Operations & Maintenance

STRESS CORROSION CRACKING—
A Caustic Experience

Here is a closer look at two instances of failure of nickel equipment in caustic environment. A falling-film evaporator developed puncture holes and vertical cracks; a problem of stress corrosion cracking occurred at a flaker drum

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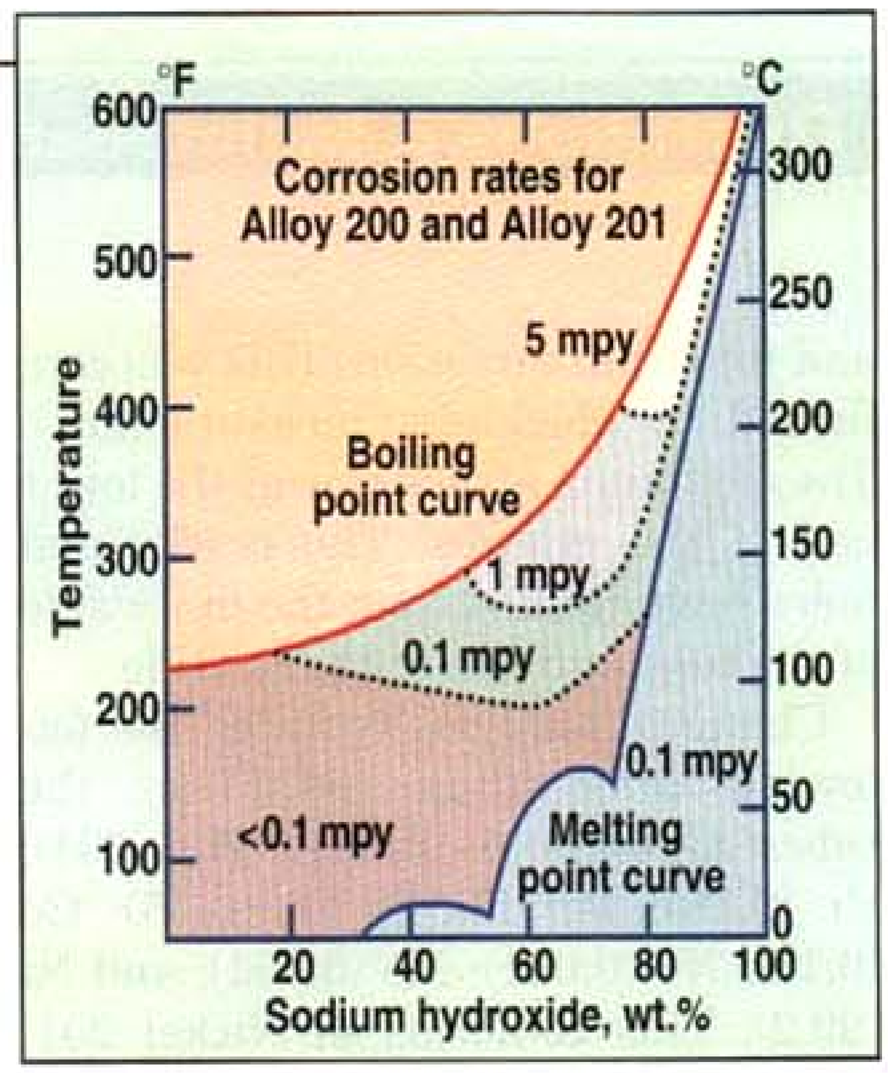

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FIGURE 1. Hot caustic will corrode Ni 200 and Ni 201. However, at a sufficiently high concentration, corrosion will begin to slow [1]. (mpy = mils/yr = 0.001 in./yr)

