

Monitoring and Eliminating Risks of Corrosion and Stress Corrosion Cracking in Kraft Pulp Digesters

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ABSTRACT

Digester corrosion, especially stress corrosion cracking, is a major topic for the pulp and paper industry as catastrophic failure of pressurized equipment may result, and risks to life and property are also significant. Also, the loss of passivation and consequent general corrosion due to modified cooking conditions remains an issue. The present work has the main objective to study the change in corrosive behavior of selected continuous digesters over time and display the value of continuous on-line monitoring and periodical passivity measurements in understanding and defining the corrosion risk development. The risks to carbon steel digesters running on modern cooking processes are demonstrated to be significant.

Keywords: continuous digester, corrosion, modified cooking, electrochemical potentials, anodic protection

1- INTRODUCTION

Corrosive conditions exist in most processes and stages of pulp and paper production. 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 may also happen. Many process changes have occurred in recent years, intensifying existing corrosion problems. These ongoing changes are primarily due to the search for improved production efficiency and reduced environmental impacts.

The warning for the pulp and paper industry came in September 1980, when a digester in North America catastrophically failed due to stress corrosion cracking (SCC) of an upper shell weld. Many other digesters were found to be cracked in inspections made after that, and even some more catastrophic failures have happened. Also, another serious corrosion problem appeared, this time in the form of accelerated shell thinning in the extraction and washing zones. In the nineties, 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. One of the fastest and easiest methods for corrosion mitigation i.e., passivation of carbon steel in alkaline conditions is anodic protection. However, it requires comprehensive design and optimum control to operate as planned.

From this perspective, the present work has the following objectives: To explain the verification and control of passivation of anodically protected continuous digesters by using periodic passivity measurements and continuous on-line monitoring, and to describe field experiences of corrosion risk development in changing conditions.

2- LITERATURE REVIEW

The variables with influence over continuous digester corrosion fall into three groups: (i) the construction materials utilized, namely carbon steel, austenitic stainless steel or duplex stainless steel. (ii) process variables such as white liquor composition, wood chips pre-treatment, cooking time and temperature, circulation of liquors, and (iii) wood species pulped [1]. These variables are discussed below.

2.1- Materials

For decades, carbon steel (especially A285 Gr C, A516 Gr 70) was the standard material for construction of continuous digesters. Process modifications intensified corrosion, prompting the equipment manufacturers to search for more resistant materials. Utilization of SA264, 304L stainless steel clad plates became common practice in the nineties. Among the austenitic grades, type 304L is the industry standard for this application. For new digesters, solid type 2205 duplex stainless steel is today a preferred material [2]. Corrosion rates for austenitic stainless steels and duplex steels are very low in comparison to carbon steels, even with modified cooking. Duplex steels are much less susceptible to SCC and

erosion [1]. However, laboratory studies and field experiences have shown that duplex stainless steels may become susceptible to general corrosion and stress corrosion cracking in hot, high pH caustic solutions containing sulfides. [3]

2.2- Process Variables

Influence of the composition of white and black liquors

In the Kraft process, wood chips are cooked in white liquor, which essentially contains sodium hydroxide and sodium sulfide. During the cook, lignin and extractives are dissolved, whilst 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 has been historically presented as a function of its inorganic constituents (Na_2S , NaOH and also $\text{Na}_2\text{S}_2\text{O}_3$). It is currently known that no straightforward relationship can be established solely between the inorganic constituents and corrosion rates [1]. It is believed, however, that sodium hydroxide, sulfide and thiosulfate have significant effect on corrosion, whereas sulfate, chloride and carbonate do not have appreciable effect [5].

The influence of inorganic compounds is as follows:

Sodium Hydroxide – Hydroxide can influence corrosion detrimentally or favorably. For passivation to occur, free hydroxide ions must be available. Whereas white liquor with 100 g/L NaOH can be very corrosive to carbon steel at elevated temperatures, the presence of a certain amount of hydroxide in extraction liquors is necessary for maintaining passivation [6].

Sodium sulfide – Higher sulfidity means larger amounts of volatile compounds (*e.g.* methylmercaptan, dimethyl sulfide, dimethyl disulfide) released during the cook, some of them corrosive to carbon steel [4]. Sulfide impairs passivation, probably by adsorption on metal surfaces [7]. In a stainless steel passivation study, Wensley [8] states that sulfide can be an SCC agent acting in three ways: as an SCC agent *per se* (thus provoking “sulfide SCC”); facilitating caustic SCC (where hydroxide is the SCC agent), probably by modifying the nature of passive film; and simply increasing the effective alkali.

Sodium thiosulfate – White liquors with high thiosulfate concentration (> 5 g/L) are corrosive to carbon steel. Thiosulfate, through formation of polysulfide, raises anodic currents and places potential at the active-passive transition, where SCC and high corrosion rates occur [9].

Chlorides – It is believed that chlorides do not play a significant role in alkaline liquor corrosive processes [10]. Chlorides are often the SCC agent to austenitic stainless steels under neutral or acidic conditions but have no role in alkaline environments.

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 basically be split into two groups: the corrosion activators and the corrosion inhibitors [11].

Activating compounds – among many products resulting from lignin degradation during the cook, small amounts of organic compounds which can form strong chelate compounds, like catechol (1-2 dihydroxybenzen) and pyrogallol (1-2-3 trihydroxybenzen) may be yielded. These substances are corrosive on alkaline pulping. Catechol could hinder passivation due to 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 [1,11].

Inhibiting compounds - Kiessling [12] 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 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, the addition of palmitic acid, $\text{C}_{16}\text{H}_{32}\text{O}_2$, reduced the corrosivity of softwood liquor to carbon steel by 15% [7]. 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 [11].

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 since synergistic interactions between the organic compounds, unknown in most cases, may play a significant role in the general corrosivity of liquors [1]. One explanation for the increased corrosion risk at the lower part of digester in modified cooking processes is that less inhibiting compounds reach there as more liquor is extracted to recovery already at the upper screens.

Influence of temperature and other process variables

Temperature influences the free corrosion 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 [10], states that some carbon steel digesters operating at temperatures above 170 °C have corroded at rates of 6 mm/yr 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.

Other process variables such as dilution factor and production rate might also influence potentials and corrosion. Intrusion of sand into the process increases abrasion and might worsen corrosion [10].

2.3- Influence of the Wood Species

Extraction liquors from softwood pulping are reportedly more aggressive than those from hardwood. The species *Pinus*, and especially Western red-cedar, *Thuja plicata* and Douglas fir, *Pseudotsuga menziesii*, are cited as corrosive species on pulping [11]. Eucalyptus is not considered particularly corrosive. Studies regarding the presence and concentration of specifically corrosive compounds produced by Eucalyptus pulping have not been identified in literature [10].

3- METHODOLOGY

The experimental method used for verification of passivation in this study is contact electric resistance (CER). The CER-technique is based on a continuous measurement between two separate surfaces that are brought into periodic contact while constant electric current is fed through the surfaces. When these two surfaces are in contact, the whole current flows through them. When the surfaces are disconnected, the metal surface will interact with the electrolyte and the current flows through the external constant resistance. The contact resistance is now calculated from the difference between the measured voltages when surfaces are connected or disconnected. The information received is the resistance of the surface under examination as real-time monitoring data.

The test specimen is manipulated in autoclave to which cooking liquor is constantly flowing through series of filters to avoid any solid particles interfering with the resistance measurement. Batch process is also possible if process environment stabilization is required. Temperature of the autoclave is adjusted to match the process temperature at the sample extraction point. The liquor sample stays pressurized and without possibility of aeration, so also the volatile compounds are present at the time of measurement.

In the CER unit it is possible to change the electrochemical potential of the test specimen by introducing a polarizing DC current feed to the test specimen. This allows simulation of different anodic protection target potentials while simultaneously measuring the surface resistance of metal sample in fixed polarization potential using a potentiostat or the specimen.

Monitoring of the surface resistance of the specimen reveals the passivation level of steel: When the resistance increases significantly (up to 2-6 decades), the resistance measurement current can no longer flow through the specimen surface when connected to inert counter point. The passive layer that prevents this has been formed when the specimen has been exposed to the liquor while the measuring points are open. When the surface resistance value is high (10-100 Ω in stainless steel and 100-1000 Ω in carbon steel), the specimen is considered as passivated. If the resistance value stays low (0.01 - 1 Ω), there are not any oxides formed, thus passivation does not exist. To avoid specimen polarisation due to current required for resistance measurement circuit when the specimen surfaces are not in contact, there is a by-pass shunt which routes the current to the resistance measurement device. Note that the resistance of the by-pass shunt affects the CER result value considered to be fully passive, therefore values over 100 Ω can be equally passive as those over 1000 Ω .

The CER technique ensures that the surface reactions take place without any disorder due to the handling of the sample. Therefore, CER results can be considered as on-line results received from oxidation or reduction reactions of the metals, indicative of the passivation status of the metal samples. Fig 1. shows the principle of the CER-measurements.

