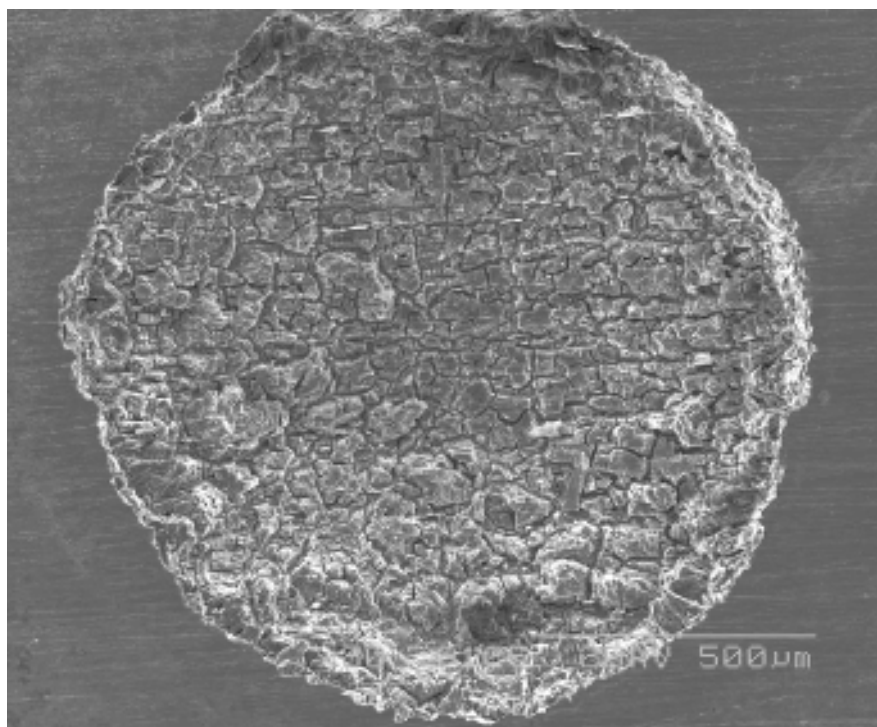


Tarja Laitinen

Thiosulfate pitting corrosion of stainless steels in paper machine environment



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Tarja Laitinen

VTT Manufacturing Technology

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Abstract

Thiosulfate pitting corrosion of austenitic stainless steels of types UNS S30403 (AISI 304L) and UNS S31603 (AISI 316L), and duplex stainless steel of type UNS S31803 (22Cr DSS) was studied in simulated paper machine environments containing chloride, sulfate and thiosulfate by cyclic polarization scans, scratch tests, Contact Electric Resistance (CER) technique and by corrosion coupon tests performed in a real paper machine. The formed pits and crevice corrosion were examined by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). The surface films were also analyzed by Electron Spectroscopy for Chemical Analysis (ESCA) and Secondary Ion Mass Spectrometry (SIMS).

Thiosulfate and chloride clearly have a synergistic effect in inducing localized corrosion. Thiosulfate is able to prevent passivation of an active stainless steel surface and able to stabilize metastable pits initiated below the actual pitting corrosion potential. The role of chloride is to initiate corrosion pits. Thiosulfate increases the possible potential range of corrosion pits to grow by lowering the repassivation potential. Hydrogen sulfide originating from thiosulfate is proposed to accelerate the anodic dissolution inside corrosion pits and crevices by forming sparingly soluble metal sulfides and by acidifying the local environment. The compositions of the black deposit enriched inside thiosulfate pits and corrosion crevices were similar to the compositions of the low-resistance surface films.

Pitting Resistance Indices (PRE) of the test materials increased in the order of UNS S30403 (PRE 19 - 21), UNS S31603 (PRE 24 - 25) and UNS S31803 (PRE 35) in accordance with the observed localized corrosion resistance in both the laboratory and field tests. All the materials corroded technically significantly in corrosion coupon tests performed in a paper machine. The bulk environment of the paper machine was very mild, but the chloride and thiosulfate ions concentrating up to high levels created favourable conditions for corrosion.

Preface

The research work of this thesis has mainly been carried out at the Technical Research Centre of Finland (VTT), VTT Manufacturing Technology, during the years 1993 - 1997. Publication I was accomplished as a part of a programme, Surface Phenomena and Corrosion of Stainless Steels in Sulphur-Containing Environments, funded by VTT. The major part of the work, Publications II - V, was carried out as a part of an other programme, Closed Loop Operation in Pulp and Paper Industry - Materials and Manufacturing Technology, funded by VTT and Finnish Industry. The financial support is gratefully acknowledged.

This thesis was supervised by Prof. Hannu Hänninen, to whom I would like to express my gratitude for his valuable advice, comments and support.

Prof. Kenneth Holmberg is also gratefully acknowledged for giving me the opportunity to finish this thesis as a part of a programme for Dr.Tech. students, funded by VTT. My group leader, Ms. Irina Aho-Mantila, has provided continuous encouragement and support both mentally and project-wise throughout the course of this work, for which I am most grateful. I thank my fellow colleagues, Ms. Leena Carpén, Ms. Ulla Ehrnstén, Ms. Outi Hyökyvirta and Prof. Tero Hakkarainen for their valuable co-operation in the area of thiosulfate pitting corrosion. I also thank the staff of VTT Manufacturing Technology for all the help and support they have given me during the course of this work.

The laboratory work for Publications III and IV was performed at the Pulp and Paper Research Institute of Canada (Paprican), Vancouver Laboratory, during my research exchange year 1995 - 1996. I am grateful to my group leader Mr. Douglas Singbeil and to my co-workers at Paprican for the valuable opportunity to get acquainted with the field of corrosion research in the Canadian pulp and paper industry. I want to thank Dr. Andrew Garner and Dr. Christian Thompson for the inspiring discussions concerning thiosulfate pitting corrosion.

Most of all, I want to express my deepest gratitude to my husband Arttu, who has provided me with the love and support only he can give during the good and especially during the not-so-good days. I am also thankful for our baby-daughter Krista for finally setting an end to this work. My mother Vappu, my father Lasse, my sister Kirsti and my parents-in-law Sirkka and Arvo have supported me greatly during the course of this work and believed in me so strongly that I was able to finish this thesis.

