

Impact of Filtrate Recycling on Corrosion of Stainless Steels in Hypochlorite Solutions

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ABSTRACT

To reduce the pollution load, industries using chlorine and its compounds are adopting filtrate recycling as part of closed-loop concept. This strategy, however, enhances the corrosivity of the process liquors. To cope this problem by understanding corrosion process prevailing in the system, detailed corrosion experiments were conducted with stainless steels AISI grade 304 and 316 (hitherto used material) in hypochlorite solutions that fails to withstand the corrosivity of the recycled liquors. The mechanism of the reaction is also discussed.

INTRODUCTION

Hypochlorites are strong alkaline oxidising agents. Out of which calcium hypochlorite solutions are frequently encountered during its manufacturing, bleaching of pulp in paper industry, sanitising, wastewater treatment etc. [1-6]. The process equipment and instrumentation made of even stainless steels suffer from severe pitting and crevice corrosion. Another undesirable aspect of hypochlorite is that they contribute to pollution. In spite of these drawbacks, its use in the industry is still continue in developing countries, for instance, as a bleaching agent in paper industry simply because of its economical viability. In recent time, people have shown more concern to the pollution aspect of hypochlorite. Consequently, paper industries are trying to adopt, among various alternatives, recycling of filtrate / process liquors inside the plant. This practice, however, aggravates the corrosivity of liquor [7]. As a result, costlier stainless steel even AISI 316 grade have started to fail at the locations (pulp washer) where they were used previously (before recycling) without any problem. In present scenario, the industries have to either go for more costly material [7] e.g. Hastelloys, titanium, Avesta 254SMO etc. or to opt for other alternate corrosion control measures. To combat the corrosion problem arose due to the recycling of filtrate/process liquors; it is necessary to make a strategy of its control. However, this will be possible only after understanding the corrosion reactions involved and identification of

the governing factors. In view of this, corrosion experiments mainly accelerated corrosion tests have been performed on stainless steels in calcium hypochlorite solutions. In addition, a few long term immersion tests, for determination of localised as well as general corrosion attack, were also done to confirm the results obtained from accelerated tests and to ascertain their long term performance in service environment.

EXPERIMENTAL PROCEDURES

Experiments have been performed on commercial grade austenitic stainless steels 304 and 316. Their chemical composition was verified with optical emission spectroscopic method [8] and the results are shown in Table I. Electrochemical polarisation tests were performed on the samples of 1.0 cm length cut from the cylindrical rod of diameter 1.4 cm. Before each test, the samples were ground by emery paper 4/0 grade followed by degreasing in acetone. two types of

Table I Chemical composition of stainless steels 304 and 316

Material	C	Mn	Si	Cr	Ni	Mo
SS-304	0.074	1.49	0.41	19.80	8.45	-
SS-316	0.071	1.90	0.48	17.49	12.70	2.18

solutions were considered in the present study i) sodium chloride solutions (NaCl) having chloride 1000 and 2000 ppm, (ii) calcium hypochlorite solutions containing 150-600 ppm OCI^- at constant Cl^- concentration. The pH of the solutions was kept at around 9. The pH and concentration were chosen to simulate the process liquor composition generally encountered in hypochlorite washer of bleaching section with / without filtrate recycling. Solutions were purged by nitrogen gas throughout the measurements to avoid the effect of dissolved oxygen. The samples were introduced into test solutions after the purging of nitrogen gas (N_2) for one hour in case of electrochemical tests.

Cyclic (anodic) polarisation, cathodic polarisation and potentiostatic (current vs. time) were the electrochemical tests performed in the present work. The scan rate was kept at 3 mV/s for anodic polarisation and 2 mV/s for cathodic polarisation measurements. Recording of the curve was started only when the sample attained a stable open circuit potential (OCP) value. The measurements were taken at 25 and 45°C, to know the effect of temperature. These experiments were performed on Potentiostat / Galvanostat Model 352 EG&G PARC, USA. Saturated calomel electrode (SCE) and a couple of graphite electrodes were used as the reference and the counter electrodes respectively.

In weight-loss experiments, the rectangular sample of the size 5.0 x 2.5 cm (thickness 0.25 cm) were used. Before exposure in test solution, coupons were finished upto 4/0 grade emery paper followed by ultrasonic degreasing in 50% acetone solution. To study the crevice corrosion susceptibility, crevices formed by the rubber band over the surface of samples, were immersed in the solutions for six weeks. The depth of attack under the crevices was measured by metallurgical microscope.

