion product film was, to some measure, protective. In the absence of this film the corrosion rates tend to be somewhat higher in certain parts of the system.

Unfortunately, the gas contains just enough organic sulfur or trace quantities of combined sulfur, which hydrogenate to hydrogen sulfide, in partial oxidation, to prevent the use of chromate and similar inhibitors, so I feel we have a somewhat more difficult problem now with natural gas than we had originally with heavy residual. But we've progressively been adding stainless shielding to our carbon steel vessels, and this is not an unduly expensive approach. We use 12-gauge sheets, pass them through the manholes, sandblast the shell during a scheduled shutdown in the area in which the cladding is to be applied. It is welded onto support bars welded to the shell. It doesn't begin to approach strip lining for complication or cost. There are considerable spans between securing welds—it goes on quite quickly, and it does seem to offer a very satisfactory protection technique. I'd be interested to hear if anybody has tried something similar with the MEA system.

Anonymous: Was there any special location where corrosion was encountered with carbonate regenerating system?

JONES: Above the demister, initially, seemed to be a bad location. This was, I believe, the area in which we first clad. We then clad down to the top bed; there are two beds of ring packing in the tower. We have, thus, been progressing downwards in the tower, from the carbon dioxide laden carbonate overhead towards the regenerated carbonate in the bottom of the tower.

We have been running a continuous Audigage monitoring, and although we haven't gotten into the position of putting guy wires on the tower, we would have to do something like that unless we had controlled our metal wastage due to corrosion.

## MEA heat exchangers

MCAHON: I don't have any help for Mr. Jones, but if we can remain on this subject for one moment more I have another question. All of this discussion so far has centered on corrosion problems in the column. We have also had severe corrosion problems in our heat exchange in the lean to foul MEA system, and we have tried to monitor our rates of corrosion by looking at coupons and corrosometer probes. We found that checking the iron content in the solution actually provided a more sensitive method for detecting variations in corrosion rate. Is anyone else having similar difficulties with corrosion in the lean to foul MEA exchangers? Perhaps our situation is a little more severe in that we have departed somewhat from the maximum recommended concentration of MEA. We have gone as high as 27% because of limited column capacity for carbon dioxide removal. I'd like to hear any comments

on this subject, if anyone has done similar things or suffered similar problems.

SIMMS: We run several amine units, normally about 20% amine. To avoid corrosion, we have found it essential to limit the total loading of our amine. If we exceed approximately 5 cu. ft. of carbon dioxide/gal. of 20% amine, that's total carbon dioxide in the foul amine, we are headed for trouble.

Second, our heat exchangers must be arranged in what I will call a vertical stack so that they are self-venting upward. If we try to reverse the flow of foul solution or arrange exchangers horizontally in series, our experience has been serious maintenance expense. By observing these two precautions, we've been able to have a very minor amount of corrosion.

In a system with three exchangers, the hottest one will be stainless, probably 304 tubes, maybe the first two, that is, the hottest and the next hottest. In the cold one, carbon steel tubes are satisfactory.

## Emergency kits

GOETTLING—Hooker Chemical: This spring, in the course of training a crew to handle emergency leaks in containers, we found that the equipment which we had for our chlorine tank cars would not fit our ammonia tank cars. As perhaps many of you know, some of the chlorine producers and large chlorine consumers have emergency equipment kits for handling leaks at valves, safety valves, and fusible plugs in tank cars, drums and cylinders.

The Chlorine Institute has adopted a design for such a kit and they are now available. In the case of the tank cars, briefly, this consists of a hood or a cap that is placed over the faulty valve or safety valve. The hood is sealed at the bottom with a rubber gasket. A yoke holds the cap in place. At each end of the yoke is fastened a hooked bolt. These bolts are hooked into the dome openings. When the nuts on the bolts are tightened, the hood is pressed against the main plate of the car until the gasket seals the leak.

