Stress Corrosion Cracking in Ammonia Urea Synthesis Corrosion of Austenitic Stainless Steel

Evidence indicates that when nickel is replaced by other austenite formers, stainless steel urea process equipment has greater resistance to corrosion.

J.M.A. Van der Horst
Surface Research, Inc.
Olean, N.Y.

The corrosion rate of many metals exposed to the reaction mixture of urea synthesis is often catastrophic. The materials most employed are molybdenum containing stainless steels *(1-6)*, but other such as titanium *(7)* and zirconium *(8)* have been proposed and used.

The Mo containing stainless steels are by no means perfect for this use, and often appear to be less than reliable. On the other hand they are preferred because of ready availability as well as suitability for field repairs. A variety of proposals have, therefore, been made to improve the resistance of these steels by modifying either the environment or the metal.

The addition of oxygen to the process stream *(9)* has certainly improved the corrosion resistance of reactors, but it is no panacea. The oxygen helps to maintain the passive film on the stainless in an otherwise reducing environment. Many investigators, e.g., Tomashov *(10)* have pointed out that the breakdown of an existing passive film is a relatively slow process which generally takes hours. Some measurements of the decay times of cathodic reduction curves of passive films on iron give values of 300- to 1,000 min. *(11)* which is in good agreement with the time of 5 hr. found for disappearance of the passive film in urea equipment after interruption of the oxygen supply. Contrary to this slow process, in urea synthesis corrosion can set in very quickly and proceed very rapidly.

Increasingly, evidence has become available that nickel is at least nonessential for corrosion protection in the urea process, and that it may well be harmful. Brusentsova et al *(12)* successfully tested two-phase steels containing 21% Cr and 5% Ni in urea synthesis. Yakabe et all *(13)* found a 25% Cr steel to have a lower corrosion rate than any of the Ni containing austenitic stainless steels; unfortunately this material is not readily weldable. A British patent *(14)* claims austenitic stainless steels containing little or no Ni. The above findings have been fully confirmed by the author in process stream corrosion tests.

Table 1 shows a weight loss comparison for three austenitic stainless steels which are essentially identical in composition except for the Ni content. The first and the third specimen were exposed to the process stream for 3 months, the second is from a process vessel wall in the same area, which had been exposed somewhat longer. Photomicrographs of the three specimens are shown in Figure 1. The 330 specimen in Figure 1 shows very severe general attack as well as intergranular corrosion. The 304 specimen is attacked less severely, and has only incipient attack at the grain boundaries. The Tenelon specimen has

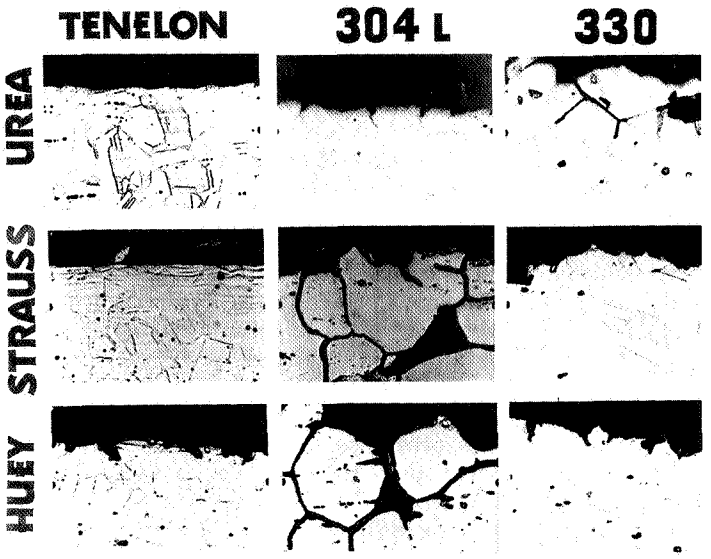


Figure 1. Specimens of Tenelon, 304L and 330 SS exposed to the urea process stream, and the Heuy and Strauss tests (mag. 500x).

Table 1
Weight loss of austenitic stainless steels subjected to process stream corrosion tests.