RESULTS

The anodic polarisation for both SS304 and 316 NaCl solutions are given in Fig. 1. According to these curves, both stainless steels are immune to pitting attack and

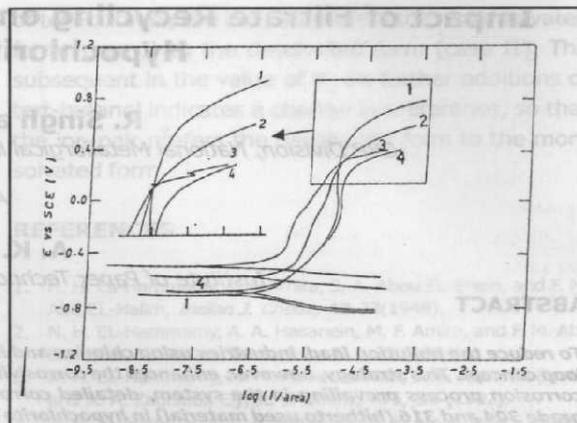


Fig.1 Anodic polarisation behaviour of 316 (curve 1-3) and SS 304 (curve 4) in sodium chloride solutions (curve 1, 2 : 1000 and 2000 ppm Cl^- at 45°C curve 4 : 1000 ppm Cl^- at 25°C).

their tendency to such attack increases with further increase in temperature and Cl^- . Increase in temperature from 25 to 45°C and Cl^- from 1000 to 2000 ppm brings down the margin of safety region (the difference between corrosion potential, E_{corr} , and critical pitting potential, E_p) against localised corrosion for SS316 to the level of SS304. Thus in case of filtrate recycling, where process liquors are expected to have high Cl^- level and temperature, 316 is likely to show limited performance which might have been performing satisfactorily otherwise.

Cyclic polarisation curves of these stainless exposed in hypochlorite solutions are given in Fig. 2. These curves

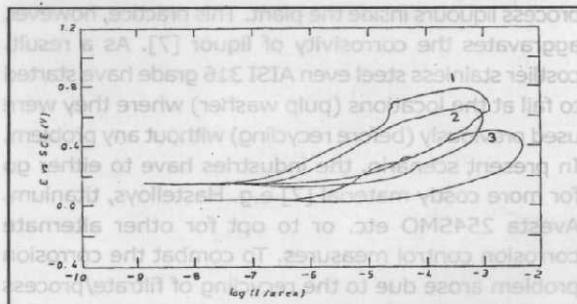


Fig. 2 Cyclic polarisation plots of 316 (curve 1, 2) and 304 (curve 3) in 450 ppm OCI^- containing hypochlorite solutions (curve 1 : 1000 ppm Cl^- at 25°C, curve 2, 3 : 2000 ppm Cl^- at 25°C).

indicate about materials tendency to either passivate or experience localised corrosion in hypochlorite solutions, which was not observed in sodium chloride solutions having same level of Cl^- . To ascertain passivation or localised attack behaviour, potentiostatic plots were recorded on stainless in hypochlorite solutions having varying constituents. The obtained curves showed the passivation tendency for SS316 only in hypochlorite solutions having Cl^- up to 1000 ppm at 25°C.

The parameters useful in ascertaining the localised corrosion (that include repassivation potential, E_p and E_c) along with E_{corr} are given in Table II and III. A general comparison for E_{corr} and E_p for various metal solution

Table II Electrochemical parameters of SS 316 in hypochlorite solutions.

Cl^- (ppm)	OCl^- (ppm)	E_{corr} (mV)	E_p (mV)	E_c (mV)
	150	132	90	
	300	137	143	
1000	450	141	163	230
	600	155	208	
1500	450	136	106	Pitting Occurs
2000	450	132	94	Pitting Occurs

Table III Electrochemical parameters of SS 304 in hypochlorite solutions.

Cl^- (ppm)	OCl^- (ppm)	E_{corr} (mV)	E_p (mV)	E_c (mV)
	150	89	39	
	300	94	57	Pitting Occurs
1000	450	105	67	
	600	109	84	
1500	450	94	29	Pitting Occurs
2000	450	40	25	Pitting Occurs

combinations shows that both steels suffer from crevice corrosion in hypochlorite solutions with a few exceptions. The tendency of crevice attack appears to be almost independent of solution concentrations in

accordance with earlier report [9].

Cathodic polarisation curves in hypochlorite solutions were recorded to find out the variation of corrosion rate with temperature and concentration of OCl^- and Cl^- . The results for SS316 and 304 are shown in Fig.3 and 4 respectively. A comparison of corrosion current density, I_{corr} (that is proportional to corrosion rate) shows an increase in corrosion rate with a rise in temperature and OCl^- (Fig. 5) and Cl^- (Fig. 6).

