

Corrosion monitoring and root cause identification in high solids concentrators

PASI NIEMELÄINEN, MARTTI PULLIAINEN, JARMO KAHALA,
AND SAMPO LUUKKAINEN

ABSTRACT: Black liquor high solids (about 80%) concentrators have often been found to suffer from aggressive corrosion. In particular, the first and second effect bodies are susceptible to corrosion attacks resulting in tube leaks and wall thinning, which limit the availability and lifetime of evaporator lines. Corrosion dynamics and construction materials have been studied extensively within the pulp and paper industry to understand the corrosion process. However, it has been challenging to identify root causes for corrosion, which has limited proactive measures to minimize corrosion damage.

Corrosion of the first phase concentrator was studied by defining the potential regions for passive area, stress corrosion cracking, pitting corrosion, and general corrosion. This was achieved by using a technique called polarization scan that reveals ranges for the passive area in which the equipment is naturally protected against corrosion. The open circuit potential, also known as corrosion potential, and linear polarization resistance of the metal were monitored online, which allowed for definition of corrosion risks for stainless steel 304L and duplex stainless steels 2205 and SAF 2906. An online temperature measurement added insight to the analysis. A process diagnostics tool was used to identify root causes of the corrosion attacks. Many of the root causes were related to process conditions triggering corrosion. Once the metal surface was activated, it was difficult to repassivate the metal naturally unless a sufficient potential range was reached.

Application: Mills can reduce corrosion risks and hence extend the lifetime of high solids concentrators.

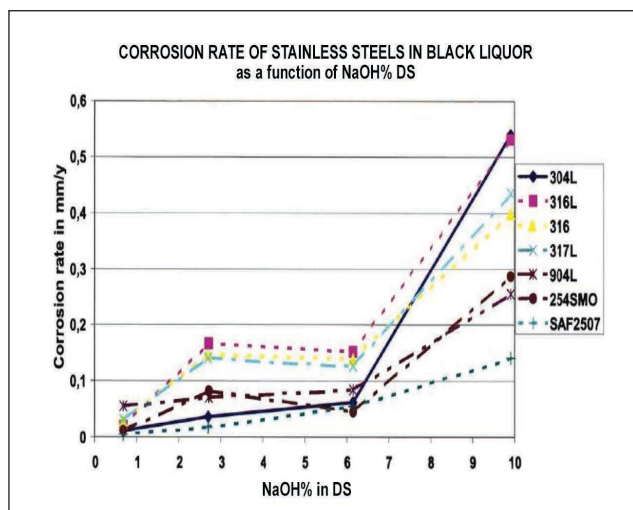
Efficiency requirements for black liquor recovery boilers have implied higher black liquor dry solids (DS). Earlier, a normal DS was 70%, but some mills now are burning as high as 78%–84% DS. As a result, the evaporation temperature increases to 165°C–170°C in concentrators and the alkali content can reach 6%–10% sodium hydroxide (NaOH) in the DS. These changes have essentially increased corrosion rates of stainless steels.

Fig. 1 shows an example of the effect of an increase in alkali content on corrosion rates of stainless steels [1]. Another factor affecting the evaporator function is scaling on the heat transfer surfaces. The main inorganic salts in scaling are sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4). In most cases, small amounts of calcium ions initiate scaling by forming calcium carbonate (CaCO_3) together with Na_2CO_3 and Na_2SO_4 . A double salt burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{CaCO}_3$) is the first sodium salt to crystallize when concentration of DS exceeds 50% [2]. Heat transfer surfaces can require washing every 3–7 days to remove scale. Scaling slightly inhibits corrosion but will not stop it because of the porous nature of the scale, and higher temperature of heating surfaces because of scaling leads to higher corrosion rate. Nevertheless, the average corrosion rate remains lower with scaling than with scale-free, bare-steel surfaces.

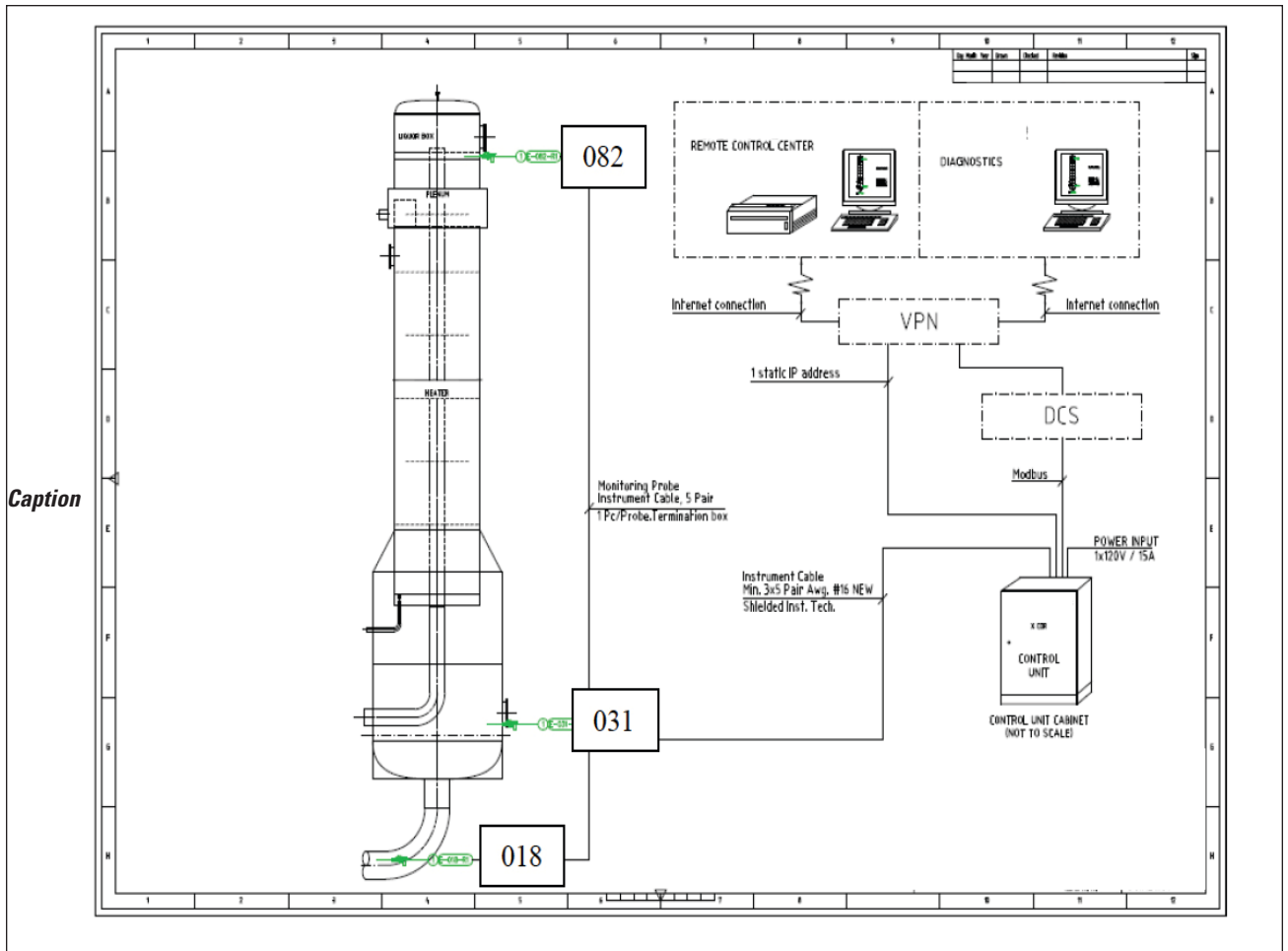
EXPERIMENTAL PROCEDURE

Corrosion monitoring of high solids concentrator

Corrosion in a black liquor concentrator was monitored with sensors at three levels of the evaporator (**Fig. 2**). The highest sensor was located above the liquor distributor plate at level 082, the second sensor below the liquor surface at level 031, and the third sensor in the liquor circulation/outlet pipe at level 018. Every sensor used a temperature sensor and a molybdenum sulfide (MoS_2) reference electrode to assess corro-



1. Corrosion rate of stainless steels in black liquor at 150°C as a function of the sodium hydroxide content of the dry solids (DS).