	C	Cr	Ni	Corrosion Loss mils./yr.	mdd*
SS 330	0.06	18.41	34.71	30.01	175.0
SS 304L	0.03	18.64	9.73	0.64	3.7
Tenelon	0.09	18.01	0.14	nil	nil

*mmd = milligrams per square decimeter per day

Table 2
Weight losses of materials exposed to the urea, process stream, and the Huey and Strauss tests.

	Tenelon	304L	330	
Urea	nil	0.64	30.0	mils/yr.
Strauss	0.63	1.04	2.05	microns/72 hr.
Huey	61.5	90.0	4.3	microns/48 hr.

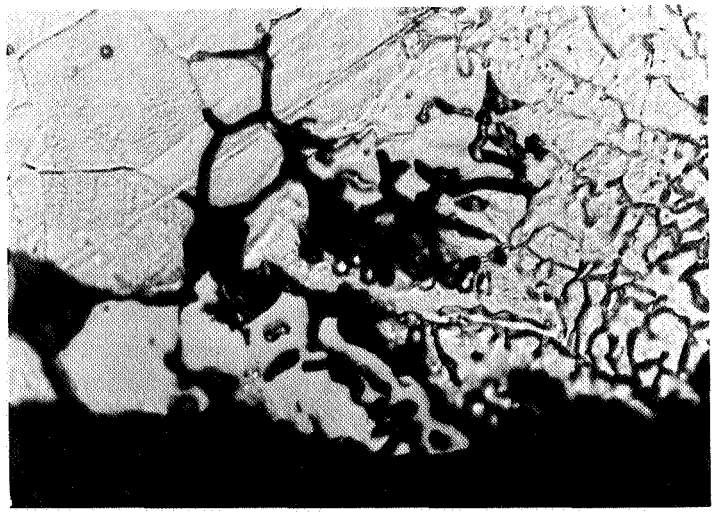


Figure 2. Surface of Huey tested weld interface 316 base metal (right), and 316 weld metal (left) with intergranular attack in base metal and etching of ferrite dendrites in weld metal (mag. 1,000x).

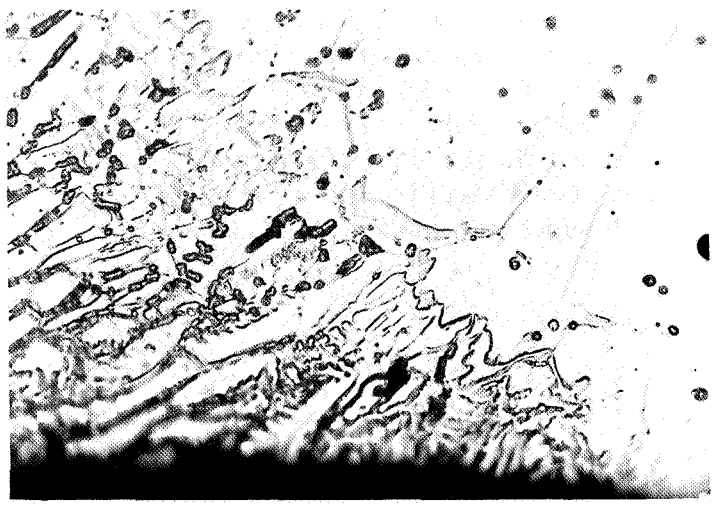


Figure 3. Surface of weld interface 316L base metal (left), and 316L weld metal (right) after 2 yr. exposure to urea synthesis environment. No evidence of attack on weld or base metal (mag. 1,000x).

zero attack.

Huey and Strauss Tests

Identical specimens out of the same plates were then submitted to both the Huey* (ASTM A279) and the Strauss** tests (ASTM A393). This was done for two reasons. First, intergranular corrosion of stainless is generally tied to the C content. Since the C content is not identical in the three metals, it was thought necessary to eliminate or confirm the possible influence of carbon. Second, the Huey test is often used as a material acceptance test for urea synthesis equipment. The use of the Huey test for this purpose is quite irrational on theoretical grounds *(15)*, since the redox potential as well as the pH of the test and of the urea environment are entirely different. It was thought useful to check the theory. The Strauss test has a redox potential closer to that of urea synthesis, but the pH is still much lower.