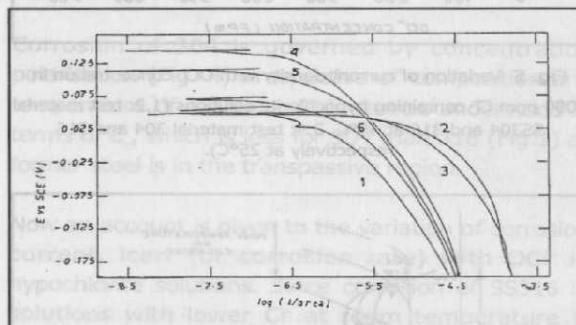


Fig. 3 Cathodic polarisation behaviour of SS 316 in hypochlorite solutions (curve 1-3 : 150 - 600 ppm OCl^- , 2000 ppm Cl^- at 45°C, curve 4-6 : 1000-2000 ppm Cl^- , 450 ppm OCl^- at 25°C)

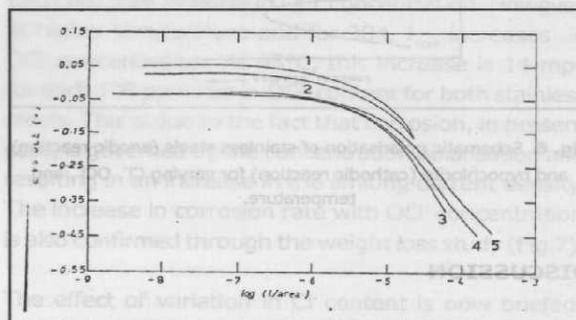


Fig. 4 Cathodic polarisation plots of SS 304 in hypochlorite solutions at 25°C (curve 1,2,4 : 1000-2000 ppm Cl^- , 450 OCl^- , curve 3, 5 : 150 and 600 ppm OCl^- respectively, 2000 ppm Cl^-).

Weight loss (coupon exposure) tests were conducted for a month period at ambient conditions. The trend of obtained corrosion rate (Fig. 7) is same as noted in the case of electrochemical experiments; however, the magnitude was considerably low in the present case as per the well-established reasons.

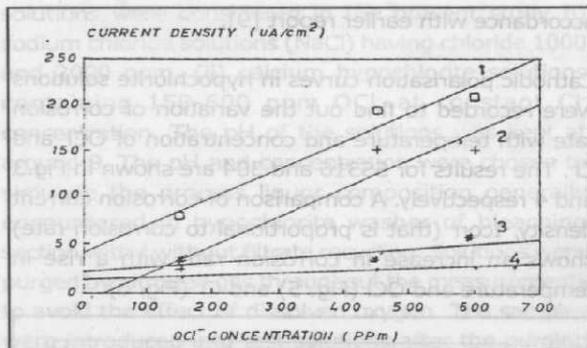


Fig. 5 Variation of current density with OCl^- concentration in 2000 ppm Cl^- containing hypochlorite solutions (1,2: test material SS304 and 316 at 45°C , 3,4: test material 304 and 316 respectively at 25°C).

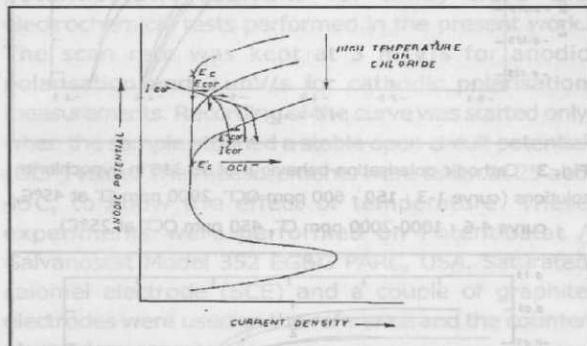


Fig. 6 Schematic polarisation of stainless steels (anodic reaction) and hypochlorite (cathodic reaction) for varying Cl^- , OCl^- , and temperature.

DISCUSSION

Nature of cathodic reactions, to a great extent, influences metallic corrosion in liquid media. Since present solutions are purged with N_2 gas in order to remove the dissolved oxygen, following cathodic reactions are possible.