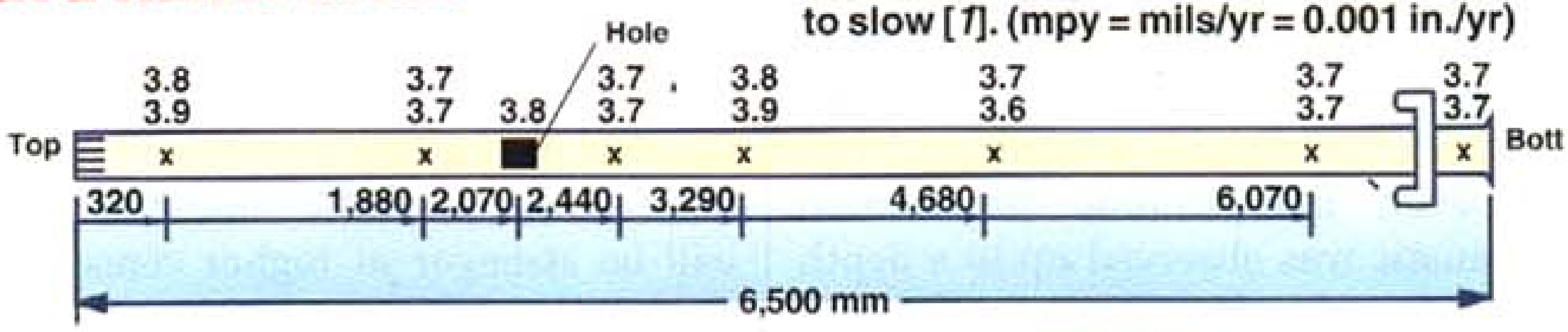

FIGURE 2. Most failures in falling-film evaporator tubes occurred between the 4,680 and 6,070 mm marks. On this specific tube, the thicknesses at marked points were all larger than the nominal 3.5 mm, except for the hole at 2,070 mm

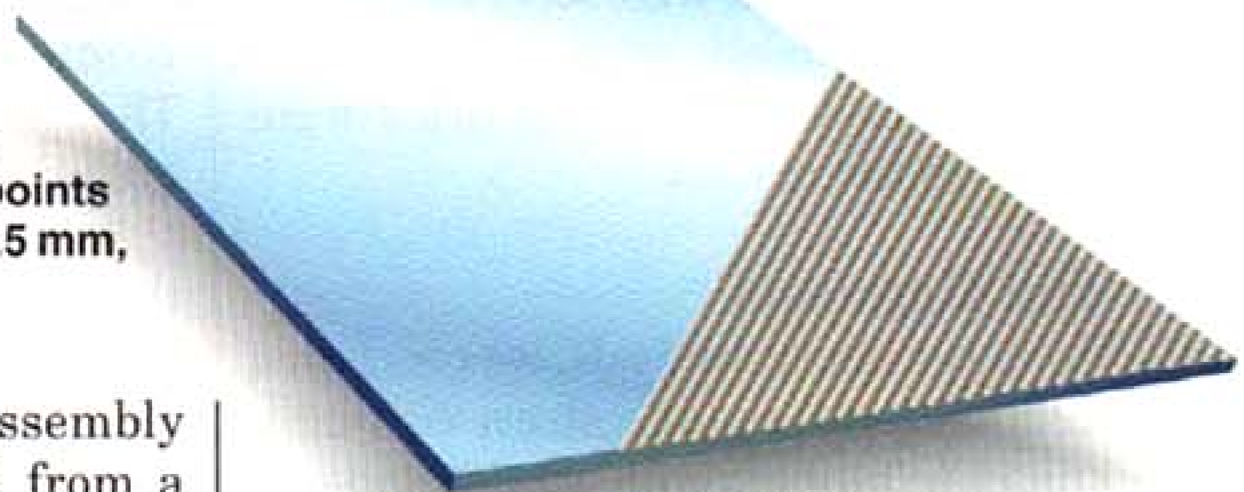

FIGURE 3. This illustration shows that corrosion left an area of grooves

Material selection references often state, in passing, that nickel is a metal of choice for equipment in corrosive service. However, the lesson we have to repeatedly learn is that Ni is corrosion-resistant — but not corrosion-proof — and that the grade of nickel makes a difference. We must keep the possibility of corrosion in mind, even with nickel alloys.

