PROCEEDINGS

OF THE

18th ANNUAL MEETING

FERTILIZER INDUSTRY ROUND TABLE

1968

accumulation of several weeks. It was also noted that evaporators that produced only 54% P_2O_5 seemed to have very few tube failures.

As a result of these problems, most of the Nionel exchangers were eventually replaced with graphite exchangers. Only a few evaporators are still existing with metal tubes, and these are almost exclusively used on acid with 50% P_2O_5 or higher strengths. Even at this concentration, if scale is allowed to accumulate, corrosion will occur. However, the higher strength acid seems to be less agressive, and the degree of cleanliness is not as critical as in more dilute acid. Some exchangers have now been in operation for more than 5 years without any major tube failure. A review of all the facts after these many years of experience, appears to indicate that the Nionel tubes might have been satisfactory if the evaporators had been boiled out every 3 to 4 days. However, this limitation would do away with one of the primary advantages of the system.

Because of these experiences, there is now a tendency to avoid the use of new materials in any position where their failure would cause a prolonged shutdown. To prevent a recurrence of the above problems the next time a new material is suggested, the initial test program should be such as to insure that the material is tested under actual operating conditions. Preliminary tests can be conducted with corrosion test spools, but before final commercial application a test set-up should be made that conforms as closely as possible to actual conditions.

A new material for the vapor head, for instance, should be exposed to the same conditions of scaling, erosion, liquor and vapor as encountered in actual operation. A new tube material should be installed in a small heat exchanger, operating in parallel with the main exchanger. This small exchanger could then be operated on its own cycle, so that the conditions in the tubes would be similar to what would be expected in the proposed commercial operation. In addition, before a material is completely accepted, it should be tested on acids produced from a variety of sources, to determine exactly what limitations potential impurities and additives may put on its use.

MODERATOR PELITTI: Thank you, Bill.

We will now hear from Russ James, a chemical engineer, and consultant on fertilizer, ammonia and synthesis gas manufacture. He is well-known in the industry through numerous articles, papers and publications. I have known him since our association at Chemico, where he was Chief Engineer of the Industrial Projects Department and, later, Director of Development. He has been active in high pressure and naphtha reforming, carbonate processes, phosphoric and hydrofluoric acids. A Yale engineering graduate, he studied economics and government at Columbia. He will talk to you about problems of corrosion in urea reactors.

Urea Reactor Lining Materials

G. R. James

CO_2 and water are corrosive at low temperature. Materials in CO_2 removal systems, where temperatures are in the range of 100 to 250°F, have long been a problem in synthesis gas purification. Operators who have seen part of their CO_2 strippers disappear or whose copper liquor regenerator has acquired a moth-eaten appearance, can testify that CO_2 in water is corrosive.

Urea reactors have the prerequisites for CO_2 corrosion at 200°F. but temperature, one of the prime factors in corrosion, is not 200°F. It is as high as 400°F, in a mixture of CO_2, water, ammonia, carbonate, carbamate and urea. Even with a high excess of ammonia at these temperatures the urea reactor mass will dissolve many corrosion resistant materials.

Fortunately, the problem, which may have seemed difficult or impossible in the early stages, has now been resolved. There are several lining systems which do allow urea reactors to give satisfactory life. Many materials have been used. Lead, silver, titanium, zirconium and stainless steel each has it own story in urea reactor service. Each has its own problems in process application, fabrication and cost.

Early Test Data

Starting with some early work by J. G. Thompson, H. J. Krase and K. G. Clark in a six inch diameter tin-lined vessel 18" long, we see that corrosion in the reactor was of prime concern in 1930.

