

Corrosion and protection of kraft digesters

ANGELA WENSLEY

AS KRAFT PULPING CONTINUES to evolve, so do the corrosion problems in continuous and batch digesters. Continuous digesters, constructed from carbon steel, were originally believed to be relatively free of corrosion problems. For two decades, corrosion was of relatively little concern in continuous digesters, and visual inspection was considered sufficient to ensure the integrity of these vessels.

The wake-up call for the pulp and paper industry occurred in 1980, when the Pine Hill digester failed catastrophically due to stress corrosion cracking (SCC). This resulted in greatly increased attention to inspection, with wet fluorescent magnetic particle testing becoming the normal method for detecting SCC.

Another decade passed before yet another serious corrosion problem manifested in continuous digesters, in the form of rapid thinning of the carbon steel digester shell in the extraction and wash zones. Although thinning had previously been experienced in a number of continuous digesters, the increased number of reports of thinning in the 1990s appears to be related to the adoption of new pulping technologies (MCC, EMCC, ITC, low solids cooking, etc.) or practices which raised the temperature in the lower part of the digester (1).

Various corrosion preventative technologies have been adopted for continuous digesters, including anodic protection, thermal spray coating, and stainless weld overlay. Each continuous digester is unique in its protection requirements; what

works in one digester may not necessarily be successful in another.

In carbon steel batch digesters, corrosion thinning has always been recognized as a problem. Various protective measures, such as stainless weld overlay or thermal spray coating were developed to protect these vessels from corrosion. Inspection of batch digesters has been increased in scope since the 1994 failure of a weld overlaid batch digester in Panama City, FL.

It is clear that we have much to learn about why digesters experience the types of corrosion that they do, and why the various kinds of protection sometimes succeed and sometimes fail. Corrosion monitoring with corrosion potential and corrosion rate monitoring probes is helping solve these mysteries. Also, laboratory corrosion testing in autoclaves filled with actual digester liquors is clarifying the corrosion behavior of materials of construction (such as carbon steel and stainless steel) and the effectiveness of anodic protection, weld overlay, and thermal spray coatings.

This paper summarizes the major corrosion problems in kraft digesters, the various protection alternatives, and the use of corrosion monitoring and autoclave corrosion testing to solve the mysteries of corrosion behavior in digester liquors.

STRESS CORROSION CRACKING

The 1980 failure of the Pine Hill digester was found to be due to a form of SCC called caustic SCC (2). The prerequisites for SCC are:

ABSTRACT

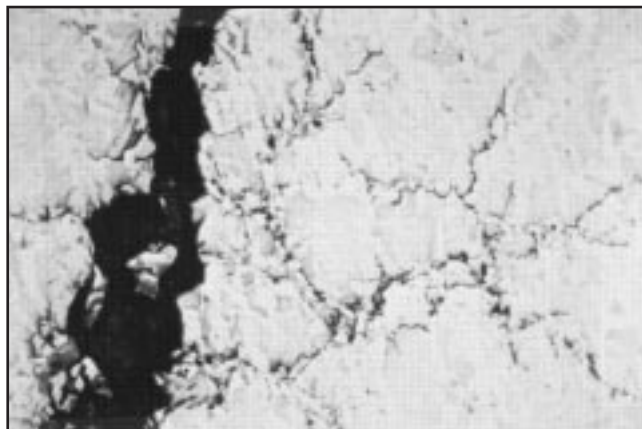
The mechanisms of corrosion and cracking in kraft digesters are reviewed, including stress corrosion cracking, general corrosion, pitting, preferential weld attack, and intergranular corrosion. Also discussed are the various corrosion protection measures, including corrosion-resisting weld overlay, thermal spray coating, and anodic protection. In situ corrosion monitoring by coupons, corrosion potential probes, and linear polarization probes is described, as well as laboratory autoclave testing in digester extraction liquors.