The passivation of carbon steel in digester conditions is a complex and multi-phased process. Passivation of metals is known to be a result of an anodic dissolution of the metal. A thin surface layer is formed and it is usually a combination of metal oxides. This layer, when dense and well developed, can protect metal well against corrosion by inhibiting the unwanted reactions with the electrolyte. Based on the electropositivity of the steel surface, the degree of ferrous ion oxidation changes, resulting in different quality oxidation layers. Some other ions available at the electrolyte, such as sulfides, can also participate in the oxide formation and change the protective ability of the passivation layer.

Fig 2. shows a polarization scan where the most relevant oxide formations and the subsequent corrosion risk potential ranges are depicted. It is only the highest degree of ferrous ion oxidation which results in dense and protective passive layer Fe_2O_3 , also known as iron (III) oxide or hematite.

When controlling the anodic protection system, reference electrodes installed to digester wall measure the potential value constantly. CER test results calibrate the potential values to provide corrosion risk information in that specific process condition. This is why it is possible to rely on potential monitoring in anodic protection control.

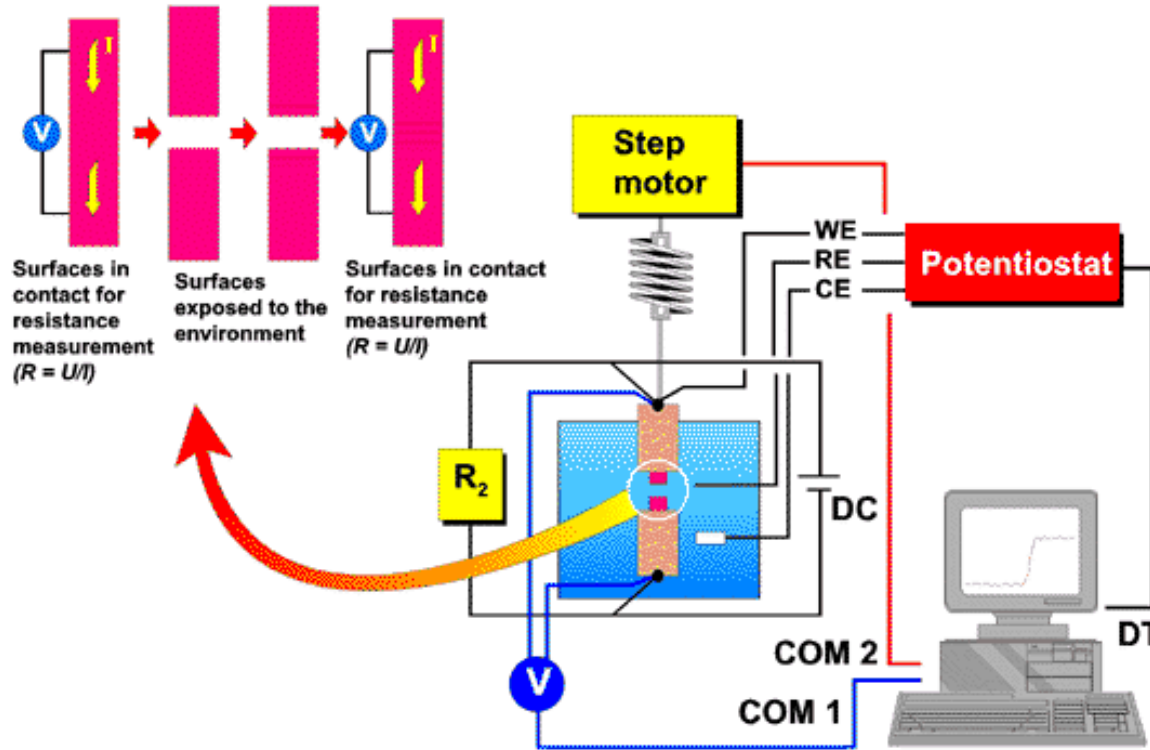


Fig 1: Principle of CER (contact electric resistance) measurement.

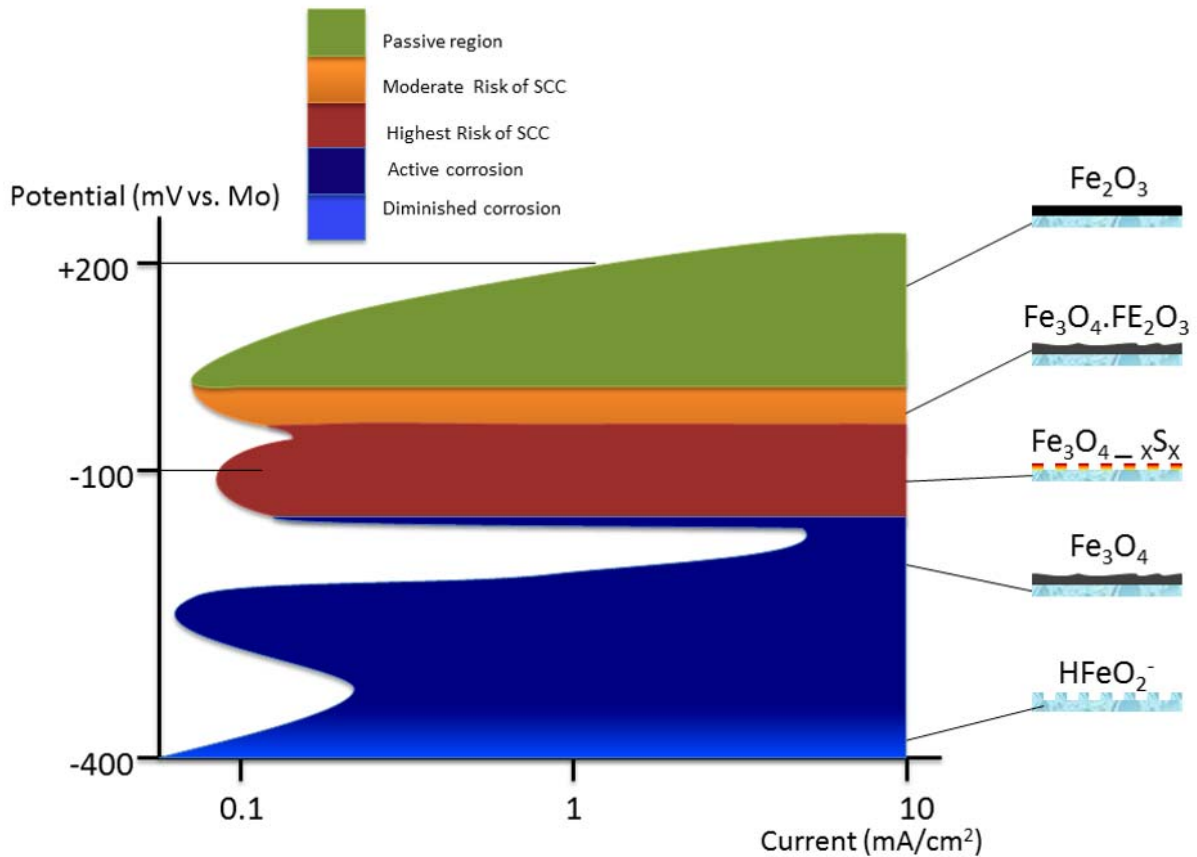


Fig 2: Schematic polarization scan showing different forms of oxide layers and corrosion risks attached to them [6].

4- CASE STUDIES

Case studies are selected in view of showing the effect of one process variable to corrosion risk potential range. The objective of publishing these selected results from different digester processes is to emphasize the fact that a seemingly small change in process can have dramatic consequences to corrosion aggressivity. These case studies also show that the electrochemical potential of steel can effectively be used to monitor and assess the corrosion risk but only after the risk ranges have been detected by CER study. The long-term potential monitoring data is presented in each case to demonstrate the change as seen by AP operators. All potential values in CER-results and potential monitoring have been measured against Mo-reference electrode.

Influence of Wood Species and Production Capacity, Digester A

Digester A is built out of carbon steel, located in Finland. It started operation in 1988 and was equipped with anodic protection system in 2002 when the cooking process was changed to Lo-Solids. The CER measurement campaign was initiated by slight wall loss noticed at wash zone which suddenly started during late 2004. The most significant process variable in this case is the periodic change between hardwood and softwood. Also change in production capacity was tested during hardwood run. The results depicted in Fig. 3-7 show that carbon steel passivates much more easily at hardwood cooking. At digesters cooking both species, anodic protection target potentials should generally be set according to softwood process requirements.