Nickel has excellent resistance to corrosion and stress cracking in concentrated and fused caustic and is the material usually used for such applications (Figure 1). Commonly used grades are Nickel 200 (UNS No N02200), with carbon 0.15 wt.% max, and Nickel 201 (UNS No N02201), with carbon 0.02 wt.% max. Composition and properties of Ni Alloys 200 and 201 are in the table on the next page.

This article focuses on two early failures of equipment in caustic environments. One is in evaporator tubes; the other is on a flaker drum. Although these occurred on the premises of one company, they represent a general problem.

Falling-film evaporator tubes

The best way to concentrate caustic soda from 50% solution to a fused mass of 99% purity is with the use of a falling film evaporator. The one under discussion developed leaks in half of the tubes in its first eighteen months of operation.

The evaporator is a harp assembly (the tubes are hung and fed from a common header) of 10 vertical tubes, 6,500-mm long, 112-mm dia. and 3.5-mm thick, made of Nickel 201 and arranged on a rectangular insulated box. Each of the tubes is fitted with an outer jacket through which molten (430°C), heat transfer salt is circulated upwards. A 50% caustic solution is fed from the top at 150°C, and flows down inside the tubes, all the while being heated by the salt. The fused caustic (99%) at the bottom end of the tubes is discharged to a flaker drum.

The evaporator was run in a standard manner. Operators and supervisors understand that corrosion increases with temperature, and also in the presence of chlorates. A small flow of 10% aqueous sucrose solution was continuously dosed to the 50% caustic feed. This is a known technique that retards corrosion without affecting the final product. The sucrose is reduced by the chlorate ion, so there is very little of either in the final product.

Most of the leaks occurred without warning. The salt level fell quickly and necessitated shutdown of the plant. The caustic was spoiled, in that it picked up nitrate and an undesirable yellow shade.

The examination

We shut down the process, removed the tubes from the jackets, and performed an inspection. The external surfaces were found to be smooth and showed a tinted coloration. There was no sign of any uniform corrosion, and there was only one leak in each of the tubes. The nature of the leaky portion of the tubes varied from small holes to modest-size but wide cracks. Most of the tubes failed in the lower third (Figure 2). In one tube, a 205-mm-long perforation was noticed in the bottom section.

The internal surface of the tubes around the failure displayed an attack-pattern of grooves, running from top to bottom. These grooves were about 15 mm wide, and ended abruptly (Figure 3). The remaining tube surface was found to be smooth

TABLE. NICKEL ALLOYS [1]		
Elemental composition:	**% in Nickel 200**	**% in Nickel 201**
C	0.15	0.02
Si	0.35	0.35
Mn	0.35	0.35
Fe	0.4	0.4
Ni	98+	98+
Si	0.01	0.01
Cu	0.25	0.25
Mechanical properties (minimum):	**Nickel 200**	**Nickel 201**
Yield strength (0.2%), N/mm³	80	105
Tensile strength, N/mm³	380	380
Elongation, %	35	35