Application:

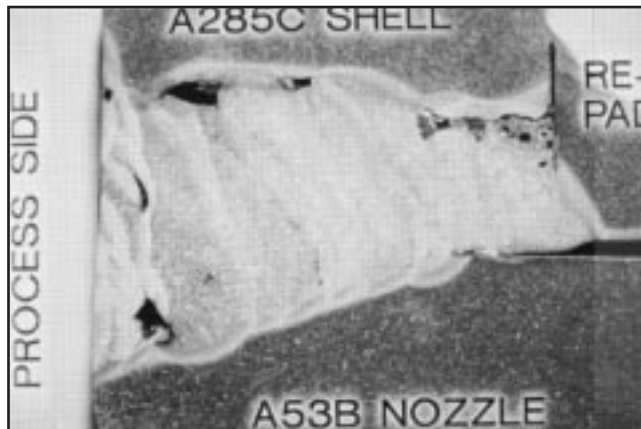
Digester owner/operators will be better informed as to the kinds of corrosion testing required to ensure selection of the best methods of corrosion protection for their digesters.

- A susceptible metal (carbon steel)
- An environment with an agent known to cause SCC (caustic)
- Tensile stress (residual tensile stress in non-stress relieved welds)
- A corrosion potential in the range where SCC is known to occur (between the active and passive corrosion behavior zones).

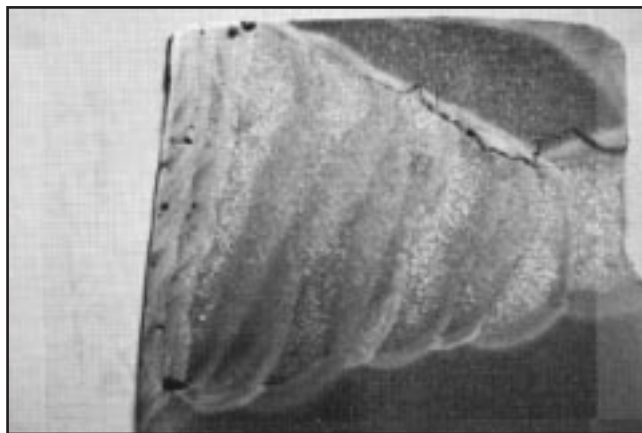
A change to the ASME Boiler and Pressure Vessel Code in the mid-1960s permitted only partial stress relief to be carried out after construction of the digester. Where the vessel wall thickness was less than 1 1/4 in. (32 mm), post weld heat treatment (PWHT, equivalent to stress for the purposes of this paper) was not mandatory. As continuous pulping gained favor in the industry, numerous partially stress relieved digesters were constructed over the next decade or so, including the Pine Hill digester.



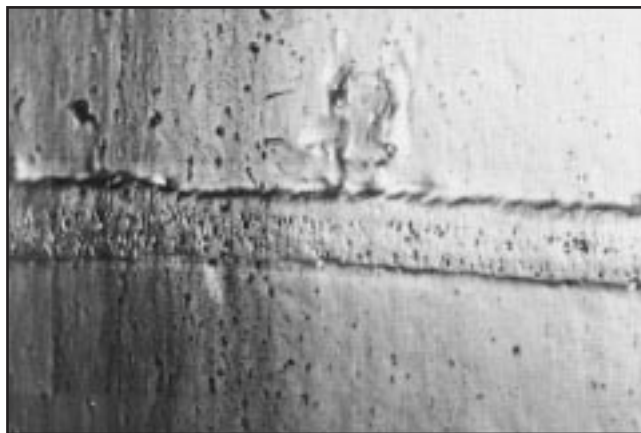
1. Caustic stress corrosion cracking in a plate from a continuous digester



2. Weld defects in a cooking nozzle weld



3. Lamellar tearing in a cooking nozzle weld



4. Bright, shiny appearance of active corrosion in a continuous digester

There is much evidence which confirms that fully post weld heat treated digesters resist SCC (3). There are a few exceptions, which suggest that better control of PWHT may be required to ensure true stress relief. If weld repairs are performed subsequent to PWHT, those welds will be susceptible to SCC unless they, in turn, are stress relieved. Local stress relief has not been as effective as the original vessel PWHT in conferring SCC resistance; perhaps half of all locally stress relieved weld repairs have experienced re-cracking.