April 1999

Tarja Laitinen

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Appendices

***Appendices of this publication are not included in the PDF version.
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(<http://www.inf.vtt.fi/pdf/publications/1999/>)***

Nomenclature

Ag/AgCl	Saturated Silver - Silver Chloride Electrode
CER	Contact Electric Resistance technique
E_{corr}	Corrosion potential, open-circuit potential
E_{nc}	Crevice potential
E_{np}	Pitting potential
E_{pp}	Repassivation potential
EDS	Energy Dispersive X-ray Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
PRE	Pitting Resistance Equivalent
	$\text{PRE} = \text{wt\% Cr} + 3.3 \times \text{wt\% Mo} + 13 \times \text{wt\% N}$
SCE	Saturated Calomel Electrode
SIMS	Secondary Ion Mass Spectrometry
SEM	Scanning Electron Microscopy
SRB	Sulfate-Reducing Bacteria

Original features

The following features of this thesis are believed to be original:

1. Thiosulfate decreases the pitting potential of stainless steels in addition to repassivation potential. The effects of thiosulfate were determined by cyclic polarization scans with a slow scan rate, 0.1 mV/s.
2. The compositions of the black deposit inside the thiosulfate pits and the compositions of the low-resistance surface films (indicating a weak surface film) were similar. The deposits inside the pits and the surface films were both enriched with chromium and sulfur and depleted in iron, when compared to the base material.
3. Thiosulfate assists the initiation of pitting corrosion on stainless steels by preventing passivation of an active surface and by stabilizing metastable pits initiated below the pitting corrosion potential. Chloride actually initiates the corrosion pits.
4. The results from the Contact Electric Resistance technique were verified with corresponding results by cyclic polarization scans, scratch tests and corrosion coupon tests performed in a paper machine. The results of the different methods complemented each other and gave a wider view of thiosulfate pitting corrosion.
5. A large series of corrosion coupon tests with several materials was conducted in five different locations in a paper machine. The duration of the corrosion coupon tests varied from 1 to 13 months.
6. Dithionite or its decomposition products increased the corrosion potential of stainless steels exposed in a real paper machine.

Dissertation

This dissertation consists of an introductory report and five appended publications (Appendices I - V).

- Publication I Salonen, T.*, Saario, T. & Likonen, J. 1994. Effect of thiosulfate on the surface film resistance of stainless steel AISI 304 in the paper-mill environment. In: Proceedings of NACE Corrosion 94. Baltimore, MD, USA, Feb. 27 - March 4. Paper No. 426. Houston, TX, USA: NACE International. 13 p.
- Publication II Laitinen, T., Likonen, J. & Heinonen, M. 1995. Comparison of CER, ESCA and SIMS surface examinations on type AISI 304 stainless steel in chloride and sulphur containing environment. In: Proc. Pulp and Paper Industry Corrosion Problems, Vol. 8. Stockholm, Sweden, May 16 - 19, 1995. Stockholm: Swedish Corrosion Institute. Pp. 271 - 283.
- Publication III Laitinen, T. 1999. Localized corrosion of stainless steels in chloride, sulfate and thiosulfate containing environments. Accepted for publication in Corrosion Science.
- Publication IV Laitinen, T. 1999. Comparison of stainless steels in simulated paper machine environment. In: Corrosion, Vol. 55, No. 9, pp. 858 - 869.
- Publication V Laitinen, T. 1999. Paper machine field testing of stainless steels. In: Pulp & Paper Canada, Vol. 100, No. 4, pp. 47 - 50.

* Salonen is the former name of the author of the thesis.

1. Introduction

At the wet end of paper machines and especially at the splash zones, pitting and crevice corrosion of stainless steels caused by chloride and thiosulfate ions is a common phenomenon. Chloride originates from the wood floated in seawater, from the supplied water and from the chemicals added to the pulp mix. Thiosulfate originates mainly from hydrosulfite (dithionite) (Garner 1982), which is a brightening chemical of mechanical pulp. Thiosulfate formation is also possible through activities of Sulfate Reducing Bacteria (SRB) (Newman et al. 1986).

Hydrosulfite brightening of mechanical pulps is performed for brightness gains 1 - 8 ISO points (Bond et al. 1990), the maximum being 10 points (Daneault et al. 1994). The reaction products of hydrosulfite decomposing in anaerobic conditions, bisulfite and thiosulfate, correspond to 95% of the original amount of hydrosulfite (Rinker et al. 1965). Hydrosulfite decomposition products in aerobic conditions are bisulfite and bisulfate (Jouan 1959). Hydrosulfite decomposition has a certain induction period, during which the concentration of hydrosulfite slowly decreases followed by an abrupt increase in the rate of decomposition suggesting an autocatalytic mechanism (Rinker et al. 1965). The decomposition rate of hydrosulfite is a function of temperature and pH, hydrosulfite concentration, bisulfite and sulfite concentrations (Lem & Wayman 1970, Danehy & Zubritsky 1974). The optimum pH value for reductive hydrosulfite brightening is 5 - 6 (Ingruber & Kopadinis 1967). The most common causes of thiosulfate formation during the hydrosulfite brightening are too low a pH, an overdose of hydrosulfite, poor mixing and insufficient retention time (Bond et al. 1990).

White water circulating at the wet end of a paper machine consists of dissolved and colloidal material originating from wood, lignin, extractives, ash and different chemicals added to the pulp mix. Residuals of chemicals like paper-making chemicals (e.g., starch, opacifiers, pigments), chemicals used for pH control (hydrogen peroxide (H_2O_2) or sodium hydroxide (NaOH)), wire and felt washing chemicals, white water cleaning chemicals, and mechanical pulp brightening chemicals (dithionite ($Na_2S_2O_4$) or H_2O_2) can be found in white water. The wet-end environment and chemistry are specific for each paper machine depending on manufactured paper grade, the quality of the fresh water

used, the brightening chemicals used, the closing level of the water system and operation temperature, but the common features are shared when manufacturing similar paper grades. A typical concentration of paper machine white water in an acid paper-making procedure using hydrosulfite-brightened mechanical pulps is presented in Table 1 (Thompson & Garner 1995).

Table 1. Typical paper machine white water composition in an acid paper-making process using hydrosulfite-brightened mechanical pulps (Thompson & Garner 1995).

Chloride Cl ⁻ [mg/l]	Sulfate SO ₄ ²⁻ [mg/l]	Thiosulfate [S ₂ O ₃ ²⁻] [mg/l]	Sulfite [SO ₃ ²⁻] [mg/l]	Temperature [° C]	pH
50 - 300	200 - 1600	0 - 50	0 - 75	45 - 55	4 - 6

The localized corrosion of stainless steels in thiosulfate-containing environments has been studied extensively. Thiosulfate pitting is known to occur in a limited potential range (Newman 1985a) and molar ratio ($[\text{Cl}^-] + [\text{SO}_4^{2-}] / [\text{S}_2\text{O}_3^{2-}]$) (Newman et al. 1989). The most sensitive area for thiosulfate pitting is in the potential range of 0... -400 mV_{Ag/AgCl} (Garner 1985) and at a molar ratio of 10 - 30 (Newman et al. 1989). The role of thiosulfate in localized corrosion has been explained in two different ways: 1) thiosulfate is reduced to elemental sulfur (S⁰), which adsorbs on a bare metal surface preventing passivation (Newman et al. 1982); or 2) thiosulfate is reduced to hydrogen sulfide (H₂S), and H₂S catalyzes the anodic dissolution of stainless steel (Tromans & Frederick 1984).

Type UNS S31603 stainless steel is the most common stainless steel used in new paper machines, typically in constructions like headbox flow surfaces, lining plates, piping, ventilation systems, tanks and hoods. Occasionally in severe environments type UNS S31603 is replaced by more corrosion resistant stainless steel UNS S31703. Secondary targets such as catwalks are usually made of type UNS S30400 or UNS S30403 stainless steels. Type UNS S31803 stainless steel is used in, e.g., suction rolls and special parts in the head boxes.

