



Erosion–corrosion of mild steel in hot caustic. Part II: The effect of acid cleaning

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Abstract

Corrosion rates of 1020 steel in 2.75 M NaOH solution at a temperature of 160 °C and velocities of 0.32 and 2.5 m/s were studied. The focus was on the effect of the acid cleaning which was performed by using strong, inhibited sulphuric acid in between the exposures to caustic. In situ electrochemical methods were used to measure the corrosion rate such as the potentiodynamic sweep and the polarization resistance method. Also used were the weight-loss method and scanning electron microscopy (SEM).

Eight electrodes/coupons were used to monitor the metal loss rate, four were placed at the low velocity section, while the other four were placed in the high velocity section of a high temperature flow. The first three coupons in each section were placed within the disturbed flow region, while the fourth was placed in a fully developed flow region.

During the exposure of mild steel to the inhibited acid, following the first caustic period, the corrosion rate increased significantly to between 3 and 10 mm/y with a few electrodes experiencing as high as 50 mm/y. The second caustic period following the acidic period typically started with very high corrosion rates (20–80 mm/y). The length of this corrosion period was typically 2–3 h with a few exceptions when the high corrosion period lasted 7–10 h. Following the very high corrosion rates experienced at the beginning of the second caustic period, the corrosion rates were reduced sharply (as the corrosion potential increased) to nearly the same levels as those observed during the passive part of the first caustic period.

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1. Introduction

In bauxite refineries which utilize the “Bayer process” in the production of aluminium oxide (alumina), a caustic solution is passed through a series of heat exchangers in order to recuperate heat. During the heat exchange process solids form on the steel surfaces by precipitation (often referred to as *scaling*) what reduces the thermal efficiency of the heat exchangers and if left unchecked can reduce or even completely stop the flow through the heat exchanger rendering it inoperable. To prevent this, the flow of caustic is occasionally interrupted and an inhibited strong acidic solution is circulated through the heat exchangers to dissolve the scale.

It was reported by Newton et al. [2] and Rubenis [1] that the corrosion rate of the mild steel heat exchanger headers was significantly increased by this cleaning (descaling) operation. The assumption was that the cleaning process also removed the protective passive film and exposed the bare steel surface to caustic at the beginning of the subsequent caustic period. It was suspected that the corrosion rate increased significantly after the inhibited acid cleaning period when compared with a stable corrosion rate observed after several days of operation [2]. Probes removed from the service before the acidic period started had major damaged areas covered with scale, which indicated that the damage had occurred early during the caustic period. Rubenis [1] stated that the ferrite steel matrix corroded only when the concentration of the inhibitor in the acid dropped below a critical value. To prove these findings in a controlled laboratory setting and to establish the exact magnitude and timing of the critical events, the previously conducted study of corrosion of mild steel in hot strong caustic solutions [3] was extended to include the effect of the *acid cleaning* period.

2. Experimental

In this new set of experiments, the whole cycle (caustic/acidic/caustic) was simulated. The conditions and duration of the two caustic periods was identical to the conditions reported in the previous paper [3]. The two caustic periods (where 2.75 M NaOH solution at 160 °C was used) were separated by an acidic period, in which a 13 wt% inhibited sulfuric acid (H₂SO₄) was circulated for 1.5 h at a temperature of 50 °C in order to remove the protective film. Corrosion was monitored as in the previous study [3]:

- Polarization resistance method was the primary technique used to measure the corrosion rate in situ at different time intervals during the experiment.
- Potentiodynamic sweeps were used primarily to obtain an indication of the corrosion mechanisms and determine the Tafel slopes for the anodic and cathodic reaction.
- Weight loss was used to calculate the time-averaged corrosion rate during the experiment.
- Scanning electron microscopy was used to investigate the appearance of the corroded surface and to check for presence of the protective surface film.

The experimental work was conducted in the high-pressure/high-temperature nickel flow loop describe in detail in the previous paper [3]. The same 1020 steel was used to make the working electrodes (coupons).

This experimental series is named “Experiment 1.2” and more or less the same experiment was repeated three times and consisted of a full caustic/acid/caustic cycle. The following steps were performed:

- The coupon were prepared by grinding with 1500/2000 grit paper, then washed by ethanol and allowed to dry. They were weighed before being installed in the test section, in order to calculate the weight loss.
- The loop was flushed with nitrogen gas to get the oxygen out of the loop.
- The test section was closed and the loop was filled with previously de-aerated caustic solution.
- The caustic solution was circulated and simultaneously heated to 160 °C.
- The test section was opened and the by-pass line was closed.
- The electrochemical measurements were started.
- Subsequently, the flow was stopped, the loop cooled and then drained and flushed by distilled water three times.
- The loop was then flushed by nitrogen gas to remove all the oxygen from the loop.
- The test section was isolated from the rest of the loop, which was filled with inhibited deaerated H₂SO₄ acid.
- The acid was heated to 50 °C, after which the test section was opened, (the by-pass line was closed) and the electrochemical measurements were started. The acidic period lasted typically about 90 min.
- The loop was then drained of the acid and flushed three times with distilled water.
- The test section was isolated again and the loop was filled with deaerated caustic. The loop was heated to 160 °C and the test section was opened (the by-pass line closed); the electrochemical measurements were restarted.
- After completion of the experiments the coupons were removed from the test section and immediately washed with ethanol. They were then dried and stored in a desiccator. The corrosion products were removed by using an diammonium citrate solution as described in the Part 1 of this paper.

The caustic solution used in this experimental series was identical to that of Experiment 1.1 [3]: electrolyte was made by dissolving 2.75 M NaOH and 1.5 wt% NaCl in de-aerated distilled water. The concentration of the inhibited acid in the acidic period was 7.2% by volume H₂SO₄. In the first repeat (Experiment 1.2-1) the concentration of the acid used was 13 vol%. This was an error, however, as seen below this did not affect the overall behaviour. The concentration of a commercial inhibitor in the acid was 0.1%.