Softwood vs. hardwood

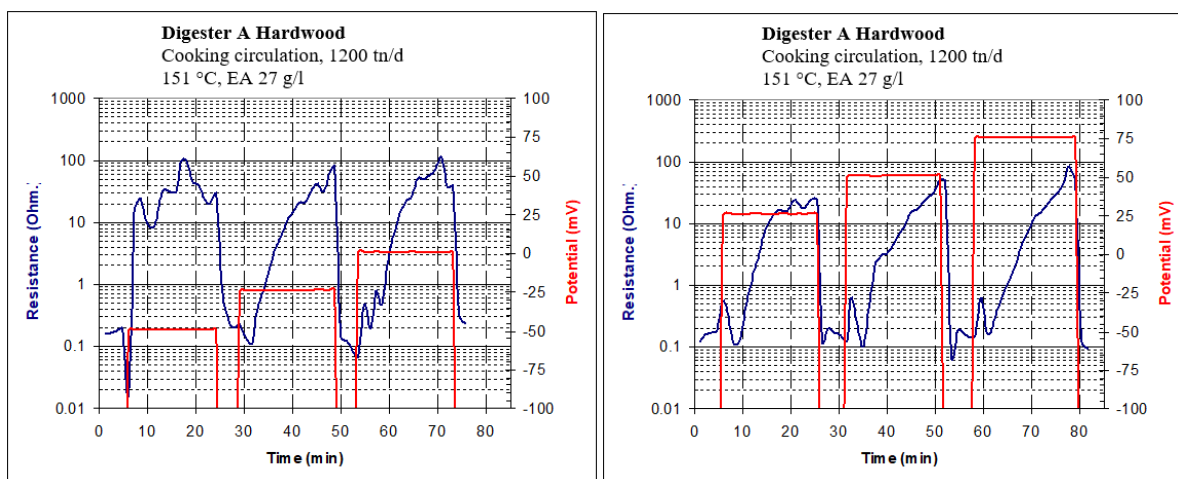


Fig 3: CER results Digester A Hardwood, cooking circulation, potentials from -50 mV to +75 mV, passivating in all potentials.

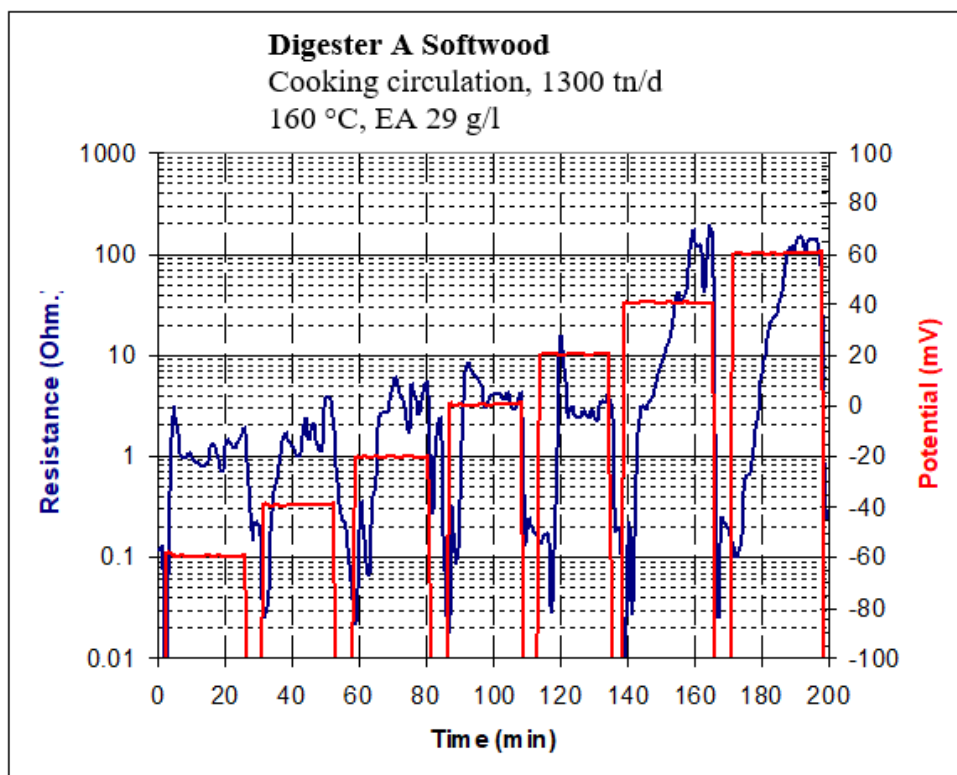


Fig 4: CER results Digester A Softwood, cooking circulation, potentials from -60 mV to +60 mV, passivating only at and above +40 mV.

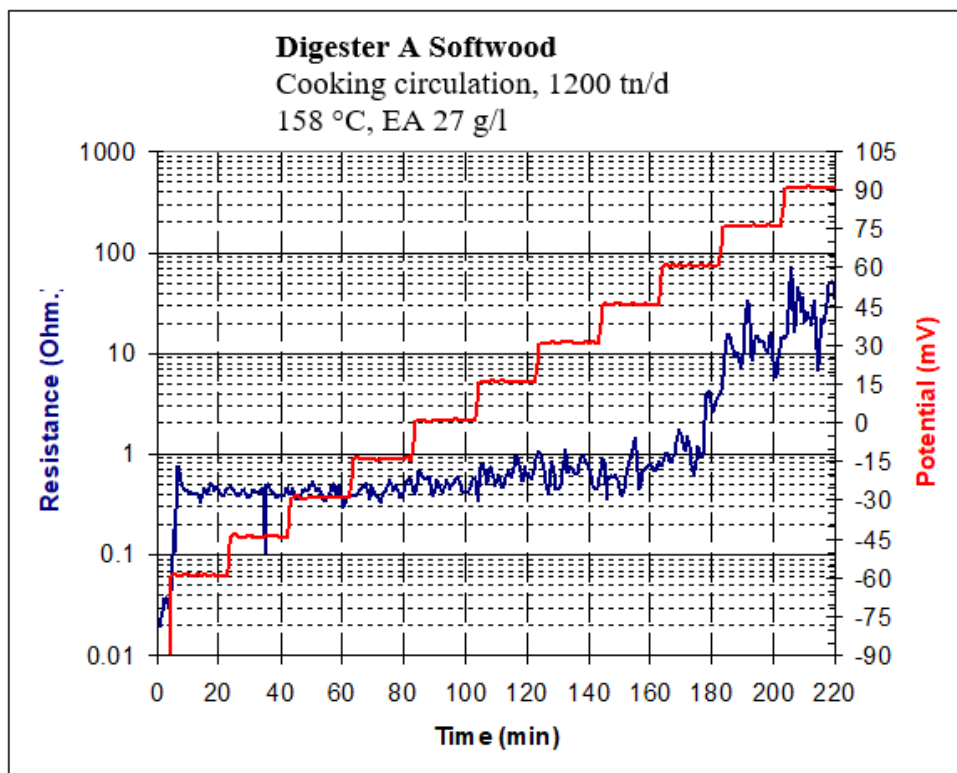


Fig 5: CER results Digester A Softwood, cooking circulation, potential sweep from -60 mV to +90 mV, starting to passivate at over +60 mV

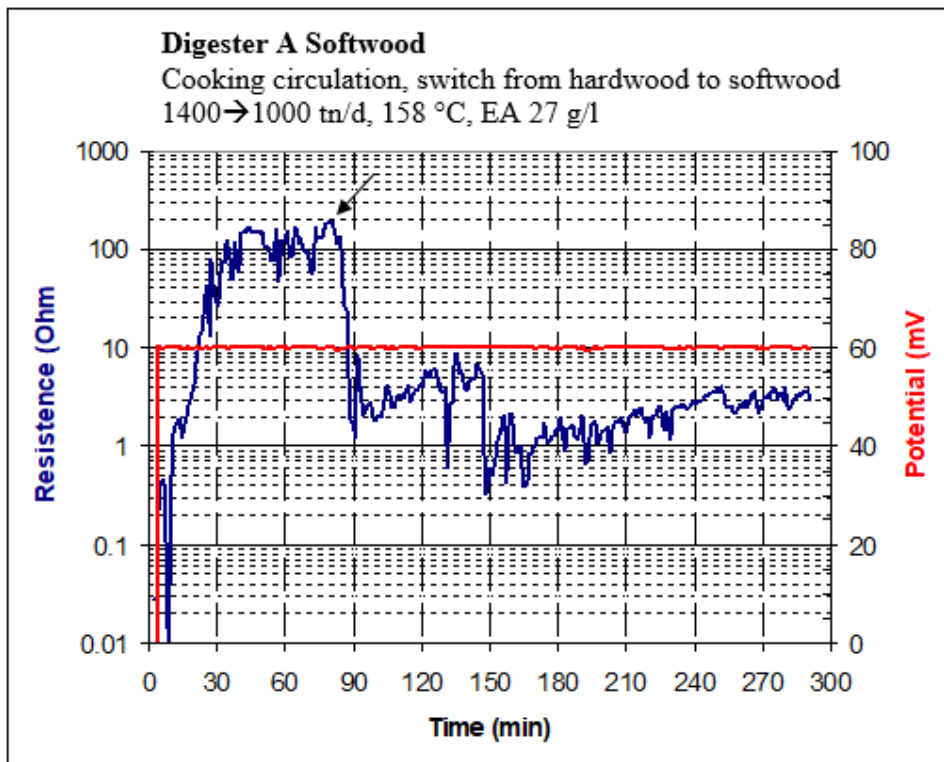


Fig 6: CER results Digester A, switch from hardwood to softwood, cooking circulation, potential constant at +60 mV, passivation collapses when switched to softwood.