2. Schematic representation of the corrosion monitoring system with sensor locations in the concentrator indicated.

sion in three different test materials: austenitic stainless steel 304L (UNS S30403), and duplex stainless steels 2205 (UNS S32205) and SAF 2906 (UNS S32906). **Table I** shows the chemical analysis for these materials.

Corrosion monitoring employs three measurements: linear polarization resistance (LPR), open circuit potential (OCP), and temperature. The LPR method measures the current created by a potential deflection in the vicinity of OCP. When the potential deflection remains below 20 mV, the current function can be assumed to be linear. In the LPR measurement, the current density (mA/cm²) is measured ($\pm \Delta i$) after applying potential deflection to both anodic and cathodic directions ($\pm \Delta E$) [3].

Linear polarization resistance R_p can be calculated according to Ohm's law (Eq. [1]):

$$R_p = \Delta E / \Delta i \quad (1)$$

Anodic R_{pa} is Eq. (2):

$$R_{pa} = \Delta E / \Delta i \quad (2)$$

Cathodic R_{pc} is Eq. (3):

$$R_{pc} = -\Delta E / -\Delta i \quad (3)$$

Anodic β_a and cathodic β_c Tafel slopes are needed to calculate corrosion current. Polarization scans in authentic environment are used to determine Tafel slopes.

The equation to calculate corrosion current is Eq. (4) [3]:

$$i_{corr} = \beta_a * |\beta_c| / (2.303 * [(\beta_a + \beta_c)]) * 1/R_p \quad (4)$$

Corrosion current (mA/cm²) can be converted into corrosion rate (CR) mm/a or mpy (Eq. [5] or Eq. [6]) [4]:

$$CR_{mm/a} = 3.28 * M / (n * d) * i_{corr} \text{ (mm/a)} \quad (5)$$

$$CR_{mpy} = 129 * M / (n * d) * i_{corr} \text{ (mpy)} \quad (6)$$

where $M_{Fe} = 55.845$ (molar mass of Fe, g/mol), $n = 2$ (number of electrons fed in the corrosion reaction), and $d_{Fe} = 7.88$ (density of steel, g/cm³).

Material	UNS	C%, max	Mn%	Cr%	Ni%	Mo%	N%
304L	304L	0.03	--	17.5–19.5	8–10	--	--
2205	S31803	0.03	2	22	5	3.2	0.18
2906	S32906	0.03	1	29	6	2	0.4

C = carbon, Mn = manganese, Cr = chromium, Ni = nickel, Mo = molybdenum, N = nitrogen.

I. Typical chemical analysis of test materials.

							Without Cr Corrosion		
Material	ASTM	Fe%	Mn% max	Cr%	Ni%	Mo%	M/n	d	M/nd
304L	304L	72.5		18.5	9		28.08	8.03	3.50
2205	S31803	67.8	2	22	5	3.2	27.84	7.805	3.57
2906	S32906	62	1	29	6	2	27.93	7.9	3.53
M		55.845	54.94	58.6934		95.95			
n		2	2	2		4			
M/n		27.9225	27.47	29.3467		23.9875			

Fe = iron, Mn = manganese, Cr = chromium, Ni = nickel, Mo = molybdenum, N = nitrogen.

II. Molar mass, valence (n), and density values for relevant stainless steel alloys.

Iron (Fe), nickel (Ni), molybdenum (Mo), and manganese (Mn) are expected to corrode electrochemically in stainless steel alloys while chromium (Cr) remains protective on the material surface. **Table II** shows the estimated M, n, and d values for stainless steel alloys relevant for this case. M/nd value for pure Fe material is 3.54 and M/nd weighted value is 3.50 for 304L, 3.57 for 2205, and 3.53 for 2906, respectively. The largest difference remains below 1.3%; therefore, Fe corrosion as CR estimation can be used for all stainless steel materials studied (Eq. [5] and Eq. [6]).

Two oxidative reactions will take place in sulfide-containing liquors on the anodic side: corrosion and sulfide oxidation reactions. Sulfide oxidation is known to disturb the separation of corrosion component from the anodic current. Consequently, the cathodic polarization resistance (R_{pc}) is a more reliable measurement for corrosion monitoring. Therefore, only R_{pc} has been used.

The following parameters were used in monitoring measurements:

- Potential deflection from OCP ± 15 mV
- 10-s duration of one R_p measurement
- 10-min time interval between measurement
- Cathodic Tafel slope $\beta_c = -15$ mV/dec
- Anodic Tafel slope $\beta_a = 21$ mV/dec

CORROSION DATA ANALYSIS

Typically, corrosion rate results are based on LPR values ($\Omega \cdot \text{cm}^2$) and potential (mV). Nevertheless, corrosion rate in mils or millimeters per year are more practical and commonly known units in industry. This conversion can be easily made

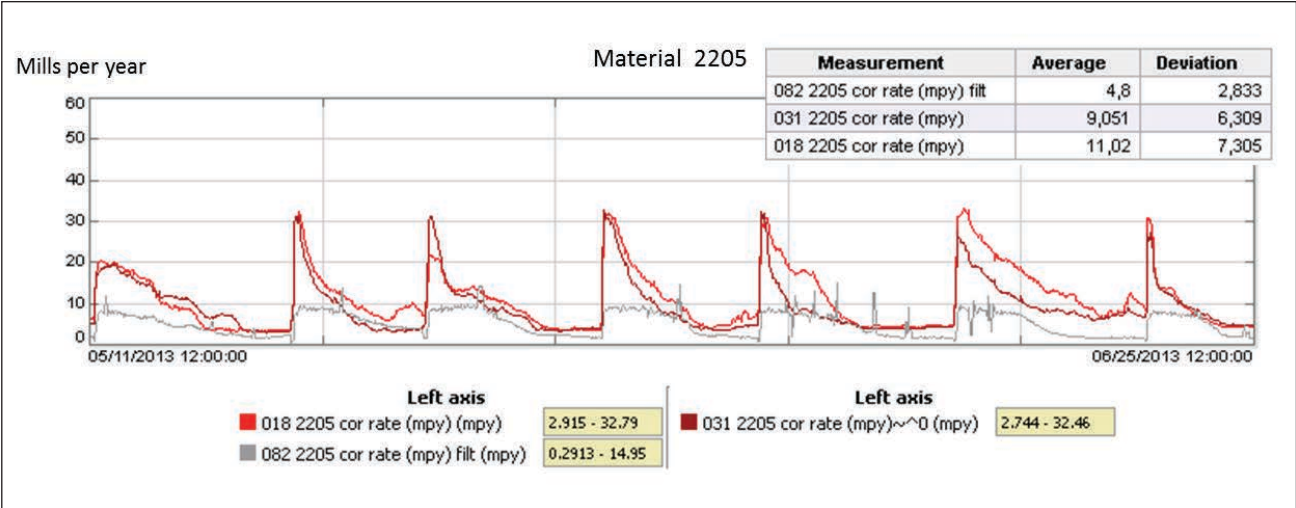
Measurement, mpy	Average	Deviation
082 2205 corrosion rate	4.8	2.833
031 2205 corrosion rate	9.051	6.309
018 2205 corrosion rate	11.02	7.305

III. High solid concentrator average corrosion rates and deviations for top location sensor 082, middle location sensor 031, and bottom location sensor 018, respectively.