The aim of the thesis was to study thiosulfate pitting corrosion occurring at the wet end of the paper machines, especially with type UNS S30403, but also with type UNS S31603 and S31803 stainless steels. Thiosulfate pitting corrosion was studied in both the laboratory and the field. The mechanism of thiosulfate pitting corrosion and the effects that thiosulfate has on stainless steels were investigated with different electrochemical corrosion-testing methods. The results gained in laboratory were verified with corrosion coupon tests performed in a real paper machine.

2. Materials and test methods

2.1 Materials

Several austenitic stainless steels and one ferritic-austenitic stainless steel typically used in paper machine constructions were included in this study. The major part of the studies was performed with UNS S30403 stainless steel. All the CER tests and ESCA and SIMS analyses were performed only with material UNS S30403. The pitting corrosion behaviour of UNS S30403, S31603 and S31803 was determined by cyclic polarization scans and scratch tests. All the test materials were exposed to a real paper machine environment in the corrosion coupon tests.

Chromium, molybdenum and nitrogen are alloyed into steels for corrosion resistance. Table 2 presents the chemical composition of the test materials together with Pitting Resistance Equivalent (PRE) index, $PRE = wt\% Cr + 3.3 \times wt\% Mo + 13 \times wt\% N$ (Suutala & Kurkela 1984, Renner et al. 1986). The ferritic-austenitic microstructure is considered more corrosion resistant than the plain austenitic microstructure. The main reason is that the ferrite phase protects cathodically the austenite phase (Magnin et al. 1987). The ferrite phase is more corrosion resistant than the austenite phase because of higher Cr and Mo contents. Cr and Mo are ferrite-stabilizing elements. N is an austenite-stabilizing element and N increases the corrosion resistance of the austenite phase.

The UNS S30403 stainless steels used for the CER tests had a slightly higher carbon content than the maximum carbon content (≤ 0.030 wt%) of grade UNS S30403. The corrosion coupon tests were performed with materials manufactured according to the Finnish SFS standards. Grade SFS 725 (UNS S30400) with a maximum carbon content of 0.050 wt% was assumed to correspond with the corrosion behaviour of type UNS S30403.

The UNS S31603 stainless steel studied by cyclic polarization scans and scratch tests contained about 0.50 wt% less molybdenum than grade SFS 757 (corresponding with UNS S31603) exposed in the corrosion coupon tests. The cyclic polarization scans and scratch tests were performed at Paprican with materials manufactured according to the North American AISI standards.

Table 2. Chemical composition (wt%) of the test materials according to the manufacturer¹⁾ or analyzed by optical emission spectrometer²⁾ together with PRE-index (wt% Cr+3.3* wt% Mo+13* wt% N) (Suutala & Kurkela 1984, Renner et al. 1986).

Material	PRE	Tests performed	C wt %	Si wt %	Mn wt %	P wt %	S wt %	Cr wt %	Ni wt %	Mo wt %	Co wt %	Cu wt %	N wt %
¹⁾ UNS S30403	21	pol. scan, scratch test	0.027	0.39	1.70	0.030	0.0006	18.2	8.2	0.40	0.13	0.34	0.095
²⁾	19	CER	0.033	0.44	1.58	0.026	0.016	17.8	8.7	0.34	0.11	0.27	-
²⁾	19	field exp.	0.040	0.46	1.48	0.021	0.005	18.4	8.6	0.10	0.16	0.20	-
¹⁾ UNS S31603	24	pol. scan, scratch test	0.012	0.50	1.20	0.029	0.001	16.3	10.2	2.0			0.050
²⁾	25	field exp.	0.030	0.56	1.51	0.027	0.004	16.9	10.7	2.6	0.22	0.26	-
¹⁾ UNS S31803	35	pol. scan, scratch test	0.016	0.46	1.42	0.021	0.001	22.1	5.7	3.0			0.17
²⁾	35	field exp.	0.020	0.51	1.46	0.025	0.002	22.2	5.7	2.9	0.07	0.18	0.18

2.2 Test methods

The main material evaluation methods used in this study were cyclic polarization scans, scratch tests, the Contact Electric Resistance (CER) technique, and corrosion coupon tests. The chemical compositions of the surface films on the CER samples were analyzed by Electron Spectroscopy for Chemical Analysis (ESCA) Perkin Elmer 5400 and Secondary Ion Mass Spectrometry (SIMS) VG Ionex IX70S. The cyclic polarization samples and corrosion coupons exposed in the paper machine were studied with a Scanning Electron Microscopy (SEM) Jeol 6400 together with an Energy Dispersive X-ray Spectrometry (EDS) Link Analytical QX2000. The scratch test samples were examined with an optical microscope.

2.2.1 Cyclic polarization scans

The test arrangement for the cyclic polarization scans included creviced samples. Pitting corrosion potential (E_{mp}) and crevice corrosion potential (E_{nc}) are different from each other. In practice, localized corrosion in paper machines, however, includes both types of corrosion, often simultaneously. Localized corrosion may start as crevice corrosion under pulp deposits and later on continue as pitting corrosion on the free surface (Publication V). In the cyclic polarization scans corrosion started under the o-rings, often as pits, and proceeded as pitting corrosion on the free surface. It was assumed that this kind of test arrangement would best correspond to the real conditions in paper machines.

Cylindrical samples for the cyclic polarization scans were machined from a thick plate, ground to a 600 grit finish, ultrasonically cleaned, rinsed with ethanol and dried. Two rubber o-rings were placed around the samples to create a tight, reproducible crevice. The test solutions were prepared from analytical grade chemicals and deionized water. The test solutions were bubbled with purified N_2 for 45 min and heated simultaneously to test temperature before the samples were immersed into the solution. About 80% of the sample area was immersed into the solution in order to avoid crevice corrosion in the connection between the sample and the wire. The pH was adjusted with dilute H_2SO_4 solution. N_2 bubbling was continued during the whole test period. The potentials

were measured against the saturated calomel electrode (SCE) and a graphite rod was used as a counter electrode. The samples were first polarized to a cathodic potential $-1.0 V_{SCE}$ for 15 min in order to reduce existing films on the sample surfaces. Cyclic polarization scans from -0.5 to 1.0 and back to $-0.5 V_{SCE}$ were performed with a scan rate of 0.1 mV/s. No IR-drop compensation was used. After completing the scan, the sample was left in the solution at open circuit potential, with the total immersion time being approximately 24 h.

The pitting potential was determined to be the potential where the current density exceeded $7.0 \text{ E-}6 \text{ A/cm}^2$. If no sign of corrosion on the sample surface was observed and the forward scan was smooth, it was concluded that the pitting potential did not exist at least below the turning point of the scan, $1.0 V_{SCE}$, even though the current density may have exceeded $7.0 \text{ E-}6 \text{ A/cm}^2$. In the cases of severe corrosion, the current density was constantly higher and the pitting potential was determined to be the potential at the current density of $1.0 \text{ E-}5 \text{ A/cm}^2$. The two current densities corresponding pitting potentials were determined based on this study. The repassivation potential was determined to be the point where the hysteresis loop was completed and the reversed scan crossed the forward scan.