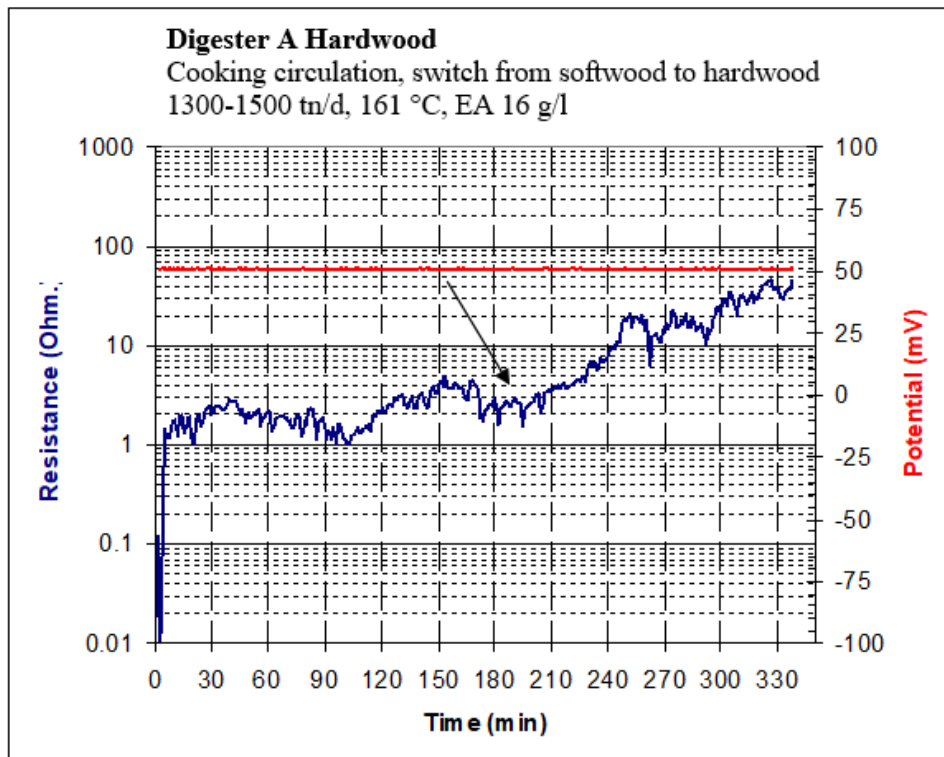


Fig 7: CER results Digester A, switch from softwood to hardwood, cooking circulation, potential constant at +50 mV, passivation starts to develop when switch to hardwood starts.

Change in production rate, hardwood cooking

In Fig. 3 passivation behavior in hardwood cooking circulation at 1200 tn/d production rate was found to be very good, passivating at all tested potentials from -50 mV to +75 mV. The situation is different when the production rate is increased to 1550 tn/d, resulting in more aggressive corrosion conditions where steel requires higher potential to passivate, Fig. 8.

Table 1. compiles all CER test results from Digester A, revealing +80 mV as the lowest possible target potential for anodic protection control.

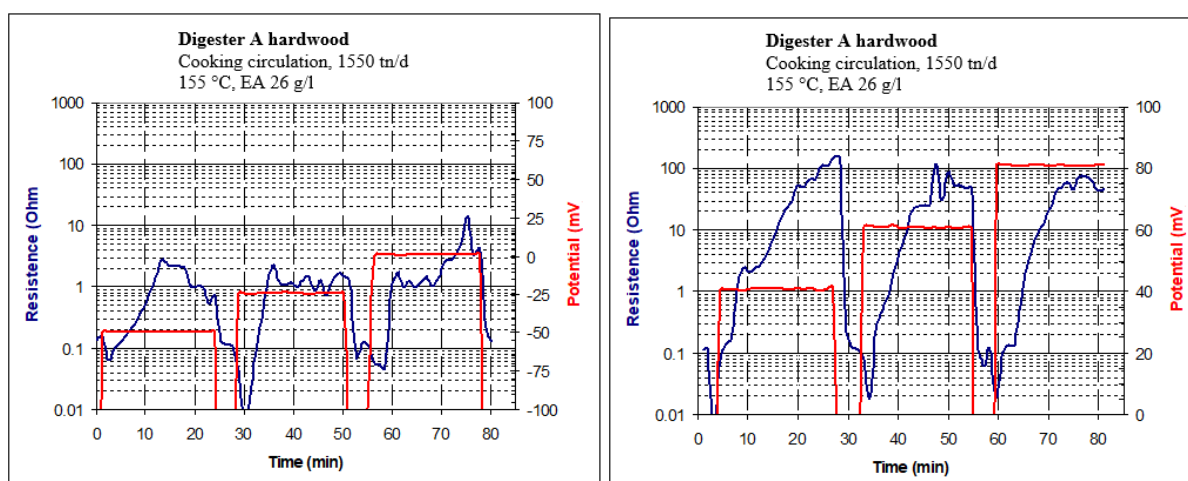


Fig 8: CER results Digester A Hardwood, production rate 1550 tn/d, cooking circulation, potentials from -50 mV to +80 mV, starting to passivate at 0 mV and fully passivating at +40 mV.

Table 1: Digester A, passivation in softwood run occurs in much higher potential than in hardwood. Increased hardwood production rate requires higher potential for steel to passivate.

Digester A Low-Solids HW vs SW			
Cooking circulation			
Potential:	Hardwood 1200 tn/d, 151°C EA 27 g/l	Softwood 1200 tn/d, 158°C EA 27 g/l	Hardwood 1550 tn/d, 155°C EA 26 g/l
-60 mV		Weak passivaion	
-50 mV	Passivating		Weak passivaion
-40 mV		Weak passivaion	
-25 mV	Passivating		Weak passivaion
-20 mV		Weak passivaion	
+0 mV	Passivating	Weak passivaion	Porous passivation
+20 mV		Weak passivaion	
+25 mV	Passivating		
+40 mV		Weak passivaion	Passivating
+50 mV	Passivating		
+60 mV		Porous passivation	Passivating
+75 mV	Passivating		
+80 mV		Passivating	Passivating
+100 mV		Passivating	

Influence of Effective Alkali Concentration, Digester B

Digester B is carbon steel, built in 1967 and located in the USA. It was equipped with anodic protection system in 1999 when severe cracking had been noticed at the top transition weld. During the CER measurements in 2018, the production was 800 tn/d of mixed hardwood. The measurement campaign was initiated when a recent process change had increased the AP current demand in the wash zone. This means that while the potential values were on target, the current required to maintain the passivity was higher than before. During the measurements, wash zone EA content was fluctuating while the temperature and production rate remained stable, so it offered a good insight on EA effecting the passivation potential. CER-Results in Fig. 9-10 show that increasing the EA concentration lowers the passivation potential. The results are compiled in Table 2.

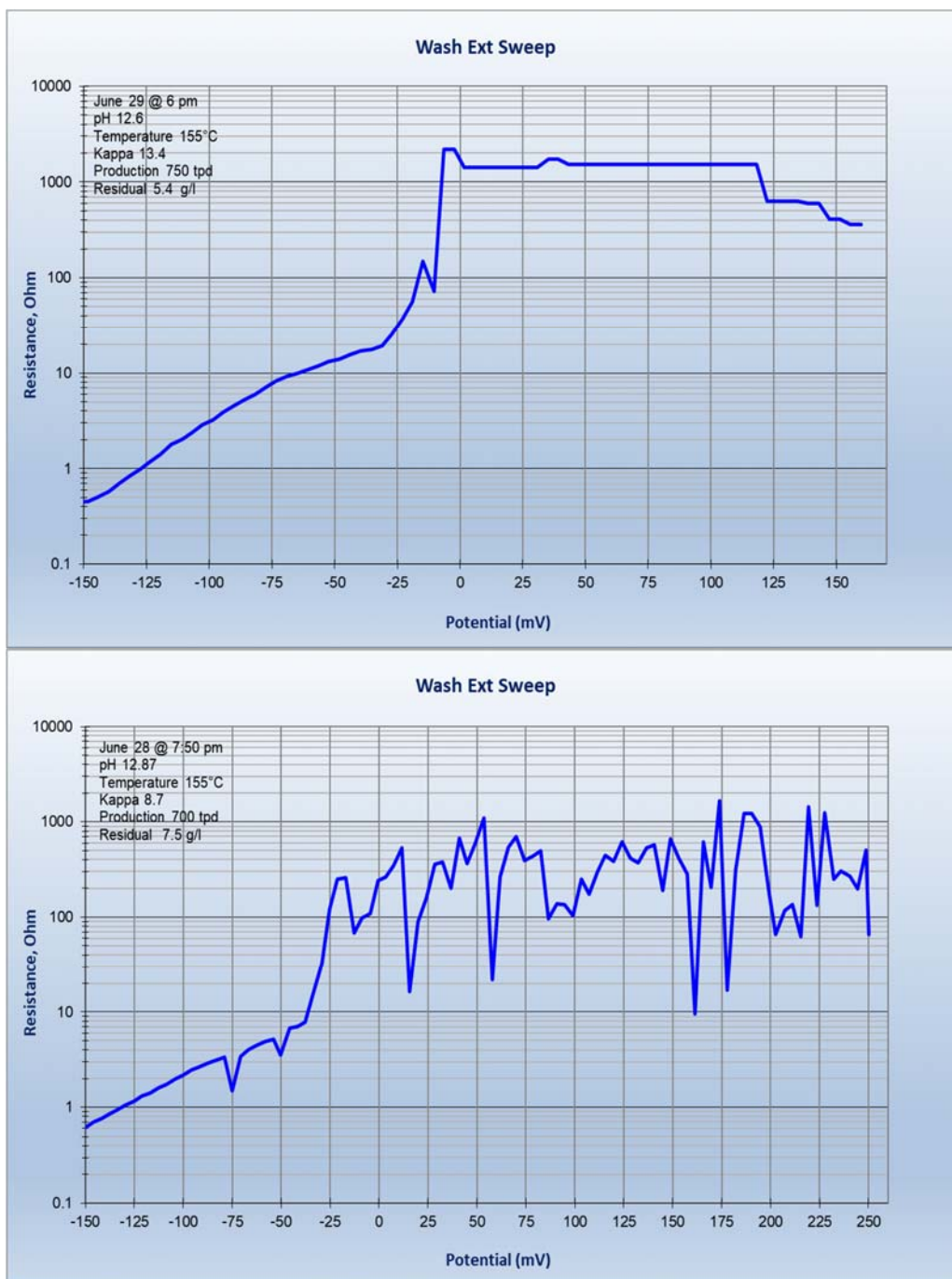


Fig 9: CER results Digester B Hardwood, wash extraction, potential sweep shows that EA increase from 5.4 g/l to 7.5 g/l lowers the passivation potential from -5 mV to -25 mV, indicating easier corrosion environment.