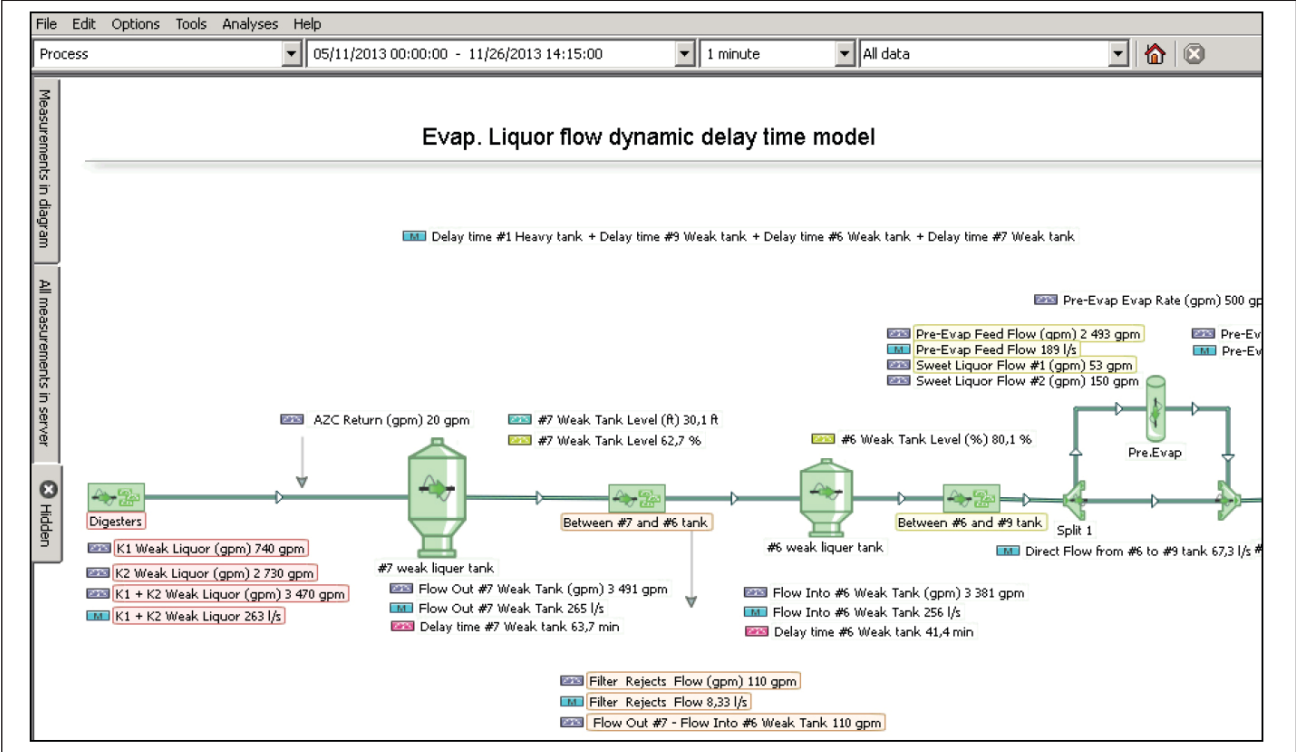
by the calculation engine using Eqs. (4)–(6). **Table III** represents the corrosion rate of 2205 in 45-day averages from the three locations of the high solids concentrator.

Signal analysis is always conducted on the basis of understanding the measurement dynamics. Typically, only averages and standard deviations combined with few other statistical entities are shown for corrosion data. However, trend curves serve much better for understanding the sources of variations. **Figure 3** presents high solids concentrator corrosion rate trend curves of a 45-day period for 2205. Strong periodic variations can be easily detected from trend curves. Corrosion rate starts from 30 mils/year and slopes down to levels of 5–10 mils/year during the following 3–5 days.

When sources of variations have been identified, the next important step is to link corrosion data to process data. This linking makes it possible to statistically connect changes in the process to corrosion peaks and other changes and to search for causal relationships. Analysis software provides tools to access different types of mill information systems and acquire data with real-time interface (**Fig. 4**).



3. Corrosion rate of material 2205 in a high solid concentrator with a 45-day trend curve for top location sensor 082, middle location sensor 031, and bottom location sensor 018, respectively.



4. User interface for the corrosion analysis model in analysis software. The model includes dynamic delay time compensation.

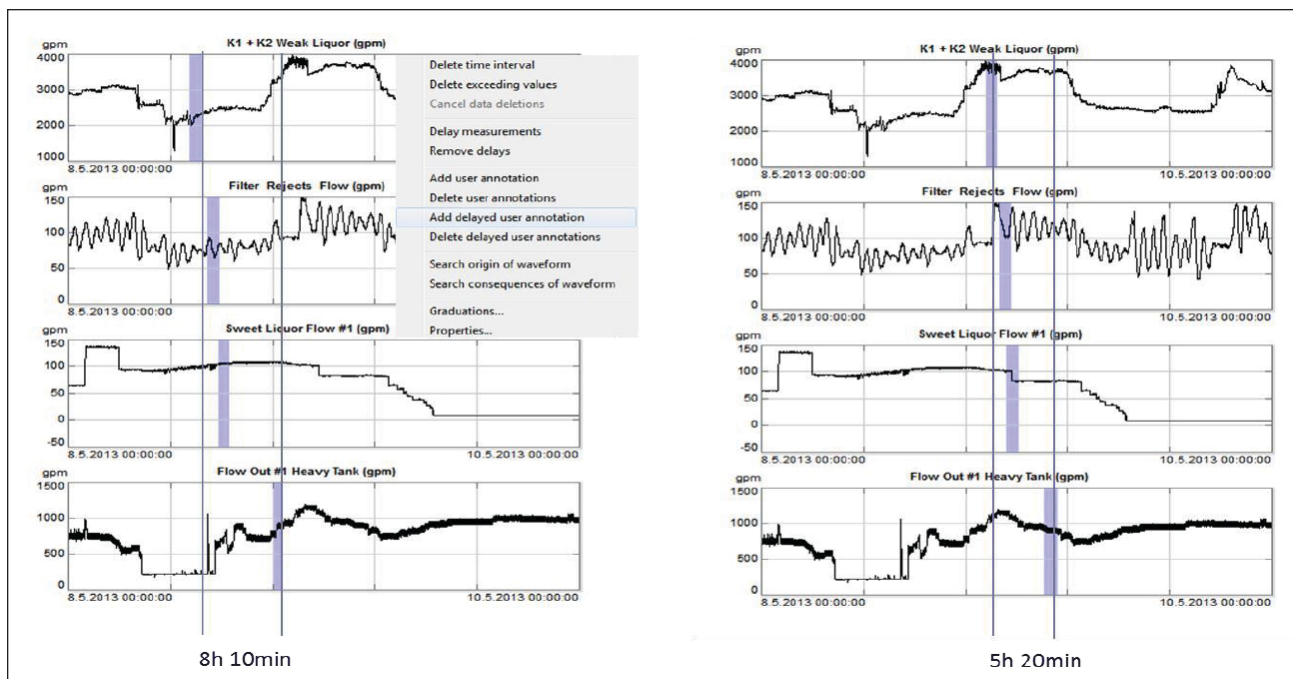
Before conducting other analyses, it is important to study process trends and filter data to include only valid values; otherwise, analyses may lead to wrong conclusions. Filtering is efficiently carried out with analysis software intuitive graphical trend tools.

Analytical tools to connect corrosion data to process data

More than 150 process measurements were included in the analysis to correlate corrosion rate variations to process data.

Descriptions follow of the analysis tools used.