In Experiment 1.2-2, the pump failed after the acidic period, and the second caustic period was started after a 48 h pause. During that period, the specimens were kept dry in a nitrogen atmosphere. The second caustic period lasted typically about 20 h.

Experiment 1.2-3 was performed 10.5 days after the Experiment 1.2.2 without replacing the specimens from the loop. Therefore, Experiment 1.2-3 started with a pre-corroded surface, which represents more accurately the actual situation in practice. In all experiments the specimens were weighed before installation in the test section in order to calculate their weight loss. Other key conditions are outlined in Table 1.

Table 1
The conditions for Experiment 1.2

Period of cycle	Temperature (°C)	Mean velocity (m/s)	
		Small-diameter pipe section	Large-diameter pipe section
Caustic	160	2.5	0.32
Acid	50	1.0	0.13

2.1. Polarization resistance measurements

All the electrochemical measurements used in this experiment were made by using the polarization resistance method, by polarizing the working electrode starting at 20 mV below and finishing 20 mV above the open circuit potential. The scan rate used was 0.1 mV/s for the caustic period and 0.2 mV/s for the acidic period. The faster scan rate was used in the much shorter acidic period in an attempt to reduce the time it took to generate the data. The Tafel slope values determined in the previous Experiment 1.1 [3] were used in this experiment for the caustic period. From the literature, the anodic and cathodic Tafel slopes values of 40 and 120 mV/decade respectively were used for the acidic period. The resulting polarization constant ($B = 13$ mV) was checked by conducting small scale glass-cell experiments under identical conditions, which were calibrated against weight loss. These measurements have indicated that the B value used in this study is conservative i.e. the metal loss rates during the inhibited acidic period were probably even higher than those indicated below.

The shape of the polarization curves obtained in the caustic was very similar to the ones obtained in Experiment 1.1 [3]. A typical polarization curve obtained for the acidic period is illustrated in Fig. 1. Unlike for the caustic period, the entire polarization curve of the acidic period was linear for all electrodes.

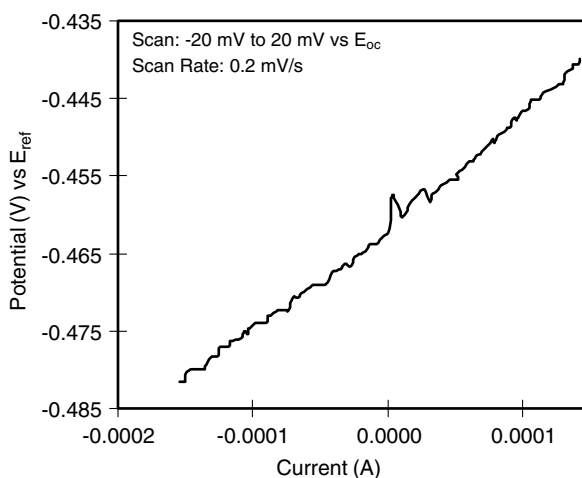


Fig. 1. A typical linear polarization resistance curve for the acid period (electrode number 1).

Table 2

Experiment 1.2: comparison of time-averaged corrosion rates obtained by using electrochemical CR_{ec} and weight loss measurements CR_{wl}

Electrode number	Experiment 1.2-1		Joint Experiments 1.2-2 and 1.2-3	
	CR_{wl} in mm/y	CR_{ec} in mm/y	CR_{wl} in mm/y	CR_{ec} in mm/y
1	4.922	4.137	5.876	10.134
2	SEM	5.043	SEM	
3	SEM	3.565	6.670	8.956
4		4.835	7.265	9.343
5	7.959	8.913	4.724	7.716
6	7.016	8.727	6.691	9.955
7	SEM	3.623	8.568	10.470
8		7.077	6.392	11.501

The time of exposure in Experiment 1.2-1 was 30 h and in Experiments 1.2-2 and 1.2-3 combined was 77 h.

2.2. Weight loss measurements

The comparison of time-averaged corrosion rates obtained by weight loss and electrochemical measurements is given in Table 2. The differences were much smaller compared to the previous experimental series (Experiment 1.1 [3]) due to an improvement in the specimen cleaning procedure after the experiment (the cleaning solution was replaced after each specimen was cleaned). In most cases the weight loss measurements gave smaller metal loss rates (typically up to 30%) which can be related to the still not perfect cleaning procedures but also is within the expected error band for polarization resistance measurements.

2.3. SEM

Three electrodes from Experiment 1.2-1 were examined by SEM, two from the disturbed flow region of the small-diameter section (electrodes 2 and 3), and one from the disturbed flow region of the large-diameter section (electrode 7). The surface view of electrode 2 is shown in Fig. 2 where a porous surface film is visible. The cross-sections of electrode 3 is shown in Fig. 3 displaying no surface film and pits up to 10 μm deep. In Figs. 4 and 5, SEM images of the cross section of electrode 7 are shown at two different locations one with a porous surface film and the other without any film. It is quite probable that the visible porous surface film which covered only part of the surface was not responsible for protection of the metal even if it might have helped achieve passivation.

Only electrode 2 from the joint Experiments 1.2-2 and 1.2-3 was examined by SEM. The cross-section of electrode 2 was examined and showed no visible film as can be seen in Fig. 6.

2.4. Time series

The measured corrosion rate and corrosion potential were plotted versus time for each electrode in Figs. 7–22. In each plot three repeats of the same experiment are shown for the corrosion rate and two for the potential. The potential is not shown for the acidic period as the same in-solution electrode was used as in the caustic experiments with an unknown

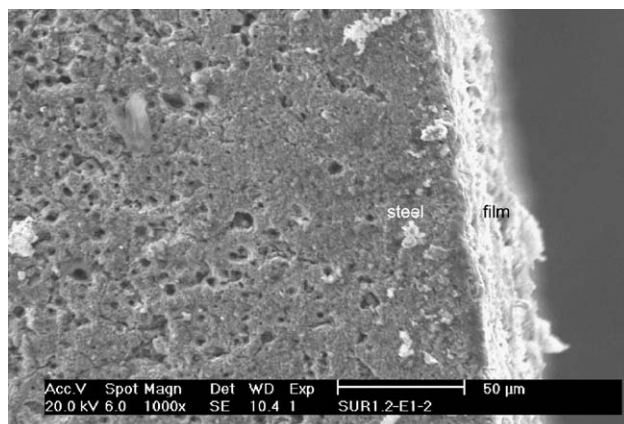


Fig. 2. SEM image of the surface of electrode 2, Experiment 1.2-1.