The results are shown in the bottom row for the Huey test, and in the center row for the Strauss test. A comparison of the surface appearance shows striking differences. The Tenelon appears unattacked in both urea and the Strauss test, but is severely attacked in the Huey test. The 304L is superficially attacked in urea with some preferential attack at the grain boundaries, but in both the Strauss and Huey tests it is literally falling apart with the grain boundaries etched out completely. The 330 has severe surface attack with pronounced grain boundary attack in urea, but is only superficially attacked in the Strauss test, and somewhat more with slight grain boundary attack in the Huey test.

Table 2 shows the respective weight losses in the Huey and Strauss tests expressed in microns per testing period with the urea weight loss expressed in mils per year. It immediately strikes the eye that 330 has a high weight loss in urea, and a low one in the Huey test. Conversely, both Tenelon and 304L are low in urea and high in the Huey test. As a matter of fact, 330 is the only material which passes the Huey test under the rules, i.e., less than 5μ /48 hr.; this material corrodes at a high rate in urea synthesis. The weight losses in the Strauss test are less significant since here intergranular corrosion is the main purpose. It would seem obvious from these comparisons that a selection of materials for urea synthesis by means of the Huey test is not well founded.

In order to meet the objection that Huey tests for urea synthesis are only used on type 316 stainless, we have also tested this material at the most sensitive point, the edge of a weld. Again the specimens come from one and the same weld bead. Figure 2 shows the results of the Huey test in the fusion zone. The base metal suffers from intergranular attack, while in the weld metal, the ferrite dendrites have been etched out. In Figure 3 the same weld is shown after several years of urea synthesis exposure; there is no attack whatsoever. The same weld Strauss tested (not shown) has no attack either.

If one compares a 316L weld that has been attacked by

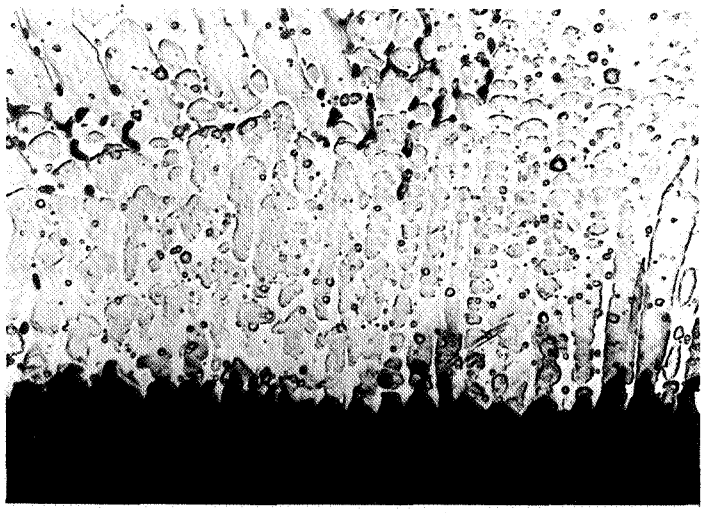


Figure 4. Surface of 316L weld after 5 months exposure to urea environment. Ferrite dendrites unattacked, austenite attacked (mag. 1,000x).

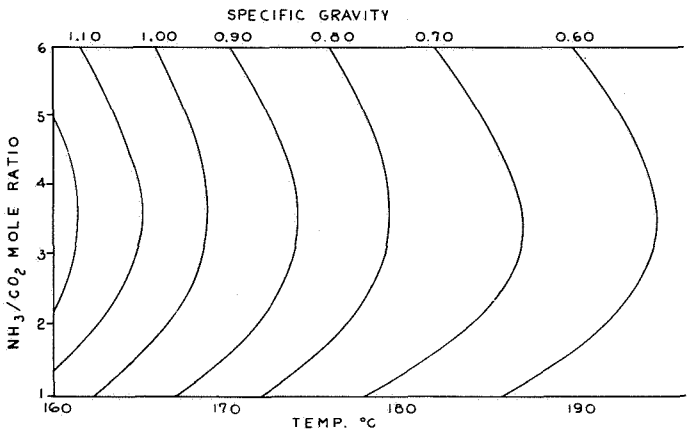


Figure 5. Urea synthesis equilibrium conditions, P = 145 kg./cm.^{2}

the urea environment, Figure 4, it is seen that the ferrite dendrites are resistant while the austenite in between is etched away, which is the opposite of what happens in a Huey test.