Originally, our chlorine kits were suitable for use on ammonia cars, but with the change of style of our angle valves this is not now the case. This suggested several questions that might well be considered by this group. Does the experience of ammonia producers with container leaks warrant having such equipment available? Have such kits been developed and are they used by ammonia producers currently? Is this something that the group should advocate? We would appreciate any comments on this subject.

MASON—Dow Chemical: When Mr. Goettling, of Hooker Chemical Corp., wrote to me about this subject, I forwarded the information to the Compressed Gas Association. It was my opinion, and CGA concurred, that any activity in this direction would properly come under CGA jurisdiction rather than this A.I.Ch.E. group. However, there is no objection to discussing the subject here and now to voice our opinions. I have been requested to serve on the CGA subcommittee to consider this subject. I shall appreciate any comments or suggestions that any of you wish to make to help in directing any activities in this line.

Vic Lane, who is the chairman of the CGA ammonia committee, has mixed emotions on such emergency kits for the reasons that Mr. Goettling mentioned. He pointed out that cars for ammonia are not as well standardized as those for chlorine. Thus such a kit might not work properly on some equipment. If so, it might be worse than nothing by giving a false sense of security. I shall be very pleased to hear com-

ments from anyone for guidance in this committee work.

## Who to call in an emergency

LAWRENCE: Mr. Mason, my first question is: whom do we call at the CGA when we have a car leaking out in the field? We have to send somebody out to check a bad car, and I guess all of us have adopted a repair kit of some kind. We have a standard kit at the plant now, and we have trained men on each shift whom we shoot out; one is a supervisor and one is an Army man on car complaints. We have certain steps to take, both on jumbo cars and on standard cars. We haven't worked with CGA or anyone over there.

I had the same general experience at Armour where we sent people out to check bad cars. I didn't realize that we had help from CGA, but there's one thing for sure, when we get a bad car out there some place, somebody's got to go out and do something.

MASON: This is the type thing that we were trying to find out. The Chlorine Institute has a very elaborate system of people, on a widely disseminated list, who are set up to take care of emergencies of this kind. Also the locations of the various kits are listed. If our ammonia industry feels that this is justified, a similar system could be established. It would be a major job, but if we think it should be done, then I feel that this should be done by CGA. If we feel that it should be done, then we should so indicate through our company CGA representative. If you would like to indicate such to me, I'll appreciate any comments you'd like to make, and you can address them to me at Midland. I would be glad to list them with what comments we have.

HELLER—Phillips Petroleum: With regard to whom you call in case of an emergency, it may be of interest that the Bureau of Explosives has established a list of people at strategic locations for all compressed gases, including anhydrous ammonia. If one is in need of some assistance, all he would need to do would be to contact the Bureau of Explosives representative in his area. The Bureau of Explosives man has access to this list of qualified individuals and you can get help very quickly.

With regard to the activities of the Compressed Gas Association, I believe that the A.I.Ch.E. should be a cooperative movement along with the CGA, and let the CGA do the basic work without duplication in the A.I.Ch.E. The A.I.Ch.E. has, through Mr. Mason and other representatives in the CGA, an avenue of communications. This way, one may funnel his comments to the agency that will be doing the basic work. I would like to see us take a stand against duplicating effort in this field.

MASON: This was really the reason for just discussing it at this point, and unless there is a reversal of our past policies to stay away from codes and setting up rules and codes (which is rightly an activity of CGA), I think our activity should be purely in advising CGA of what we think should be done, and conveying to them any ideas that we may have. Let the CGA actually set it up.

ROYCE—Collier Carbon & Chemical: I'd like to add that our company has been working in this line for the last several years. One of the things that we have found helpful is that we have developed a postcard mailer that we put on the inside of the tank car dome at the time of loading. Anything that the customer sees faulty in the way of relief valves, unloading valves, or

gauges he notes to our attention and drops it back in the mail so that we have that car earmarked when it comes back into the plant. Aside from that, in our normal repair we maintain relief valves on stock in the plant from the tank car people, which has been generally the extent of repairs. But we found that this postcard mailer has been most helpful.

