Influence of cooking conditions on continuous digester corrosion in a Brazilian pulp mill

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ABSTRACT: Digester corrosion is costly because of repairs, replacement of components and upgrade of materials, and losses in connection with unplanned outages. Risks to life and property also are significant, especially if catastrophic failure of pressurized equipment occurs. From the 1980s to present, corrosion problems in many pulp and paper mills worldwide have been intensifying, some resulting from materials and design aspects of the digesters themselves or later process modifications. The main focus of this study is the corrosive behavior of continuous digesters with modified processes. We discuss actual corrosion cases in two continuous digesters at a pulp mill in Brazil and the protection measures adopted. Results of electrochemical testing, metallurgical analyses, corrosivity testing, and field inspections are discussed. In one case, a carbon steel digester experienced rapid thinning on its top sections, with wall loss of 5 mm over 30 months following a process change. In the second case, also following a process change, a unique, type 316 stainless-clad continuous digester was found to have an altered electrochemical profile, indicating prospective corrosion hazards. This prompted studies and protective measures that are unique for stainless cooking vessels. The risks to carbon or austenitic stainless steel digesters running on modern cooking processes are shown to be significant. The effectiveness of the protective technologies, and their compatibility, was proved, and the need to consider these technologies upon cooking retrofit projects was established.

Application: This paper describes two specific cases of digester corrosion and protection and relevant processes and construction materials. The information may be useful to mills that have switched to newer cooking processes, or plan to do so.

Corrosive conditions exist in most pulp and paper production processes and stages. Conditions within a mill encompass pHs ranging from strongly acidic to highly alkaline. The industry incurs the high cost of repair, unforeseen downtime, and material upgrade requirements. Accidents also happen. Many process changes have occurred in recent years, intensifying existing corrosion problems. These ongoing changes primarily result from the search for improved production efficiency and reduced environmental impacts.

Continuous digesters were once considered relatively free of corrosion problems. Since their introduction on an industrial scale in the late 1950s, and over the following two decades, continuous digester corrosion was not a major concern at the mills, with rare exceptions where particularly corrosive wood species were pulped. Continuous digesters were then usually built out of carbon steel, and complete post-weld heat treatment was not widely practiced. Visual examinations were regarded as sufficient means for inspecting these vessels.

The warning for the pulp and paper industry came in September 1980, when a digester in Pine Hill, AL, USA, catastrophically failed because of stress corrosion cracking (SCC) of an upper shell weld. Many other digesters were found to be cracked after that. One more decade went by until another serious corrosion problem appeared, this time in the form of accelerated shell thinning in the extraction and washing zones. In the 1990s, a growing number of cases of thinning were recorded. These cases were apparently related to the adoption of several modified cooking technologies that presented, as a common feature, higher temperatures at the lower zones of the digester.

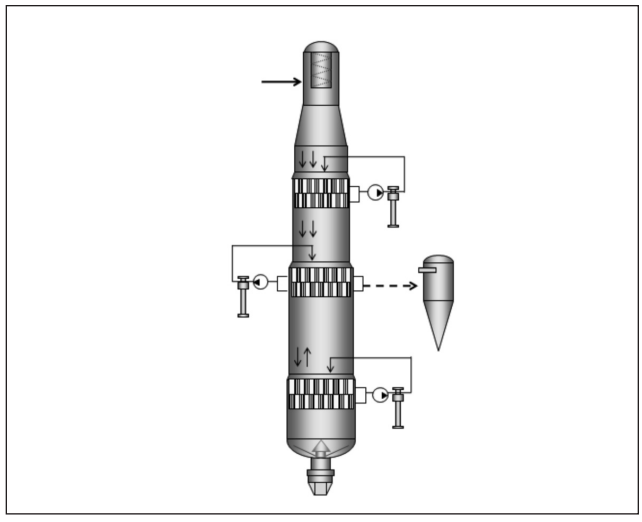
It became clear that much remains to be learned about corrosion in continuous digesters. Each digester has a unique combination of corrosion conditions, requiring correspondingly different protection approaches. Several technologies came into use to protect existing digesters, including anodic protection, thermal spray coating, and stainless steel weld overlays [1].

From this perspective, we set the following objectives for our analysis: 1) to verify the corrosive behavior of continuous digesters, especially with modern cooking processes; and 2) to describe field experiences with digester corrosion, discussing the studies and protective approaches adopted in these cases.

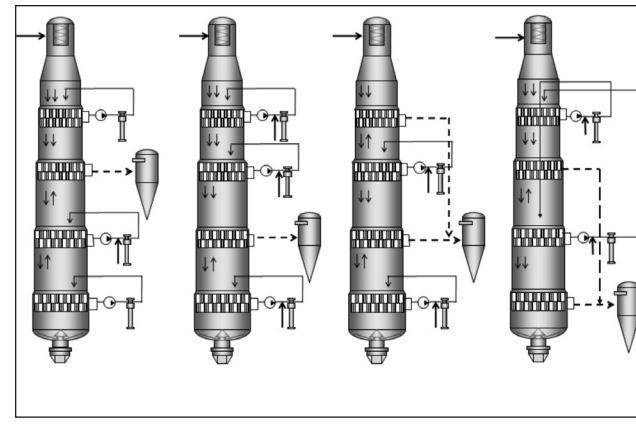
LITERATURE REVIEW

Contemporary kraft cooking

By the early 1980s, most pulping processes used the conventional cooking method, in which all of the cooking chemicals (i.e., white liquor) are added at the beginning of the process (**Fig. 1**). Impregnation and concurrent cooking take place



1. Conventional cooking.



2. Examples of modified cooking arrangements.

above the extraction screens. Under such conditions, hydroxide concentration is greatest at the beginning of the impregnation stage, decreasing gradually while the pulping reactions progress and alkali is depleted.