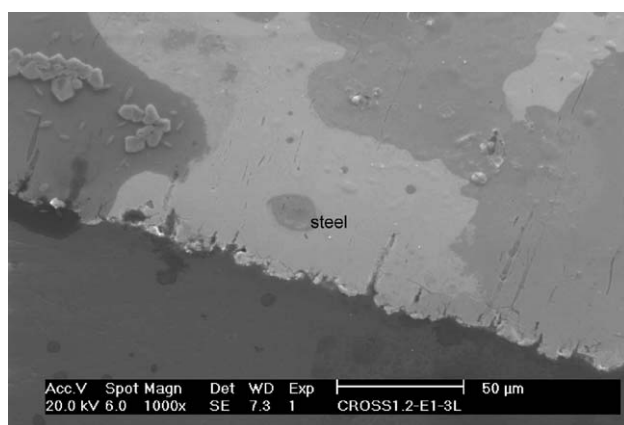


Fig. 3. SEM image of the cross-section of electrode 3, Experiment 1.2-1.

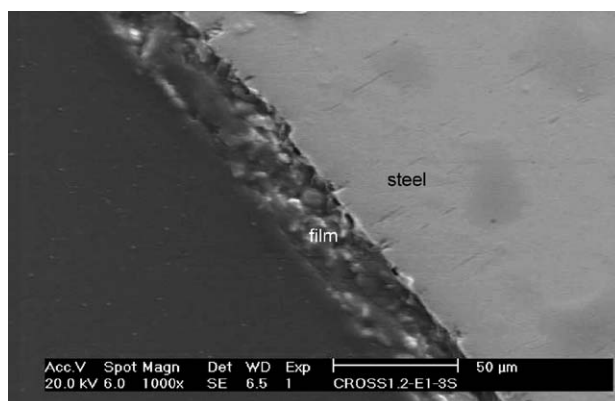


Fig. 4. SEM image of the cross-section of electrode 7, Experiment 1.2-1 showing some surface film.

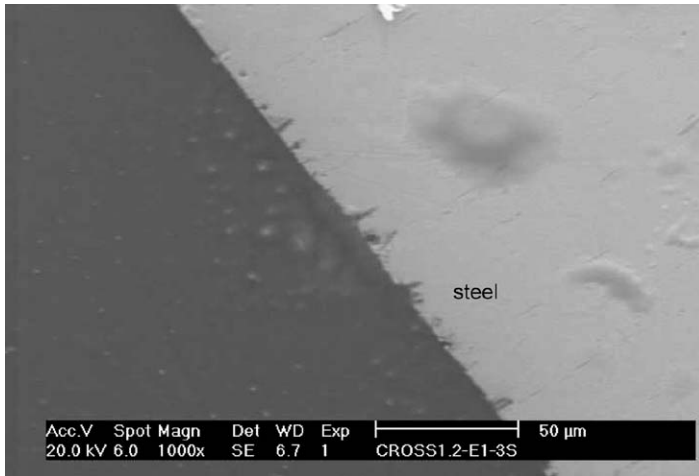


Fig. 5. SEM image of the cross-section of electrode 7, Experiment 1.2-1 showing no surface film.

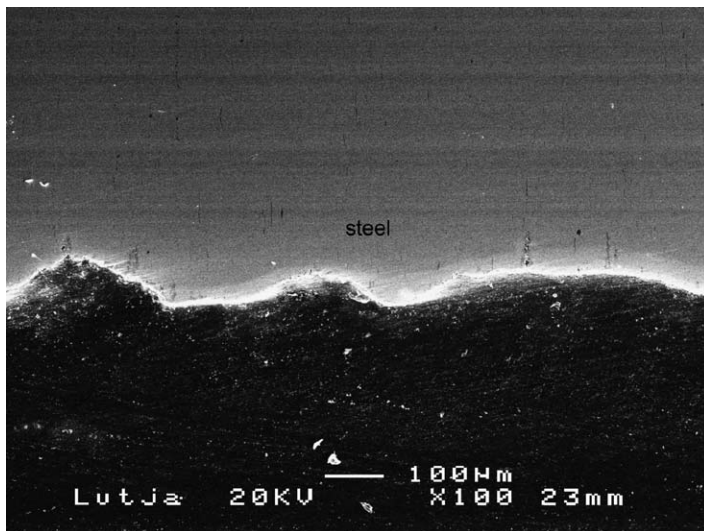


Fig. 6. SEM image of the cross-section of electrode 2, Experiment 1.2-2/3 showing no surface film.

reference potential offset between the two. The following conclusions can be drawn from the results shown below:

- Most of the electrodes in all three repeats of the present experiment started the first caustic period with a high corrosion rate typically 10–100 mm/y, what can definitively be termed as “active” corrosion.¹ After a short period of time, ranging from 0.5 to 3 h, the

¹ The reason that this behavior was not observed in the previous experimental series (Experiment 1.1) is that in those experiments the data logging was not started soon enough and “missed” the high corrosion rates present at the very beginning of the experiments.