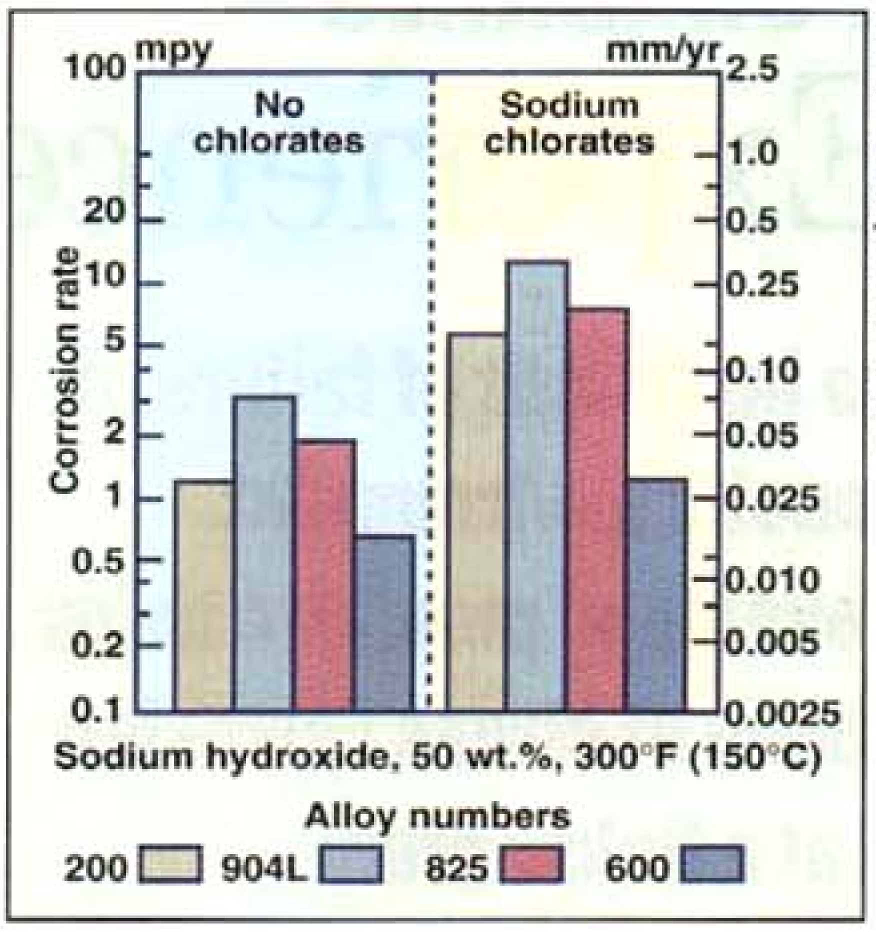

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FIGURE 4 (left). Chlorates in caustic solution caused greater corrosion of four Ni alloys [1].

and free from corrosion. This was confirmed by thickness measurements. The maximum attack was at the lower end of the grooves. The cracks and holes have started from the inner side of the tube and run to the outside.

Chemical analysis revealed the following composition (wt.%) of the tubes: C (0.01); Al (0.001); Ti (0.001); Cr (0.16); Mn (0.30); Fe (0.15); Co (0.16); Nb (0.001); Mo (0.001); and Ni (99.2). This conforms to Nickel 201, which is the prescribed material usually selected for this duty. Metallurgical examination under an optical microscope (photos are unfortunately unavailable) showed twinned grains that are normal for annealed nickel. However, intergranular penetration of caustic was observed up to a depth of 2 to 3 grains. No specific metallurgical deterioration was observed at the heavily corroded area. Some scattered, round graphite particles were found in the matrix.

The diagnosis

From the above analysis, we concluded that intergranular stress-corrosion cracking, coupled with accelerated corrosion by overheated caustic, might have caused the failure. The presence of stress, caustic soda and high temperature is necessary for such a situation to occur in localized areas.

A possible source of stress is the thermal cycles during startup and shutdown, or process interruptions. Operators must ensure uniform and continuous flow of a thin layer of the liquid along the wall of the tube in a falling film evaporator. If there are any restrictions, the flow will tend to become localized, will stop flowing after some time, and will end as a teardrop.

The abrupt ending of the bottommost grooves indicated that this had happened. A stationary band of caustic got overheated at the bottom of the tube where the heat transfer salt is at its highest temperature. This led to accelerated and localized corrosion and subsequent failure. We know from other tests that the presence of small amounts of chlorate also accelerates attack on nickel. Unfortunately, chlorates are a characteristic of a membrane-cell chlorine-alkali plant. Figure 4 (which, unfortunately, does not include data on Nickel 201) shows that a five-fold increase in corrosion occurs in 50% caustic at 150°C, and the effect will be stronger at higher concentrations and temperatures.