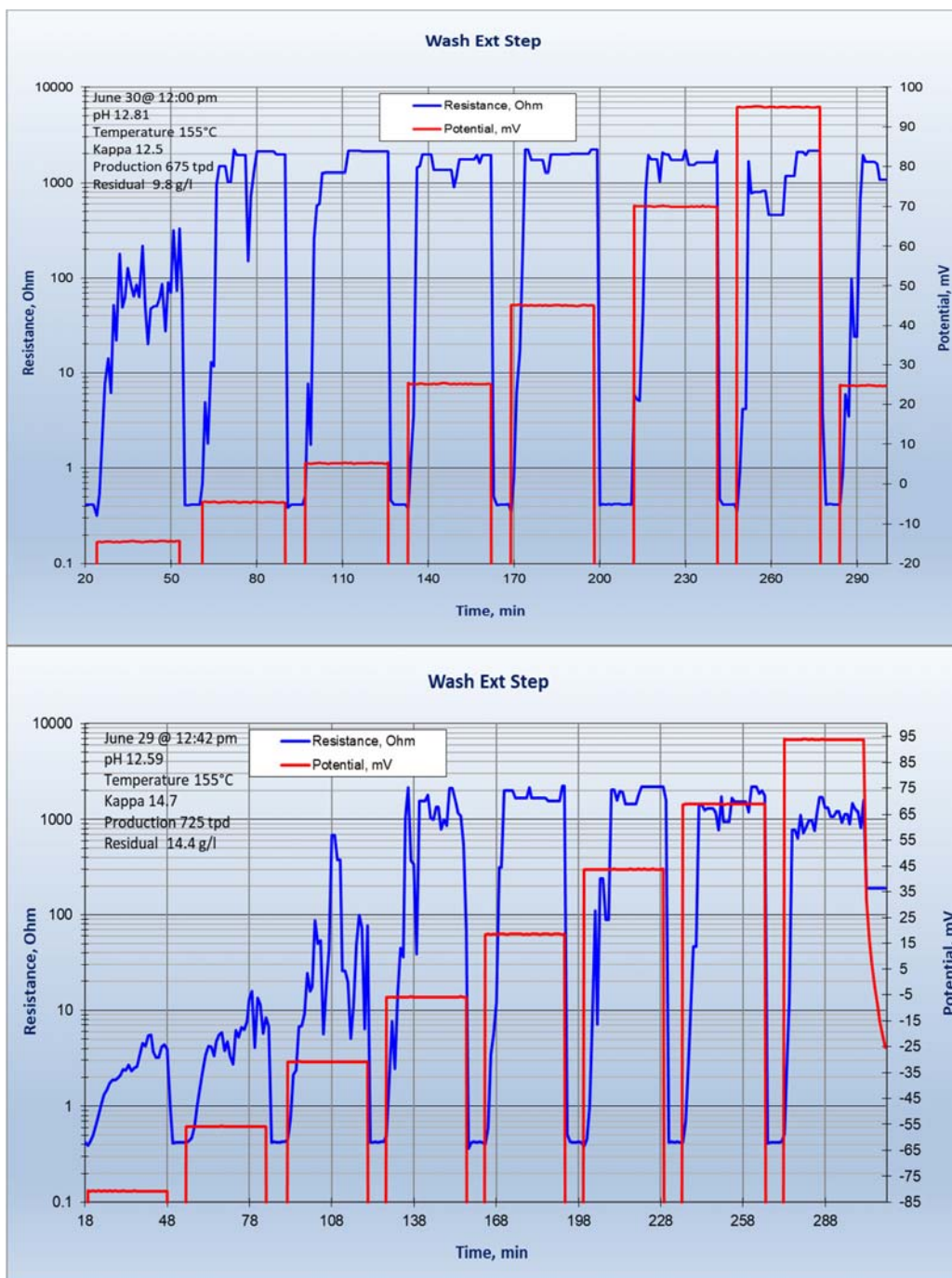


Fig 10: CER results Digester B Hardwood, wash extraction, potential steps show that EA increase from 9.8 g/l to 14.4 g/l lowers the passivation potential from -15 mV to -30 mV, indicating easier corrosion environment.

The discrepancy in passivation potentials between step tests and potential sweep is the time factor: In step test the time spent in one stable potential setting is longer, allowing the slow passivation process to develop. Sweep displays the passivity which has already started developing at lower potentials.

Table 2: Digester B, hardwood process, passivation occurs in lower potentials (easier) when EA is higher.

Digester B, Extended cooking mixed HW, EA effect				
Wash extraction				
Potential:	EA 5.4 g/l 750 tn/d, 155°C Potential sweep	EA 7.5 g/l 700 tn/d, 155°C Potential sweep	EA 9.8 g/l 675 tn/d, 155°C Potential step	EA 14.4 g/l 725 tn/d, 155°C Potential step
-80 mV	Weak passivation	Weak passivation		Weak passivation
-60 mV	Weak passivation	Weak passivation		Weak passivation
-50 mV	Weak passivation	Weak passivation		
-40 mV	Weak passivation	Weak passivation		
-30 mV	Weak passivation	Porous passivation		Porous passivation
-25 mV	Weak passivation	Passivating		
-20 mV	Porous passivation	Passivating		
-15 mV	Porous passivation	Passivating	Porous passivation	
-10 mV	Porous passivation	Passivating		
-5 mV	Passivating	Passivating	Passivating	Passivating
+0 mV	Passivating	Passivating		
+5 mV	Passivating	Passivating	Passivating	
+20 mV	Passivating	Passivating		Passivating
+25 mV	Passivating	Passivating	Passivating	
+40 mV	Passivating	Passivating	Passivating	Passivating
+50 mV	Passivating	Passivating		
+60 mV	Passivating	Passivating		
+75 mV	Passivating	Passivating	Passivating	Passivating
+80 mV	Passivating	Passivating		
+100 mV	Passivating	Passivating	Passivating	Passivating

Influence of Process Temperature

After the EA content, temperature is the most important process factor affecting steel passivation. Generally, at low temperatures steel passivates more easily, provided that enough free hydroxide is available. The CER measurements (Fig. 11-15) with temperature as the only variable are compiled from different measurement campaigns.

Temperature can also boost the natural passivation process in some conditions. The increased reaction rate at elevated temperatures can enhance the build-up of oxide layer on the steel surface at alkali concentration level which is not quite enough for spontaneous strong passivation. The following results (Fig 12) show the specimen resistance measured during heating period, when autoclave is heated up to normal process temperature. The importance of EA level is also emphasized: High EA passivates the specimen spontaneously at all temperatures, low EA will not develop strong passivation while the intermediate EA starts to improve oxide layer resistance after temperature increases. Note that the spontaneous passivation refers to passivation by formation of magnetite, existing at a quite narrow potential band below potential region where sulphur merges with the oxide layer making it porous. In anodic protection technique this is not yet considered as safe potential.