Modified cooking practices became available in Scandinavia from the late 1970s through the 1980s. The technology evolved from laboratory research at the Swedish Forest Products Research Laboratory (STFI) and the Royal Institute of Technology (KTH), of Stockholm, which investigated the influence of digester operation on pulp properties. Specifically, their research identified methods to attain extended delignification through improved selectivity, so that lignin is selectively removed from wood, while degradation of polysaccharides is minimized, as expressed by pulp viscosity at a given kappa number.

Kamyr AB, now part of Metso, developed modifications to the digesters according to the STFI and KTH specifications, and nearly all systems supplied from 1986 incorporate these features by design, or the possibility to implement them by uncomplicated changes [2].

Modern kraft cooking is presented in a number of types and commercial names. **Figure 2** presents typical arrangements of some contemporary, modified cooking processes [3].

Modified cooking and corrosion

Although the modified cooking processes can achieve their objectives in terms of pulping yield and fiber properties, corrosion problems have been linked to them. The possible reasons for higher corrosivity with these processes include the following:

1. *Higher temperatures* in the lower zones of digesters. Extended or iso-thermal cooking operations typically increase the temperature in the washing zone by about 30°C [1].
2. *Higher sulfidity*, releasing larger amounts of volatile, corrosive compounds during the cook [4]. Sulfide is also an SCC agent [5].
3. *Low lignin contents* in the washing zone as a result of extractions. As lignin could have inhibiting effects, its removal may intensify corrosion [6]. The same concept applies to heartwood extractives removal [3].
4. *Higher production rates* (higher liquor and chip flows) increasing erosion, abrasion and thus corrosion [6]. An increased output from an existing digester also implies higher temperature and/or alkali charge, for a given H factor.
5. *Higher extraction temperatures* [1].
6. *Operating with lower hydroxide residuals* [3].

Types of corrosion in continuous digesters

The types of corrosion that affect continuous digesters built from carbon steel include 1) uniform corrosion, 2) SCC, 3) pitting corrosion, 4) preferential weld corrosion, and 5) erosion-corrosion. For digesters built from stainless steel, corrosion typically is 1) SCC, or 2) intergranular attack (IGA) [1].

Variables influencing continuous digester corrosion

The variables with influence over continuous digester corrosion fall into three groups: 1) the construction materials used, namely carbon steel, austenitic stainless steel, or duplex stainless steel (currently the only well-established variable); 2) process variables such as white liquor composition, wood chip pretreatment, cooking time and temperature, circulation of liquors, etc; and 3) wood species pulped [7].

Materials

For decades, carbon steel (especially A285 Gr C, and A516 Gr 70) was the standard material for construction of continuous digesters. Process modifications intensified corrosion, prompting equipment manufacturers to search for more resistant materials. Use of SA264, 304L stainless steel clad plates became common practice in the 1990s. Among the austenitic grades, type 304L is the industry standard for this application. Type 316L is not commonly used. For new digesters, type 2205 duplex stainless steel is now preferred [8]. Lean duplex, type 2101, also has become an option for new vessels. Corrosion rates for aus-

tenitic stainless steels and duplex steels are very low in comparison with carbon steels, even with modified cooking. Duplex steels are much less susceptible to SCC and erosion [7].

Process variables and liquor composition

In the kraft cooking process, wood chips are cooked in white liquor, which essentially contains sodium hydroxide and sodium sulfide. During the cook, lignin and extractives are dissolved while cellulose fibers are separated. The resulting product is black liquor, consisting of the residual inorganic compounds after pulping, plus numerous extractives and organic compounds produced by lignin fragmentation reactions [4].

The corrosivity of cooking liquors historically has been presented as a function of its inorganic constituents (sodium hydroxide, sodium sulfide, and sodium thiosulfate). It is currently known that no straightforward relationship can be established solely between the inorganic constituents and corrosion rates [7]. Hydroxide, sulfide, and thiosulfate are thought, however, to significantly affect corrosion, whereas sulfate, chloride and carbonate do not have appreciable effect [9].

Influence of inorganic compounds

The influence of inorganic compounds is as follows:

Sodium hydroxide – Hydroxide can influence corrosion detrimentally or favorably. Whereas white liquor with 100 g/L sodium hydroxide can be very corrosive to carbon steel at elevated temperatures, the presence of a certain amount of hydroxide in extraction liquors (e.g., 10-20 g/L) is necessary for maintaining passivation [10].

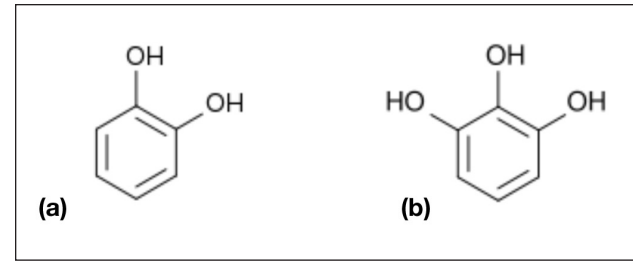
Sodium sulfide – Higher sulfidity means larger amounts of volatile compounds (e.g., methylmercaptan, dimethyl sulfide, and dimethyl disulfide) released during the cook, some of which are corrosive to carbon steel [4]. Sulfide impairs passivation, probably by adsorption on metal surfaces [11]. Wensley [10] states that sulfide can be an SCC agent acting in three ways: as an SCC agent (thus provoking sulfide SCC); by facilitating caustic SCC (where hydroxide is the SCC agent), probably by modifying the nature of passive film; and simply by increasing the effective alkali.

Sodium thiosulfate – White liquors with high thiosulfate concentration (>5 g/L) are corrosive to carbon steel. Thiosulfate raises anodic currents and places potential at the active-passive transition, where SCC and high corrosion rates occur [5]. Passivation is impaired by this species, as observed by Hazlewood [11].