Dynamic delay time model compensates process delays on the basis of a dynamic model (e.g., tank surface levels and flows into and out from the tanks). Delay time compensation is an essential preprocessing step before correlation analysis in processes with long delays (Fig. 5). Best correlations rank correlation coefficients from strongest to weakest and discover the most similar signals to the target signal (Fig. 6). Waveform identification analyzes target signal (e.g., corrosion rate) trend curve shapes and identifies similar shapes in other



5. Dynamic delay time model to track process delays and compensate delays before correlations analysis.

signals. This tool deals with time delays automatically without any specific delay time model (Fig. 6). State comparison compares two periods (e.g., high versus low corrosion rate periods) and indicates signals with highest differences between the periods. Principal component analysis (PCA) is a multivariate analysis method that reduces the sources of variations in high amounts of process variables to relevant calculated variables called principal components (Fig. 6). Hence, PCA allows for the detection of potential root causes for a phenomenon affected by multiple factors.

RESULTS

Short-term variations in corrosion rates

Corrosion rate was found to strongly correlate with the evaporator line washing. The washing procedure induces higher passivation in all materials, as can be seen from the increase in the corrosion potential. During washing, corrosion rate retains the level before washing although scale is removed (Fig. 7).

When entering into the evaporator, hot black liquor quickly activates washed, bare material surfaces, as indicated by a decrease in the corrosion potential and an increase in the corrosion rate. Quickly after washing (<4 h), a new scale layer initiates. Scaling reduces metal surface proportion with a direct liquor contact with the bare metal. This decreases the average corrosion rate by about 40%–60% compared with the corrosion rate just after washing (Table III and Fig. 8).

Hot black liquor corrosion of austenitic and duplex stainless steels has been recently studied in a Finnish research project [5]. This project showed that the corrosion potential of these steels should be >30 mV versus MoS₂ electrode for per-

fect passivation. These potentials are capable of preventing stress corrosion cracking (SCC). In this study, the steels remained passive even with a maximum potential of +300 mV.

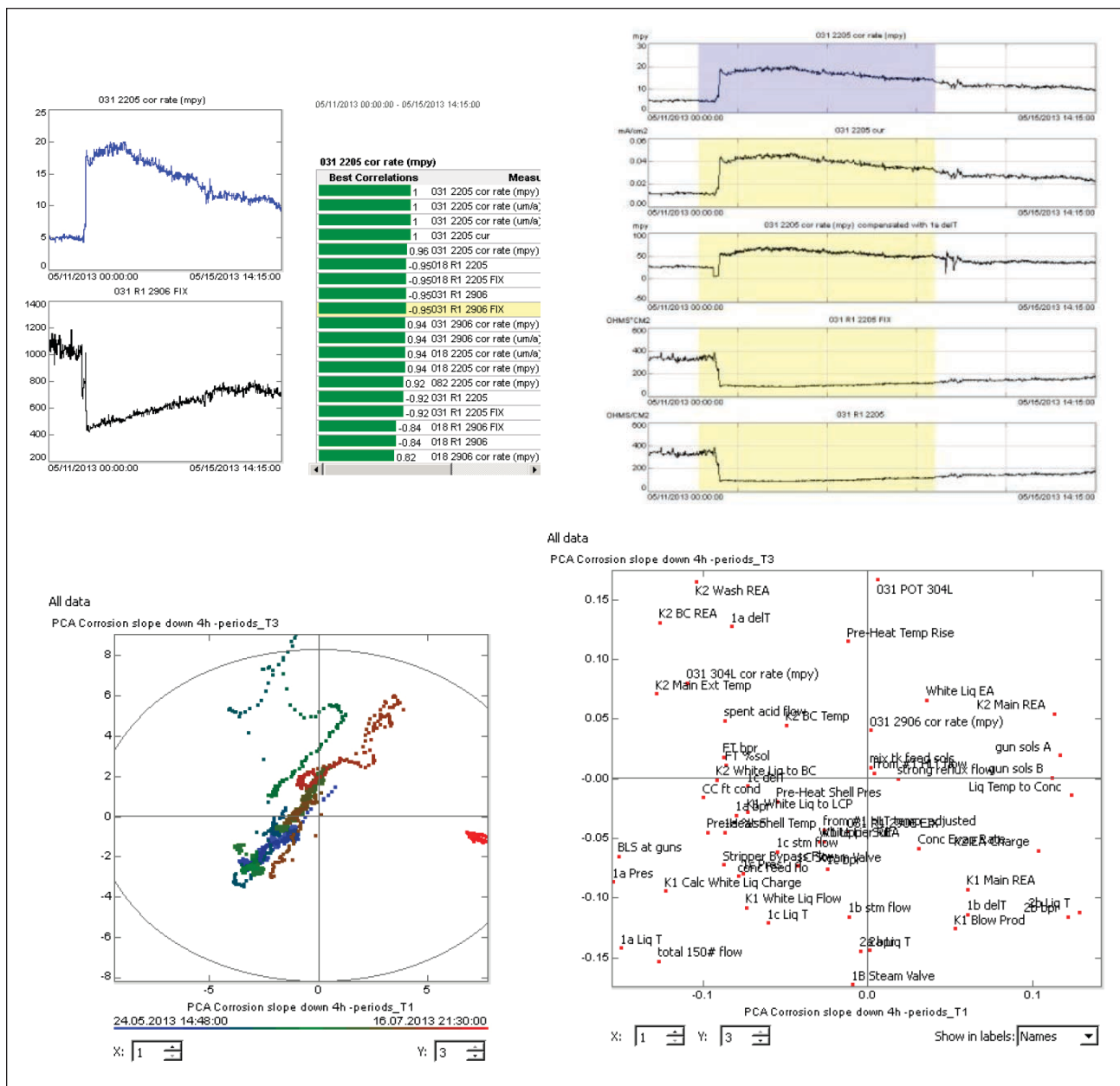
Corrosion rates for different materials and locations in a high solids concentrator are shown in Fig. 9. Figure 10 represents the corrosion rate correlated to time after line washing. Washing induces a high corrosion rate that stabilizes in a couple of days to a lower level.

Fig. 11 shows the correlation between corrosion rate and difference in temperature. Depositing scale hinders heat transfer between steam and black liquor. The measured difference in temperature difference indicates the thickness of the scale layer and implies the need for washing of the heat transfer surfaces when the evaporator reaches too low of a heat transfer efficiency. A rapid decrease in corrosion rate is seen in Fig. 11 after initiation of scaling. In the course of time after washing, the scale covers larger parts of the metal surface, hence reducing the average corrosion rate. Although this is a positive phenomenon, the reduction of the evaporator efficiency is a disadvantage.

Increased corrosion risk in relation to process changes

Increases in corrosion rates were noticed between March and June 2013. Corrosion peaks after line washing became higher, which increased the average corrosion levels (Fig. 12).

Figure 13 represents process variables with the greatest changes between periods A (March) and B (June). Analysis software easily provides all the changes in the process between the periods. Nevertheless, linking of process knowledge to statistical methods is essential to reliably select the



6. Different ways to present analytical results: best correlations (top left), waveform identification (top right), and principal component analysis (bottom).

most relevant process changes. In this case, the average corrosion rate increased about 60% from 5.7 mpy (A) to 9.1 mpy (B) at level 031 in the concentrator. According to the analysis, a lower effective alkali charge to the Kamyr digester, decreased white liquor strength to the Kamyr digester wash cycle, decreased spent acid flow, and increased pressure of the preheat shell were the most important factors contributing to higher corrosion values in the concentrator (Fig. 13).