## Low temperature storage

WALTON: On low temperature storage, one of the problems that's facing us now and has a number of times in the past is: what is the proper method of fire protection for low temperature storage? Here I'm talking about, not only ammonia, but cryogenic storage in general, and this can be liquid ethylene, liquid CO, and so on. It has always seemed to me that providing fire hydrants and monitors around such storage is rather useless.

You usually find the insurance carrier insists that you do so. I'd be interested in the thoughts of anybody in the group here as to what is the proper method of fire protection for low temperature storage.

SCHWAB—Factory Insurance Association: With respect to this problem of low pressure storage, I had the questions asked of me quite a while back, "What might happen if a line of liquid ammonia would break and ignite? Could you ever sustain such a fire from the ammonia gushing out of the line?" I got various opinions, but I do not know of anyone who experienced such a thing. Has such an occurrence happened to anyone in this group?

MASON: I think Bill Bulkley pointed out in his experiment that the chances for fire of the ammonia itself are so remote as to be practically nil. We know that ammonia-air mixtures are combustible only in the range of about 17 to 23%. This percentage can exist under dynamic conditions in such a small area that a fire will go out if you do have any such fire, and it would have to be reignited. The possibility of a continuing flame, or of a fire being started which can't be put out, when the ammonia is coming out of a pipe is, I think, so remote as to be negligible.

There is one other comment I'd like to make while I'm here: another appeal to all of you who know of any additional storage tanks or low pressure storage tanks. I'd like to have you give me the name of the company and the location, the size, and the operating pressure of these tanks.

## Ammonia pipeline problems

SCHWAB: With regard to that ammonia pipeline problem, during this meeting I heard of one such occurrence concerning liquid ammonia gushing out of the tank farm.

There is another problem involved here too, this field of low temperature ammonia storage is relatively new, and it is not as completely well understood as I would like it to be. There is also the problem of insurance; what are you going to do with regard to this huge value in ammonia at \$60/ton? How are you going to supply the fire protection, and just what is the hazard?

HELLER: Perhaps the incident Mr. Schwab mentioned may have been one of our experiences. We had a header fail on a refrigerated barge compressor and it spewed liquid ammonia. There may have been sources of ignition around but we had no fire. We did lose a

man. He happened to run through the stream of liquid ammonia and froze to death. But there was no fire as a result of this particular accident.

KUENZLY: I can't talk about any leaks from major storage tanks that caught on fire, but about 20 years ago in one of our bottling plants at Pittsburg, I think it was a flanged gasket let loose and spewed liquid ammonia onto a light bulb, which did not have vapor-proof protection on it. The bulb broke and ignited the ammonia. Apparently there was the right condition of draft and it did sustain combustion. The rafters of the building caught on fire, which resulted in very slight damage. I've seen quite a few ammonia leaks, but I've never seen one of them catch on fire without a really hot source of ignition such as this particular one; it was the only one I'd ever seen where we had a fire.

## Flammability and toxicity

JACKS—M. W. Kellogg: We have paid a lot of attention to the fire hazard of ammonia. We have the insurance people very vitally interested in this along with us. As a result of this, sometimes we give so much attention to the protection against the fire that we forget to put the toxicity protection ahead of it. Of course, there's no insurance for any company that would sustain a lot of people being killed from ammonia escaping and moving in the air toward a populated area.

Another thing that worries me a little is that when I talk to potential customers of ammonia storage, they sometimes say that they want to have water sprinkler systems over ammonia storage. Now I don't mean deluge nozzles, which have definite value when you get a small leak and want to deluge that leak with water. If you get a fair-sized leak and you turn on a sprinkler system you could asphyxiate a lot of people with the fumes that would be generated by the water that would, of course, supply the heat to generate the ammonia cloud. The point here is that we sometimes worry so much about fire, that we forget the seriousness of the toxicity.

