UREA PLANT SAFETY PROBLEMS

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SunOlin has a Montecatini urea plant with full liquid recycle of carbamate. This plant and urea plants, in general, pose quite a number of metallurgical problems which are rather interesting and appear frightening at times because of the unpredictability of corrosion patterns and the fact that the amount of information available in the literature on corrosion rates of different materials is extremely limited.

Corrosion rates

Table 1 is a compilation of some corrosion rates in a urea-ammonium carbamate environment, urea plant synthesis system. The letters after some of the figures in Table 1 code the source of the data. The code is not given because permission to release the sources has not been given. One will note that zirconium shows the lowest corrosion rate, next is 329 stainless steel and Ni-O-Nel, and next is Carpenter 20. (Additional data have been included in Table 1 since its original presentation.)

I have not been able to find anyone who has tried Carpenter 20 in valves or pipe in urea or urea carbamate service.

Stainless steel—317, 316, and 304

Type 317 stainless is next. There is some limited information that it appears better than 316 where one has higher temperatures, in the neighborhood of 340 to 350°F, however, this is not thoroughly established. Type 316, of course, is the standard workhorse in the urea plant. Different samples of Type 304 show extremely variable performance. In one case a sample shows good corrosion resistance, and in another case it corroded away completely.

General experience is that 304 is perfectly satisfactory for urea but not for urea carbamate mixtures. Most of the corrosion rates shown in Table 1 are based on samples in the reactor where there is urea, carbamate and excess ammonia. Next is 17-4PH Mo stainless steel; SunOlin has no experience with this but we do with 15-4PH Mo stainless steel, which has looked very good. Then tantalum with which we have no direct experience; and titanium which has been tried as valve trim and which has held up very well.

Next is Hastelloy F. One manufacturer of urea uses this as their standard for valve trim.

Inconel, Incolloy, and Hastelloys

Next is Inconel and Incoloy, which don't stand up too well. And then the Hastelloys, B and C. We have a piece of valve trim of Hastelloy B, which shows very severe corrosion. Other samples that corroded away completely in the test include: 310, 325, 330, nickel, Inconel, Monel, Incoloy, Duriron, Ni-Resist, and silver, as some of the earlier urea experience showed in a rather expensive way. Another source of data, however, showed 310 to have a low rate of corrosion.

Experience has been spotty, and what seems to be satisfactory for a few months in a particular location, may upon examination in a future shut down prove to show corrosion.

Reactor failure

There was an experience in another company, where a multilayer reactor failed shortly after its initial operation. It failed due to cracking through the layers. After a great deal of investigation the failure was considered to be due to stress corrosion due to contamination of the water in the jacket of the reactor. After this incident, the word was spread around the country, by The M. W. Kellogg Co., in this regard and a number of people, including ourselves, have stopped using water in the jacket of the reactor.

It was also mentioned at The San Juan Symposia that a urea reactor failed in Germany. This is recorded in the literature (1). This also was attributed to stress corrosion due to contamination of water in the jacket. Anyone who may be operating urea reactors with a water jacket might well consider this.

Contamination by sulfur compounds

Another problem that revolves around urea reactors is contamination of the CO_2 by sulfur compounds. In SunOlin's case, this has happened several times when we were putting new catalysts into service: shift catalysts or new catalysts where we had to change a few reformer tubes. We feel that one has to be below 1 ppm of H_2S in the CO_2 going to the reactor, in order to avoid losing the protective film in the stainless lining of the reactor.

One would be quite interested in knowing if anyone has established any different limits than this, or has had different experience. It becomes rather frustrating sometimes when one is putting new catalyst into service, to have to wait for days for the sulfur to be removed from it. The urea plant is just sitting idle waiting until the sulfur content gets down to a limit that one feels is safe.

Letdown block valves

The next problem in urea plants that has been annoying to us is the inability to maintain a workable

TABLE 1. CORROSION RATES IN A UREA-AMMONIUM CARBAMATE ENVIRONMENT. UREA PLANT SYNTHESIS SYSTEM.