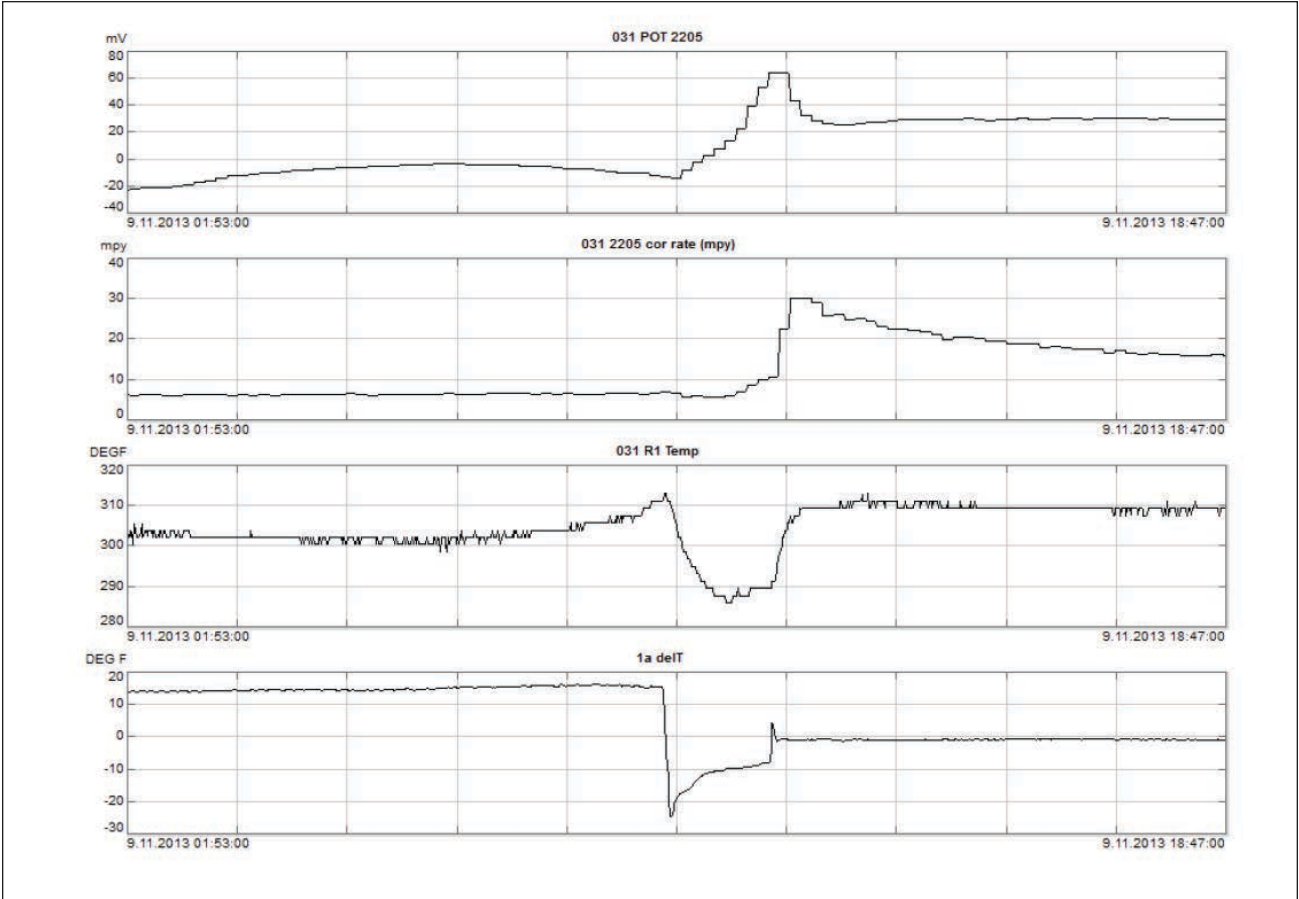
Comparing different corrosion slopes

Corrosion trends occasionally displayed different types of slopes between washings of the concentrator (Fig. 14). State

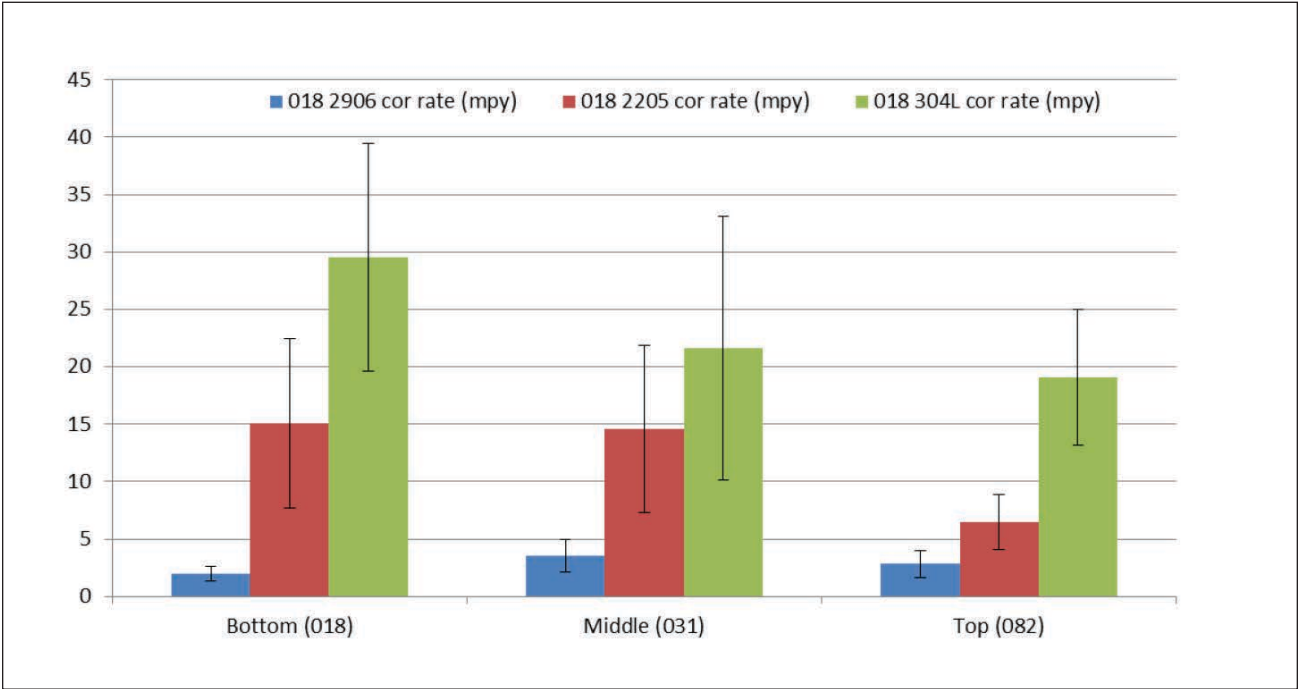
comparison analysis identified numerous process changes between the relevant periods (Fig. 15). Spent acid flow and pH are shown in Figs. 14 and 15. This implies that spent acid may affect washing procedure and corrosion rates. However, further studies are needed for a reliable conclusion.