WHITE: Going back to the question of what we're going to do about these spills for protection, it's quite a problem, and if there's any chance of cold liquid ammonia being inflammable, I would say then there is no question but we should have dikes around tanks to contain it and handle it with our own work force.

Second, these tanks all should be located at some distance, which each of us will have to decide, from other facilities and other inhabitants. I know the American Standards Association is right now about to set up those distances as a maximum. In the case of ammonia, as Bill Bulkley has illustrated, you can get a fire around ammonia spills at the initial evaporation rate. When the gas temperatures are high enough, you can, of course, have a flame, where it is cold, you can't. At San Juan we talked about this; since then I poured some on the ground, waited until it settled down, and tried to ignite it; I couldn't, except right on the outside, where you would get a little flashing. It would not burn at all where you had the liquid ammonia around.

I regret to say I didn't think of spraying it and lighting it. I believe I could try that and I would get the flashing on the outer edges of the fog. I would not be a bit afraid of trying it, and I think it would flash and then extinguish itself from the extreme cold. As Bill Mason pointed out, the ignition ranges are rather narrow and just that one zone on the outer edge of the fog would have that range.

Whether we should dike around a tank or not, I

guess we each have to decide that for ourselves. Certainly it would be better to contain it where you could handle it. But if you're close to some place where it could drain and perhaps not do as much damage as around a lot of people, you might have a choice to make. Of course, the best thing is to prevent it, and that's the reason we're spending so much time on it.

## Fire retardant materials

WHITE: There were a couple of points that I wanted to mention, one is that on these insulating compounds that would burn ordinarily, the inhibitors used are the phosphates. I'd like to put into the record an article that deals with these different phosphates. This article is in Industrial and Engineering Chemistry, Product Research and Development (December, 1963), and it's by J. J. Anderson of Virginia Carolina Chemical Co.

This article classifies the different phosphate inhibitors. I think there's about four different classes of compounds, and there's only one of them that he found that would be permanent; the others are more or less temporary, in that over a period of three or four years they would—I believe he used the word "sublime"—so that after that time they would actually not inhibit the flame as well as when they were first put in there.

The other fire retardant paint that I found is actually a flame barrier. You can spray this on Styrofoam and it will char, it will blacken, but it will actually insulate the Styrofoam or the urethane so that it will not melt with a very intense flame. This is made by ALBI Manufacturing Co. at 98 East Main St., Rockville, Conn. I would certainly recommend that anyone worried about a flame barrier, rather than an inhibitor, look into this.

## More research needed

JONES: I was rather engaged with the insurance gentleman's concern about fire with respect to ammonia because I believe that many of us hope that if we did get a major spill perhaps the best thing that could happen would be that it would take fire and burn; it might be better to rain weak nitric acid rather than have a dangerous gas cloud enveloping people.

However, to pass on from that, other conversations here—we had Bill Bulkley of American Oil, and Jack Reed of Imperial Chemical Industries,—have suggested the magnitude of the downwind cloud. I believe the American Oil figure for steady state was an evaporation rate of 1,800 lb./min., whereas the initial flash rate was 110,000 lb./min. Conceivably, under these circumstances, the downwind effect would be very much further than the 2,500 to 5,000 ft. mentioned by the American Oil work.

In our experience, we have observed distances of this order or larger, with very modest size spills. That is a very strong smell of ammonia, shall we say, but in relation to a few tons spilt, rather than a few thousand tons. It seems almost incredible that one would be secure at 2,500 to 5,000 ft. downwind.

Perhaps the thing to do is to consider whether one mightn't take the U. S. Naval Research attitude in the fracture safe design and construction of the tank. This would cost a little more, but it might be wise to have the assurance of extreme reliability in the prime container and dispense with the dike.