Chlorides – The role of chlorides in alkaline liquor corrosive processes is not considered to be significant [3]. Chlorides are often the SCC agent to austenitic stainless steels, but acting in nonalkaline environments.

Influence of organic compounds

The influence of organic compounds in black liquors, which vary with wood species, is more complex. Within the specific context of this work, the organic compounds in black liquor can be split into two basic groups: the corrosion activators and the corrosion inhibitors [12].



3. Lignin degradation during the cook can produce organic compounds, which can form strong chelate compounds, such as (a) catechol and (b) pyirogalol.

Activating compounds – Among many products resulting from lignin degradation during the cook, small amounts of organic compounds that can form strong chelate compounds, like catechol (1-2 dihydroxybenzen) and pyrogallol (1-2-3 trihydroxybenzen), may be yielded. These substances (**Fig. 3**) are corrosive on alkaline pulping. Catechol could hinder passivation through its ability to form metallic complexes with iron and de-stabilize iron oxides, dissolving carbon steel in alkaline liquors. Pyrogallol increases the corrosion rates to carbon steel by stimulating the sulfide corrosive reaction [7,12].

Inhibiting compounds – Kiessling [6] added lignin (60 g/L) to white liquor from a Swedish mill and conducted potentiostatic tests. The lignin addition decreased the current density by a factor of 3. He concluded that lignin acts as a corrosion inhibitor to carbon steel digesters. Hazlewood [11] assumed that organic extractives such as resins, tannins and fatty acids, which occur at considerable concentration differences in different wood species and ages, could have inhibiting properties. In his experiments, addition of palmitic acid ($C_{16}H_{32}O_2$) reduced the corrosivity of softwood liquor to carbon steel by 15% [3,11]. Tannin has been cited in literature as having the ability to form an organometallic compound with iron in alkaline solutions. Tannates of alkaline metals act as inhibitors and can reduce the corrosivity of black liquors to carbon steel [12].

In summary, the complex solution of organic and inorganic compounds known as black liquor may contain multiple corrosion activators and inhibitors. However, their individualized study may lead to mistaken conclusions because synergistic interactions between the organic compounds, unknown in most cases, may play a significant role in the general corrosivity of liquors [7].

Influence of temperature and other process variables

Temperature influences the free potential, being an operational factor with strong influence on digester corrosion. Corrosion increases exponentially with temperature. Wensley, in her proprietary report AWE3005 written for the mill and cited by Paoliello [3], states that some carbon steel digesters

operating at temperatures above 170°C have corroded at rates of 6 mm/year as verified in the field. The combined effects of elevated sulfidity, high temperatures, and low residual alkali are greater than the individual contributions of each factor. Temperature also influences SCC in terms of severity and velocity [10].

Other process variables, such as dilution factor and production rate, also might influence potentials and corrosion. Intrusion of sand into the process increases abrasion and might worsen corrosion [3].

Influence of the wood species pulped

Extraction liquors from softwood pulping are reportedly more aggressive than those from hardwood. Pinus species, and especially western red-cedar, *Thuja plicata,* and Douglas fir, *Pseudotsuga menziesii*, are cited as corrosive species on pulping [12]. Eucalyptus is not considered as particularly corrosive. Studies regarding the presence and concentration of specifically corrosive compounds produced by eucalyptus pulping have not been identified in literature [3].

Corrosion protection technologies

As noted, marked increases in corrosion rates were observed in continuous digesters, and several technologies against corrosion started to be applied, highlighting anodic protection (AP) systems and stainless steel weld overlays. Thermal spray coating is still another suitable technology, although not as widely used. Carbon steel weld buildup appears a complementary technique for restoration of the original thickness. Stainless steel lining is seldom used at present [1,3].

METHODOLOGY

A number of experimental and observational methods, both in-situ and in laboratory, have been used by the mill to support the discussions and conclusions (**Table I**).

CASE STUDIES

Case studies focusing two continuous digesters of a Brazilian pulp mill are presented here. Given that one carbon steel and one stainless steel digester are in question, these rather distinct circumstances naturally gave rise to correspondingly different technical approaches (**Table II**).

Digester 1

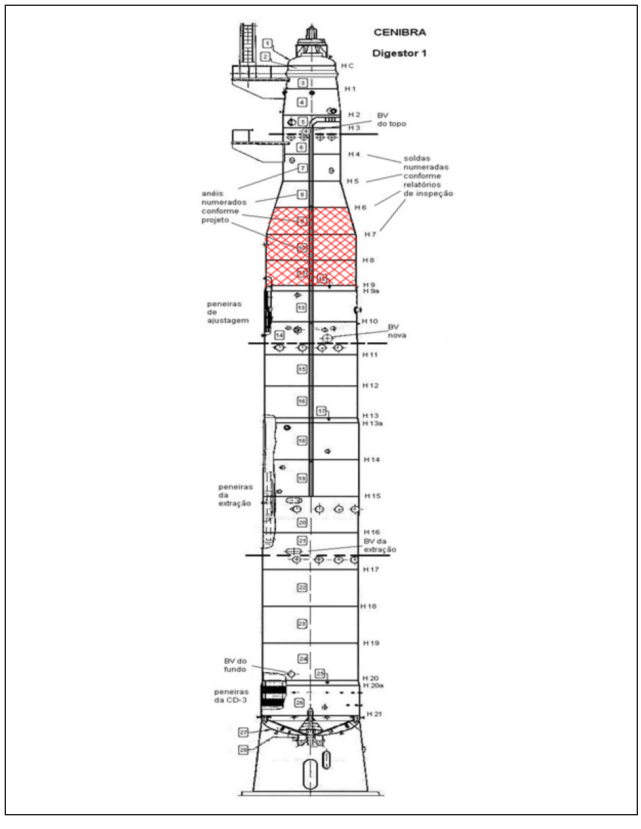
Digester 1 is built in carbon steel, with top sections in stainless steel clad plates. It started operations in 1977 and has always exhibited a favorable service history from its first start-up until 2000, without presenting any significant corrosion