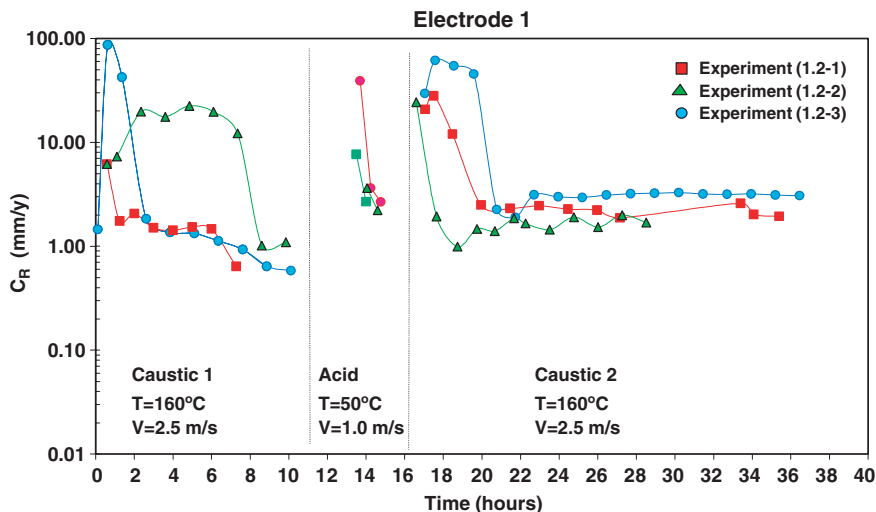


Fig. 7. Corrosion rate vs. time for electrode 1, Experiment 1.2.

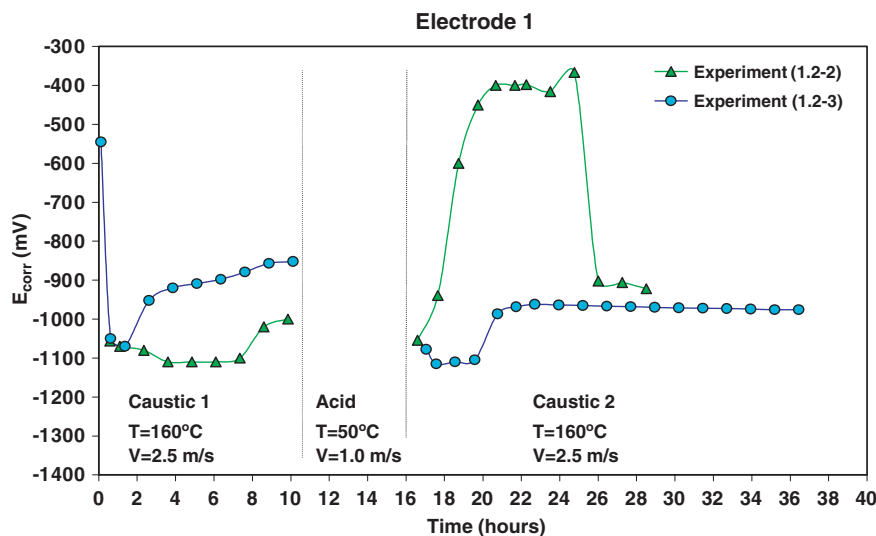


Fig. 8. Corrosion potential vs. time for electrode 1, Experiment 1.2.

corrosion rate was reduced significantly (below 3 mm/y) and stayed low until the acid was introduced. This reduction is most likely related to the formation of passive surface films which lead to an increase of the corrosion potential as observed below. The exceptions were electrode 1 (shown in Fig. 7) and electrode 3 (shown in Fig. 11) both from Experiment 1.2-2, for which the length of the active period was much longer: 8–9 h. As in the case of electrode 1 in Experiment 1.1. [3], it can be speculated that this is related to the very high turbulence levels associated with the flow passing through the inlet section of the sudden pipe constriction. Nevertheless, the effect seems to appear only in small fraction of the cases almost at random.

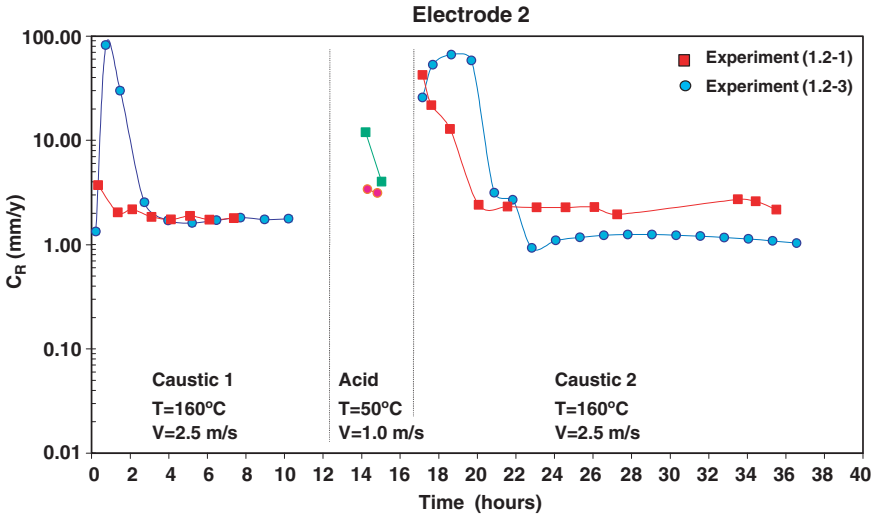


Fig. 9. Corrosion rate vs. time for electrode 2, Experiment 1.2.

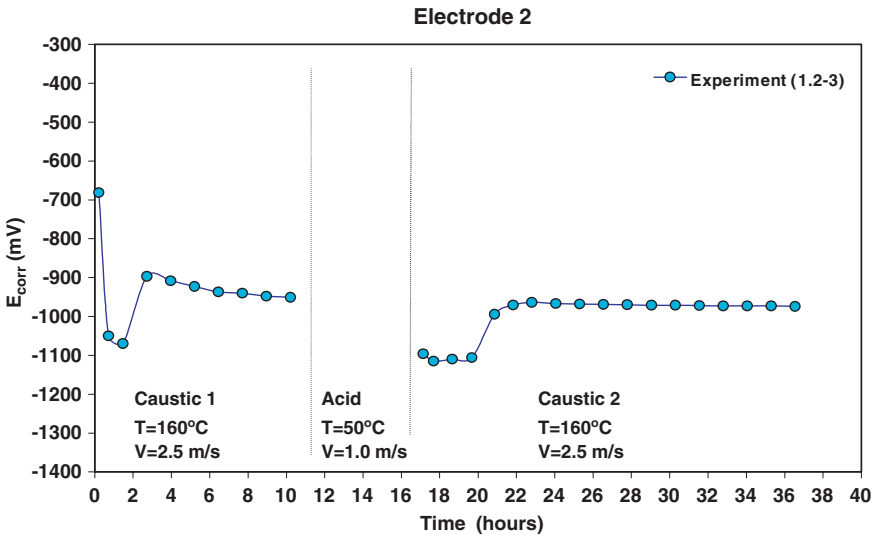


Fig. 10. Corrosion potential vs. time for electrode 2, Experiment 1.2.