A TAPPI JOURNAL survey published in 1989 revealed that nearly

75% of all continuous digesters had cracking (4). Interestingly, the cracking was only confirmed to be SCC in a relative handful of cases; otherwise, the cracking was often presumed to be SCC. It is my opinion that much of the cracking observed in digesters is actually from original construction, such as cold (hydrogen) cracking, lamellar tearing, or brittle cracking. Progressive corrosion thinning or grinding for inspection may reveal such cracking years after the vessel went into service.

Misidentification of cold cracking as SCC may lead to misguided repairs; SCC preventive measures may have been adopted for vessels

which never had SCC. Digester owner/operators would benefit from a metallographic examination of samples (e.g., boat or core samples) removed from locations where cracking is found. Figure 1 shows the microstructure of a carbon steel digester plate with caustic SCC; the crack path prefers to follow ferrite-pearlite or ferrite-ferrite grain boundaries. Figures 2 and 3 are cross section views of cooking nozzle welds which have numerous defects, including lamellar tearing, but no SCC.

SCC has been a painful reality in many continuous digesters. Of the available preventive measures,



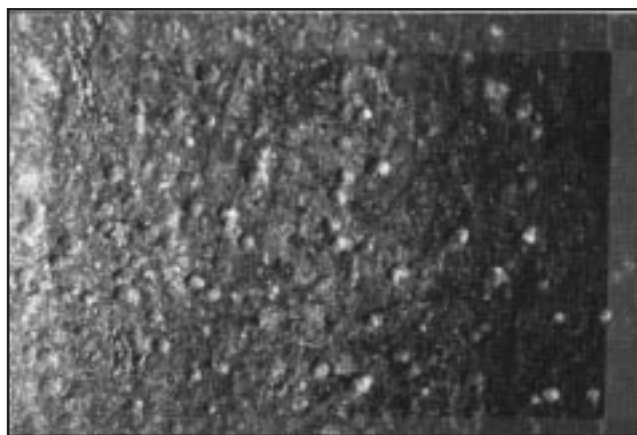
5. Nonuniform thinning in the wash zone of a continuous digester



6. "Spikes" on the wall of a continuous digester, between the cooking and extraction screens



7. Erosion-corrosion behind an extraction screen



8. Hemispherical pitting believed due to muriatic acid cleaning

anodic protection has probably had the most success in mitigating SCC. It is a relatively easy task to raise the corrosion potential of a carbon steel digester shell outside the range of SCC susceptibility. *In situ* corrosion monitoring may be very useful in determining whether a particular zone in the digester is in the SCC range. The SCC range may be determined by corrosion testing in autoclaves containing actual digester liquors.

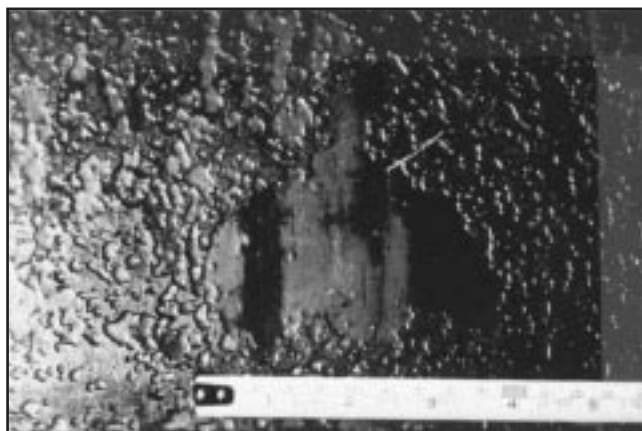
CORROSION THINNING

Rapid digester shell thinning has occurred at corrosion rates exceeding 200 mpy (mpy = mils per year,

200 mpy = 5 mm/y) (5). The TAPPI Task Group on Continuous Digester Thinning defined rapid thinning as a corrosion rate exceeding 20 mpy (0.5 mm/y). Unlike SCC, which tends to occur in the upper parts of digesters (impregnation zone), rapid wall thinning tends to occur toward the bottom of the digester (extraction and wash zones). The consequence of thinning is the eventual consumption of the corrosion allowance (typically 1/4 in., or 6 mm), which has led to de-rating of vessels.