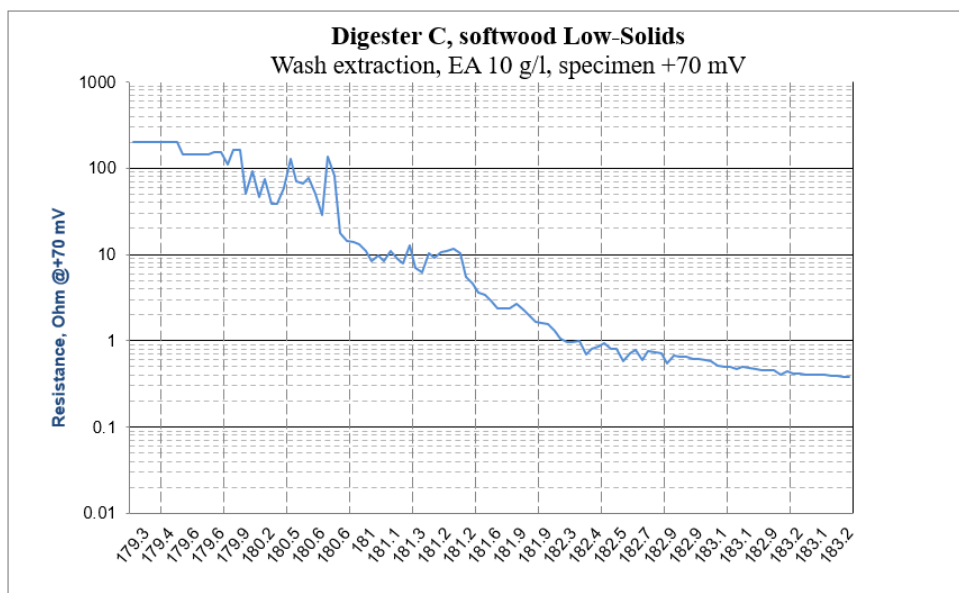
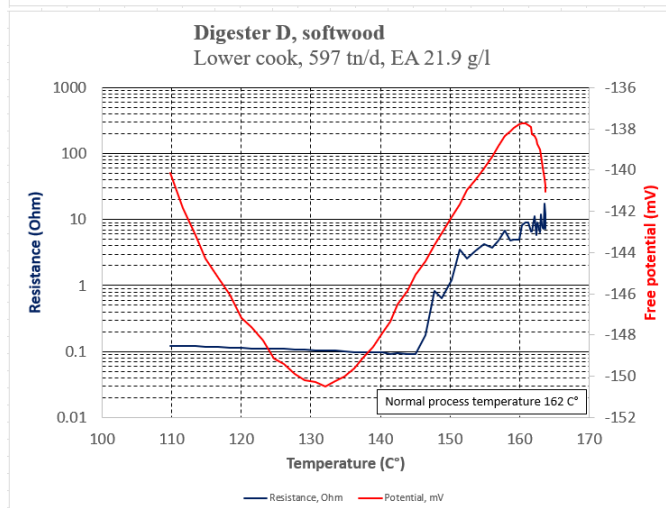
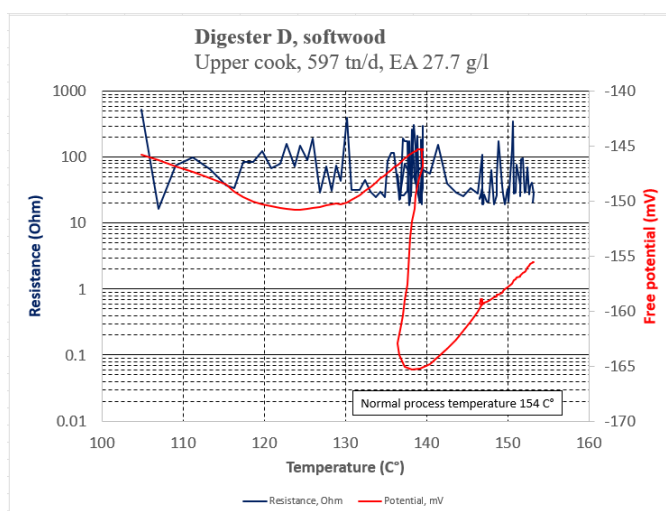


Fig 11: CER results Digester C softwood, Lo-Solids, wash extraction, carbon steel specimen maintained at +70 mV. Increasing temperature over 1.5 hours measurement session destroys the passivation layer after just two degrees temperature change.



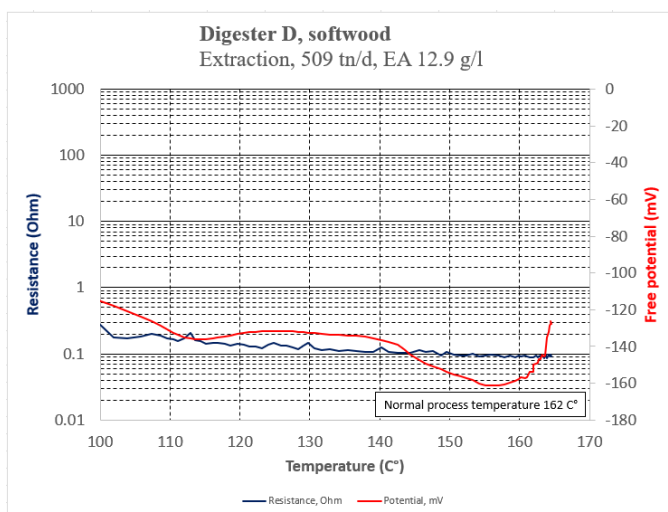


Fig 12: CER results Digester D softwood, showing the effect of temperature increase in three different conditions where the steel specimen is at free potential, without any AP current feed. Upper cook with highest EA level presents quite high resistance values throughout the temperature range. Lower cook with less EA starts to develop stronger passivation boosted by temperature increase at above 145 C°. Extraction liquor has the lowest EA and steel does not passivate at all at free potential region.

As stated earlier, development of a strong passivation layer is a time-dependent process. The sweep test where one factor is constantly changing, will give slightly different results than the step test where all variables are maintained stable. Given enough time, step tests will usually show passivation in lower potential.

A series of measurements were conducted in a Finnish digester with Compact cooking process, an objective was to find out the passivation potential limit for wash zone anodic protection after the process change was made. The results (Fig 13-15) show that while passivation occurs very fast in all tested potentials at 115 °C, at 140 °C the passivation starts at +50 mV and at 150 °C +75 mV is required.

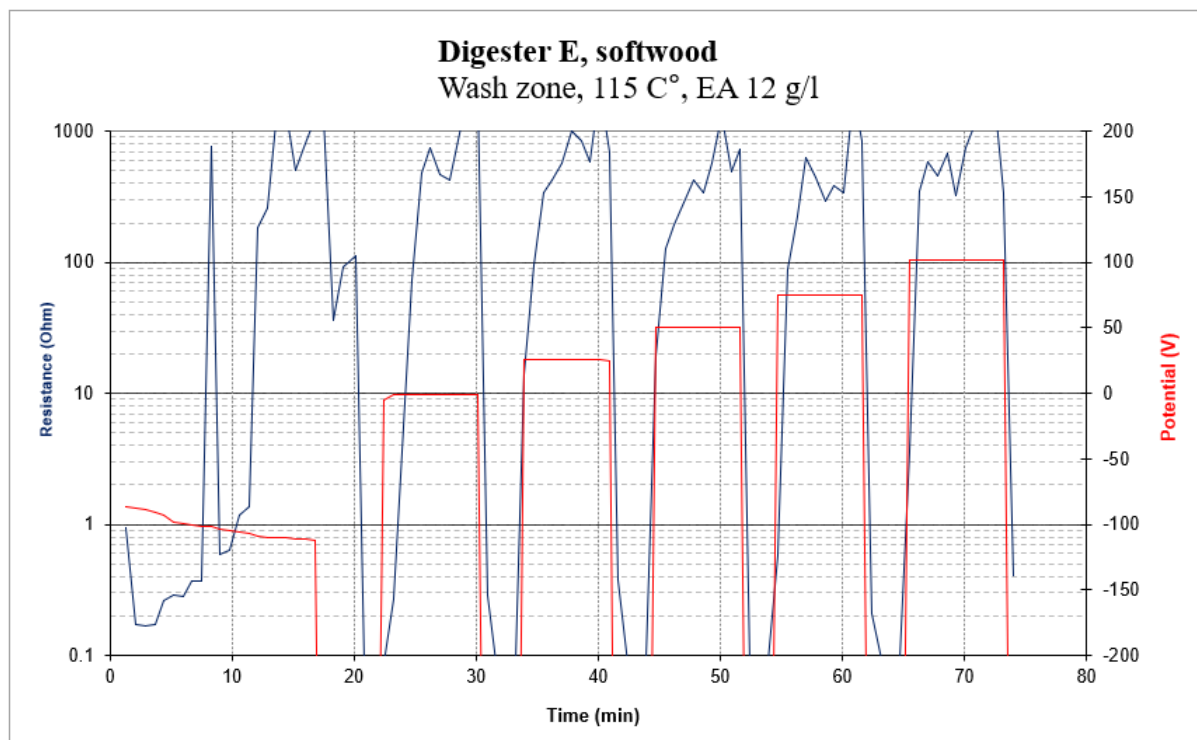


Fig 13: CER results Digester E, softwood, wash zone with very low 115 C°. As expected, passivation occurs spontaneously already at free potential and stays strong throughout the tested potentials.