Unit	Technique	Description	Location and Time
Digester 1	Corrosivity tests and black liquor composition analysis to specify the alloy for overlaying.	Determination of liquor corrosivity to candidate alloys. Chemical composition analysis (NaOH, Na_2S, $Na_2S_2O_3$, Na_2SO_4, Na_2CO_3, and NaCl).	At specialized laboratories in Canada, February 2004.
	Visual examinations and thickness surveys.	Measurements using Krautkrämer DM4 ultrasonic thickness gauges and 5 MHz piezoelectric transducers, per ASME V.	In-situ in May 2003, October 2003, April 2004, and September 2004. Annually to 2010.
Digester 2	Continuous measurement of potentials.	Potential measurement against Mo reference electrodes	In-situ from January 2005.
	Measurement of digester passivation potentials using contact electric resistance (CER), a proprietary technique.	Determination of passive film resistivity, under free or fixed potentials, in an autoclave and instrumentation connected to the actual digester environment.	In-situ in March 2005 and April 2007.
	Metallurgical analyses.	Sensitization assessment per ASTM A262 "Practice A – Oxalic Acid Etch Test for Classification of Etch Structures of Austenitic Stainless Steels."	At specialized laboratories in Brazil and Canada, 2007.
	U-bend corrosion tests	Corrosion tests per ASTM G58 – "Standard Practice for Preparation of Stress-Corrosion Test Specimens for Weldments."	At a specialized laboratory in Canada. November 2006, February and August 2007.
	Visual examinations and nondestructive testing.	Dye penetrant testing per ASME V.	In-situ. Annually to 2010.

I. Experimental and observation techniques.

Unit	Material of Construction	Vessel Code	Start-up Year	Principal Modifications and Events
Digester 1	SIS1430 Swedish carbon steel (SIS2352 Swedish stainless steel clad plates in top eight courses)	SPVC	1977	Change from conventional cooking to a proprietary process in November 2000.
				Installation of anodic protection system in May 2003.
				Application of weld overlay to shell courses 9, 10, and 11 in September 2004.
Digester 2	SA 264, 316 ELC clad plates	ASME VIII-I	1995	Change from ITC to a proprietary process (process A) in October 2004.
				New process change, to a proprietary process (process B) in May 2006.
				Installation of corrosion monitoring in January 2005, and of anodic protection in January 2008.
				Replacement of a cracked bottom scraper in 2010.

II. Process changes, modifications, and protective implementations to digesters 1 and 2.



4. Digester 1. The vessel is constituted by shell courses numbered from 1 to 27 from the top. The cross-hatched area indicates the region affected by rapid thinning.

problems in the many periodic inspections conducted. No measurable wall loss occurred within this period. The inspection conducted in August 2002, however, revealed a sudden and intense corrosion thinning process on the shell and blank plates in the upper part of the digester, shell courses (rings) 9, 10, and 11 (**Fig. 4**).

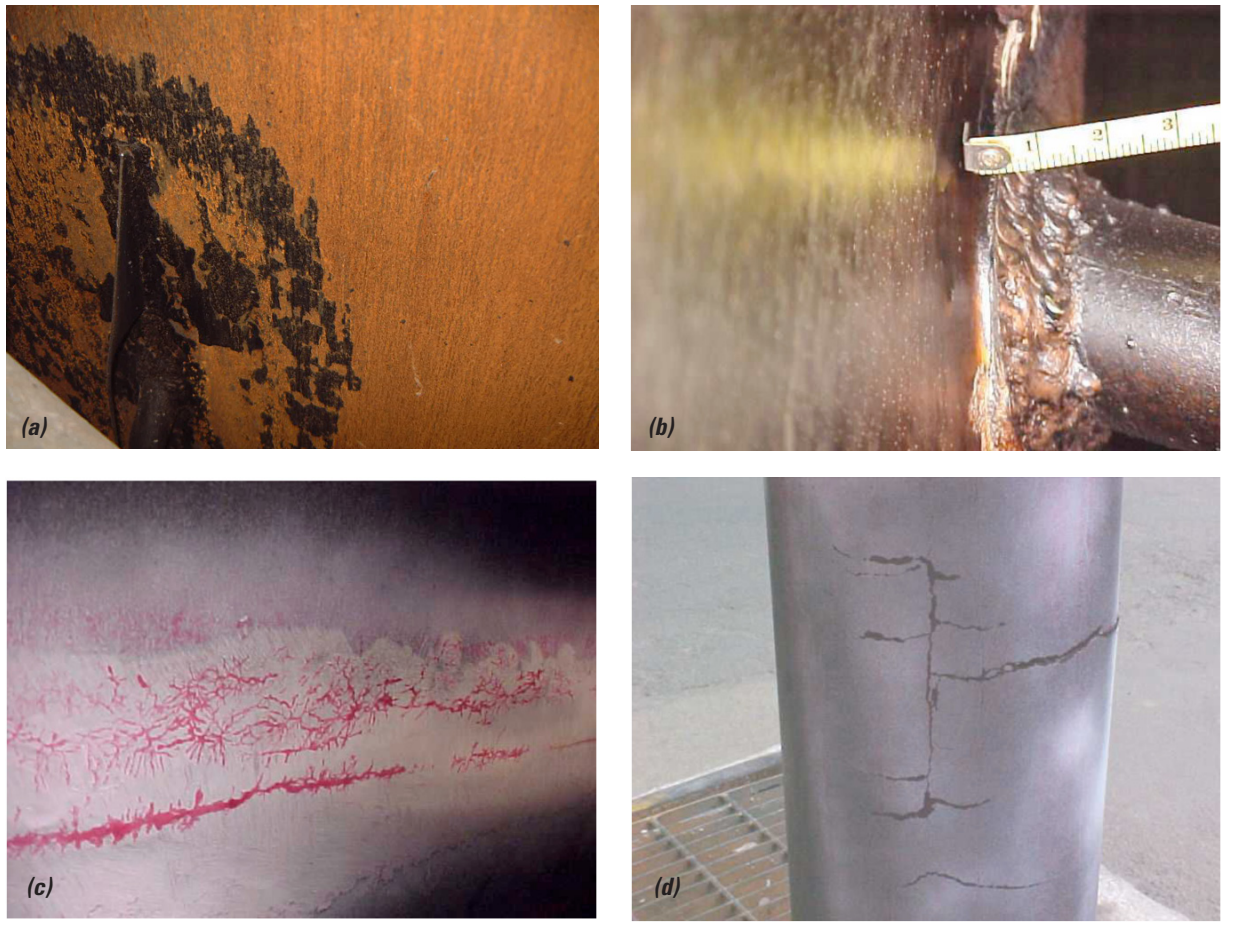
Wall losses of around 4 mm, on average, with respect to the previous inspections, were initially measured. The visual appearance of the metallic surfaces indicated an active widespread corrosion process all over the walls. No pitting or other localized forms of corrosion were seen. From this elevation downwards, the corrosion gradually decreased its intensity.