The corrosion morphologies of digester thinning appear to be as varied as the numbers of digesters. The

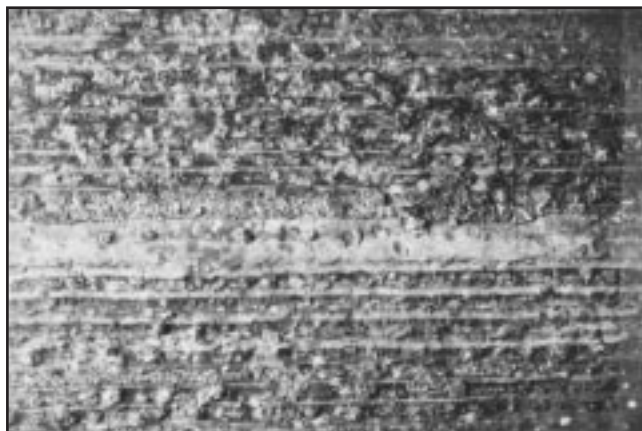
digester wall may experience smooth, uniform reduction in thickness. Sometimes, the corroded area is found to be bright and shiny on inspection (Fig. 4). Alternatively, the wall may experience non-uniform attack. Pitting corrosion is discussed in the following section. Many vessels exhibit a "corrugated" or "rippled" surface morphology, with the vertical corrugations angled slightly in the direction of rotation of the outlet device (Fig. 5). There are also bizarre forms of corrosion morphology, such as "spikes" or uncorroded metal remaining after the surrounding metal has been corroded away (Fig. 6). Behind screens the digester



9. Severe, sharp-edged pitting in an EMCC digester



10. Preferential attack of a circumference seam weld



11. Corrosion thinning of FCAW carbon steel buildup



12. Anodic protection with centrally-mounted cathodes

shell may corrode at an even faster rate, and exhibit features of erosion-corrosion (Fig. 7).

Rapid thinning is the result of active corrosion, which occurs at relatively low values of corrosion potential. Corrosion potential monitoring is extremely useful in assessing whether a particular zone in a digester is experiencing active potential (high corrosion rates) or passive potential (higher values of corrosion potential, which are characterized by low corrosion rates). Again, laboratory autoclave testing is useful in establishing the potential ranges for active and passive behavior.

The corrosion potential in a digester usually varies with time, as

the result of changes in temperature, liquor concentration, wood species, and operating parameters such as dilution factor. Excursions from passive to active behavior may be frequent, or the vessel may exhibit relatively constant active (undesirable) or passive (desirable) corrosion potentials. Knowledge of this is valuable in assessing which corrosion preventive measure to employ. Anodic protection may not be completely effective in mitigating thinning in vessels where the corrosion potential tends to fluctuate widely.

PITTING CORROSION

Pitting corrosion of carbon steel digester shells may occur by two different mechanisms. Muriatic acid

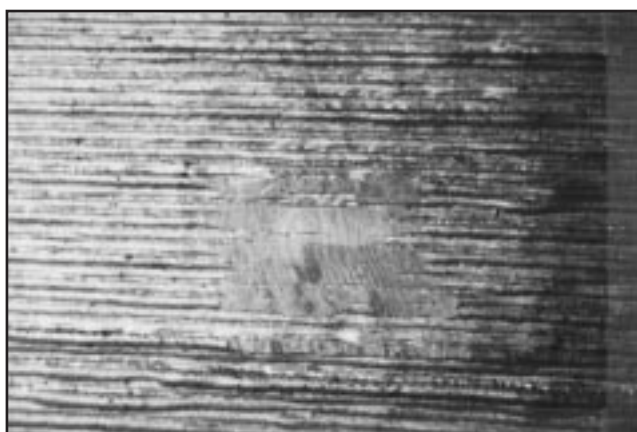
cleaning at an excessively high temperature, or with poor circulation, or with inadequate inhibitor concentration, may produce pitting. Such pits are typically rounded and hemispherical in shape (Fig. 8). Repeated acid cleaning damage may result in rougher appearance.