DISCUSSION

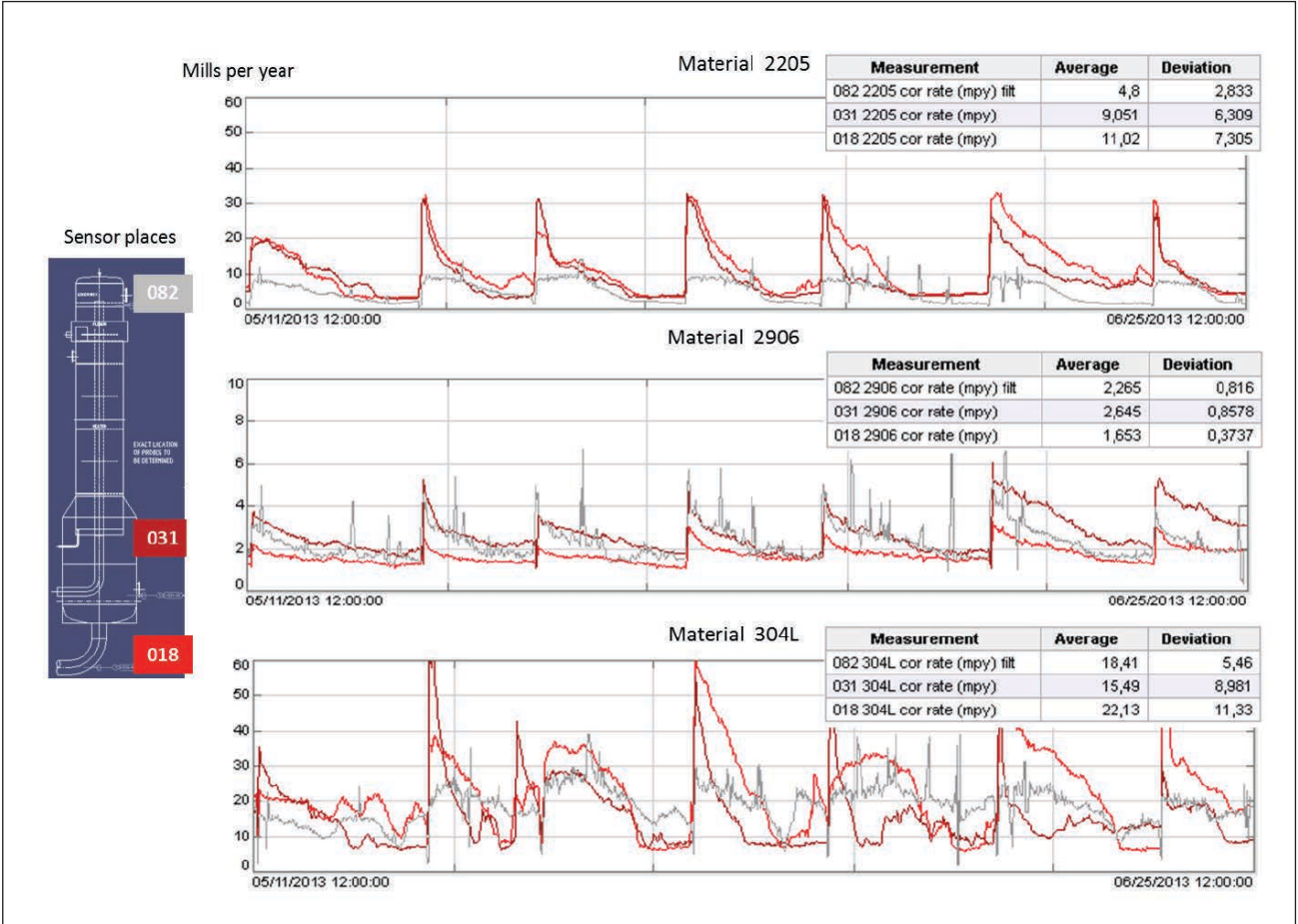
Linear polar resistance measurement is not the best possible method for determining corrosion rates in cases where porous scale deposits on metal surfaces. Electrochemical impedance spectrometry (EIS) is a better method to specify the effect of scaling on corrosion rate. However, EIS is an arduous



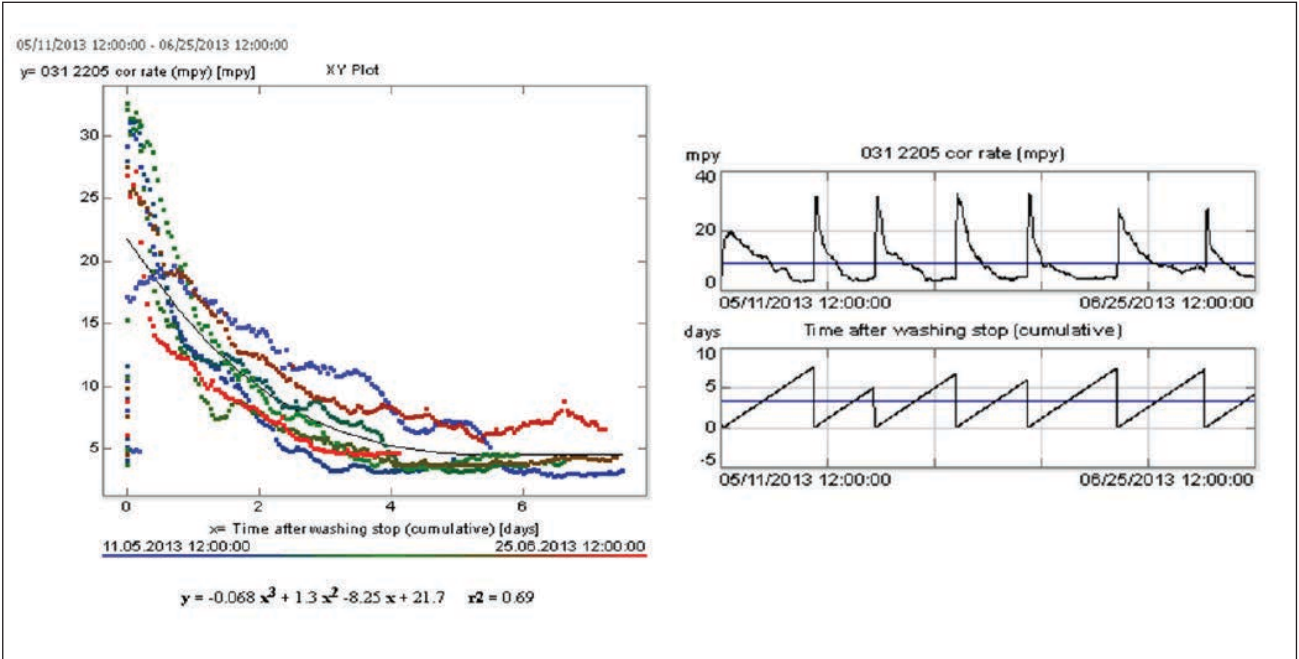
7. Effects of a washing procedure on corrosion behavior in the evaporator.



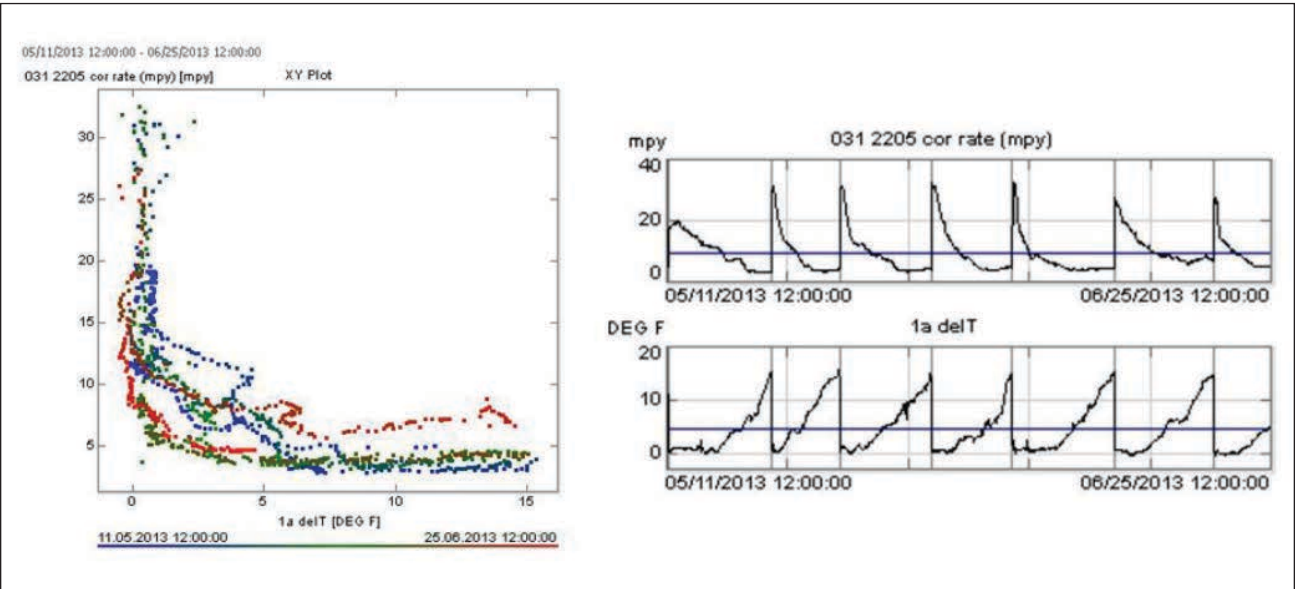
8. Corrosion rate averages and deviations after 0–4 h evaporator washing with large deviations caused by different scale initiation times after washing.