At a 2 mm/year corrosion rate (verified in three inspections using the average values for each ring per method in Table I), the Code minimum permitted thickness would soon be reached. A definition as to the protective steps to be adopted became an urgent matter. A decision was then made in favor of installation of an anodic protection (AP) system, which was the reliable option with the fastest delivery time and requiring the shortest outage for installation. AP was installed in May 2003.

Also in May 2003, SCC was observed around the digester circumference at the beginning of the clad plates that form the top separator, right above the thinned areas, requiring repairs and crack grinding. In October 2003, the 316L central pipe failed, completely destroyed by SCC, and was replaced by a new pipe in 2205 duplex stainless steel.

Figure 5 presents the main corrosion aspects observed in digester 1.

However, there remained yet another issue to be addressed.



5. Corrosion aspects observed in digester 1: (a) and (b) shell corrosion thinning, (c) stress corrosion cracking (SCC) on the stainless clad plates of the upper zone, (d) central pipe destroyed by SCC.

The total losses of the thinned walls of digester 1 up to the AP installation had been 5 mm. In some locations the remaining thickness was close to the code-allowed minimum. The mill therefore needed to build up part of the lost thickness on the thinned shell courses. The mill decided to resort to the additional security afforded by 110 m^2 stainless steel weld overlay, in ER312 alloy with 3 mm thickness, applied during October 2004.

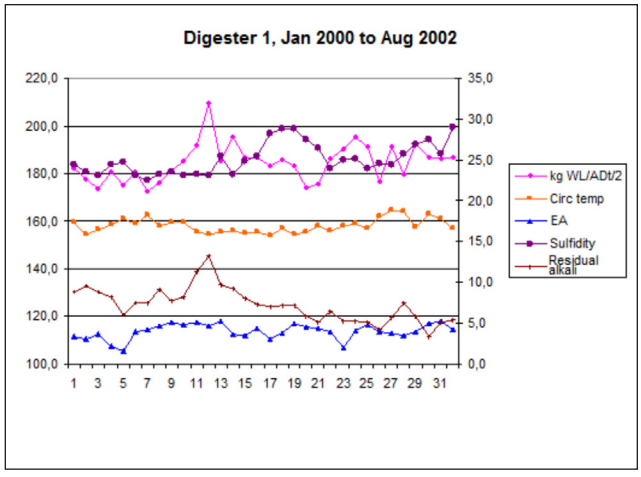
The change in corrosion behavior of digester 1 was attributed to a process change in November 2000, from conventional cooking to a proprietary process. The new cooking process, aimed at an increased yield, involved a larger dosage of white liquor to the top in relation to other processes. A review of operational parameters from 2000 to 2003 revealed that the most significant change was that sulfidity increased from 23% to 29% over the period (**Fig. 6**). The circulation temperature also increased slightly, from 159°C to 161°C, and residual alkali decreased from 8 to 4 g/L NaOH, factors regarded as being of limited significance. An unusually high thiosulfate concentration (14.7 g/L) found in digester 1 liquor also could have contributed to corrosiveness.

The reasons for the corrosion onset in the upper part of the digester could not be determined. The corrosion in the top of a carbon steel digester typically is negligible because of relatively low temperatures and high hydroxide concentration in this environment [3]. The corrosive attack would be expected to take place in lower zones (extraction and wash) where temperatures are elevated and residual alkali is lower.

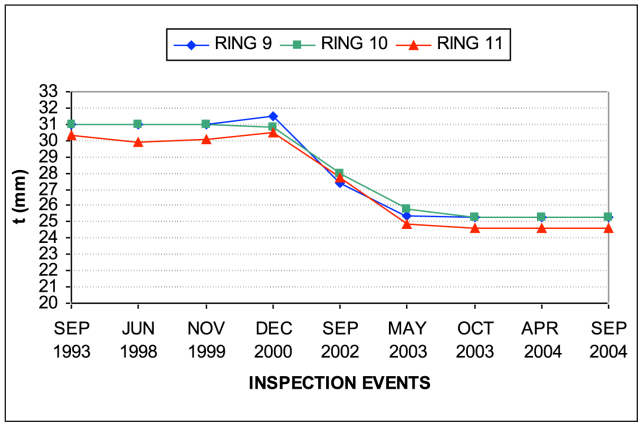
Despite this remaining undefined issue, all the facts and findings concurred with the same actions and solutions. With AP and weld overlay, digester 1 received the most effective protective technologies currently available in industry. At a considerable cost, they afforded an "open" remaining life to digester 1 with respect to corrosion, as well as reliability levels to international standards. The corrosion rates after AP (**Fig. 7**) have been negligible, as witnessed by permanent electrochemical control and periodic inspections.