Pitting corrosion can also occur due to the digester liquor (6). Such pits are typically irregular in shape, and may tend to undercut the adjacent metal. Pitting damage is relatively difficult to repair, although in some cases of extensive pitting resulting from EMCC operation, the pits tend to coalesce over time to produce a relatively smooth surface (Figure 9).

Pitted surfaces present a problem



13. Anodic protection with wall-mounted cathodes



14. Stainless steel GMAW overlay in the wash zone of a continuous digester



15. SCC in the carbon steel at the edge of the stainless steel weld overlay band in the impregnation zone of a continuous digester



16. HVOF thermal spray being applied by a robot arm in the wash zone of a continuous digester

for protection of the digester by such methods as stainless weld overlay or thermal spray coating. Surface preparation may involve grinding or, in cases of severe pitting, arc gouging. Anodic protection, on the other hand, requires no surface preparation, and may be the only alternative where pitting is extensive and deep.

PREFERENTIAL WELD CORROSION
Welds in continuous digesters, in particular the circumferential and vertical seam welds, often experience preferential corrosion attack compared with the surrounding carbon steel plate (Fig. 10). There are two

reasons for this: the microstructure of welds is inferior (being more like a casting, and coarser grained than the plate metal, which typically has a finer-grained banded structure from hot rolling); also, welds may contain significantly more silicon than the base metal.

High silicon content has been correlated with higher corrosion rates for steels in kraft liquors; welds made with E7018 filler (the most common welding electrode employed in digester repairs) can have considerably more silicon than the plate metal.

In the early days, North American

digesters were made with SA285-Grade C carbon steel, specially modified to have low silicon content. Seam welds were also capped using low silicon welding consumables. Modern carbon steel digesters are made from SA516-Grade 70 carbon steel, which has an appreciably higher silicon content than the modified SA285-Grade C.

High silicon welds not capped with low silicon weld metal will tend to corrode relatively rapidly. Slow corrosion of a low silicon weld cap, or progressive grinding for digester weld inspection, may expose the underlying high silicon

content weld metal to the digester environment, with the result that the welds "suddenly" seem to experience rapid preferential attack.

Where weld corrosion has progressed below the corrosion allowance, the welds must be restored. The use of high preheat (300°F, or 150°C), temper bead welding, and post-heat (500°F, or 260°C) may preclude the necessity of PWHT where otherwise it might be required. The almost universal use of a high silicon content weld filler such as E7018 for such repairs may result in the repair still being susceptible to preferential thinning, unless corrosion preventive measures are employed.

Banding of repaired weld seams with stainless steel weld overlay is not recommended, as the carbon steel at the overlay band edges is susceptible to SCC. Thermal spray coating may be an effective way to protect weld seams (a 12-in., or 30-cm, wide band would be appropriate). Anodic protection has also been effective in protecting repaired weld seams, particularly from SCC.

CARBON STEEL WELD BUILDUP

Carbon steel weld buildup has been done in many digesters which have experienced thinning to near or below the corrosion allowance. Such buildup can at best be considered a stop-gap measure, as it will continue to experience rapid thinning at even a more rapid rate than did the digester shell (Fig. 11).

An alternative to carbon steel weld build-up, even when corrosion has proceeded below the corrosion allowance, may be application of stainless steel weld overlay. The ASME Boiler and Pressure Vessel Code permits credit to be given for some or all of the overlay thickness in the design thickness calculation. The weld procedure must be qualified as a groove weld, rather than an overlay, but this is a technicality. This alternative may

avoid the unnecessary step of first applying a layer of carbon steel weld buildup before overlaying with stainless steel. Anodic protection may only be partly successful in protecting carbon steel weld buildup applied to restore wall thickness in the wash zone.

ANODIC PROTECTION

As a corrosion preventive measure, anodic protection has been very successful against SCC (7–9). Theoretically, anodic protection should also stop corrosion thinning, and it has been successful in this regard in many vessels; however, there have also been cases where anodic protection has not been able to reduce corrosion rates in the lower zones of digesters to acceptably low values.