2.2.2 Scratch testing

The scratch test samples (5 mm by 5 mm) were prepared from thick stainless steel plates by sawing. Wires were attached to the scratch test samples with mechanical joints and the samples were moulded in epoxy. The samples were ground to an 800 grit finish, cleaned with ethanol and dried. The test solutions were prepared from analytical grade chemicals and deionized water and the pH was adjusted with dilute H_2SO_4 solution. The test solutions were bubbled with purified N_2 for 45 min and heated before the test. N_2 bubbling was also carried out during the test. The potentials were measured against the saturated calomel electrode (SCE) and a graphite rod was used as a counter electrode. A maximum of three sequential tests was performed in the same solution. The potential level was set and then the samples were scratched manually with a diamond pen (usually two scratches per sample). After scratching the current density was measured for 15 min.

The results of the scratch tests were divided into three categories (pits, minor pits, no pits). If the current density during the test grew steadily after scratching, and pits were visible under optical microscopy inspection, the environment was considered corrosive and marked as 'pits'. The mark 'minor pits' indicated cases where small spikes in current density were observed after scratching, and one or few small pits were visible under optical microscopy inspection. When current density remained steady after the scratching and no pits were observed with optical microscopy, the environment was characterized by the mark 'no pits'.

2.2.3 Contact Electric Resistance

The CER technique is a novel in-situ method based on an accurate measurement of the electric resistance of surface films. The surface film resistance can be determined in the very initial stages of water and anion adsorption, in the formation and destruction of oxide and hydride films and in electrochemical incorporation of cations (Marichev 1991). The CER technique has a wide measurement capacity that ranges from 10^{-9} to $10^5 \Omega$ (Saario 1995). A detailed description of the CER technique has been presented earlier (Saario & Marichev 1993). The principle of the CER technique is to feed direct current through two surfaces, for example the surfaces of a fatigue crack or two separate samples, which at a constant frequency are moved into contact and out of contact. The voltage is continuously measured over the moving surfaces. During the formation of surface films, which are insulators or semiconductors, a voltage drop proportional to the resistance appears, according to Ohm's law. The development work of the CER technique was directed towards achieving a tool for solving practical corrosion problems (Saario 1995).

The samples used in the CER tests were cylindrical and had a diameter of 2 mm. The samples were periodically taken into contact and out of contact at a frequency of about 0.3 Hz. The accuracy of the displacement, produced by a piezoelement, was better than 3×10^{-9} m, and the repeatability of the contact position was estimated to be better than 1×10^{-10} m. The potentials were measured against the saturated calomel electrode (SCE) and a platinum plate was used as a counter electrode. Before starting the measurement, the samples were polarized to a cathodic potential ($-1.0 V_{SCE}$) for 30 min in order to reduce the existing films. After the cathodic polarization, the surfaces were assumed to be clean, which was

agreed to be the initial stage. When the measured voltage signal had stabilized, the potential was changed stepwise in 100 mV steps towards anodic potentials. The electrolytes were prepared from deionized water and from analytical grade chemicals.

The change in the surface film resistance by about an order of magnitude or more was considered to result from real modification in the surface film. Negligible surface film resistance is assumed to correlate with a surface film of easy dissolution of the material creating conditions for initiation of corrosion. High surface film resistance is considered to correlate with a passive surface film.

2.2.4 Corrosion coupon tests

Corrosion coupons (100 mm by 50 mm) were prepared from stainless steel plates in as-received condition by sawing and drilling two mounting holes per coupon. The edges of the mounting holes and the edges of the coupons were ground to a 600 grit finish, and the coupons were numbered. The coupons were cleaned in acetone and ethanol baths with ultrasonics. The ground edges were etched with pickling solution (5 wt% HF + 22 wt% HNO₃) for an hour and cleaned with water and acetone. The corrosion coupons were installed horizontally in different parts of the paper machine in such a way that there was about 80 mm free space between the coupon and the paper machine construction, thus allowing the free entrance of white water and pulp mix on the coupon surfaces. The coupons were insulated from the paper machine.

After the field exposure, the corrosion coupons were divided into three categories according to the severity of the corrosion. The coupons marked 'no corrosion' were in as-received condition, and no corrosion could be detected. The second category marked 'minor corrosion', included corrosion coupons with small pits ($\varnothing < 100 \mu\text{m}$) and some crevice corrosion. It was assumed that such small corrosion pits and crevices were metastable and would passivate. The third category marked 'major corrosion', included pits over 100 μm in diameter and large areas of crevice corrosion, which were considered to continue their growth and to be technically significant.

3. Summary of the main results

3.1 Comparison of the test methods

Potentiodynamic methods have been postulated to be not sensitive enough to detect pitting corrosion at low (≤ 10 ppm) thiosulfate concentrations because of the slow diffusion rate of thiosulfate (Garner 1985). In an earlier study, a scan rate of 0.2 mV/s was used by Newman et al. (1982). Usually, thiosulfate pitting corrosion is investigated by weight loss or scratch tests. The slow scan rate, 0.1 mV/s, used in this study was, however, able to reveal the strong effect of thiosulfate on pitting and repassivation potentials on UNS S30403 and UNS S31603 stainless steels (Publications III & IV).

Cyclic polarization scans and the CER technique are somewhat similar test methods. In both methods, the aggressive ions of the solution have to locally break the passive film as a function of potential in order to induce localized corrosion. The cyclic polarization scans and the CER tests were both started by cleaning the samples at a reductive potential in order to remove the protecting passive film (Publications I & II & III & IV). The development and the possible rupture of a passive film was detected in cyclic polarization scans as changes in the current density and in the CER tests as relative changes in the surface film resistance. The CER technique reveals the state of the surface film and, thus, the susceptibility to corrosion, but is not able to directly determine the initiation of pitting corrosion (Publications I & II). The CER technique was able to detect the enhanced anodic dissolution of stainless steel caused by thiosulfate (Publication III).

Thiosulfate pits nucleate rather in mechanical defects in the passive film than in sulfide inclusions (Newman et al. 1982). In the scratch tests, the passive film protecting the metal is broken only from a small area. The small area turns anodic compared to the large, passive remaining surface area and possible localized corrosion is expected in the scratched area. The scratch tests do not reveal the actual pitting potential, but merely the possibility of pitting in a certain environment (Publications III & IV).