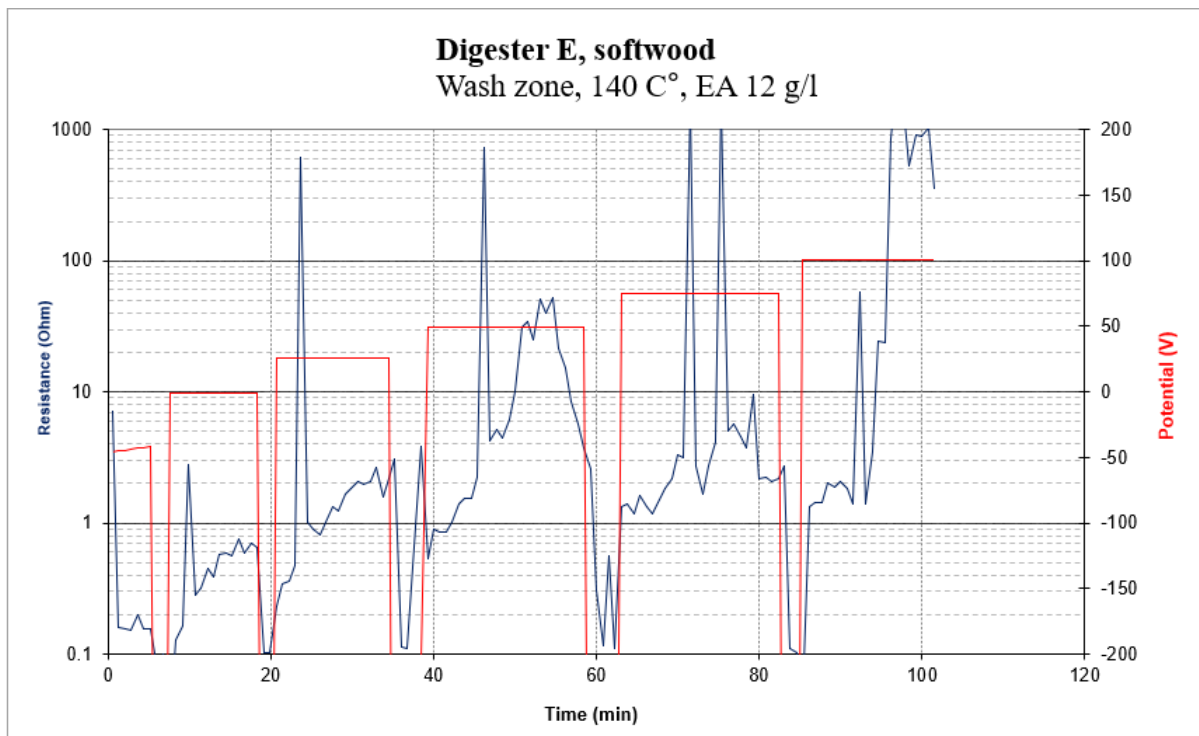


Fig 14: CER results Digester E, softwood, wash zone with 140 C°. The first attempt to passivation occurs at +50 mV but only at +100 mV the oxide layer resistance indicates full passivation.

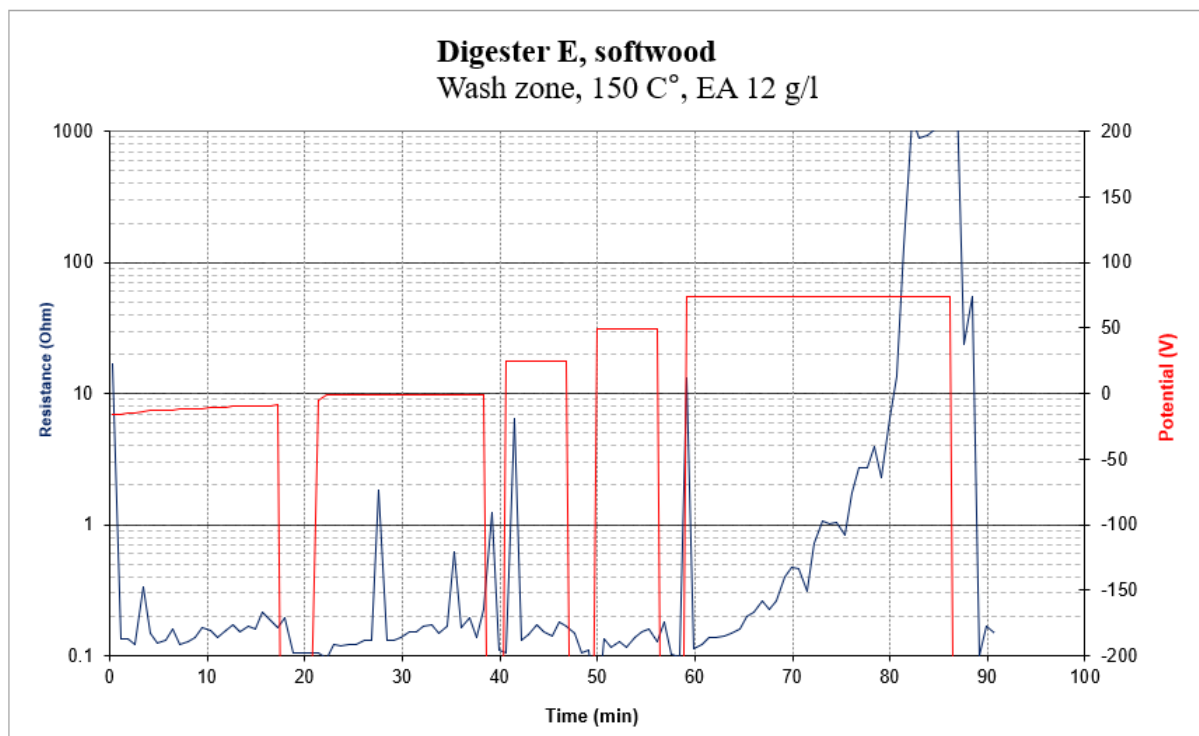


Fig 15: CER results Digester E, softwood, wash zone with 150 C°. There is not any sign of passivation until after longer than usual step at +75 mV.

4- CONTINUOUS ON-LINE POTENTIAL MONITORING

Based on in-situ CER measurements we can define the potential regions that have corrosion risks and should be avoided. With the new cooking methods, new risk potential regions have appeared in regions formerly regarded as safe. For example, CER-result shown in Fig 16 displays two potentials where the oxide layer resistance suddenly drops, indicating porous or unstable passivation. When anodic protection is installed, it is possible to manipulate the electrochemical potential of the digester steel by modifying the amount of protection current fed to the digester wall. In a properly designed anodic protection system, the digester is divided into different zones that can be controlled individually, based on the specific electrochemical environment in each zone. Anodic protection system is controlled in potentiostatic mode, which means the protection current is adjusted automatically to reach a preset potential target. For the monitoring of the anodic protection performance, potential trend measured from each reference electrode installed in the digester wall is the most important information.

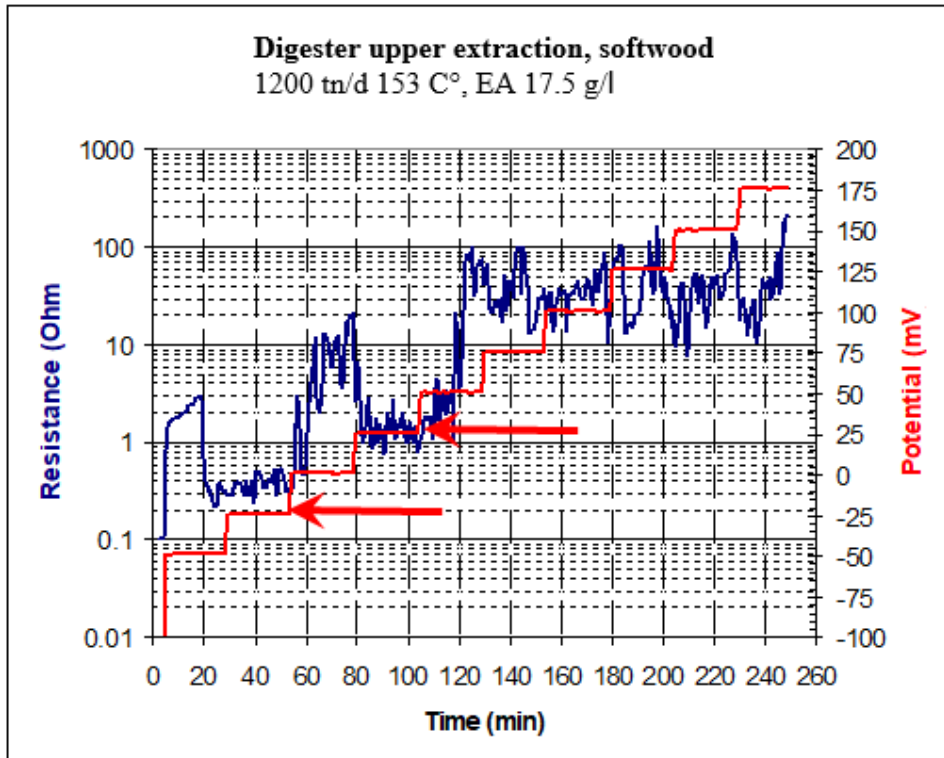


Fig 16: Example of CER measurement result which shows corrosion risk potential regions at -25 mV and +25 mV. The oxide layer resistance drops indicating porous and unstable passivation.

Even if anodic protection system has not been installed, receiving electrochemical potential information from the digester helps identifying the corrosion risks and the proportion of runtime exposing the digester to corrosion risks. Figures 17 and 18 show potential monitoring without and with anodic protection respectively.