Remedial measures

The operators were taught that better procedures make a difference.

1. Ensure an unbroken film of caustic solution on the inside surface of the tube. Maintain proper distribution of feed, and vertical alignment of tubes.

2. Maintain strict control of chlorates in the feed.

3. As far as possible, take care to see that the tubes are operated without subjecting them to the stress of frequent thermal cycles.

The flaker drum

No one wants to manually break up solid NaOH for packaging. For this reason, the flaking machine was invented. Central to the machine is a rotating, water-cooled cylinder, the flaker drum.

The one that corroded operates as follows: The cylinder is dipped 10–20 mm into a dipping vat, which is constantly fed by melted caustic soda. A film of 0.8 to 1.3 mm forms on the surface of the cooling cylinder and crystallizes. It is subsequently cooled to 55°C during rotation of the cylinder and then scraped off. This flaker operates at 600°C on the caustic side, and at 45°C on the water side.

In this plant, the cylindrical drum, of 2,260-mm dia. and 1,800-mm length, is made of 18-mm-thick nickel plate with carbon steel side covers (Figure 5). There are two equidistant internal retainer rings (stiffeners) welded to the drum and each has parallel grooves 3 to 4 mm deep on the outer surface. The material of construction is low-carbon nickel conforming to DIN 17751 Gr 2.4066.

The drum developed a circumfrential crack 600-mm long in one of the grooves within six months of commissioning. To arrest further extension of the crack, through-holes were drilled at the end of the grooves, and then the welder cut a 10-mm-deep V-groove. The entire crack was repaired by welding with nickel filler rod.

Two months later the crack extended to the two adjacent grooves and reached a total length of 2,300 mm. The location of the crack was exactly on the outside wall of the internally provided stiffeners. After another welding repair, as above, the plant was returned to service. Shortly, we detected a similar crack, this one in the groove adjacent to the cover plate opposite to the drive end.

The diagnosis

The cracks have occurred at the outside wall of the retainer-rings locations. Considering the short span of six months in service during which these cracks appeared, it is evident that these are not perforating cracks due to corrosion. A corrosion rate of 100 to 200 mm/yr for nickel in fused caustic is required to develop such cracks.

A logical interpretation is that the cracks originated from the internal surface and then propagated outward. This is why the later cracks could not be detected by dye-penetrant checks. As the internal fluid is deaerated