Conditions which promote corrosion

Over a number of years I have noticed in a variety of urea plants that stainless steel corrosion is directly connected with certain operation conditions, or rather "environmental aberrations." Corrosion is invariably found on stainless exposed to ammonia rich vapors where the metal forms a "cold spot", when a film of reaction fluid is exposed to vapor with high ammonia content, and when urea conversion has accidentally failed to take place and the resulting ammonia-rich liquid is heated.

A careful analysis has turned up that these cases have the following characteristics in common: a liquid phase with an unconverted NH_3/CO_2 mole ratio>4:1 and free NH_3:H_2O mole ratio>2:1; free NH_3 is the NH_3 left after deducting 2 moles NH_3/mole CO_2.

It is well known that Ni is a very readily complexed by ammonia. An entire branch of the Ni-ore extraction industry is based on this phenomenon. Such Ni ammines are more stable than other simple metal ammines. The Ni chloride hexammine $[Ni(NH_3)_6]Cl_2$ has, for instance, a 100 mm. vapor pressure at 125°C, compared with 71°C for the corresponding iron ammine *(20)*.

I have observed that, in areas of changing liquid composition adjacent to heavily corroded stainless steel, deposits of pure iron oxide could be found, analyzing at 80% Fe, i.e., corresponding to a suboxide. The area of iron oxide deposition corresponded in terms of process equilibrium to a lower NH_3 content than the corroded area. This indicates that the iron ammine complex is only marginally stable in the process environment, and very readily decomposes when the environment changes somewhat.

An ore extraction process for Mn[16] with an NH_3-CO_2 solution relies on the fact that MnO dissolves readily when NH_3:CO_2 >4.5, and precipitates when NH_3:CO_2<4. Incidentally, when the presence of iron interferes with the manganese extraction, hydrogen sulfide is added as an activator. It is well known that urea synthesis melts become much more agrgressive when they contain trace amounts of H_2S *(17, 18)*.

It is probable that a layer of carbamate ions is adsorbed at the metal surface, perhaps to the oxygen layer of passivity. This layer must still be in place since it takes many hours of normal operation under conditions of complete oxygen starvation before passivity breakdown.

Under the abnormal operating conditions set out above, i.e., high NH_3:CO_2 and NH_3:H_2O ratios; the breakdown of passivity is instantaneous. It is postulated that while the combination Ni-oxide-carbamate adsorb is insoluble in the environment, the ammine complex is quite soluble, and that the same is true for the corresponding Fe complex. The Fe complex being less stable quickly decomposes when the NH_3 levels drops.

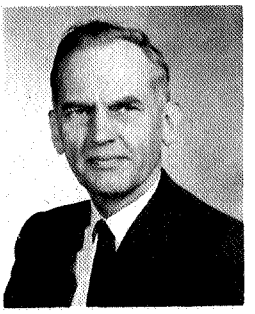
A possible confirmation of complex formation may perhaps be found in some Russian findings. Empirical equilibrium equations giving the mixture density of the synthesis reactor effluent indicate the highest density at a ratio NH_3:CO_2= 3.5:1 instead of 2:1, the figure corresponding to plain carbamate, Figure 5 *(21)*,. At a 63% conversion ratio this translates in terms of unconverted ammonia into a NH_3:CO_2 ratio in the area of 6:1, and at a 57% conversion ratio into a 5.5:1 NH_3:CO_2 ratio.

Ni detector

It has been observed that traces of Ni can be found in the product when corrosion takes place, long before Fe is detected. It is suggested that a sensitive Ni detector in the product stream would detect the beginning of corrosion long before the product turns red due to the presence of Fe. Such an instrument would also detect corrosion in the early stages, possibly even before major damage to process equipment has occurred. #