- In the acidic period, the corrosion rate increased significantly for all electrodes and in all experiments to values much higher than those recorded during the first caustic (passive) period, despite the presence of the inhibitor. In most cases the corrosion rate stayed between 3 and 10 mm/y with a few electrodes experiencing as high as 50 mm/y. Only a few measurements (typically 2 or 3) were taken during the acidic period, since the duration of the acidic period was relatively short. Across the three repeats of the experiments there were no significant differences in the corrosion rate for all electrodes.

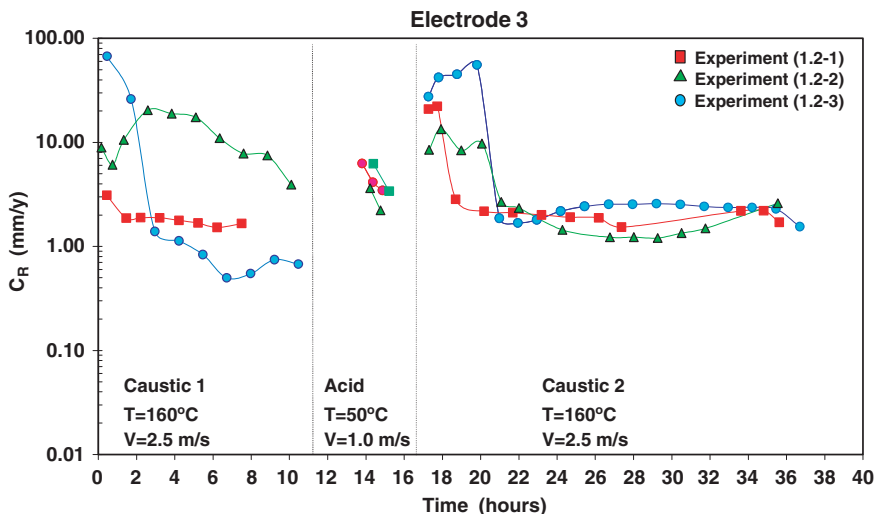


Fig. 11. Corrosion rate vs. time for electrode 3, Experiment 1.2.

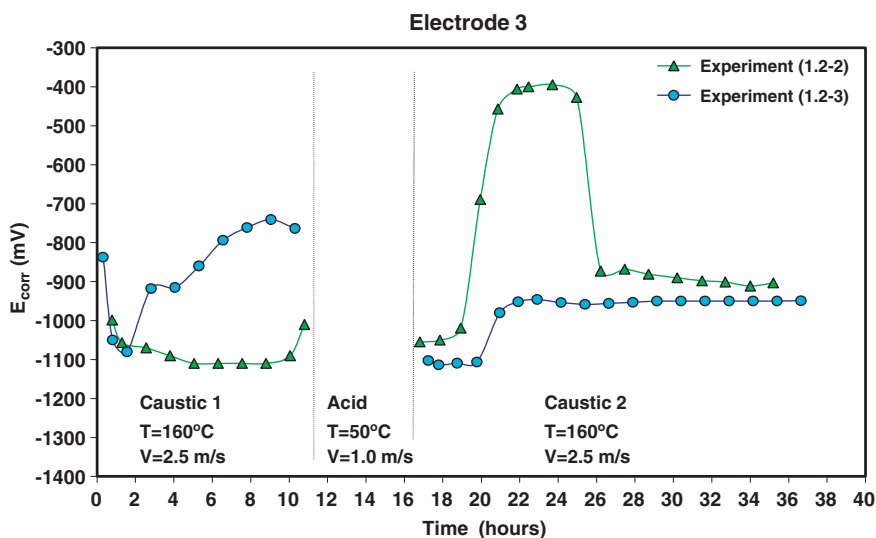


Fig. 12. Corrosion potential vs. time for electrode 3, Experiment 1.2.

- The second caustic period started with extremely high corrosion rates (20–80 mm/y) which are much higher than those observed during the active part of the first caustic period or the acidic period. The length of this very high corrosion period was typically 2–3 h except in the case of electrodes 7 and 8 in Experiment 1.2-3, when it lasted 7 and 10 h respectively. The reasons for these dangerous exceptions remains unclear as they cannot directly be linked to flow conditions particularly for the case of electrode 8, which experiences the “mildest” flow conditions of all eight electrodes.

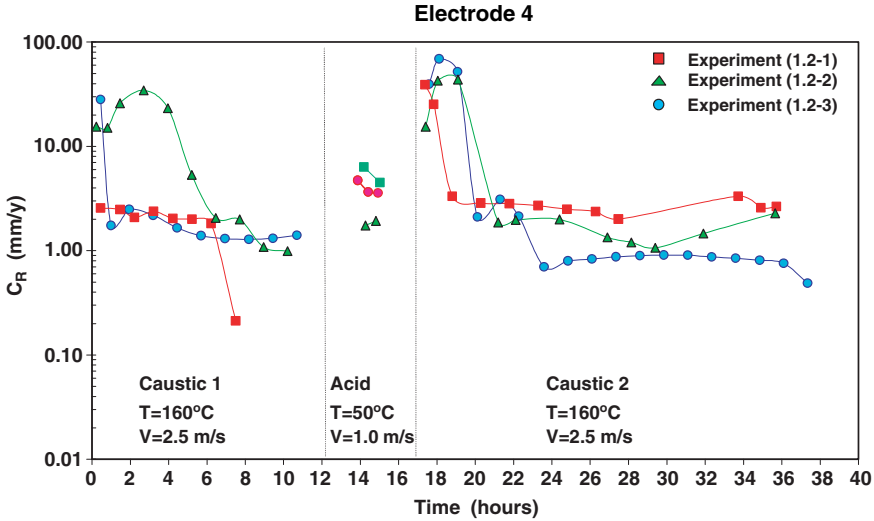


Fig. 13. Corrosion rate vs. time for electrode 4, Experiment 1.2.