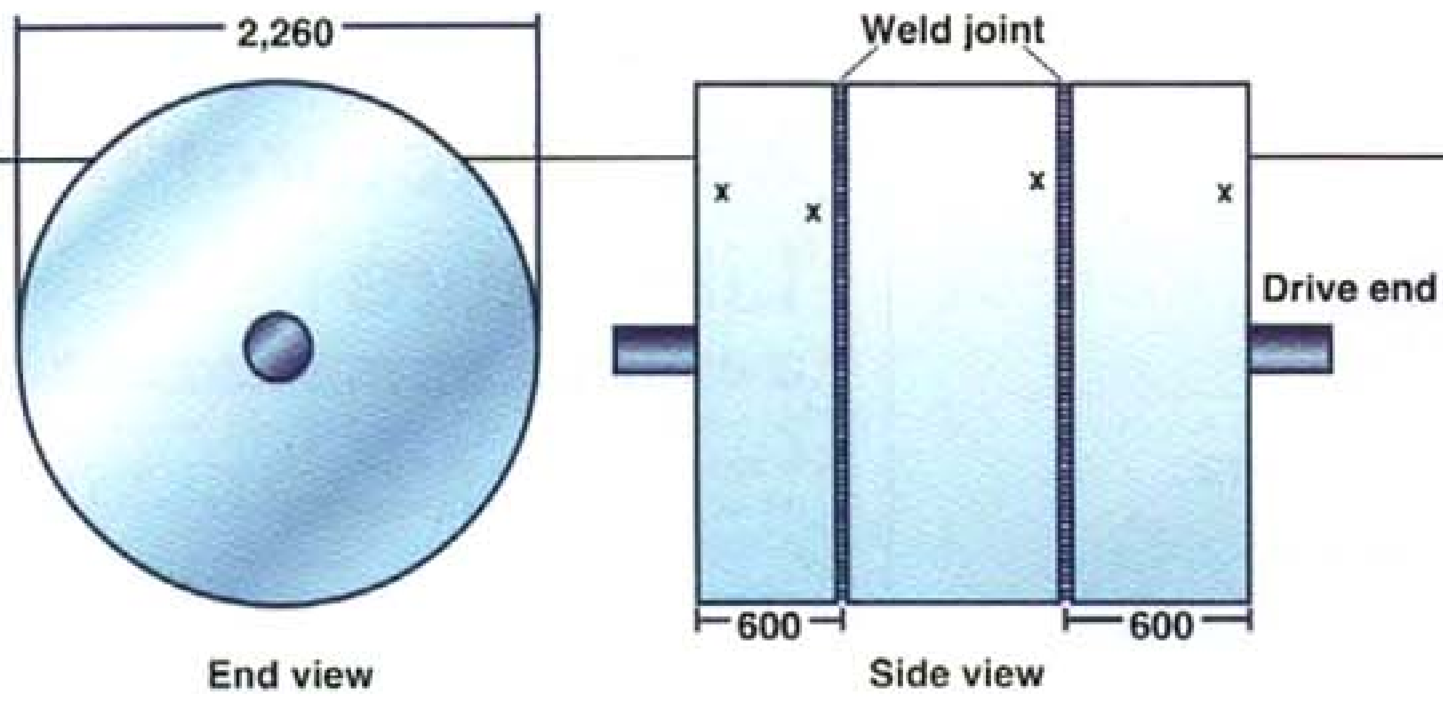

FIGURE 5. Failure occurred in the grooves of the flaker drum. The thickness at four marked points was nominally at the specified 15 mm (dimensions above are in mm)

water, a failure emanating from inside cannot be due to corrosion.

The only plausible mechanism left is related to stress. We concluded that the presence of leftover stress after metalworking and fabrication, due to inadequate stress relief, initiated the cracking process. The wide temperature difference between the inner and outer surface of the drum wall, and the cyclic heating and cooling, produced thermal stresses. In addition, the side plates and the stiffeners put a bending restraint on the drum wall.

Under such a situation, the cold face will be under tension and the hot one will be under compression. The stress level may not be sufficient to initiate any cracks in the plate, but the weld-points of the stiffener rings and the end plates could act as stress raisers. Under changing stress levels, due to cyclic heating and cooling, the equipment can end up cracking from thermal fatigue. The residual stress after weld repairs of the cracks also added to the overall stress level. Subsequent development of cracks near the side-plate joint reinforces this argument.

Remedial measures

On prolonged heating above 315°C, carbon precipitates at grain boundaries as graphite and embrittles the metal. Under the influence of stress, grain boundary cracking occurs. Nickel 201 would have been a better choice in this case. Following the investigation, the plant replaced the flaker drum with one made of Nickel 201. ■

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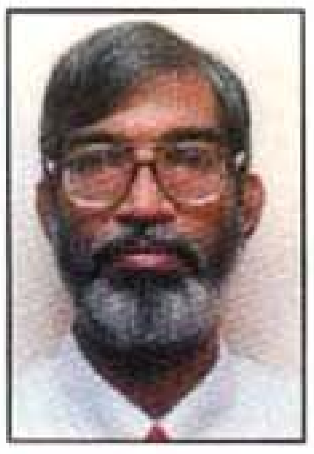
Reference:

1. Shillmoller, C. M., "Alloy Selection for Caustic Soda Service," NiDI Technical Series No 10019, Nickel Development Institute, Toronto, Ont., Canada, 1988.

Author



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