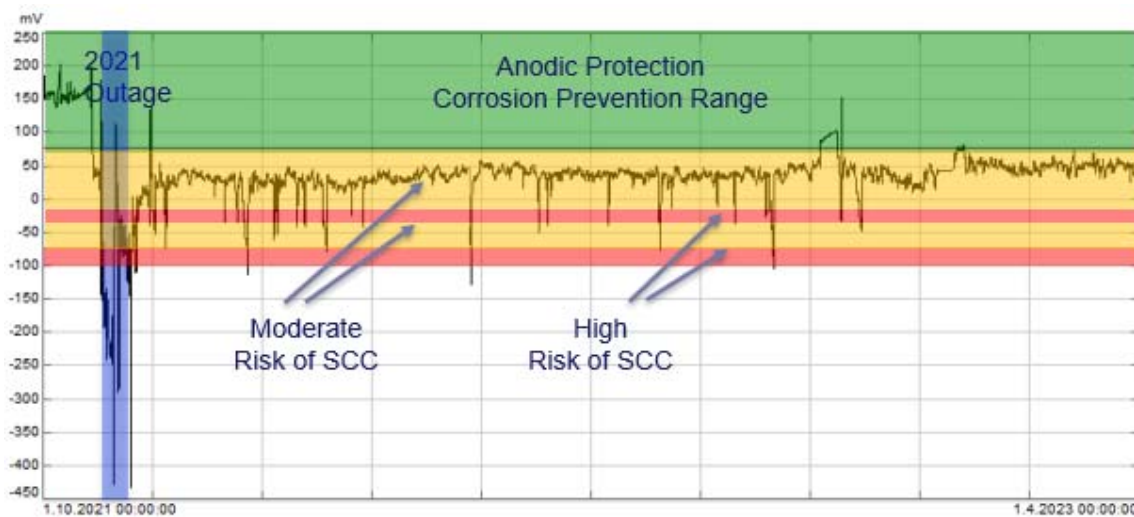


Fig 17: Example of potential monitoring utilized to upper extraction zone corrosion risk assessment. Monitoring of natural potential in the process, no anodic protection applied. Excursions to the high SCC risk range are quite short, although frequent.

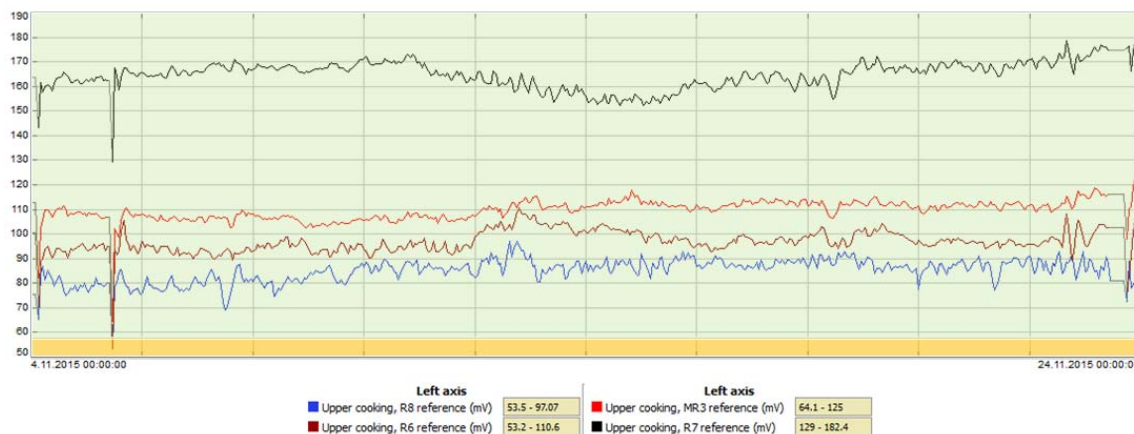


Fig 18: Example of potential monitoring showing excellent performance of anodic protection system on upper cooking zone: All potential values are at safe region.

5- DISCUSSION

To be sure about the potential range where the anodic protection passivates and protects against corrosion it is important to work in the right potential region (passive region). To be able to tune in the anodic protection system correctly it is important to do CER measurements as it can be difficult to define the passive region accurately with any other method.

CER measurements have been routinely conducted for over 20 years now. The results state that the high resolution of CER enables the chemical variations on the liquor as well as the temperature changes and their influence on passivation to be seen. Also the differences between the types of pulping fibers, vessel zones and different types of pulping modifications can be investigated.

CER measurement campaign requires setting up a liquor sample line from the digester circulation to be investigated, hauling a movable equipment container near the sample valve and then conducting several days worth of test runs, while the cooking process needs to be representative of the normal operation. This is an exercise that cannot be repeated very often, so the only feasible method of monitoring the passivity of the digester is by on-line monitoring the electrochemical potential of the vessel wall. Provided that the process stays the same, maintaining the potential in the target region, defined by CER measurements, ensures the non-corroding status of the digester. Additionally, the current feed for the protection circuit needs to be considered as the current density required reflects the quality of the passivation layer. A perfect oxide layer restricts current flow efficiently and results in relatively low current requirement.

Intentional or unintentional process variations are not uncommon in kraft digester process. From the CER-results we can see the significant effect of temperature and effective alkali concentration (EA) on passivity potential regions. Therefore, for a comprehensive anodic protection monitoring, receiving continuous information also of temperature and EA is clearly beneficial. Usually, each reference electrode probe already includes a temperature sensor but measuring EA directly from the digester has not been commercially possible until recently. Now there is a new method for EA measurement built in a probe that can be installed to vessel wall, similar to a reference electrode. These alkali profile probes reveal the EA level exactly at the measuring point and the information can be transferred to anodic protection control system, for finetuning of AP target potential.

6- CONCLUSIONS

This work concentrated on defining the conditions where rate of corrosion reactions can be significantly reduced in a kraft pulp digester. The equipment used for the task is CER (contact electric resistance) where the ohmic resistance of the passivation layer on a carbon steel specimen can be measured in a process sample drawn directly from a sample point. The resistance value achieved, and the rate of resistance increase indicates whether the steel is passivated or at corrosion risk. In CER measurements, the electrochemical potential of the specimen can be manipulated with direct current feed, a method exactly like anodic protection. Therefore, accurate potential targets for anodic protection system control can be defined with CER measurements.

After the safe potential regions have been defined with CER, the assessment of steel passivation status can be done by monitoring the electrochemical potential of digester wall. Continuous on-line monitoring requires permanent reference electrodes installed to the vessel wall. The reference electrodes with integrated temperature sensors are the key equipment in anodic protection control. As there are variations in the cooking process over time, measuring effective alkali concentration directly from the digester would be advantageous.

Based on the various CER experiments and observations on digester corrosion for over 20 years of field surveys, and considering the discussions presented, the following conclusions can be drawn:

- the cooking method considerably affects electrochemical potentials, passivation region, and consequently the corrosion behavior of continuous digesters
- every digester and cooking process is unique and requires individual assessment of corrosion risks
- online corrosion monitoring together with safe potential ranges defined by CER is an effective tool in order to continuously monitor corrosion risks
- key variables influencing the passivation of steel in the CER-tests presented, are wood species, process temperature and effective alkali level

6- LITERATURE CITED

1. Klarin-Henricson, A., *Corrosivity of liquors in continuous digesters*. TAPPI J., 3(7): 13 (2004).
2. Tuthill, A. (editor), "Stainless steels and specialty alloys for the modern pulp and paper industry", Nickel Development Institute, Toronto, 2002, pp. 27 - 31.
3. Bhattacharya, A., Singh, P. M., Electrochemical behavior of duplex steels in caustic environment, *Corrosion science* 53 (2011) pp. 71-81.
4. Klarin-Henricson, A., *Corrosivity of black liquors from a modern digester to a high dry solids concentrator*. *Proceedings of the 11th International Symposium of Corrosion in the Pulp and Paper Industry*, TAPPI, Charleston, SC, 2004, p. 75.
5. Wensley, A., Charlton, R.S., *Corrosion studies in Kraft white liquor: potentiostatic polarization of mild steel in caustic solutions containing sulphur species*, *Corrosion J.* 36 (8) 385 (1980).
6. SAVISALO, H., PULLIAINEN, M., KEROLA, T., "Corrosion of Kraft Continuous Digesting: The Results of In-Situ Electrochemical Testing", *Proc. 5th International Symposium on Corrosion in the Pulp and Paper Industry*, (1986)
7. Hazlewood, P. E., "Corrosivity of pulping liquors". Ph.D. thesis, Georgia Institute of Technology, Atlanta, GA, 2006.
8. Wensley, A., Leavitt, A., Paoliello, F.A., *Stress corrosion cracking of stainless steel in continuous digesters*, *TAPPI 2008 Engineering, Pulping and Environmental Conference Proceedings*, TAPPI PRESS, Atlanta, p.29.

9. Crowe, D. C., *Stress corrosion cracking of carbon steel in kraft digester liquors*. The Institute of Paper Chemistry, Appleton, Wis., 1989. Available [Online]
<https://smartech.gatech.edu/bitstream/1853/2505/1/tps-339.pdf> > [10Apr2010].
10. Paoliello, F. A., “Corrosão de digestores contínuos”. M.Sc. dissertation. Universidade Federal de Viçosa – UFV, Viçosa – MG, Brazil, 2010.
11. Singh, P. M., Anaya, A., *Effect of wood species on corrosion behavior of carbon steel and stainless steels in Black liquors*, Corrosion Science, 49 (2) 497 (2007).
12. Kiessling, L., *A study of the influence of modified continuous cooking processes on the corrosion of continuous digester shell*, *Proceedings of the 8th International Symposium of Corrosion in the Pulp and Paper Industry*, Stockholm, 1995, p. 12.