Anodic protection has been successfully employed in combination with stainless steel overlay, to protect the overlay band edges from SCC. It may also be effective in preventing corrosion at pinholes or other defects in the overlay.

There are two philosophies regarding anodic protection of digesters. One employs central cathodes (Fig. 12); the other, wall-mounted cathodes (Fig. 13). The range of potentials where anodic protection can provide effective protection against corrosion thinning is quite narrow, perhaps as low as 50 mV (at lower corrosion potentials the digester experiences active corrosion at a high rate; at higher potentials the digester experiences transpassive corrosion, also at a high rate). The inherent instability of the reference electrodes (stainless steel, silver, or molybdenum) used for controlling anodic protection systems may be of this magnitude in the lower zones of continuous digesters.

The anodic protection potential range may also vary from digester to digester, as a result of differences in liquor composition. Autoclave testing in actual digester liquors is a very

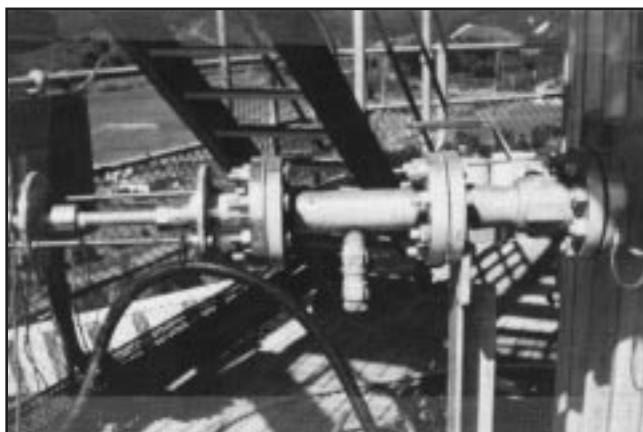
good method for determining the anodic protection potential range (superior to the polarization curve method). Such testing can also be used to establish the most effective control potential for an anodic protection system.

STAINLESS WELD OVERLAY

Stainless steel weld overlay is the application of a corrosion resisting barrier by welding (10–12). Austenitic stainless steels of minimum composition 18% Cr, 8% Ni predominate for overlay application, although nickel-base alloys have also been extensively used. Welding processes employed include submerged arc (SAW), gas metal arc (GMAW), shielded metal arc (SMAW), and flux-cored arc (FCAW). A TAPPI Technical Information Paper exists describing how to ensure the overlay application is sound.

Stainless steel weld overlay has been applied in batch digesters for at least 40 years to protect the carbon steel shell from corrosion thinning. Although many batch digesters experience severe corrosion only in particular zones, the trend has been to weld overlay them completely. This has been done either all at once (usually it is possible to take a batch digester off line for the required time), or in stages over several years. Many batch digesters have been re-overlaid after about 20 years, because the original overlay has corroded or worn.

In my experience, stainless steel weld overlay which meets the minimum compositional requirements outlined in the TAPPI TIP resists corrosion in most digester liquors. Much of the corrosion observed in old overlay may be due to inadequate alloy content. I also believe that higher minimum alloy contents may be required in particularly aggressive digester environments. Figure 14 shows a 22% Cr, 12% Ni GMAW overlay which has resisted corrosion in a digester with an extremely aggres-



17. A corrosion probe installation in a continuous digester

sive liquor.