3.2 Corrosion resistance of test materials in the paper machine environment

The PRE indices of the test materials increased in the order of UNS S30403 (PRE 19- 21), UNS S31603 (PRE 24 - 25) and UNS S31803 (PRE 35) in accordance with the observed localized corrosion resistance in both the laboratory and field tests (Publications IV & V). For UNS S30403 the critical chloride concentration where E_{np} values start to decrease and localized corrosion is induced was about 100 mg/l (Publications III & IV). Sulfate inhibited the initiation of pitting in chloride and thiosulfate-containing environments at the molar ratio $[Cl^-]/[SO_4^{2-}] < 0.5$ (Publications III & IV). The inhibiting effect of sulfate has been proposed to be based on the competitive adsorption with chloride ions (Leckie & Uhlig 1966). In the CER tests, the detrimental effect of thiosulfate was observed already at the molar ratio $([Cl^-]+[SO_4^{2-}])/[S_2O_3^{2-}] < 130$ (Marichev et al. 1993). In the corrosion coupon tests, technically significant corrosion, both pitting and crevice corrosion was observed during one month's exposure time on UNS S30403 corrosion coupons, which were located in the wire section of the paper machine, in the splash zone (Publication V).

In the case of type UNS S31603 stainless steel the critical chloride concentration where E_{np} values start to decrease and localized corrosion is induced was about 200 mg/l (Publication IV). Sulfate slightly enhanced the pitting (Publication IV). In the corrosion coupon tests, technically significant corrosion, both pitting and crevice corrosion, was observed during two months' exposure time on UNS S31603 corrosion coupons located in the wire section of the paper machine, in the splash zone (Publication V).

For UNS S31803, the chloride concentration had to be at least 500 mg/l before any localized corrosion could be observed (Publication IV). The sulfate concentration or the molar ratio $[Cl^-]/[SO_4^{2-}]$ of the solution had no effect on pitting on UNS S31803 (Publication IV). In addition, material UNS S31803 suffered from technically significant crevice corrosion and some minor pitting when exposed for 13 months to the pick-up section of the paper machine, in the splash zone (Publication V).

Pit initiation on higher-alloyed materials demanded a more aggressive environment, which took a longer time to concentrate from the bulk

environment (Publications IV & V). The more corrosion resistant alloys contained molybdenum, which is known to cause a 5- to 10-fold decrease in the active dissolution rate occurring inside the pits after the dissolution of a few atom layers of the alloy (Newman 1985b). On the other hand, a porous, thick layer of molybdenum-rich oxide precipitating on the pit walls at an early stage of pitting decreases corrosion rate and favours repassivation of the pits (Qvarfort 1998). A higher potential in general is required to maintain a localized corrosive solution causing stable pitting on the more corrosion resistant Mo-containing alloys.

The location of the corrosion coupons in the paper machine seemed to be a very important factor in determining the severity of the localized corrosion that occurs. The corrosion conditions were most aggressive at locations where the corrosion coupons were occasionally wet and dry during the paper machine running time, thus enabling chloride and thiosulfate ions to concentrate from the bulk environment. The determined molar ratios in the bulk environment were not at the most aggressive range of thiosulfate pitting, but the concentrated deposit on the corrosion coupons provided an aggressive corrosion environment. Temperature was not the most determining factor for the observed corrosion phenomena.

Dithionite or its decomposition products increased the corrosion potential (E_{corr}) of UNS S31603 up to $0.4 V_{\text{Ag/AgCl}}$ in a simulated paper machine environment (Carpén 1999). Increasing the dosage of dithionite was also observed to increase the corrosion potentials of stainless steels in the measurements performed in a paper machine (Publication V). Once dithionite or its decomposition products have raised the corrosion potential of stainless steels, the high chloride content of the concentrated deposits can initiate pitting corrosion. Thiosulfate present in the concentrate would further ease pitting corrosion by decreasing the pitting potential and by enlarging the possible pit growth range towards negative potentials (Publications III & IV & V).

3.3 Pits and surface films

The pits formed in solutions containing chloride and sulfate were typically deep, partly closed and free of any visible deposit (Publications III & IV). Where thiosulfate was present in the otherwise similar solutions, the pits were open,

full of black deposit and 3 - 6 times larger in size (Publications III & IV). The black deposits inside the pits and crevices occur in the case of thiosulfate-induced localized corrosion (Newman et al. 1982, Tromans & Frederick 1984, Garner 1985, Varjonen et al. 1989).

All the pits formed on UNS S30403 and UNS S31603 were enriched in chromium and copper and depleted in iron, when compared to the base material (Publications III & IV & V). Chromium enrichment has been observed in pits initiated in MnS inclusions on type UNS S30403 steel (Ke & Alkire 1995) and in the black deposit inside thiosulfite pits on type UNS S30403 and S31603 steels (Tromans & Frederick 1984, Varjonen et al. 1989, Varjonen et al. 1995, Ehrnstén et al. 1996). Sparingly soluble copper sulfide has been proposed to form during the corrosion process owing to the dissolution of traces of copper in stainless steel (Wranglen 1974). Nickel enrichment was detected only in the black deposit inside the pits developed on UNS S30403 steel (Publication IV).

The difference between the two types of pits was the amount of sulfur detected. When thiosulfate was present in the solution, the pits contained very high amounts of sulfur and no chloride (Publications III & IV & V). Without the thiosulfate addition, the pits contained only small amounts of sulfur and traces of chloride (Publications III & IV).

The surface films formed during the CER tests in solutions containing thiosulfate were analyzed by ESCA and SIMS. The surface film with a low electrical resistance contained more chromium and sulfur and less iron than the surface film with a high electrical resistance (Publication II). A similar kind of enrichment and depletion of elements occurred inside the pits during active corrosion as in the surface films in corrosive environments (Publications II & III & IV & V).

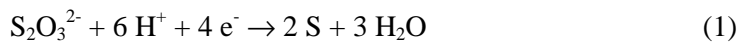
3.4 Mechanism of thiosulfate pitting

Thiosulfate pitting corrosion was observed both in laboratory tests and in corrosion coupon tests performed in a paper machine. The different test methods used revealed several aspects of thiosulfate pitting corrosion. Thiosulfate affected the phenomena of pitting corrosion by preventing the passivation of an

active stainless steel surface and by accelerating corrosion in the pits already initiated.

As observed in the CER tests, the surface film resistance of UNS S30403 was negligible in the presence of thiosulfate, thus indicating an active surface or a non-protective surface film (Publication I). On the other hand, in the presence of chloride the surface film resistance of UNS S30403 was high, indicating passivation in the potential range below E_{np} (Publication I). When the solution included both thiosulfate and chloride, thiosulfate caused a negligible surface film resistance despite the presence of chloride (Publications I & II). Severe localized corrosion of stainless steels is not known to be caused by thiosulfate alone. Therefore, thiosulfate is not able to initiate pits, but thiosulfate either hinders passive film formation on an active surface or forms a very weak, non-protective surface film on stainless steel. The role of chloride is to initiate the pits.