Table 1 shows the results of 4

Table I— Resistance of Metals to the System Urea-Water-Ammonium Carbamate at 142° C. under Pressure

SAMPLE	NON-FERROUS COMPOSITION					4-DAY TEST LOSS	7-DAY TEST		
	Carbon	Chromium	Nickel	Silicon	Other elements		Loss	Penetration per year	
						Mg./sq cm /day	Mg./sq cm./day	Inches	Mm
1 (Duriron)				14.5		0 024	0 012	0 00021	0 00533
2 (Silver)					Ag 99.9		0 050	0 00025	0 00089
3 (Illium G)	0 5	21.5	58 5	1.4	Cu, 8; Mo, 3; W, 2	0 069	0 066	0 0012	0 0505
4 (Chromium)						0 14 (gain)	0 084	0 0017	0.0432
5 (Lead)							0 11	0 0014	0 0356
6 (Nickel strip)							0 15	0.0025	0 0635
7 (Pioneer)		20	38	4	Mo, 3, some C, Cu, Mn	0.029	0.17	0 0031	0 0787
8 (Corrosiron)				12		0.68	0 175	0 0037	0 0940
9 (Rezistal 4)	0 23	18	22 5	2.9		0.90	0.95	0 017	0 432
10 (Stellite)	2 (approx.)	15 33			Co, 40–75; W, 10–17		1.1	0 019	0 483
11 (Invar)			36				1 49	0 027	0 686
12 (Cimet 1)	0 7	29	1			0 77	36	0 87	22.10
13 (Cimet 2)	1	20	60	1.4		0.97	0 10 (gain)		
14 (Rezistal 5)	0 31	11	36	2		1.4			
15 (Hylnickel S)	0 15	17	21			1.7			
16 (Cyclops 17-B)	0.20	6 3	2	1		1 7		0.053	1.346
17 (Block tin)							2.68		
18 (Ferro Molyb. A 111)					Mo, 5.75		57	1 07	27.18
19 (Delhi cast)	0.45	17	3			4.4			
20 (Bethlehem chrome steel)	0.35	15 5	0.3		W, 3.5	4.5–6 9*			
21 (Silchrome)		18 5	0 4	3.0		5 7			
22 (Delhi rolled)	0 09	20 0				6.5			
23 (Enduro A)	0 09	17.0	0 35			14 0			
24 (Duraloy)	0 32	23 5	1 1			17 0			
25 (Chrome iron)	0 13	14 8			V, 1.2	17 0			
26 (Unioy 282S)	0 30	28 3				19.0			
27 (Chrome iron)	0 13	14 0				34.0			
28 (Electrolytic iron)	0 02			0 01		43 0			
29 (Chrome iron)	0 20	24 0				59			
30 (Unioy 1409)	0.09	12 4	0 5			84			
31 (Vanadium alloy steel)		13 6			V, 0.5	97			
32 (Rezistal 7)	0 9	5 5	0 3			101			
33 (Carpaloy 1)	0 1	14 0				109			
34 (Ascoloy 33)	0 09	10 5				143			
35 (Carpaloy 3)	0 27	20 0			V, 0.7	174			
36 (Unioy 1809)	0 10	18 8	0 5			179			

* Range of triplicate samples.

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RESULTS OF CORROSION TESTS
IN UREA PILOT REACTOR

Sample	Non-Ferrous Composition				Loss	Relative Penetration
	C %	Cr %	Ni %	Si %	Mg./sq. cm.	
1. Chromium	-	-	-	-	0.21 gain	0
2. Tantalum	-	-	-	-	0.10 gain	0
3. Duriron	-	-	-	14.5	2.4	1.0
4. Nickel	-	-	-	-	13.2	4.3
5. Illium G	0.5	21.5	58.5	1.4	12.5	4.4
6. Rezistal 4	0.23	18.0	22.5	2.9	37.0	13.9
7. Lead	-	-	-	-	67.4	17.3
8. Aluminum	-	-	-	-	55.4	59.9
9. Enduro KA 2	0.15	18.0	8.5	<0.75	308.0	114.3
10. Tin	-	-	-	-	506.0	252.1
11. Zinc	-	-	-	-	Complete Solution	

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day and 7 day tests at 142°C. (288°F.) and 50 to 75 atmospheres. It appeared from this work that operation under the given conditions would be reasonable with lead, silver, chromium and nickel liners, and that various chrome-nickel alloys also would have application.