Material	Rate, in./yr.	Material	Rate, in./yr.
Zirconium	0.0001	17-4 PH Mo stainless steel	0.003
202 Stainless steel	0.0020	15-4 PH Mo stainless steel	0.001
304 Stainless steel	0.0015	Tantalum	0.0034
304 Stainless steel (sensitized)	Corroded away		0.00067 (S)
304L Stainless steel	0.0016	Titanium	0.0068
309 Stainless steel	0.007		Nil (G)
	0.022 (R)		0.0058 (R)
	0.055		0.0197 (R)
	0.0185 (R)		Nil (G)
310 Stainless steel	Corroded away	Hastelloy F	0.0019
	0.0024 (R)		0.0070
	0.0018 (R)		0.0025 (G)
316 Stainless steel	0.0011		0.00092 (G)
	0.0089	Hastelloy B	0.024
	0.0047 (S)		0.052
	0.025 (G)		0.0418 (R)
	0.019 (G)		0.071 (R)
316 Stainless steel (sensitized)	0.0041	Hastelloy C	0.020
316 L Stainless steel	0.0013		0.056
	0.0030		0.0114 (S)
	0.0086 (S)		0.042 (G)
	0.074 (G)		0.030 (G)
	0.039 (G)	Inconel X	Corroded away
317 Stainless steel	0.0013	Inconel 600	Corroded away (R)
	0.0072 (G)		Corroded away (R)
	0.0216 (G)	Inconel 700	0.029
317L Stainless steel	0.016 (G)	Incoloy 804	0.0008
	0.0069 (G)		0.057
325 Stainless steel	Corroded away		0.041 (S)
329 Stainless steel	0.0010	Incoloy 901	Corroded away
330 Stainless steel	Corroded away	Nickel	Corroded away
Ni-O-Nel (Incoloy Alloy 825)	0.0011	Illium G	Corroded away
Carpenter 20	0.0011	Monel	Corroded away
Carpenter 20 Cb	0.0056 (R)	Nimonic 75	Corroded away
	0.0355 (G)	Duriron	Corroded away
	0.0061 (S)	Ductile Ni-Resist	Corroded away
	0.030 (G)	Silver	Corroded away
	Corroded away (R)	Lead (antimonial)	Corroded away
Carpenter 20 Cb 3	0.0075		
	0.085 (G)		

Note: Data collected by N. H. Walton, SunOlin Chemical Co., Claymont, Del. Letters such as (R) denote source of data.

letdown-block valve in the reactor letdown line. We started out and still have globe valves, series 1,500 lb., 316 stainless valves. These started out with a Hastelloy C trim; a piece of the collar that's used to fasten the plug on the stem was cut in half and the corrosion was rather startling.

It is particularly apparent in threaded areas, and we theorize that stresses that are set up in machining the threads may cause the material to be more susceptible to corrosion. In an attempt to get around this, titanium trim was tried in these valves, and the titanium stands up well. The difficulty is that where the seat ring screws into the 316 body of the valve, the threads don't last too long in the body, and the seat ring then comes loose and the valve isn't of much use.

A number of manufacturers have given up completely in trying to maintain block valves in their reactor letdown line. However, some attempts are being made to provide better designs. There is one valve manufacturer who recently has designed a new valve for this particular service. It would be of interest to know of anybody's experience along these lines which has been satisfactory.

Safety valve operation

Another problem in urea plants is the maintenance of safety valves in an operable condition due to the high melting temperature of urea, carbamate, and urea-carbamate mixtures. One is likely to get solidification in the throat of the safety valve, particularly those on the urea reactor and those in the carbamate systems. Steam tracing or steam jacketing is probably not the answer here because if one has a stagnant condition of urea and carbamate, as heat is applied and time proceeds, the chemistry of the reaction proceeds to biuret and triuret and cyanuric acid, and so on, in the relief valve; it then becomes completely blocked and solid.

Some companies have block valves under their safety valves, and they change them at regular intervals. This is a rather controversial attack on the problem.

Some states and some insurance companies do not care for this solution, others permit it. We have tried one device which works for a large safety valve, and that is, injection of water through a small tubing line right up into the throat of the valve, on a continuous basis, to keep the valve washed clean. This works well on the carbamate separator valve where the throat of the valve is fairly large. However, in the case of the first stage carbamate pumps where the throat of the valve is very small, this does not work as well.

Air injection

Another problem that affects corrosion in urea plants is whether a particular urea plant is one which employs air injection in order to maintain the passivity of the stainless steel material of construction. Where one has air injection one has one set of problems; where one does not have air injection in another process one has materials which apparently stand up satisfactorily, materials that do not perform satisfactorily where one has air injection.

Aluminum bronzes, for instance, have been used satisfactorily in trim of valves where there is no air present in the system.

One problem which has been a bother is the vented gas from the first stage carbamate absorber. It is necessary to take a small vent there, in processes where you use air injection into the CO_2, in order to remove inerts from the system. This vent gas consists of the inerts, that is, oxygen and nitrogen, some ammonia, and some hydrogen, which is present in the CO_2 as a result of the solubilities in the MEA system.