Thiosulfate is able to reduce to sulfur on the metal surface in the pH and potential range prevailing in an acid paper-making process according to the reaction (1) (Pourbaix & Pourbaix 1990):



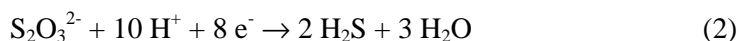
Sulfur is suggested to block the adsorption sites of hydroxyl ions, which are the precursors in the formation of the passive layer (Marcus et al. 1984, Elbiache & Marcus 1992). Above a critical coverage of the surface by sulfur, which was found to be 0.7 - 0.8 monolayers, the formation of passive film is prevented (Marcus et al. 1984). Molybdenum decelerates the formation of critical sulfur coverage hindering passivation of the metal surface. Molybdenum is observed to bond to and remove sulfur on the active stainless steel surface. It is suggested that the presence of chromium enhances the molybdenum induced desorption of sulfur. Two molybdenum atoms bond to and remove one adsorbed sulfur atom on a stainless steel surface. (Elbiache & Marcus 1992, Marcus 1995)

Thiosulfate made it easier for chloride to initiate pits. Thiosulfate caused a decrease in pitting potential on materials UNS S30403 and S31603 compared to the corresponding E_{np} in similar solutions without the thiosulfate addition (Publications III & IV). Thiosulfate and chloride clearly have a synergistic

effect in inducing localized corrosion. Thiosulfate could assist chloride to initiate pits by affecting the passive film on stainless steel or by affecting the initiation and passivation of metastable pits below the actual pitting corrosion potential. The CER results indicated that thiosulfate had no effect on the already formed passive film on stainless steel (Publications I & II). Thiosulfate is also suggested to be reduced only on the bare alloy surface, not on the passive film (Duret-Thual et al. 1997). It seems more probable that thiosulfate stabilizes the metastable pits formed below the actual pitting potential by accelerating the anodic dissolution process inside the pits and, thus, lowering the pitting potential.

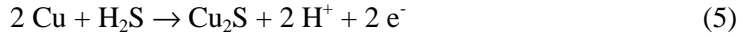
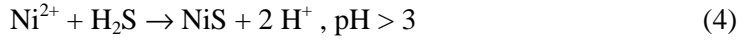
Thiosulfate increased the hysteresis loop and the possible potential range of pits to grow. The repassivation potentials on materials UNS S30403 and S31603 decreased remarkably in solutions containing thiosulfate compared to the corresponding E_{pp} values in similar solutions without thiosulfate (Publications III & IV). Thiosulfate accelerated the corrosion rate in pits already initiated (Publications III & IV).

When thiosulfate is present in a solution, it is able to migrate into the growing pits. The environment inside the pit is too acidic and too reducing to keep thiosulfate stable. The formation of hydrogen sulfide through the reduction of thiosulfate is possible according to reaction (2) (Pourbaix & Pourbaix 1990). When no thiosulfate is present in a solution, sulfide inclusions initiating pits in solutions containing chloride could be the source of the sulfur observed inside the pits (Publications III & IV). Pits initiated in MnS inclusions have been observed to show a high intensity of S (Ke & Alkire 1995). The growing pit dissolves the inclusion and some sulfur (S^{2-}) is released. The conditions inside the pit (acidic, reducing) reduce sulfur to hydrogen sulfide according to reaction (3) (Pourbaix & Pourbaix 1990).



The calculated potential - pH diagrams reveal that hydrogen sulfide is stable at potentials below -250 mV_{SCE} and $\text{pH} < 3$ (Pourbaix & Pourbaix 1990), i.e., in conditions prevailing inside the pits and crevices. In a system containing nickel and copper as well as sulfur and water, hydrogen sulfide can form stable

sulfides with Ni²⁺ (NiS) and Cu (Cu₂S) above -500 mV_{SCE} according to reactions (4) and (5) (Chen et al. 1983).



The main acidifying reaction in pitting corrosion is the hydrolysis of chromium Cr³⁺ (Brown 1970, Suzuki et al. 1973). Additionally, in the above metal sulfide forming reactions (4) and (5), hydrogen ions (H⁺) are produced, which enhance the acidity inside the pits. The formation of metal sulfides consumes metal cations and, thus, accelerates the dissolution of stainless steels. Metal sulfides precipitate and deposit in the order of their solubility. Iron probably migrates out of the pits as cations or forms soluble ferrous chloride (Varjonen et al. 1995, Ehrnstén et al. 1996).

4. Summary of the thesis

The main objective of this thesis was to investigate how thiosulfate affects stainless steels of types UNS S30403, S31603 and S31803 in simulated paper machine environments using several electrochemical laboratory test methods and by corrosion coupon tests performed in a real paper machine. Thiosulfate is a corrosive decomposition product of hydrosulfite, which is a brightening agent of mechanical pulp. When the hydrosulfite brightening process is used, thiosulfate ions are most probably present at the wet end of the paper machine.

The test methods that were employed, cyclic polarization scans, scratch tests, the CER technique and corrosion coupon tests gave corresponding results for thiosulfate pitting corrosion. The results of the test methods complemented each other, which gave a wider view of thiosulfate pitting corrosion. In cyclic polarization scans the slow scan rate of 0.1 mV/s that was used was able to reveal the effect of thiosulfate on pitting and repassivation potentials. The scratch tests merely determined the possibility of pitting in a certain environment instead of the actual pitting potential. The CER technique detected the enhanced anodic dissolution caused by thiosulfate. The corrosion coupon tests revealed the effect of the concentration of corrosive ions, the aggressive locations in a paper machine and the fact that hydrosulfite increases the corrosion potential of stainless steels.

The PRE-indices of the test materials increased in the order of UNS S30403 (PRE 19 - 21), UNS S31603 (PRE 24 - 25) and UNS S31803 (PRE 35) in accordance with the observed localized corrosion resistance in both the laboratory and field tests. Chloride was the most powerful element that affected the corrosion resistance of the materials. For UNS S30403, the critical chloride concentration inducing localized corrosion was about 100 mg/l, for UNS S31603 about 200 mg/l and for UNS S31803 about 500 mg/l. Sulfate slightly inhibited the initiation of pitting on UNS S30403 steel with the molar ratio $[Cl^-]/[SO_4^{2-}] < 0.5$.

All the materials corroded technically significantly in the corrosion coupon tests, even though the bulk environment in the paper machine was very mild. The corrosion conditions were most aggressive at locations where the samples were occasionally wet and dry during the paper machine running time, thus

enabling chloride and thiosulfate ions to concentrate from the bulk environment. The brightening agent, hydrosulfite, increased the risk of corrosion not only by being a source of thiosulfate, but also by increasing the corrosion potential of stainless steels. Pit initiation on higher-alloyed materials demanded a more aggressive environment, which took a longer time to concentrate from the bulk environment. On materials with a higher PRE index, the observed corrosion was crevice corrosion, on lower-alloyed materials both pitting corrosion on free surfaces and crevice corrosion were present.

In the presence of thiosulfate, a passive surface film cannot be formed on an active stainless steel surface, as demonstrated by the CER measurements. Thiosulfate is proposed to reduce to sulfur, which prevents the passivation of a stainless steel surface. Thiosulfate also stabilizes the metastable pits formed below the actual pitting corrosion potential, which can be observed by the lower pitting potentials of UNS S30403 and S31603 in solutions containing thiosulfate and chloride, when compared to the E_{np} values in corresponding solutions without thiosulfate. Thiosulfate increases the possible potential range of pits to grow by lowering the repassivation potential to $-400... -500 V_{SCE}$.