(a) Water reduction

In case of alkaline solutions, water reduces according to following reaction

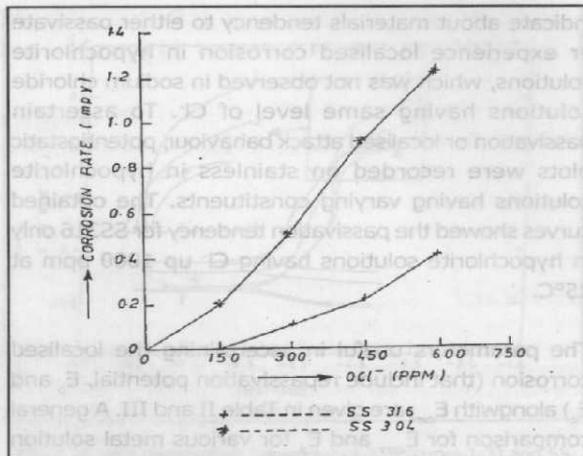
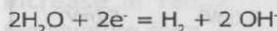


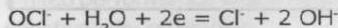
Fig. 7 Variation of corrosion rate (measured through mass loss) with OCl^- in solutions having 1500 ppm and temperature 45°C , for SS316 and 304.



Its standard reversible potential, $(E^0)_{\text{H}_2\text{O}/\text{OH}^-}$ is -0.775 V (SCE).

(b) Hypochlorite reduction

Reduction of OCl^- to Cl^- is governed by following reaction



Standard reversible potential, $(E^0)_{\text{OCl}^-/\text{Cl}^-}$, for above reaction may be calculated from

$$(E^0)_{\text{OCl}^-/\text{Cl}^-} = 0.917 + 0.0295 \log \frac{\text{OCl}^-}{\text{Cl}^-}$$

For present solutions, $(E^0)_{\text{OCl}^-/\text{Cl}^-} = +1.18\text{ V}$ (SCE)

It is important to mention that in case of OCl^- free solutions e.g. sodium chloride, water reduction will be the only cathodic reaction. However, in hypochlorite (having OCl^- as well) solutions, corrosion of steel will be govern by both reduction reactions (a & b) at the cathodic sites. Out of H_2O and OCl^- reduction (where both exist), the later dominates being OCl^- a strong oxidant (compare E^0 for $\text{H}_2\text{O}/\text{OH}^-$ and OCl^-/Cl^- reaction).

Effect of process parameters on localised corrosion

Due to OCl^-/Cl^- in hypochlorite solutions, for which E^0 is 1.184V, E_{corr} of stainless steels shifts to more anodic direction as compared to those in chloride solutions (Fig. 1 & 2). Consequently, the anodic polarisation curves exhibit (i) truncated passivation region indicating steel to passivate (curve 1 in Fig. 2) or (ii) steels in transpassive region showing localised corrosion (curve 2 & 3 in Fig. 2). From anodic polarisation curves (Fig. 2) and potentiostatic plots, one observes that E_{corr} is less than E_c for SS316 in hypochlorite solutions of varying concentrations (upto 600 ppm) having 1000 ppm Cl^- at 25°C (Table II). This indicates that the tested steel is not likely to pit under such conditions (illustrated schematically in Fig.6). However, lesser value of E_p than E_{corr} (Table II) shows it to be susceptible to crevice corrosion in these solutions. When Cl^- amount increases to 1500 ppm or more (200 ppm) and/or temperature is enhanced to 45°C in presence of fixed concentration of OCl^- SS316 shows tendency of experiencing both pitting and crevice corrosion. This may be understood through the schematic Fig. 6 which depicts that E_c and E_{corr} are expected to be modified such that E_c is less than E_{corr} resulting in both type of localised corrosion when Cl^- and temperature are increased. Almost similar behaviour is noted for SS 304 (Table III) also.

Experiments done by immersing sample (SS304 and 316) with artificial crevices, for six weeks, showed the crevice attack. Maximum pit depth under the crevice is 0.056 mm for SS316 and 0.795 mm for SS304 respectively, at room temperature, irrespective of solution concentrations. The degree of attack on 316 is within the acceptable limit (10) while from crevice corrosion standpoint SS304 fails. However, a rise in temperature or Cl^- concentration will aggravate this performance of steels (Fig.6).

Cathodic polarisation and corrosion rate

Cathodic polarisation curves (Fig.3) show that corrosion of 316 at low Cl^- and temperature (1000 ppm Cl^- , 25°C) in hypochlorite solutions is governed by activation

polarisation. This is also supported by the observation that $E_{\text{corr}} < E_c$ since then the stainless steel is under passivation (Fig. 6) and hence concentration polarisation is not feasible. When temperature is increased, corrosion is governed by concentration polarisation (Fig.3). This is expected because these changes lower E_c for stainless steels due to destabilisation of the passive film [3, 11] resulting in the shift of corrosion potential to the transpassive region.

Corrosion of 304 is governed by concentration polarisation (Fig. 4) irrespective of composition and temperature of solutions. This can be understood in terms of E_c , which is less for 304 than 316 (Fig.1) as former steel is in the transpassive region.