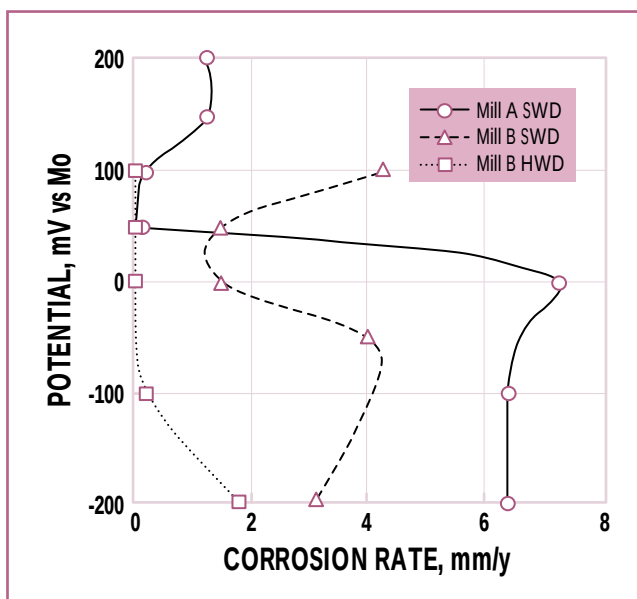
In continuous digesters, stainless weld overlay bands were applied over seam welds to protect them against SCC. In many digesters, this resulted in serious SCC in the carbon steel at the overlay band edges (Fig. 15). Nickel-base weld overlay bands appear to be particularly prone to edge SCC. Overlay banding is no longer recommended for welds in the impregnation zone; bands lower in the digester should be inspected carefully for cracking. On the other hand, application of stainless weld overlay to protect large surface areas in the lower part of the vessel from corrosion thinning has been very successful.

Autoclave testing in liquor from the digester to be overlaid has confirmed that highly alloyed GMAW stainless steel weld overlays are highly resistant to corrosion (13). Alloy 625 nickel-base GMAW overlay, while still having very good corrosion resistance, experiences transpassive dissolution at high corrosion potentials.

THERMAL SPRAY

Thermal spray coatings have been applied for both SCC and corrosion protection in both batch and continuous digesters. Most success has been obtained with thermal spray applied by the arc spray process, and the HVOF (high velocity oxygen fuel process). Arc spray is a low velocity process which requires application of at least 80 mils (2 mm) thickness to overcome porosity problems; HVOF is a high velocity process which produces less porous coatings and is typically applied at 30 mils (0.75 mm) thickness. Figure 16 shows automatic application of HVOF thermal spray using a robot arm. Plasma spray (intermediate velocity) coatings have been employed, but these have tended to fail.

The main advantage of thermal spray over weld overlay is that it does not produce a SCC-susceptible heat affected zone in the carbon steel substrate onto which it is applied. On the other hand, its bond to the substrate is



18. Corrosion polarization curves for SA516-Grade 70 carbon steel obtained by autoclave corrosion testing in actual digester liquors

mechanical, not a metallurgical one. Surface preparation requirements are stringent to ensure good bonding. Autoclave testing of HVOF thermal spray coatings in actual digester liquors has confirmed that these coatings are not fully penetrated by the liquor after 10 days exposure at 170°C (13).

CORROSION MONITORING

Digester corrosion can be monitored with corrosion coupons mounted inside the vessel [(e.g., on the screens, or screwed onto the vessel wall as in the case of thin layer activation (TLA) coupons (14)] or by means of corrosion probes installed in one or more zones of the vessel. Retractable corrosion probes (Fig. 17) offer the possibility of corrosion potential monitoring, instantaneous corrosion rate monitoring, or corrosion coupon exposure at any time while the vessel is operating. The corrosion data provided may be useful in scheduling work to be done in the upcoming shutdown.

Corrosion potential monitoring reveals the corrosion behavior of the vessel (active, passive, transpassive—or fluctuating between these states). When a corrosion polarization curve (discussed below) is available, corrosion potential measurements can also be used to estimate the corrosion rate at the zone in the digester where the probe is located. None of the available reference electrodes (stainless steel, silver, or molybdenum) is stable, and the reference electrode potential itself tends to fluctuate with differences in liquor composition or tempera-

KEYWORDS

Alkaline digesters, anodic protection, coatings, corrosion, corrosion mechanisms, corrosion prevention, corrosion tests, cracks, digesters, joining, kraft digesters, materials testing, metal joining, overlays, pitting, protective coatings, reaction mechanisms, stress corrosion, test methods, welding.

ture. Nonetheless, corrosion potential monitoring is an invaluable tool for assessing digester condition.