The environment inside the corrosion pits reduces thiosulfate migrating from the solution to hydrogen sulfide according to the potential - pH diagram. Hydrogen sulfide is proposed to accelerate the anodic dissolution of stainless steel by forming sparingly soluble metal sulfides and by acidifying the local environment. A black deposit enriched in chromium, sulfur and copper and depleted in iron, when compared to the base material, was determined in all the pits and crevices formed in thiosulfate-containing environments. The surface films with low electrical resistance contained more chromium and sulfur and less iron than the surface films with high resistance. A similar composition of elements was observed inside the pits during active corrosion as in the surface films in thiosulfate-containing corrosive environments.

Summary of the appended papers

Publication I (Appendix 1) describes the Contact Electric Resistance (CER) technique experiments performed on type UNS S30403 stainless steel in a simulated paper machine environment containing chloride, sulfate and thiosulfate. The surface films formed were analyzed by Secondary Ion Mass Spectrometry (SIMS).

In Publication II (Appendix II), CER measurements were carried out on stainless steel type UNS S30403 in a simulated paper machine environment containing chloride, sulfate and thiosulfate. The analysis of surface films formed on UNS S30403 was performed by SIMS and Electron Spectroscopy for Chemical Analysis (ESCA). The analysis results were compared with the CER results.

Publication III (Appendix III) compares the results gained by different electrochemical methods on thiosulfate pitting corrosion on type UNS S30403 stainless steel in a simulated paper machine environment containing chloride, sulfate and thiosulfate. The test methods studied were cyclic polarization scans, scratch tests and the CER technique. The pits and crevices formed were investigated by SEM and analyzed by EDS.

Publication IV (Appendix IV) discusses the behaviour of stainless steels type UNS S30403, UNS S31603 and UNS S31803 in a simulated paper machine environment containing chloride, sulfate and thiosulfate. The susceptibility of the materials to localized corrosion was estimated with cyclic polarization scans and scratch tests. The corrosion pits and crevice corrosion formed were investigated by SEM and analyzed by EDS.

Publication V (Appendix V) provides corrosion coupon test results for materials UNS S30403, UNS S31603 and UNS S31803 exposed to different parts of a real paper machine for a maximum 13 months. The paper machine environment contained chloride, sulfate and thiosulfate. The corrosion pits and crevice corrosion formed were investigated by SEM and analyzed by EDS.

References

- Bond L. D., Sweeney N., Giust W., Whiting P., Fluet A. & Fairbank M. G. 1990. Controlling thiosulphate production during hydrosulphite bleaching. In: Preprints A of the 76th annual meeting of CPPA. Jan 30 - 31, 1990, Montreal, Canada. Montreal: Canadian Pulp and Paper Association (CPPA). Pp. A33 - A36.
- Brown, B. F. 1970. Concept of the occluded corrosion cell. *Corrosion*, Vol. 26, pp. 249 - 250.
- Carpén, L. I. 1999. Ruostumattoman teräksen SFS 757 pistesyöpyminen simuloidussa paperikoneympäristössä. Espoo: VTT Technical Research Centre of Finland. 28 p. (VTT Manufacturing Technology Report VALB291). In print.
- Chen, C. M., Aral, K. & Theus, G. J. 1983. Computer-calculated potential pH diagrams to 300°C. Ohio, USA: Electric Power Research Institute. 122 p. (EPRI NP-3137, Vol. 2).
- Daneault, C., Robert, S. & Dionne, P.-Y. 1994. Groundwood post-refining hydrosulphite bleaching. *Pulp & Paper Canada*, Vol. 95, pp. T277 - T281.
- Danehy, J. P. & Zubritsky, C. W. III 1974. Iodometric method for the determination of dithionite, bisulfite, and thiosulfate in the presence of each other and its use in following the decomposition of aqueous solutions of sodium dithionite. *Analytical Chemistry*, Vol. 46, pp. 391 - 395.
- Duret-Thual, C., Costa, D., Yang, W. P. & Marcus P. 1997. The role of thiosulfates in the pitting corrosion of Fe-17Cr alloys in neutral chloride solution: electrochemical and XPS study. *Corrosion Science*, Vol. 39, pp. 913 - 933.
- Ehrnstén, U. M., Likonen, J., Carpen, L. I. & Varjonen, O. A. 1996. Studying localized corrosion in stainless steels with surface-sensitive methods. *Materials Characterization*, Vol. 36, pp. 279 - 289.

Elbiache, A. & Marcus, P. 1992. The role of molybdenum in the dissolution and the passivation of stainless steels with adsorbed sulfur. *Corrosion Science*, Vol. 33, pp. 261 - 269.

Garner, A. 1982. Sources of thiosulphate in paper machine white water, Part I - Decomposition of stored sodium hydrosulphite solutions. *Pulp and Paper Canada*, Vol. 83, pp. 20 - 28.

Garner, A. 1985. Thiosulfate corrosion in paper machine white water. *Corrosion*, Vol. 41, pp. 587 - 591.

Ingruber, O. V. & Kopadinis, J. 1967. Hydrosulphite bleaching, Part I. Decomposition of hydrosulphide (dithionite) solutions with and without pulp. *Pulp and Paper Magazine of Canada*, June, pp. T258 - T267.

Jouan, R. 1959. Étude expérimentale de quelques réactions très rapides d'oxydation, par l'oxygène moléculaire, de solutions salines aqueuses. III. - Oxydation des solutions aqueuses de dithionite de sodium. *Chimie Physique*, Vol. 56, pp. 327 - 357.

Ke, R. & Alkire, R. C. 1995. Initiation of corrosion pits at inclusions on 304 stainless steel. *Journal of Electrochemical Society*, Vol. 142, pp. 4056 - 4062.

Leckie, H. P. & Uhlig, H. H. 1966. Environmental factors affecting the critical potential for pitting in 18-8 stainless steel. *Journal of Electrochemical Society*, Vol. 113, pp. 1262 - 1267.

Lem, W. J. & Wayman, M. 1970. Decomposition of aqueous dithionite. Part I. Kinetics of decomposition of aqueous sodium dithionite. *Canadian Journal of Chemistry*, Vol. 48, pp. 776 - 781.

Magnin, T., Lardon, J. M. & Amzallag, C. 1987. Coupling effects between the α and γ phases during corrosion fatigue of an α/γ duplex stainless steel. In: Richie, R. O. & Starke, E. A. (eds.). *Proceedings of 3th International Conference on Fatigue and Fatigue Thresholds*, Vol. 3. West Midlands, United Kingdom: Engineering Materials Advisory Services Ltd. Pp. 1221 - 1228.

Marcus, P., Teissier, A. & Oudar, J. 1984. The influence of sulphur on the dissolution and the passivation of a nickel-iron alloy - I. Electrochemical and radiotracer measurements. *Corrosion Science*, Vol. 24, pp. 259 - 268.

Marcus, P. 1995. Sulfur-assisted corrosion mechanisms and the role of alloyed elements. In: *Corrosion mechanisms in theory and practice*. P. Marcus and J. Oudar (eds.). USA: Marcel Dekker Inc. Pp. 255 - 257.