The nominal thickness of digester rings 9, 10, and 11 is 31 mm. The inspection report from the September 1993 outage shows that their average thickness was close to nominal at that time (31.0 mm, 31.0 mm, and 30.3 mm, respectively). Similar data were reported in inspections done in 1998, 1999, and 2000.

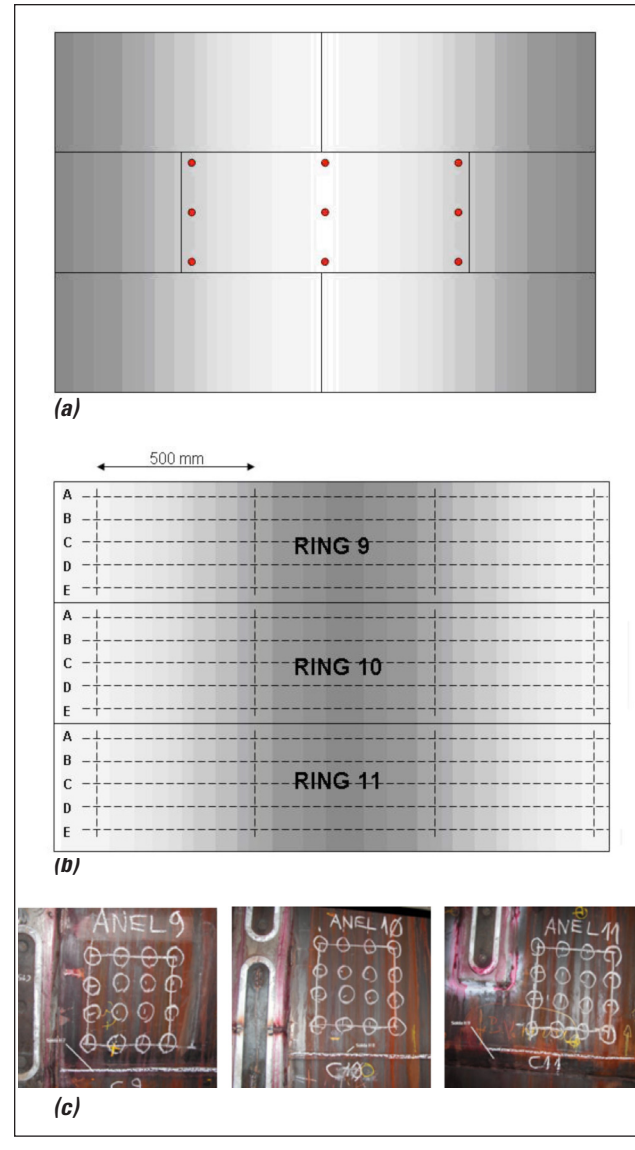
Historically, thickness measurements of digester 1 were



6. Digester 1 process data from 2000 to 2002 reveal an increase in sulfidity. Other parameter changes were regarded as unimportant.



7. Thinning progress; anodic protection system installed as of May 2003.



8. Details of (a) original, regular ultrasonic testing (UT) grid; (b) denser grid after corrosion onset; (c) specific grid to verify the anodic protection effectiveness.

carried out using a regular ultrasonic testing (UT) grid with nine points (3×3 matrix) on each rectangular shell plate (**Fig. 8a**). After 2002, with the corrosion onset, a denser grid was adopted with five elevations per ring and with points at every 500 mm around the ring, giving approximately 190 points per ring (Fig. 8b).

Additionally, from the installation of AP in May 2003, special UT grids were set on rings 9, 10, and 11 to accurately, repeatably check the effectiveness of AP (Fig. 8c). These 16-point matrices were used along four inspection cycles until weld overlay was applied in October 2004. The wall loss observed after AP is virtually nil.

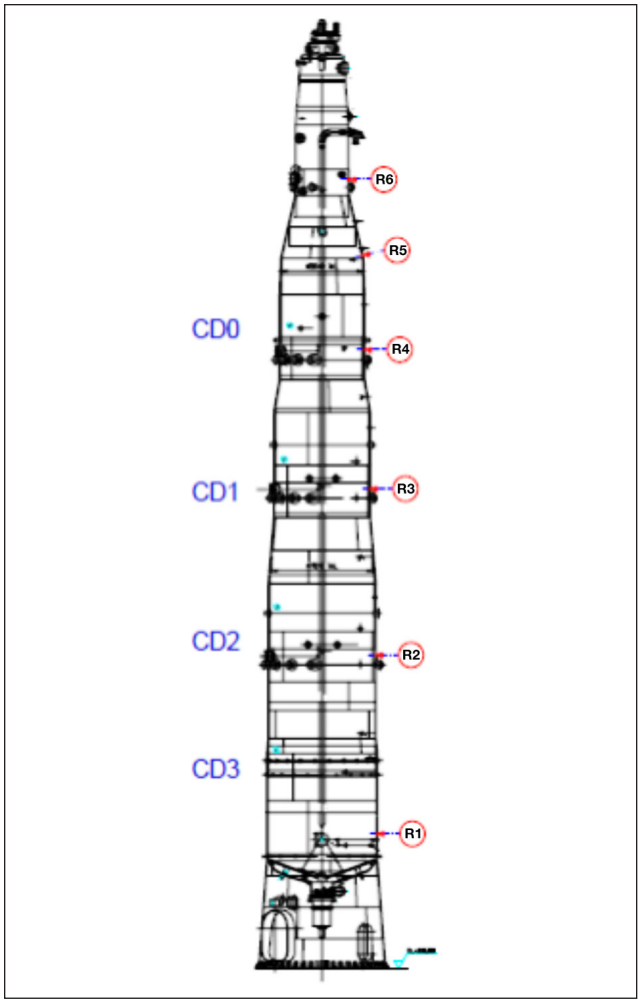
Corrosion rates for this report were established on average values for each shell course, not based on localized forms of corrosion.