Now an account is given to the variation of corrosion current, i_{corr} (or corrosion rate) with OCl^- in hypochlorite solutions. Since corrosion of SS316 in solutions with lower Cl^- at room temperature is governed by activation polarisation, i_{corr} is not expected to vary with OCl^- to a considerable extent. Fig.5 shows that the corrosion rate increases only by 1 mpy for each 100 ppm increase in OCl^- concentration. However, at higher temperature and for 304, i_{corr} increases in OCl^- concentration. At 45°C, this increase is 14 mpy for each 100 ppm rise in OCl^- content for both stainless steels. This is due to the fact that corrosion, in present case, is governed by the concentration polarisation and resulting in an increase in the limiting current density. The increase in corrosion rate with OCl^- concentration is also confirmed through the weight loss study (Fig.7).

The effect of variation in Cl^- content is now briefed. According to Fig.6, at higher Cl^- level, E_c tends to decrease causing the shift of corrosion potential in negative (active) direction resulting in an increase in i_{corr} when steel is in the transpassive region. Experimental results (Fig. 3 & 4) show the similar behaviour. The effect of temperature on corrosion rate is significant. For example, at $\text{OCl}^- = 450$ ppm and $\text{Cl}^- = 2000$ ppm, corrosion rates of steels increase by about 63 mpy when temperature of liquid raises from 25 to 45°C.

Effect of system closure

System closure enhances OCl^- and Cl^- contents and temperature of the process liquors [11]. This may be noted from present study that SS316 is an acceptable material in existing bleach plant washer which has Cl^- and OCl^- upto 1000 ppm and 200 ppm respectively at ambient temperature. However, material becomes unacceptable due to severe localised corrosion in the process conditions expected to be encountered in the washer after filtrate recycling (i.e. having Cl^- and OCl^- upto 2000 ppm and 600 ppm respectively and temperature $\approx 50^\circ\text{C}$). Moreover, at higher temperature, corrosion rate increases tremendously with an increase in OCl^- concentration. Further it should be noted that SS304 suffers from unacceptable degree of corrosion even in the unrecycled liquors.

Performance of materials and corrosion control

In hypochlorite solution (having upto 1000 ppm Cl^-) at ambient temperature, SS316 does not experience pitting whereas 304 does. Both steels experience crevice corrosion though the degree of attack on SS316 is acceptable. The corrosion rate of SS304 is roughly four times that of SS316. Stainless 316 is found as an acceptable material for handling hypochlorite solutions in the existing (unrecycled) plant conditions. At higher temperature, the degree of crevice corrosion will increase and SS316 may also suffer from mild pitting. However, 316 may still be considered by closing crevices with the help of smoother welding and improved design, wherever possible. It should be noted that the application of SS316 would be affected by the change in temperature, $\text{OCl}^- / \text{Cl}^-$ contents of the solutions. Thus with increased 'closed-cycle', application of 316 also becomes questionable. Instead, stainless steels 904L, 317L and 2205 may be better materials. However, this has to be verified by doing similar experiments on the later type of stainless steels for a given degree of recycling. The other alternative is to enhance the performance of SS304 / 316 by developing the electrochemical protection system in the aggravated conditions. For this, the results of present study will be the basic tool. The electrochemical protection of these

steels will be beneficial since (i) fabrication procedures for SS304 / 316 are well known and (ii) the protection system may be installed for the already existing plants.

Though the tests solutions were deoxygenated, the results of the present study are useful for bleach plant also as the presence of oxygen in hypochlorite solutions does not significantly affect the corrosion mechanism. This has been confirmed experimentally also and is attributed to lower E^0 and I_0 for O_2/OH^- system than OCl^-/Cl^- one [12].

CONCLUSIONS

- (i) In hypochlorite solutions, corrosion of steels is governed by hypochlorite ion reduction at the cathode.
- (ii) Stainless steel 316 appears to be an acceptable material in the existing bleach plant condition while SS304 suffers from considerable localised attacks, i.e., pitting and crevice corrosion.
- (iii) As a result of system closure, SS316 is also found prone to localised corrosion. The effects of temperature dominate over the constituents of liquors. However, these entire factors act in unison to make the suitability of 316 questionable.
- (iv) In view of the increasing demand of filtrate recycling as a pollution control measure, there is need of evaluating the performance of more corrosion resistant materials, e.g. SS 904L, 2205, Avesta 254 SMO, Hastelloys, etc. Alternately, the performance of SS 304 / 316 may be upgraded through the electrochemical protection.

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