MASON: There is one possible misconception that I would like to clear up about Styrofoam. A statement was made that it would burn like mad. The original

Styrofoam would continue to burn when ignited, but the foam that is recommended for these tanks will not burn without external flame. It will melt if the temperature is high enough; but when an external flame is removed from the foam it will not continue to burn.

Bill Bulkley, who is the chairman of the general safety group of A.I.Ch.E. suggested that some more experimental work should probably be done. Our subcommittee has instructed me to poll the various low pressure ammonia tank owners and operators to see if they believe their companies would be favorable to the financial support of some more experimental work on a larger scale. This work would include the effects of large spills of ammonia and the causes and effects of roll-over of the contents of large low pressure tanks. This poll is by no means a definite commitment, but let us have a show of hands of those who believe their companies would probably be willing to participate in financial support of such a research program. . . . It appears that this subject should be pursued further.

Anonymous: Those of us in the contracting industry who are concerned with installing all these tanks would, I'm sure, like to participate in that, so include us in your list.

## Leakage of combustible gases

SIMMS: I'd like to read a report from the Asahi Chemical Industry in Japan. This is a very brief report concerning the leakage of combustible gases from the cold box of nitrogen wash section; the date: March 13, 1962; damage: none, potentially great, however.

"As the nitrogen wash plant is operated at a low temperature, all of the equipment is packed in an airtight box and insulated with slag wool. If combustible gases leak out, this cold box comes to exceed the limit for explosion. We measure continuously the gases in the box using a Rauter gas analyzer which checks the state of gases by sending in nitrogen so that the safety of equipment can be maintained. A large gas leak was discovered soon after the plant was put in normal operation, but a prescribed gas leak test had shown nothing wrong following the overhaul of the plant.

At that time, however, the Rauter gas analyzer showed an abnormal composition of gases in the cold box. So the plant was shut down immediately and work was started to find the leak. The leak point was soon found and repaired. Operation was stopped for four days, but an explosion was prevented.

The leak was from the gland of the valve installed inside the cold box. Because of the analyzer, we could easily find an abnormal state of gases inside the box. We realized that leak was often from the valve gland, therefore, the construction of the valve has been remodeled so that the gland part comes out of the box, leaving the body inside as it is. This helps make repair work easy. Thus, the problem of leak has been solved."

## Preventing roll-over

WHITE: I would like to mention what we propose to do to prevent roll-over in the anhydrous ammonia tanks. We are planning to install a 2-in. steel heater well from the top to the bottom of the tank and insert an electrical heating tape. We will then experiment to find out exactly how much heat we'd need to prevent temperature stratification in the storage tank.

It is our thought that a steel well going all the way down to the bottom, that could be just warmed up maybe just one degree above the ammonia inside the

tank, would keep the evaporation that would start from this ammonia in the bottom going all the way to the top. This would start a chimney effect just from one source. I realize that we're hitting in the dark on this because we still don't understand why light density ammonia will stay on the bottom below some cold heavy ammonia. I might throw out one point that we discussed, that perhaps our curves on the densities of ammonia at different temperatures under these pressures have not been really resolved.

SIMMS: I don't know where you're returning your condensate from your refrigeration compressors, but in the event that you're returning it over the top, you might want to consider what the benefits might be, circulationwise, by returning this condensate near the bottom.

WHITE: In order to eliminate as many nozzles on the bottom of the tank as possible, we have put everything through the top. We've been a little reluctant to do this until we know why, in our tank, we have worse trouble than anybody else. I believe we have a little poorer insulation on the bottom as compared to other tanks, and I'm a little worried that this may be the reason that we have more temperature differential. If that's the case, I hesitate to add more heat to the bottom of the tank.

RYAN: There was a comment made that one could not use tank mixers on such tanks due to the diameter. In the oil business, they have been faced with stratification for many years and do use mixers on tanks of equal diameter to these refrigerated ammonia tanks.