The weld overlay durability has proven satisfactory.

Digester 2

Digester 2 had its first start-up in 1995. Its shell is fabricated in 316 ELC stainless steel clad plates. ELC stands for extra low carbon, denoting a carbon content of <0.015%, to minimize sensitization upon the post-weld heat treatment stage.

The original cooking process was ITC. In October 2004, in an effort to increase the pulping yield, the cooking process was modified to a proprietary process (process A). As a precaution, an electrochemical potential monitoring system, comprising six molybdenum reference electrodes, was installed in January 2005. The electrochemical profile changed in connection with the new process, but was still within acceptable potential levels, especially if residual alkali was controlled (previous tests had indicated that increasing residual alkali to 12.3 g/L significantly improved passivation). A contact electric resistance (CER) test conducted in March 2005 showed that, at any potential above -60 mV versus molybdenum, digester 2 was passivated. The measured open circuit

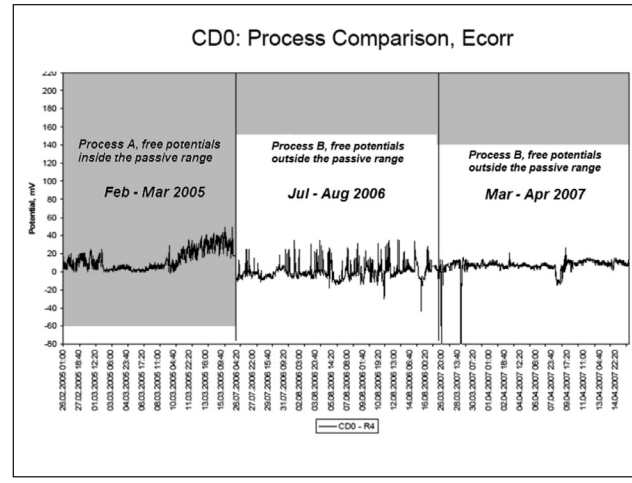


9. Digester zones and screens arrangement, CD0 to CD3.

potentials (Ecorr) were consistently above this level, thus confirming the feasibility of operations under cooking system A.

In May 2006, the cooking system was converted to another process (process B). Along with a new feeding system, the cooking modifications afforded a remarkable output increase from digester 2. **Figure 9** depicts its current arrangement. From this point on, however, the monitoring system indicated unfavorable electrochemical potentials with regard to the risk of SCC, without the possibility of correction via operational parameters.

Simultaneously, new CER tests conducted in 2006 and 2007 revealed that the shell passivation ranges of potentials had also changed. CER establishes the passivation range by measuring the electric resistance of shell passive film at selected potentials, either free or forced. The potential range that permits a sufficiently resistive and stable protective oxide surface film to build characterizes the passive range [3]. **Figure 10** presents the electrochemical changes observed (the digester upper region [the CD0 screen] appears as a reference, with similar conditions elsewhere in the vessel). **Table III** summarizes the electrochemical profile of digester 2 with process B.



10. Electrochemical changes in connection with the process change. The shaded areas indicate the passive range of potentials.

Digester zone	Ecorr, average, mV	Passive Limit, mV	Condition
CD0	10	>140	Nonpassivation at all zones. Ecorr far from passive limits.
CD1	10	>120	
CD2	20	>100	
CD3	15	>75	

III. Electrochemical profile with process B.

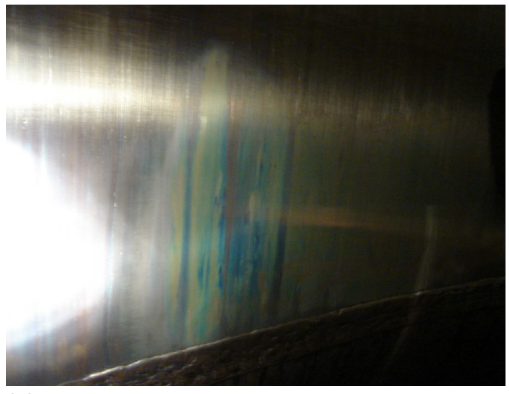
Additionally, after the process change in 2006, a peculiar blue coloring was observed on the digester internal surfaces (**Fig. 11**). This provoked debate and differing opinions. The AP supplier asserted [3] that the phenomenon was linked to the weakening of the passive layer on the material. Wensley et al. [10], in turn, defined the bluish film as mixed oxides of iron and chromium ($FeO\text{-}Cr_2O_3$) inherent to stainless steel passivation. The blue color is, according to this judgment, an interference color resulting from light passing through the passive film.

Additional digester tests

Additional tests were conducted to support decision making as to the protection needs of digester 2 (Fig. 11).