There has been considerable concern about maintaining a vent, sufficient in quantity, to keep the hydrogen-oxygen relationship in the vent gas outside of the explosive limit range. This means that one has to waste more ammonia than one would if one were not concerned with this. It would be of considerable interest to determine whether other people are concerned with this, what precautions they take, or how they look at this problem.

Passenger-freight elevators

Another problem which is largely a safety problem in urea plants, not only at SunOlin but at others, is the maintenance of the passenger-freight elevator on the prill tower. Prill towers, of course, are fairly tall; people being what they are today, one needs to supply elevators for operators to get up and down the tower for maintenance work. The maintenance of such elevators in many cases is an extremely difficult problem.

At SunOlin there is seldom a week that goes by that we don't have the elevator maintenance people in several times a week. We have problems with interlocks, with door switches, the emergency cables, and the main cables. Then what happens is that when an interlock doesn't work, one gets the elevator up to the floor but can't get the door open, so an operator or a mechanic gets frustrated and pokes a hole in the wall and reaches in and releases the interlocks so he can open the door and get in. It's almost impossible to stop this, but you have a condition which is potentially very dangerous. We have tried chrome plated contacts and silver plated contacts. The call buttons at the floors are another problem. This is extremely difficult, expensive, and an annoying safety problem. Anybody that has solved this in their plant or has any suggestions or hints could help a number of us and perhaps save some lives.

Crevice-type corrosion

On 316 stainless steel, one of the things which we have run into a number of times is crevice-type corrosion. For example, in the reactor letdown line, mentioned previously, we have 1,500 lb. valves. These valves have bonnets which have ring-type joints. Three of the valves stood in an upright position in the original installation. One of them lay over on its side. On this particular valve the ring in the bonnet developed a leak. This happened time after time. When this valve was taken apart, the bonnet was taken off, one found severe corrosion at the bottom of the ring-type joint there.

Flexitallic gaskets

Another case where corrosion has been found is the face of the flanges where one uses a Flexitallic gasket, where the I.D. of the Flexitallic gasket is smaller than the I.D. of the pipe, which is normal for Flexitallic gaskets. One has an area there of perhaps a quarter of an inch in width where the faces of the flanges are exposed and in effect are a crevice. Recently, it was necessary to replace two flanges because the corrosion had proceeded and undermined the surface where the Flexitallic gasket was sealing. Thought is being given to the desirability of ordering special Flexitallic gaskets where the I.D. of the gasket closely approaches the I.D. of the pipe.

Clad carbamate absorbers

The last incident to be mentioned here is something that happened which was a little frightening. We have a first stage carbamate absorber. The vessel itself is a clad vessel, 316 clad. There's a 16-in. manhead on the vessel which is carbon steel with a 316 liner. Each time we opened this absorber the liner was found to be buckled and puckered. Each time this happened it was beat back into position and anchored in one or two places with a plug weld.

Several months ago at this particular manhead, a leak was found at the reinforcing plate telltale. The plant was shut down and the absorber manhead opened. The liner was found to have a crack in it. The liner was completely removed and the carbon steel manway nozzle was found to have corroded to a depth of about 1/2 in., over about 14 in. of the circumference of the weld between the manway nozzle and the vessel.

Plug welds for liners

It was repaired by filling in with weld, and then putting the liner back with plug welds on 4-in. centers. This was the quickest thing to do. We put telltales under the liner in the manway nozzle itself, and when we started up, one of these leaked. On shutting down it was checked for leakage again. It was found that one of the plug welds was leaking, it was repaired and the unit put back in service again.

Plug welds for liners are frowned on today, however, there's a problem here as just what is the proper answer; should one go to a solid 316 manway nozzle, or stripline the nozzle?

These are a few problems which have been encountered in urea manufacturing technology; there are many more.

LITERATURE CITED

1. Chemie Arbeit (January, 1959).

DISCUSSION

SORELL—M. W. Kellogg: First of all, I agree with you completely on your diagnosis of crevice corrosion; this is a familiar term in corrosion technology describing localized corrosion of passive metals in sheltered, oxygen impoverished areas. It is frequently encountered in threaded and flanged joints. In fact, the term gasket corrosion is used to describe the special form of crevice corrosion on flange faces experienced in your plant. This mechanism probably accounts also for the corrosion of Hastelloy C threads described by you. Hastelloy C, like Cr-Ni stainless steel also forms a complex chrome/iron oxide film which confers corrosion resistance. Thus, in threaded joints where free access of oxygen is prevented, this passive film tends to break down and localized attack is a distinct hazard. Note, incidentally, that these remarks apply equally to Alloy 20 which also requires an adequate supply of oxygen or some other oxidizing agent to maintain passivity.