The same year further work by K. G. Clark and V. L. Geddy produced relative corrosion penetration figures for various metals in a test autoclave operated at somewhat higher temperature, 165°C. (335°F) and approximately 110 atmospheres (Table 2). It can be seen that results in the two tables do not agree on actual corrosion rates, but that those materials with lower rates do generally correspond.

Test Data on Corrosion

Additional, more recent data in Tables 3 through 6 show results of corrosion tests in actual operating reactors.

From these tables it is again apparent that several materials are

Table 3

LOCATION OF SPECIMENS:
Urea Reactor 3 ft. below top head of reactor in liquid - spool was mounted horizontally next to vessel wall.

AERATION:
Moderate

TOTAL TIME IN TEST:
115 days

AGITATION:
Slight

TEMPERATURE:
Ave. 181 °C
357 °F

REMARKS:
Type 316 ELC is used in construction of this plant. No failure encountered but general corrosion observed.

METAL	SAMPLE	CORROSION RATE in./yr. Ave.	
Titanium	1	0.0031	
Ni-o-nel	1	0.009	
Carpenter 20	1	0.010	
Hastelloy C	1	0.017	
316 ELC SS	1	0.030	
Ni-o-nel	2	0.061	
Silver	1		0.025 Destroyed in test
Silver	2	>0.025	Destroyed in test
Aluminum 1100	1	>0.061	Destroyed in test
Aluminum 1100	2	>0.063	Destroyed in test
Carpenter 20	2	>0.070	Destroyed in test

Table 4

LOCATION OF SPECIMENS:
Urea Reactor directly on top of sparger plate in bottom of reactor.

AERATION:
Some slight amount of air

TOTAL TIME IN TEST:
58 days

AGITATION:
3400-3800 lb/hr. of NH₃, CO₂, Urea soln. thru 31¾" ID vessel

REMARKS:
Type 316L (¼" liner) stainless steel sparger plate in use. One plate failed in three months by general corrosion. During this test, corrosion was less than in the past as judged by iron in product and condition of sparger plate.

METAL	SAMPLE	CORROSION RATE in./yr. Ave.
Type 304 SS	1	0.0018 Etched
Type 202 SS	1	0.0031
Type 302 SS	1	0.0042 Lightly etched
Type 202 SS	3	0.0056
Type 302 SS	2	0.0090 Lightly etched
Type 201 SS	1	0.024 Heavily etched
Type 202 SS	2	0.096 Missing after test
Type 202 SS	4	0.11 Missing after test
Type 304L SS	1	>0.12 Missing after test
Type 201 SS	2	>0.1° Missing after test

Difference in corrosion rates of duplicate specimens and complete disappearance of Type 304L makes value of test doubtful. The conditions of exposure apparently varied along the length of the rack.

satisfactory in urea reactor service, although the order of preference is by no means clear.

It is also apparent that location of samples in the reactor has a definite effect. Thus one sample located a short distance from another may have a markedly different rate of corrosion. This may be indicative of actual differences in reactor conditions, not of the questionable validity of test results.

Oxygen

There has been considerable work done on the effect of oxygen on reactor linings; however, there is not a great deal of information available on corrosion related to oxygen content. Table 7 illustrates the effect of oxygen on titanium corrosion and Table 8 gives information on the combined effect of sulfur and oxygen. Thus for titanium the results illustrate that oxygen decreases the corrosion rate and sulfur increases it markedly.

The data in Figure 9 show that

Table 5

LOCATION OF SPECIMENS:
Urea Reactor on top of sparger in bottom of reactor.

AERATION:
Moderate to slight

TOTAL TIME IN TEST:
125 days - Out of service six months

AGITATION:
Extensive; 3400 to 3800 lb./hr. throughout.

TEMPERATURE:
Ave. 190 C
375 F

REMARKS:
Type 316L sparger has failed by general corrosion. Disagreement between duplicate samples on two support rods may be due to sparger flow pattern, but opens results to question.