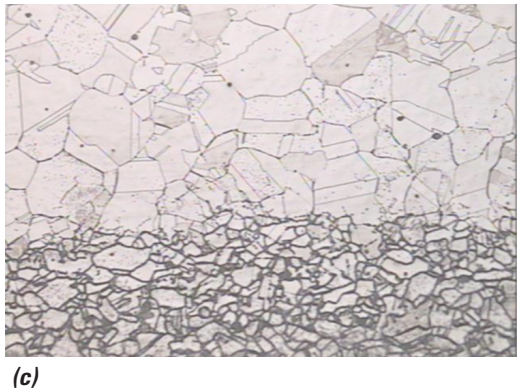
Metallurgical tests – Samples of digester 2 material were sent to laboratories to verify whether the metallurgical structure was sensitized, which would increase the susceptibility to SCC and IGA; if confirmed, the need and urgency of installation of AP would be reinforced. The results showed that no bulk sensitization of digester material on the process side had occurred, thus attenuating this specific concern [3].

Corrosion tests – U-bend corrosion tests were conducted with materials similar to those used in the digester construction, and exposed for 190 h and 712 h to liquors containing hydroxide residuals comparable with those typically encoun-



(a)

(b)



(c)

11. Corrosion aspects and studies of digester 2: (a) peculiar blue color, (b) U-bend specimen with stress corrosion cracking after 712 h in liquor with 25 g/L NaOH at 165°C, (c) metallurgical analysis indicating absence of bulk sensitization of material.

tered in continuous digesters (10 and 25 g/L NaOH). All specimens tested for 712 h experienced SCC. This led to the conclusion that austenitic stainless steels subject to severe tensile stresses are at risk of SCC when immersed in typical digester liquors [10]. Digester 2 could therefore be at risk at stressed regions, including welds, cold-formed sections, and parts subject to piping loads or significant thermal expansion.

Final decision as to the protective technology for digester 2

With all the results taken into consideration, the mill decided to install an anodic protection system comprised of 27 cathodes and 12 reference electrodes (including the pre-existing six) to digester 2 in October 1997, and operated it through January 2008. Thereafter, and still today, permanent potential monitoring and annual inspections control the corrosive behavior of digester 2 and the AP performance.

Justification for AP in digester 2

The tests and analyses carried out to assess the digester 2 corrosion risks under the new cooking process yielded somewhat conflicting results. Operation at unfavorable electrochemical conditions and the strange blue coloring, together with the results from corrosion testing, were major concerns faced by mill management. The blue coloring prompted different opinions from respected specialists, reinforcing that uncertainties in the understanding of digester corrosion mechanisms still exist.

In light of these considerations, and since the digester is a critical asset whose failure is unacceptable, a conservative managerial decision had to be made. Thus, considering all the testing results, which did not provide any guarantees that digester 2 was free of corrosion problems, an AP system — likely the first one in a stainless digester — was installed during the October 2007 outage. Since then, the equipment has been operating within potentials defined as safe. As the corrosion rates of digester 2 were negligible, consistent with the austenitic material, the AP exclusively aimed at SCC and IGA protection. We must stress that, in spite of the period of operations at adverse electrochemical conditions, digester 2 did not come to experience an observable SCC process. SCC is known to appear after an incubation period, during which the phenomenon cannot be observed [13]. To minimize any remaining risks to digester 2, even protected by AP, it undergoes periodic inspections during mill outages, with visual examinations, ultrasonic surveys, and dye penetrant testing, still to the present day.

CONCLUSIONS

Based on the various experiments and observations on digester corrosion conducted throughout this work, and considering the discussions presented, the following conclusions can be drawn:

- The cooking method considerably affects electrochemical potentials, passivation range, and consequently, the corrosion behavior of continuous digesters. The contemporary, modified cooking systems significantly increase corrosion in relation to conventional cooking.
- Under such conditions, even austenitic stainless steel digesters are at risk of SCC. When subject to elevated tensile stresses (e.g., welds), this material is susceptible to SCC under conditions typically encountered in modern cooking.
- Corrosion protection measures, with due time frames and budget allocations, must be considered whenever an existing digester is to be retrofitted to a newer cooking process. The length of a mill outage is often a major influence on choosing the suitable protection. Unlike weld overlay, a more

time-consuming application, an AP system can be installed in less than four days.

• Whether a digester in service will suffer SCC is not simple to determine in advance, because damage only appears after a period of incubation. Metallurgical analyses (as to sensitization) and corrosion testing can help assess the risks, supporting managerial decision-making as to the need of protection.

• Anodic protection is an option for corrosion control in a continuous digester. A properly specified and applied weld overlay also provides adequate protection, with satisfactory durability. These technologies are mutually compatible and have been used together successfully.

Note that this work does not attribute higher intrinsic corrosiveness to any specific proprietary cooking process. All process changes cited were implemented to existing digesters operating with mill-specific conditions. Thus, the studies and conclusions drawn are mainly intended and useful for corrosion comparison when different cooking processes were applied to a single digester. The risks involved were duly agreed between mill and vendor. **TJ**

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ABOUT THE AUTHORS

This study began when our mill experienced out of the ordinary cases of digester corrosion and protection, making for a rich, perhaps unique technical experience that might be useful for other mills as well.

This research deals with diverse cooking processes and digester construction materials, and was supported by a number of field and laboratory studies. It also received the contribution of respected consultants who worked with the mill engineers. Another distinct feature is that the corrosion risks and protection needs of a stainless steel clad digester, a rare context, were discussed and studied.

The most difficult aspect of this study was to determine the real protection needs as a function of how prone to SCC the digester was and to correlate process data with potentials changes and corrosion behavior.

It has been shown that cooking processes actually affect the corrosion behavior, and that any process changes must consider the adoption of protection technologies. We also note that SS digesters are prone to SCC cracking under modern cooking.

This study will be useful to mills that have shifted to newer cooking processes or plan to do so in the near future. It provides perspectives on consequences that can be expected, and countermeasures to be considered.

Studies as to the corrosivity of eucalyptus liquor are very rare in the literature, and research on that topic could be a worthwhile next step. Follow-up on the performance of our protected digesters over time might provide interesting information in the future.

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