Instantaneous corrosion rate monitoring can be accomplished using the linear polarization resistance (LPR) technique. Such monitoring may give helpful information on the effects of process changes or upsets on corrosion of the digester. A typical LPR monitoring probe has two electrodes of digester steel (e.g., SA516-Grade 70). These also serve as weight loss coupons. The average weight loss corrosion rate can be compared with the integrated area under the corrosion rate versus time curve to calibrate the LPR instrument.

Corrosion probes can also be employed to insert weight loss corrosion coupons. These may be of digester steel, or of candidate repair materials (coupons of different carbon steel weld metals, stainless overlay, or thermal spray). Such coupon monitoring is also very useful in assessing corrosion during acid cleaning, batch cooking on startup, or trials of alternative cooking technologies.

AUTOCLAVE CORROSION TESTING
Corrosion testing can also be performed outside the digester, in autoclaves containing actual digester liquors (13). Specimens of digester steel, or other candidate materials can be exposed in the autoclave. Autoclave testing permits testing in samples of the same digester liquor,

the temperature to be held at a constant value, and the corrosion potential to be controlled at a constant potential. This eliminates much of the variability inherent with *in situ* corrosion testing in digesters.

The most useful product of autoclave corrosion testing is the "corrosion polarization curve," which describes the corrosion rate versus corrosion potential behavior of a particular material of construction (e.g., SA516-Grade 70 carbon steel). Figure 18 shows the corrosion polarization curves for SA 516-Grade 70 carbon steel in three different digester liquors.

CONCLUSIONS

1. Corrosion mechanisms affecting digesters constructed from carbon steel include stress corrosion cracking, general corrosion thinning, pitting corrosion, preferential attack of welds.
2. Impregnation vessels and the impregnation zones of continuous digesters with non-stress relieved welds are at highest risk of stress corrosion cracking.
3. High temperature ($\geq 160^\circ\text{F}$) muriatic acid cleaning can result in severe pitting corrosion of the digester shell.
4. Anodic protection has been highly successful in stopping stress corrosion cracking in digesters; it can also reduce the rates of general corrosion thinning.
5. A sound (porosity and crack free) corrosion resistant weld overlay completely protects the digester shell from corrosion, although the heat affected zones at overlay edges may be susceptible to stress corrosion cracking in the impregnation zone.
6. Thermal spray coatings can provide protection of the digester shell without introducing heat affected zones; however, liquor may completely penetrate the

coatings if they are porous.

7. Laboratory autoclave testing is a useful method for assessing the corrosivity of digester liquors and the optimum method of corrosion protection. TJ

Wensley is pulp and paper corrosion specialist, Bacon Donaldson Consulting Engineers, 12271 Horseshoe Way, Richmond, BC, Canada V7A 4V4.

Received for review June 28, 1995.

Accepted May 1, 1996.

Presented at the TAPPI 1995 Engineering Conference.

LITERATURE CITED

1. Kiessling, L., *Pulp and Paper Industry Corrosion Problems* (8): 12(1995).
2. Bennett, D. C., *Pulp and Paper Industry Corrosion Problems* (4): 2(1984).
3. Singbeil, D. and Garner, A., *Materials Performance* 34(10): 9(1985).
4. Wensley, A., *Tappi J.* 72 (8): 211(1989).
5. Wensley, A., *TAPPI 1993 Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 71.
6. Maspers, E., *Pulp and Paper Industry Corrosion Problems* (8): 1(1995).
7. Munro, J. I., *TAPPI 1983 Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 181.
8. Kiessling, L., *TAPPI 1989 Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 659.
9. Singbeil, D., *Pulp and Paper Industry Corrosion Problems* (6): 109(1989).
10. Eriksson, T., Börjesson, E., and Johansson, L., *Pulp and Paper Industry Corrosion Problems* (8): 58(1995).
11. Workman, R., *TAPPI 1995 Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 173.
12. Hulsizer, P., *TAPPI 1995 Engineering Conference Proceedings*, TAPPI PRESS, Atlanta, p. 193.
13. Wensley, A., *Pulp and Paper Industry Corrosion Problems* (8): 26(1995).
14. Boulton, L., Wallace, G., Barry, B. J., et al., *Pulp and Paper Industry Corrosion Problems* (6): 67(1989).