METAL	SAMPLE	CORROSION RATE in./yr. Ave.	SAMPLES DESTROYED IN TEST
Zirconium	1	<0.0001	304 Sensitized
Type 309 SS	1	0.0007	Type 310 SS
Type 329 SS	1	0.0010	Type 330
S.S. Carpenter 20	1	0.0011	Illium G
Ni-o-nel	1	0.0011	Nickel
Type 316	1	0.0011	Monel
Type 317 SS	1	0.0013	Hastelloy C
316L SS	1	0.0013	Inconel
Type 304 SS	1	0.0015	Inconel X
Type 304L SS	1	0.0016	Incoloy
Hastelloy F	1	0.0019	Incoloy 804
Type 202 SS	1	0.0020	Incoloy 901
316L SS	2	0.0030	Nimonic 75
Cu - Mo	1	0.0030	Cast iron
316 Sensitized	1	0.0034	Ni-Resist Type II
Titanium	1	0.0041	Duriron
Hastelloy F	2	0.0068	Type 325
Type 316	2	0.0070	
Inconel 700	1	0.0089	
Type 309 SS	2	0.019	
Type 309 SS	1	0.055	

Table 6

LOCATION OF SPECIMENS:
Pilot plant reaction autoclave in open glass tubes immersed in reactor.

TOTAL TIME IN TEST:
7 days

TEMPERATURE:
180 °C
355 °F max.

REMARKS:
Test specimens 15 mm. diameter x 30 mm. long. Pressure about 250 atms. (3750 psi) max.

METAL	CORROSION RATE in./yr. Ave.	
Silver	0.033	
Stellite	0.39	
Monel	0.39	
Al Bronze	0.42	
Lead	0.42	Actual corrosion plant autoclave
M7 (18 Ni, 8 Cr, 7 Mo)	0.85	

Table 7

LOCATION OF SPECIMENS:
In reactor, position not given.

AERATION:
None

TEMPERATURE:
Ave. 196 C
385 F

AGITATION:
Considerable

REMARKS:
Pressure 260 atmospheres.

METAL	S ppds. g/cu m	ppm by wt	CORROSION RATE in./yr. Ave.
Titanium (all tests) O₂ ppm			
44	0.012	6.0	0.0040
380	0.015	7.5	0.0014
790	0.011	5.5	0.0008
2360	0.012	6.0	0.0008

the reduction of corrosion rates as oxygen increases is more pronounced with stainless steels than with titanium. This is one of the reasons for the preference given presently to stainless reactor linings, when adequate oxygen content is present.

Table 3 gives the results of a 115 day test, with the samples near the top of a 316 ELC lined reactor, in which air was being introduced. Note the relative positions of titanium and 316 SS, and the variation in two samples of Carpenter 20. Aeration was probably responsible for the destruction of both silver specimens.

Table 4 again shows data from samples suspended in a 316 ELC lined reactor. They cover different materials and at a different loca-

Table 8

LOCATION OF SPECIMENS:
In Reactor - Position not stated

AERATION:
None

TOTAL TIME IN TEST:
33 to 63 days

AGITATION:
Considerable

TEMPERATURE:
Ave. 176 °C
349 °F

REMARKS:
Pressure 240-250 atmospheres

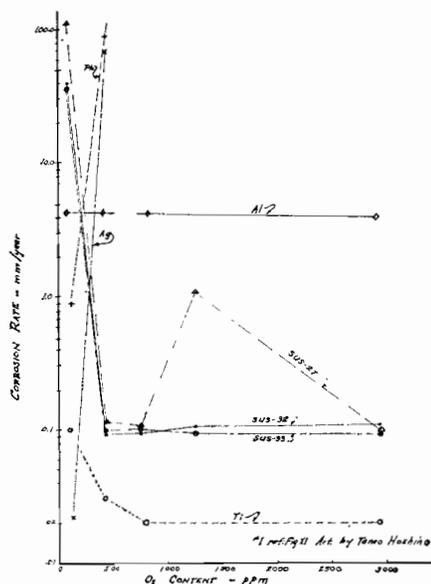| O₂	8-9 ppm	9-250 ppm	0.3-0.5%	1-1.5%
S ppds, g/cu m(ppm)	0.004(2)	0.02(10)	0.1(50)	0.5(250)
METAL	IPY	IPY	IPY	IPY
Titanium	0.0024	0.0033	0.016	0.089
Titanium 10-15 Cr	0.020	0.026	0.091	0.54
Titanium 6-7 Cr	0.0033	0.0035	0.033	0.18
Titanium 2-4% Mo	0.0021	0.0026	0.011	0.14
Lead	0.0037	0.015	0.34	Destroyed
Monel alloy 400	0.023	0.25	Destroyed	Destroyed
Inconel alloy 600	0.025	0.35	Destroyed	Destroyed