Marichev, V. A. 1991. A new possibility of application of electron tunneling effects in electrochemical double layer structure investigations. *Surface Science*, Vol. 250, pp. 220 - 228.

Marichev, V. A., Saario, T. & Molkanov, V. V. 1993. Prevention of localized corrosion caused by thiosulfate in paper mill environment. In: *Proceedings 12th International Corrosion Congress, Corrosion Control for Low-Cost Reliability*, Vol. 2. Houston, TX, USA: NACE International. Pp. 826 - 833.

Newman, R. C., Isaacs, H. S. & Alman, B. 1982. Effects of sulfur compounds on the pitting behavior of type 304 stainless steel in near-neutral chloride solutions. *Corrosion*, Vol. 38, pp. 261 - 265.

Newman, R. C. 1985a. Pitting of stainless alloys in sulfate solutions containing thiosulfate ions. *Corrosion*, Vol. 41, pp. 450 - 453.

Newman, R. C. 1985b. The dissolution and passivation kinetics of stainless alloys containing molybdenum - I. Coulometric studies of Fe-Cr and Fe-Cr-Mo alloys. *Corrosion Science*, Vol. 25, pp. 331 - 339.

Newman, R. C., Wong, W. P. & Garner, A. 1986. A mechanism of microbial pitting in stainless steel. *Corrosion*, Vol. 42, pp. 489 - 491.

Newman, R. C., Wong, W. P., Ezuber, H. & Garner, A. 1989. Pitting of stainless steel by thiosulfate ions. *Corrosion*, Vol. 45, pp. 282 - 287.

Pourbaix, M. & Pourbaix, A. 1990. Potential - pH diagrams for the system S-H₂O, from 25 to 150°C. Influence of access of oxygen in sulphide solutions. Bryssel: Centre Belge d'Etude de la Corrosion. 44 p. (Cebelcor Rapport 299, Vol. 159, Rapports Techniques).

Qvarfort, R. 1998. Some observations regarding the influence of molybdenum on the pitting corrosion resistance of stainless steels. *Corrosion Science*, Vol. 40, pp. 215 - 223.

Rinker, R. G., Lynn, S., Mason, D. M. & Corcoran, W. H. 1965. Kinetics and mechanisms of the thermal decomposition of sodium dithionite in aqueous solution. I & EC Fundamentals, Vol. 4, pp. 282 - 288.

Renner, M., Heubner, U., Rockel, M. U. & Wallis, E. 1986. Temperature as a pitting and crevice corrosion criterion on the FeCl₃ test. *Werkstoffe und Korrosion*, Vol. 37, pp. 183 - 190.

Saario, T. & Marichev, V. A. 1993. A new contact electric resistance technique for in-situ measurement of the electric resistance of surface films on metals in electrolytes at high temperatures and pressures. In: *Proceedings 12th International Corrosion Congress, Corrosion Control for Low-Cost Reliability*, Vol. 6. Houston, TX, USA: NACE International. Pp. 4325 - 4331.

Saario, T. 1995. Development and applications of the Contact Electric Resistance technique. Helsinki: Helsinki University of Technology. 33 p. (Report TKK-V-A13).

Suutala, N. & Kurkela, M. 1984. Localized corrosion resistance of high alloy austenitic stainless steels and welds. In: *Proceeding Stainless Steel 1984*. Gothenburg, Sweden, Sep 3 - 4, 1984. London: Institute of Metals. Pp. 240 - 247.

Suzuki, T., Yamabe, M. & Kitamura, Y. 1973. Composition of anolyte within pit anode of austenitic stainless steels in chloride solution. *Corrosion*, Vol. 29, pp. 18 - 22.

Thompson, C. B. & Garner, A. 1995. Paper machine corrosion and progressive closure of the white water system. In: *Pulp and Paper Industry Corrosion Problems*. Stockholm, Sweden, May 16 - 19, 1995. Stockholm: Swedish Corrosion Institute. Pp. 207 - 216. (Vol. 8).

Tromans, D. & Frederick, L. 1984. Effect of thiosulfate on crevice corrosion of stainless steels. *Corrosion*, Vol. 40, pp. 633 - 639.

Varjonen, O. A., Ehrnstén, U. M. & Hakkarainen, T. J. 1989. Effect of thiosulfate on the pitting corrosion of stainless steels in paper machine environments. In: Pulp and Paper Industry Corrosion Problems. Finland, Helsinki, Sep 29 - Oct 1, 1989. Helsinki: The Finnish Pulp and Paper Research Institute. Pp. 303 - 313. (Vol. 6B).

Varjonen, O., Carpén, L. & Ehrnstén, U. 1995. Thiosulfate pitting of molybdenum alloyed stainless steel (SS 2343) in chloride/sulphur environments. In: Pulp and Paper Industry Corrosion Problems. Stockholm, Sweden, May 16 - 19, 1995. Stockholm: Swedish Corrosion Institute. Pp. 254 - 262. (Vol. 8).

Wranglen, G. 1974. Pitting and sulphide inclusions in steel. Corrosion Science, Vol. 14, pp. 331 - 349.

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Title Thiosulfate pitting corrosion of stainless steels in paper machine environment			
Abstract <p>Thiosulfate pitting corrosion of austenitic stainless steels of types UNS S30403 (AISI 304L) and UNS S31603 (AISI 316L), and duplex stainless steel of type UNS S31803 (22Cr DSS) was studied in simulated paper machine environments containing chloride, sulfate and thiosulfate by cyclic polarization scans, scratch tests, Contact Electric Resistance (CER) technique and by corrosion coupon tests performed in a real paper machine. The formed pits and crevice corrosion were examined by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). The surface films were also analyzed by Electron Spectroscopy for Chemical Analysis (ESCA) and Secondary Ion Mass Spectrometry (SIMS).</p> <p>Thiosulfate and chloride clearly have a synergistic effect in inducing localized corrosion. Thiosulfate is able to prevent passivation of an active stainless steel surface and able to stabilize metastable pits initiated below the actual pitting corrosion potential. The role of chloride is to initiate corrosion pits. Thiosulfate increases the possible potential range of corrosion pits to grow by lowering the repassivation potential. Hydrogen sulfide originating from thiosulfate is proposed to accelerate the anodic dissolution inside corrosion pits and crevices by forming sparingly soluble metal sulfides and by acidifying the local environment. The compositions of the black deposit enriched inside thiosulfate pits and corrosion crevices were similar to the compositions of the low-resistance surface films.</p> <p>Pitting Resistance Indices (PRE) of the test materials increased in the order of UNS S30403 (PRE 19 - 21), UNS S31603 (PRE 24 - 25) and UNS S31803 (PRE 35) in accordance with the observed localized corrosion resistance in both the laboratory and field tests. All the materials corroded technically significantly in corrosion coupon tests performed in a paper machine. The bulk environment of the paper machine was very mild, but the chloride and thiosulfate ions concentrating up to high levels created favourable conditions for corrosion.</p>			
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