Literature cited

1. Lees, T.A. "Safety in Air and Ammonia Plants," a CEP Technical Manual, 8 40 (1966).
2. Walton, N.H., *Ibid.*, 36
3. Edstrom, J.O., and B. Skold, *J. Iron Steel Inst.*, No. 7 207,854 (July 1969).
4. Brocart, J., *Corrosion Anti-Corrosion*, No. 3, **14**, 116 (1966) C.A. 65, 6821C.
5. Strigin, A.F., and E.V. Akimov, *Khim. Prom.*, No. 4, *45* 298 (1969).
6. Van Wijk, W. Th., *Der Ingenieur*, 4, W65-72 (1968).
   Douglass, J.J., "Corrosion Applications of Explosion Bonded Reactive Metals," paper presented at NACE Northeast Regional Conference, Buffalo (October 23, 1969).
8. Wentworth, T.O., U.S. Patent 3,236,888 (February 1, 1963).
9. Van Waes, J.P.M., U.S. Patent 2,727,069 (December 13, 1955).
10. Tomashov, N.V., "The Theory of Corrosion and Protection of Metals," Champter XIII, Macmillan Co., New York (1966).
11. Nagayama, M., and M. Cohen, *J. Electrochem. Soc.*, 140 , 670 (1963).
12. Brusentsova, B.M., et al, *Zásheh. Metal.*, No. 4, 2, 494 (1966).
13. Belgium Patent 564,504 (May 26, 1965).
14. British Patent 1, 192,044 (May 13, 1970).
15. Vassal, M., Conference Internationale des Arts Chimiques, Journees Techniques de Paris, Aciers Speciaux, Paris (1965).
16. Dean, R.S., *Mining Eng.*, No. 1, 4, 55 (1952).
17. Yakabe, M., et al, Belgium Patent 664,504 (May 26, 1955).
18. Strukov, N.M., et al, *Khim. Prom.*, No. 4, **46**, 294 (1970).
19. Wendlandt, Wesley W., and James P. Smith, "The Thermal Properties of Transition Metal Ammine Complexes," Elsevier Publishing Co., New York (1967).
20. Kucheryavyi, V.I., *Zh. Prikl. Khim.*, 3 629 (1969).



VAN der HORST, J. M. A.

DISCUSSION

UMBERTO ZARDI, SNAM Progetti, Milan, Italy: I want to report about an experience we had in a urea plant in Italy. This plant is based on the SNAM Progetti ammonia stripping process. In this plant we have equipment that operates at very high pressure and temperatures (nearly to the condition of the reactor). The reactor effluents enter this equipment where a very high excess of ammonia is used as a stripping agent.

We found out that when we did not use this ammonia agent we had very high corrosion in this equipment, which was made of 316L stainless steel. During the period of operation with ammonia injection we had much better conditions. I wonder if this experience can be explained by the theory that you make. Our experience is in disagreement with your theory.

VAN DER HORST: It certainly would seem so. No I don't know the details of your process and what actually your operating conditions are at various points, but the reason I came to this conclusion is that I have found repeatedly in various plants of entirely different design that at locations where there is a high ammonia content, that is where you get corrosion.

I cannot judge about your experience because I have no idea what your actual chemical composition was.

ZARDI: Through the background of traditional processes it can be said that when a low ratio of ammonia to CO_2 is used, critical conditions for corrosion are obtained. In other words, if a plant is operated with a too low ammonia-CO_2 ratio this means very critical conditions for corrosion in the reactor and downstream. When this plant is properly operated with the proper ratio, this corrosion factor disappears. The operators were asked to keep the ratio to a certain level—ammonia-CO_2 og 3:1—otherwise they could get in trouble with the corrosion.

VAN DER HORST: Well, that's about normal. I am more specifically speaking of instances where the ammonia ratio is the plant itself may be quite normal but where at certain points in the synthesis loop accidentally the ammonia ratio becomes much higher. Incidentally, just recently my views have been confirmed by people at Sherritt Gordon in Ft. Saskatchewan who also do a lot of work with ammonia because they're trying to dissolve nickel out of the ore.

Their views were in good agreement with my findings as to various locations where corrosion was found in their plant.

Q. Are there any plants using autoclaves with the Tenelon liner, and also if they do have the Tenelon lining, do they have oxygen injection into the system?

VAN DER HORST: To my knowledge, there are no plants with a Tenelon lining, and therefore the oxygen question does not apply. I've never heard of a plant that has a tenelon lining.

Q. Did your test do any work at all on the stress corrosion characteristics of this – what do you call it, Tenelon?

VAN DER HORTS: Of the stress corrosion characteristics of Tenelon?

Q. Yes.

VAN DER HORST: No. And personally I have never seen stress corrosion of an austenitic material in urea synthesis.