Figure 9

tion. The wide variation in corrosion rates is probably due to non-uniform conditions on top of the sparger. The object of this table is to show the difference between the rates of corrosion that can be obtained with the same materials in the same reactor.

Table 5, at relatively high temperature, shows zirconium at the top of the list, and other samples again with widely varying corrosion rates, as much as 80-fold in the case of 309 SS. Titanium is far down the list, maybe due to location or possibly the sample had been improperly heat treated before testing. Worthy of notice in this test are the many materials that proved to be unsatisfactory.

Table 6 gives results of a pilot test for a short period. It shows silver at a high corrosion rate but significantly better than other materials. In this case air was not used. The lack of oxygen proved the downfall of all materials but silver.

Silver and lead both react ununfavorably to oxygen content as illustrated in Figure 9. They also react unfavorably to a combination of oxygen and sulfur compounds. Limits for satisfactory operation of reactors with relatively thick silver linings have been set by one operator at 25 ppm O_2, when there is 300 ppm sulfur in the CO_2 used.

Process Considerations

Use of higher temperatures in reactors results in increased conversion of ammonia and CO_2 to urea. For example, if a given mixture at 180°C would provide a yield of 60%, the same initial mixture at 200°C might provide a yield of 65% of the CO_2 introduced.

Thus a more expensive liner with capacity for higher temperature operation may be justified, because either the same size reactor can provide more capacity, or recycle facility cost will decrease for the same output.

Summary of Materials in Commercial Use

Stainless Steel—316 ELC appears to be an economical material for urea reactor liners. It is used with various amounts of oxygen and in thicknesses of approximately ½ inch. Finish on the interior of the vessel and design to allow for even flow of materials and even distribution of oxygen are important factors in maintaining a protective oxide film on the liner.

Temperature limit is approximately 200°C (392°F).

Cost of material for a shaped stainless steel liner might be $2.50 per pound. Finished cost will depend on the fabrication technique used.

Titanium—Although know-how for titanium fabrication is limited, it has been used successfully in urea reactor design. Titanium is not as dependent on oxygen for satisfactory service life, thus eliminating requirements for oxygen injection. Also because of a lower corrosion rate, the period between inspection shutdowns may be increased and the cost of upkeep lowered.

Titanium treatment before installation is important in maintaining its resistance to urea reactor corrosion. Proper annealing can reduce titanium corrosion by as much as 80%.

Thickness of titanium liners is as low as ⅛ inch in clad material. They can be installed by two or three of the major vessel fabricating shops in the U.S. Various installation techniques are used. Besides clad plate in lower pressure units even solid titanium has been employed.

Cost relative to stainless steel is two or three times on a weight basis.

Temperature limit is approximately 200°C (392°F).

Zirconium—First use of zirconium for reactor lining produced failure in welds, which could not be X-rayed because of installation technique. Later design produced a satisfactory liner which loosely fits inside the pressure vessel, with a purge between the shell and the liner. At present, either the purged liner or one in which the steel shell is shrunk on the liner is used.

Zirconium liners have been approximately ⅜ inch thick. They can be fabricated by techniques and welding similar to that used on titanium. Corrosion of zirconium in urea reactor service is practically nil.

Cost relative to stainless steel is about 4 or 5 times on a weight basis.

Temperature limit is approximately 215°C (420°F).