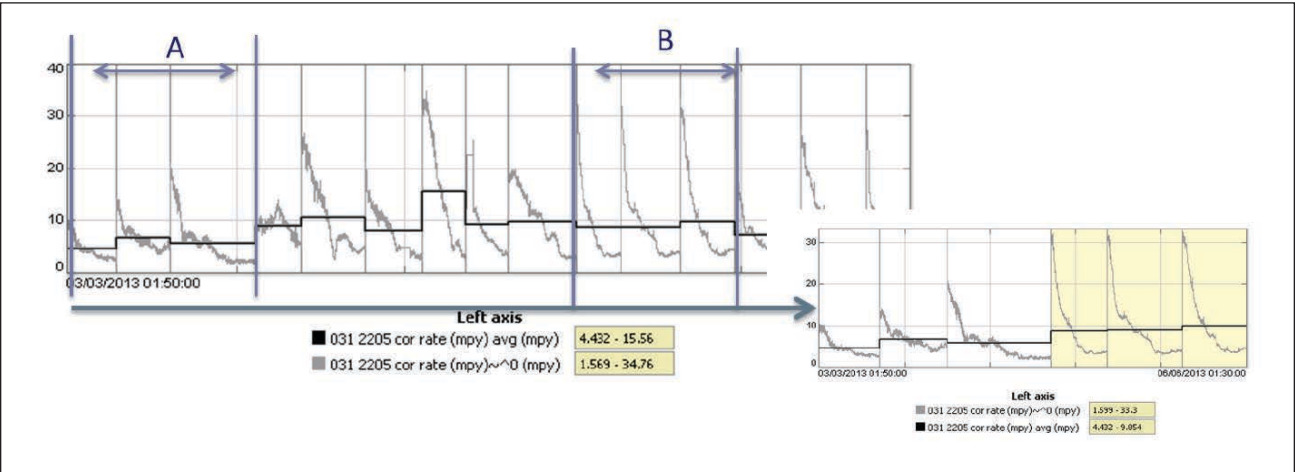
9. Corrosion rates for different materials in a high solid concentrator.



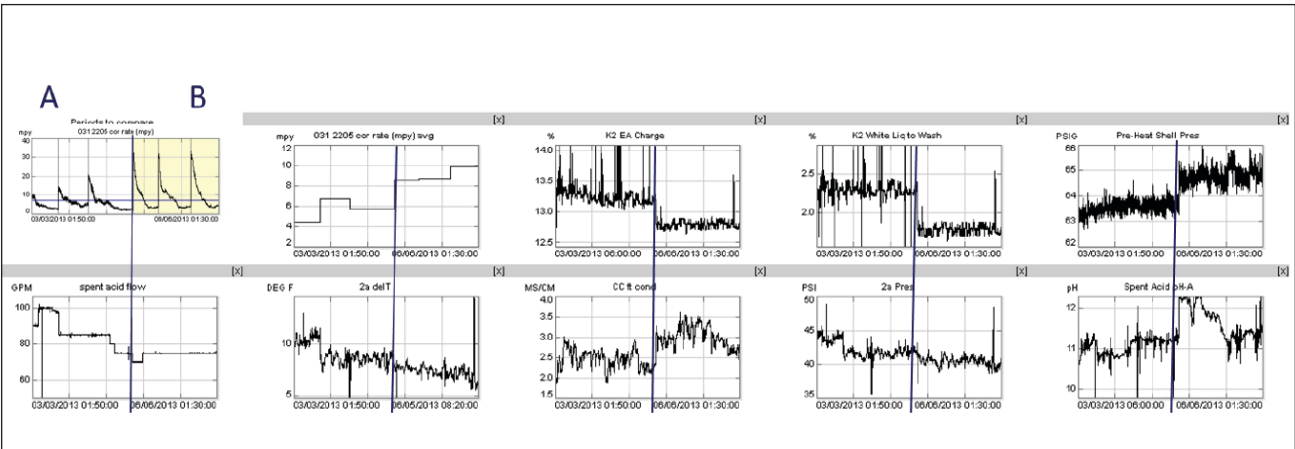
10. Correlation of corrosion rate and time after line washing.



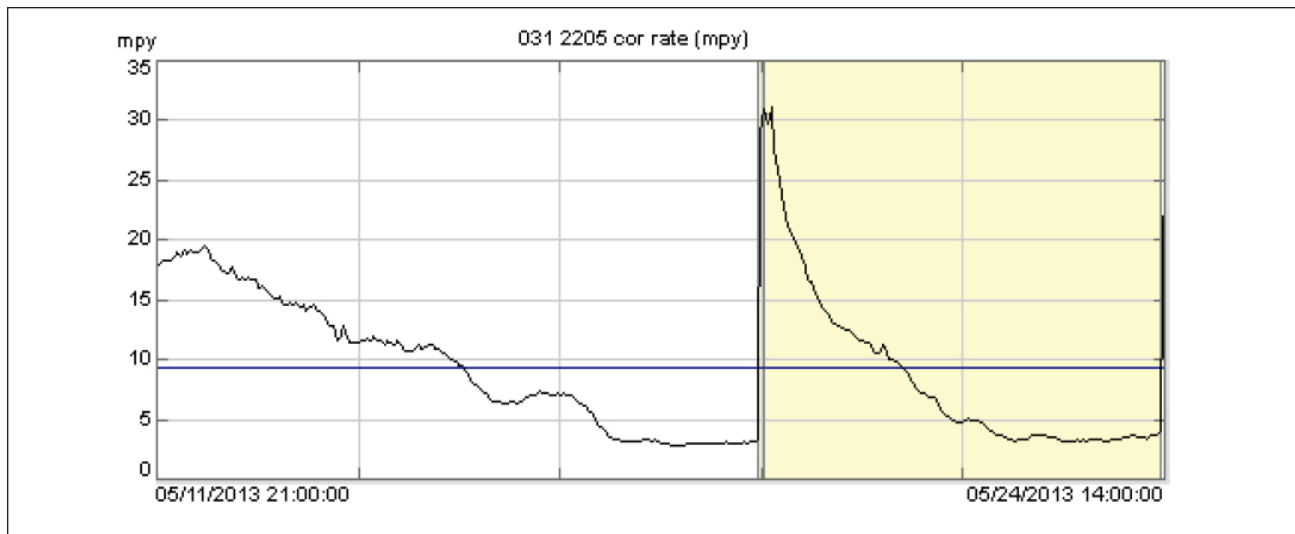
11. Correlation of corrosion rate and temperature difference in a concentrator.