Reference was made earlier to a German article describing a urea reactor failure; this paper was published in the January, 1959, issue of the magazine Chemische Arbeit. Briefly, it described an explosion killing 5 people and injuring several others caused by massive brittle fracture of a multilayered urea reactor operating at 2500 lb./sq.in. As Mr. Walton pointed out, the failure is attributed to intergranular stress corrosion cracking by ammonium nitrate. Trace quantities of this salt were present in the cooling water which circulated through an external coil. The failure apparently occurred as the result of a leak in that coil which permitted water spillage on the hot shell with consequent evaporation to dryness and nitrate deposition on the reactor wall. It is readily apparent that a mere few parts per million of dissolved solids can form salt deposits, similar to water stains on kitchen ranges. Multilayer vessels appear to be particularly vulnerable to stress corrosion cracking because, in addition to high stress levels, there is always a possibility of water entrapment between layers.

The United States experience mentioned earlier was quite similar in nature, except that the cooling water was contained in an external, pressurized jacket rather than in a coil. Again the failure was attributed to the deposition of ammonium nitrate, resulting from sudden depressuring and consequent flashing of the hot jacket water. The failures originated inside vent holes which were inadvertently flooded with jacket water as the result of leaking hose connections.

Before closing, I would like to stress the important difference between pressurized and nonpressurized water jackets with respect to potential stress cracking hazard. As was pointed out in a previous session, The M. W. Kellogg Co. advocates external water cooling as the most positive protection against overheating of the metal shell in the event of insulation failure. Open water troughs and jackets with natural overflow are used for jacketing secondary reformers and hot downstream equipment in our recent designs. It is evident that high concentration or precipitation of dissolved solids in atmospheric water jackets is an extremely unlikely occurrence so long as continuous overflow is maintained.

LAWRENCE—Central Nitrogen: On elevators, Nort, have you ever attacked this problem with the useful tool of this committee, statistically checking them around the country, to see if anybody does better? And the reason I asked is this: in the two elevators that I've worked with, one was open almost completely, and the other one is completely enclosed. The one that was open had very little contact trouble; of course, these are all sealed contacts. The one that we have closed now at Terre Haute, we're running a good race with Nort on keeping that elevator running.

So I agree this is a fairly serious problem, since these things take you way up in the air and someone is going to reach his arm back some day and get an arm sheared off at least and bleed to death on a stuck elevator or drop out of the thing or fall off trying to crawl out of it. So my question would be to this group: has anybody statistically or otherwise determined some way to improve these? This question about keeping the thing open and keeping a good air draft up through it, does that ring any bells.

WALTON: This has other aspects of safety, too. For instance, as a part of my corrosion inspection I began to wonder what the steel was like—the supporting steel on the inside of this closed in elevator shaft. We took some of the aluminum sheets off to look at it and it's rather sad-looking steel. When it's closed in, it is extremely hard to get to it to inspect it regularly or to coat it and keep it painted. This is another safety problem in urea plants. What is a satisfactory coating system for the steel of a prill tower? This is a real problem.

Anonymous: I don't have any experience in a urea plant, in particular, but two things that you were talking about interested me, one is this threaded gland apparently you have. I think when you cut those threads you have a tendency to expose end grain and you may be getting in some end grain attack and a roll thread will probably help you somewhat.

KUENZLY—Shell Chemical: We have had some experience along your line of letdown valves. And we started, as you probably know, with two parallel trains of letdown valves with block valves on both sides. However, we were shut down by the auxiliaries more than we were with the letdown valves, so we finally, as you know, eliminated one train and the block valve on the upstream side and only had one on the downstream side. If you have a proper designed letdown valve you can go between shutdowns or annual changes.

The other question I had was: in your corrosion tests I presume there was oxygen present in the reactor?

WALTON: Yes. These were mounted in a spool in the bottom of the reactor, so you had the oxygen present with the CO_2.

KUENZLY: Then we also experienced this corrosion on the threaded valve seats, and I think we got around that by actually welding up the bottom of the things. You may have to do a little machining, and lapping afterwards if you get a little warping—but that seems to solve the problem.

We have experienced this so-called end grain corrosion in places where you cut across to the way the plate is rolled, and it really chews it right out. We had that problem in the bottom of the distributor baffle in the inlet of the reactor, where we finally solved that by welding over and peening.