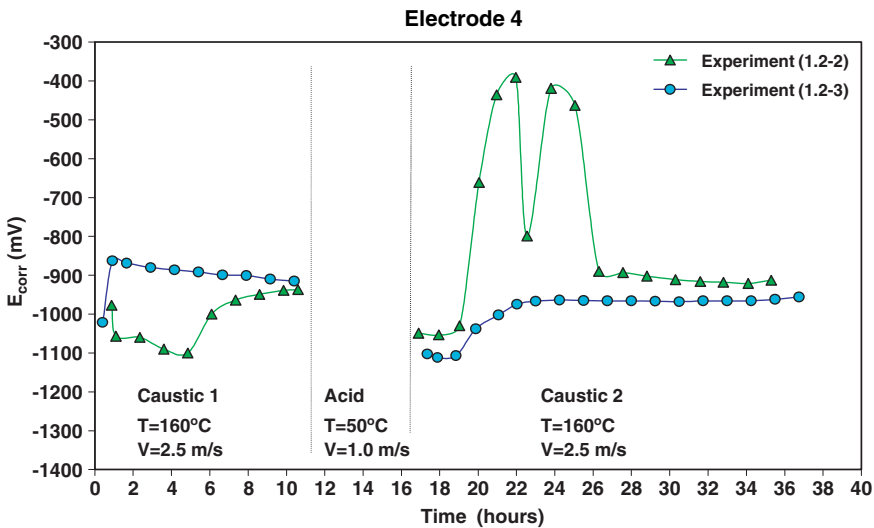


Fig. 14. Corrosion potential vs. time for electrode 4, Experiment 1.2.

- The extremely high corrosion rates observed during the second caustic period, indicate that during the acidic period the surface of the steel has been changed in a way which makes it very vulnerable to a severe attack by caustic. This change goes beyond removing the protective film as the corrosion rates in the beginning of the second caustic period were higher than those observed at the beginning of the first caustic period when the initial surface was film free (freshly ground). Also the effect of the acid seemed “permanent” as no difference in corrosion behavior was observed for the cases of continuous Experiments 1.2-1 and 1.2-2 vs. the interrupted and delayed Experiment 1.2-3.

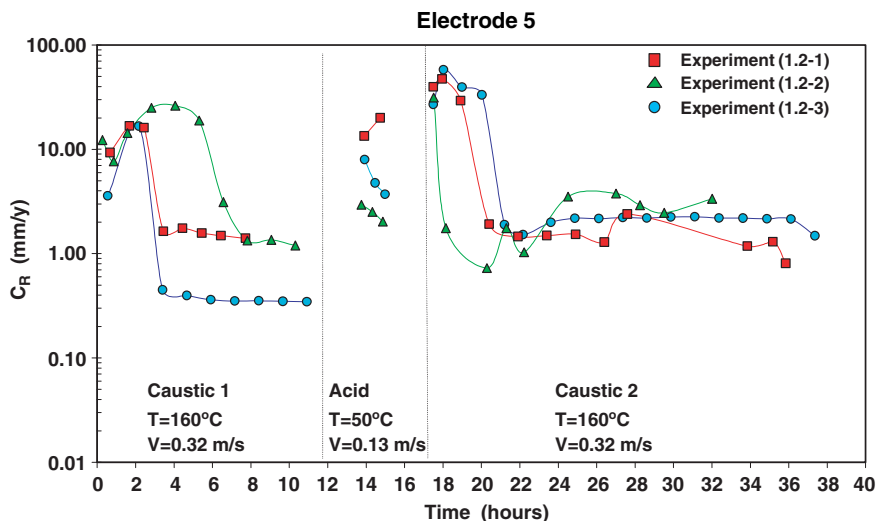


Fig. 15. Corrosion rate vs. time for electrode 5, Experiment 1.2.

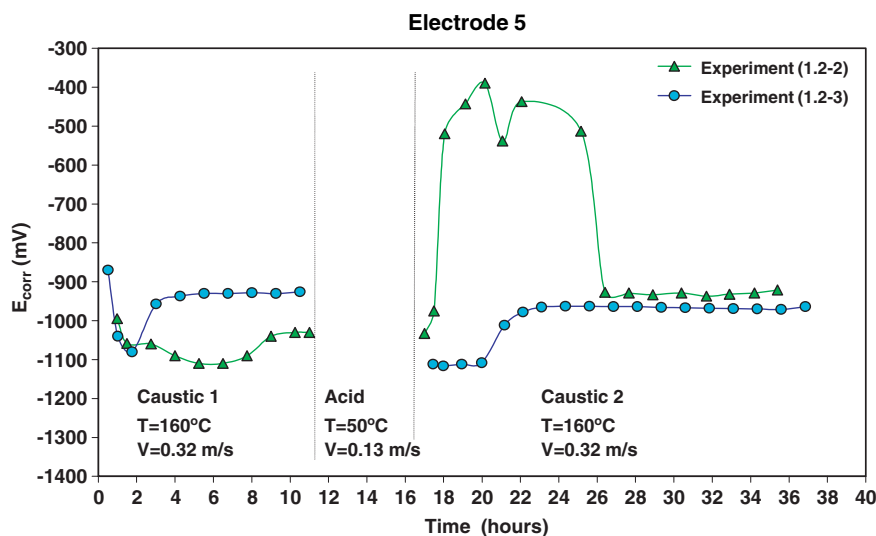


Fig. 16. Corrosion potential vs. time for electrode 5, Experiment 1.2.