Silver—Long a standard with many designers, silver has generally been replaced with stainless steel using oxygen injection.

Thickness of silver linings has been, in some cases, as much as ¼ inch.

Cost of silver (min. $24/lb.) is now considered prohibitive when compared with 316 ELC, titanium or zirconium on an over-all basis.

Temperature limit is approximately 200°C (392°F).

Lead—One of the earlier liner materials, lead has now largely been replaced by others, except in the oil slurry process, wherein no oxygen is used and oil coating lowers the corrosion rate of the lead.

General

Figures given herein on cost cannot be taken as indicators of comparable completed vessels. The complete vessel cost will depend on items that are related to the lining design, but not necessarily dependent upon it.

A comparison of the various corrosion data presented does not allow a definite conclusion as to which is the best lining. The answer will be determined in large measure by process and equipment considerations. One designer may

have adapted his process and equipment to one material, with as good a result as obtained by another designer with a different liner.

Conclusion

While the information in this report is necessarily brief, it is apparent that there are several satisfactory lining materials for urea reactors, as well as several factors to be considered relative to their selection.

Some of the important ones are:

1. Process to be used
2. Pressure vessel fabrication technique
3. Availability of manufacturing facilities
4. Availability of repair facilities.

The data contained in the tables indicate that results of tests with corrosion spools in urea reactors can be frequently contradictory and sometimes misleading. And that generalizations cannot be made except on the basis of actual plant experience.

Acknowledgment

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MODERATOR PELITTI: Thank you, Russ.

Next on the panel is Philippe Moraillon. Mr. Moraillon received his Chemical Engineering degree in 1945 from the Ecole Nationale Superieure de Chimie in Paris. In 1946 he joined the Chemical Department of Saint-Gobain, which was later merged with the Chemical Division of Pechiney.

In Rouen, Mr. Moraillon played an important part in the development of many Pechiney-Saint-Gobain's fertilizer and phosphate processes. For the past three years he was Manager of fertilizer operations; first at Montargis and then at Bordeaux. He is presently assigned to the Pechiney-St. Gobain main office in Neuilly as Chief Engineer of the Fertilizer Division.

Mr. Moraillon has been active in technical meetings in Europe, and has presented papers at some of the conferences of the International Superphosphate Manufacturers Association. He has recently conducted a survey on the use of plastic materials in a number of fertilizer plants, and will report to you on European experience with the use of plastics for fertilizer applications.

Some European Experiences with the Use of Plastics in Fertilizer Plants

P. Moraillon

People who have known the fertilizer industry some twenty years ago should no doubt remember that wood and lead were widely used for reaction tanks, gas or vapor ducts, sulfuric and phosphoric acid piping, launders, scrubbers, stacks, etc. After operating for some time under the usual severe conditions, these materials underwent considerable deterioration and their maintenance cost was high. It is no wonder then that as soon as plastics became available, they received wide acceptance from fertilizer manufacturers and that their use spread quickly, in spite of some early failures caused by insufficient knowledge of their properties and lack of experience of equipment manufacturers.

No doubt this audience is well-acquainted with the use of various plastics in the States. So, my topic will be limited to European experience, mainly French, with the use of plastics in the fertilizer industry. The information I have collected covers a great number of French plants, a few in the Netherlands, Belgium, Italy, and also equipment supplied by French manufacturers to plants in Spain, Jugoslavia, U.S.S.R., Morocco, Lebanon and Senegal.

We will review successively the use of different plastics in sulfuric acid handling and metering, superphosphate manufacture, phosphoric acid manufacture, granulated fertilizers production and bagging.

Sulfuric Acid—Handling and Metering

The manufacture of phosphoric acid, superphosphate and some grades of granulated fertilizers consumes sulfuric acid.

Piping

Rigid unplasticized PVC pipes are extensively used for acid concentrations between 70 and 94% H_2SO_4.

Normal PVC is usually satisfactory when the temperature is not over 40°C. For instance in a plant in Nantes, a pipe 79/90 mm. in diameter and 250 m. long has been in service since 1954.

Some plants prefer high im-