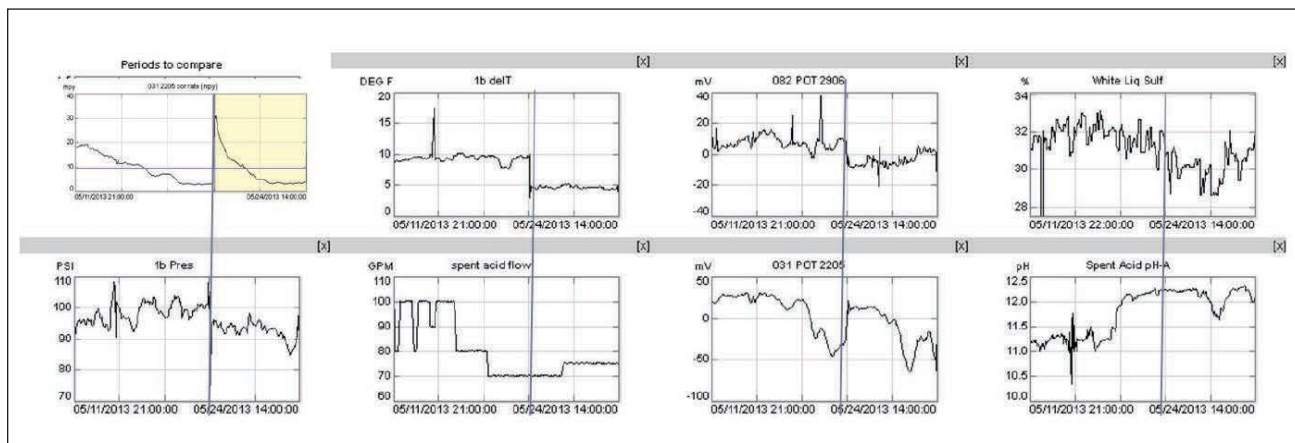
12. Change in the corrosion dynamics observed between periods A (March 2013) and B (June 2013).



13. Measurements with highest changes between lower (March 2013, A) and higher (June 2013, B) corrosion risk periods.



14. Different corrosion rate slopes between high solid concentrator washings.



15. The variables with the largest changes between lower (left) and higher (right) corrosion risk periods.

method to use in online monitoring. Therefore, a more practical approach would be to determine functional correction factor or factors for LPR measurement and to use these to obtain a more reliable corrosion rate for scaled surfaces.

Furthermore, a smoother startup procedure after evaporator washing should be developed. Hot black liquor rapidly activates corrosion when fed into the washed concentrator. Roughly half of the corrosion takes place during the first 24 h after washing, which corresponds to only 20% of the process time between washes.

Monitoring corrosion using electrochemical methods combined with real-time data analysis is new to the pulp and paper industry. More research, tests, and data analysis should be conducted to confirm the effects of scaling, DS, and process variables on the corrosion resistance of materials of construction.

A more comprehensive way to manage corrosion is needed. This new way could consist of three steps: selection of the right construction material for the industrial process, online

monitoring, and an online analysis of corrosion and process data together. The results from corrosion/process data analysis could be the basis for process runs in conditions that are as resistant to corrosion as possible.

CONCLUSIONS

Duplex stainless steel SAF2906 was found to be the most corrosion resistant material in a high solids, hot black liquor concentrator. These findings were from test trials at an evaporation plant where online corrosion monitoring was combined with process data using powerful analysis software. The average corrosion rate ranged between 1.8 and 2.9 mpy. It was also found that the risk for SCC in this environment was the lowest with SAF2906. The average corrosion rate of the duplex stainless steel 2205, which was the material used in the concentrators at this plant, was between 8 and 10 mpy.

Austenitic stainless steel 304L was the least corrosion resistant of the studied materials. The average corrosion rate ranged between 15 and 21 mpy. This material is not recom-

mended to be used in concentrators. The 304L shows high SCC risk and 2205 moderate SCC risk when the potential remains below +30 mV against the MoS₂ electrode. If the potential exceeds +30 mV, both materials remain safe from SCC.

Corrosion rates are highest when hot black liquor enters into the concentrator after washing. In addition, decreases in potentials activate material surfaces. In less than 4 h after washing, scaling initiates a decrease in corrosion rates. Corrosion slowly decreases and the potential trends usually increase slowly towards the next washing time. Another aspect that needs to be considered is that at the start of the washing cycle, potentials rapidly increase to +60–120 mV (much higher than the typical values which remain below +30 mV) and effectively passivate the metal surfaces. Metal surfaces thereafter remain passive until hot black liquor is fed into the evaporator.

Scaling decreases the corrosion rates of the alloys tested but the scaling decreases heat transfer efficiency considerably. For efficient corrosion management, the right construction material, on-line corrosion monitoring, and on-line analysis of corrosion and process data are needed. **TJ**

LITERATURE CITED

1. Klarin, A. and Kottila, M., "Caustic corrosion in black liquor evaporators," *TAPPI Eng., Pulping Environ. Conf.*, TAPPI PRESS, Atlanta, GA, USA, 1996.
2. Euhus, D.D., Shi, B., Rousseau, R.W., et al., "Control of soluble scale in black liquor evaporators and concentrators: part 1. Pilot plant studies," *TAPPI Fall Conf. Trade Fair*, TAPPI PRESS, Atlanta, 2002.
3. ASM International Handbook Committee, *Metals Handbook*, 9th edn., vol. 13, ASM International, Materials Park, OH, USA, 1989, p. 33.
4. Corrosion Doctors, "Corrosion rate conversion," Kingston Technical Software Co., Kingston, ON, Canada, 2016. Available [Online] <http://www.corrosion-doctors.org/Principles/Conversion.htm> <18July2016>.
5. Finnish Metals and Engineering Competence Cluster, "Demanding applications—DEMAPP final report," FIMECC Publication Series No. 3 2009–2014, FIMECC Oy, Tampere, Finland, 2014.

ABOUT THE AUTHORS

Although corrosion dynamics and construction materials have been studied extensively within the pulp and paper industry, identifying the root causes for corrosion has been challenging. This has limited proactive measures to minimize corrosion damage. The idea for this particular research project came from earlier work that we had completed. Many pulp mill evaporators have suffered from corrosion attacks and we have actively monitored several cases before. The challenge has always been in identifying the underlying reasons for corrosion. In this case, we got much further by using a powerful process diagnostics tool.

Much information relating to corrosion risks was collected during the study. The real challenge was to correlate these findings with the process parameters (i.e., to find the root causes of corrosion risks). Using a powerful process diagnostics tool, we were able to identify some root causes of the corrosion attacks, including some related to process conditions triggering corrosion.

The challenges of having vast amounts of data and trying to figure out corrections online were very interesting. A lot of commercial data analyses packages are available on the market, but the key in this case was to use something that is fast and gets to the root causes in minutes. This gives the operator



Niemeläinen



Pulliainen



Kahala



Luukkainen

time to react to corrosion issues and also provides a tool to learn best practices from the process.

The project allowed for a mill study of various process scenarios and discovery of a less corroding formula. Ultimately, the mill was able to reduce corrosion risks and hence extend the lifetime of its vessels. This work would apply to other mills in the industry with similar corrosion issues.

One of the key steps is to develop a user-friendly dashboard for operator and manager level employees so they take immediate action and tune their processes out of corrosion-risky zones. Ultimately, this will lead to increased availability and maximized lifetime of evaporators.

Niemeläinen is president, Savcor Forest Oy, Surrey, BC, Canada. Kahala is vice president of Process Analysis, Savcor Oy, Espoo, Finland. Pulliainen is a Savcor Fellow and Luukkainen is an application specialist, Savcor Oy, Mikkeli, Finland. Email Niemeläinen at pasi.niemelainen@savcor.com.