- Following rapid corrosion observed at the beginning of the second caustic period, the corrosion rates were reduced sharply (as the corrosion potential increased) to nearly the same levels as those observed during the passive part of the first caustic period.
- The corrosion rates observed during the acidic period of Experiment 1.2-1 when higher concentration inhibited acid (13 vol%) was used, were typically higher than the corresponding corrosion rates observed during Experiments 1.2-2 and 1.2-3 when lower concentration inhibited acid (7.2 vol%) was used.

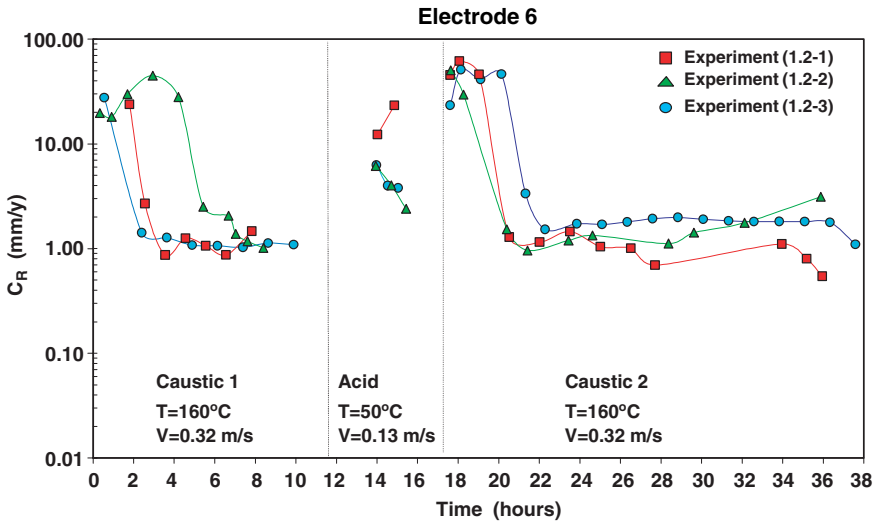


Fig. 17. Corrosion rate vs. time for electrode 6, Experiment 1.2.

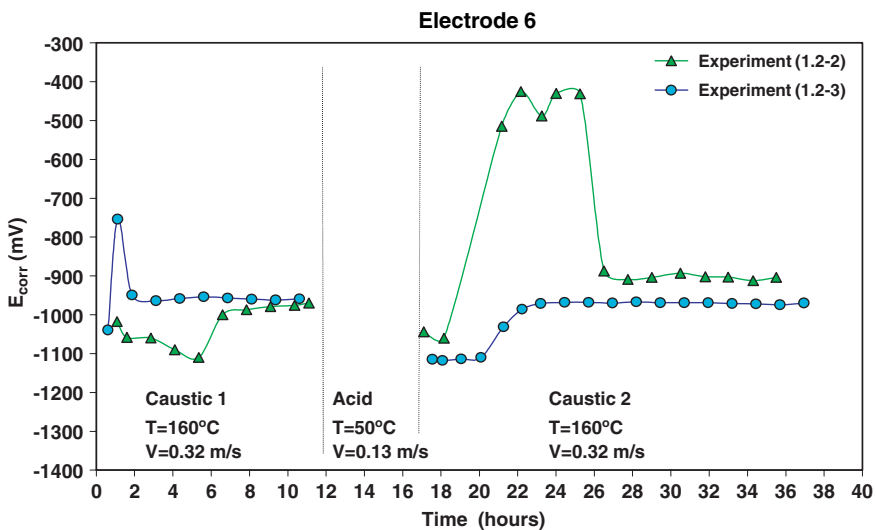


Fig. 18. Corrosion potential vs. time for electrode 6, Experiment 1.2.

- Overall, the turbulence level seems to have had some effect on the rate of metal loss as in three of the four cases of delayed passivation described above, the electrodes involved were located in the disturbed flow region. On the other hand, the mean flow velocity, which was nine times lower in the large-diameter section, had no systematic effect on the corrosion rate.
- In general, all eight electrodes demonstrated similar behavior during the three periods (caustic/acidic/caustic) in all three repeated experiments. In any particular experiment the variation in the corrosion rate was small across the eight electrodes.

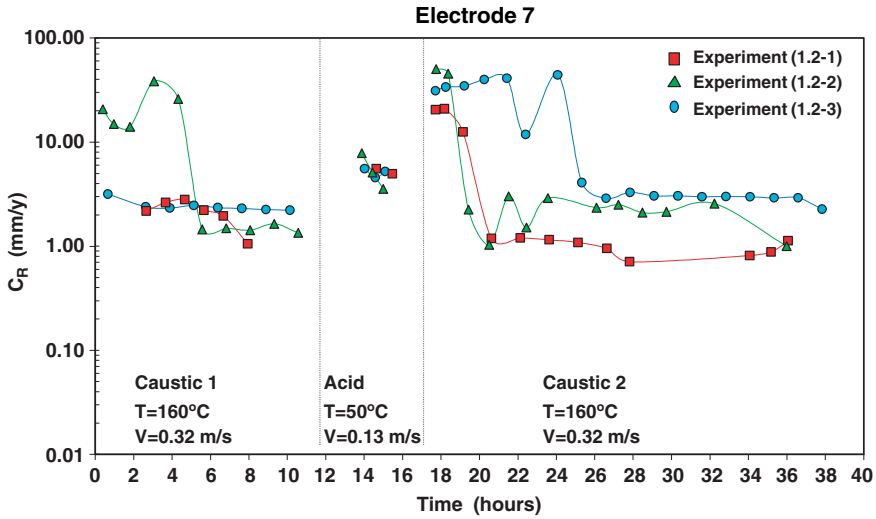


Fig. 19. Corrosion rate vs. time for electrode 7, Experiment 1.2.

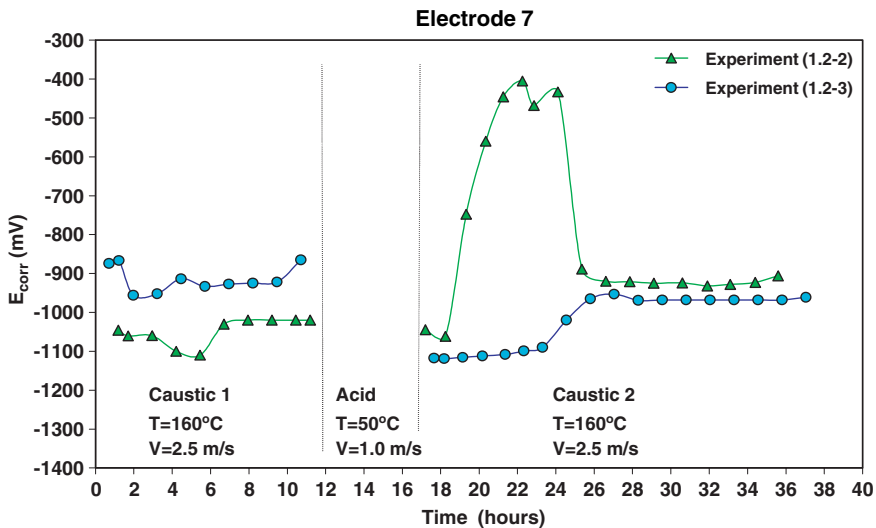


Fig. 20. Corrosion potential vs. time for electrode 7, Experiment 1.2.

3. Conclusions

The aim of this research project was to investigate the erosion–corrosion of mild steel in caustic solutions and in particular the effect of the acidic cleaning period. The problem studied is related to the metal loss problem found in the bauxite refineries’ mild steel heat exchangers. Some of the most important findings are summarized below.

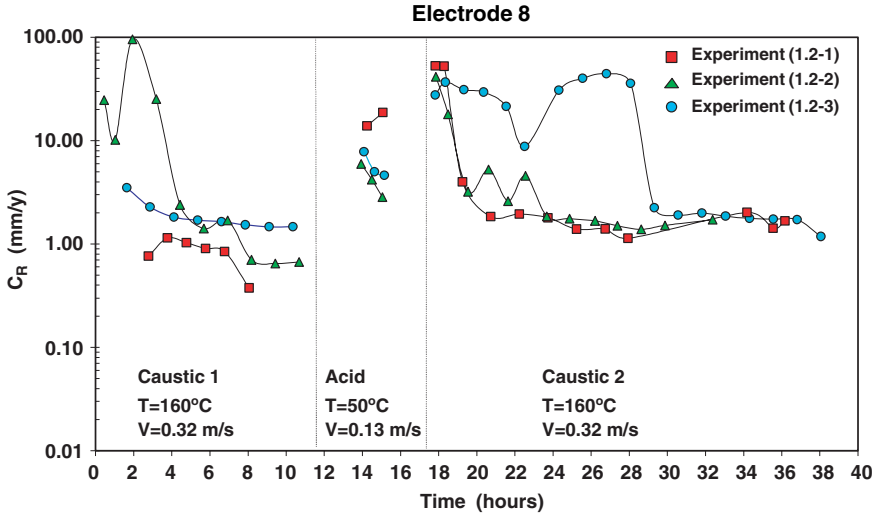


Fig. 21. Corrosion rate vs. time for electrode 8, Experiment 1.2.

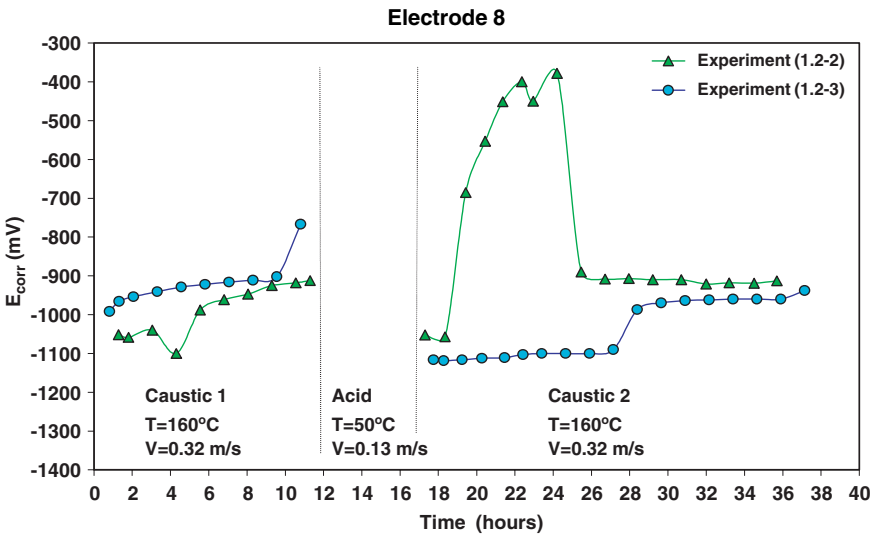


Fig. 22. Corrosion potential vs. time for electrode 8, Experiment 1.2.

- When freshly ground specimen were exposed to hot caustic they initially corroded at very high rates typically 10–100 mm/y for up to 3 h in most cases. Subsequently, the corrosion rates were reduced significantly (below 3 mm/y) and stayed at this level until the acid was introduced. This reduction was most likely related to the formation of passive surface films which also lead to an increase of the corrosion potential.
- In the inhibited acidic period following the first caustic period, the corrosion rate increased significantly for all electrodes and experiments, typically between 3 and 10 mm/y with a few electrodes experiencing as high as 50 mm/y.

- The second caustic period following the acidic period typically started with very high corrosion rates (20–80 mm/y). The length of this corrosion period was typically 2–3 h with a few exceptions when the high corrosion period lasted 7–10 h. The reasons for this behavior remain unclear as it cannot directly be linked to high flow rates or disturbed flow conditions. The extremely high corrosion rates observed indicate that during the acidic period the surface of the steel has changed in a way which made it very vulnerable to a severe attack by caustic. This change goes beyond removal of the protective film. Following the very high corrosion rates experienced at the beginning of the second caustic period, the corrosion rates were reduced sharply (as the corrosion potential increased) to nearly the same levels as those observed during the passive part of the first caustic period.

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