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Evaluation of Stainless Steel Grades in Pulp Bleach Plants

At the NACE conference Corrosion 87' in San Francisco, March 9-13, 1987, results and experiences were presented from more than eight years' use of the stainless steel UNS S31254 (Avesta 254 SMO) in paper mill bleach plants. References from 20 different installations were given, including a description of the corrosive environment, type of equipment and performance of the alloy.

Since the presentation supports the results from two previous investigations from the Scandinavian pulp and paper industry, they are opening this issue of ACOM and followed by the NACE report. These previous reports were both presented at the Fourth International Symposium on Corrosion in the Pulp & Paper Industry in Stockholm, May 30-June 2,1983.

Performance of a High Molybdenum Stainless Steel in the Pulp and Paper Industry

by
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Summary

The corrosion conditions in two of the most exposed parts of the pulp and paper mill, i.e. the bleach plant filter washers in the C and D stages and the recovery boiler scrubber, have been analyzed. In the filters, the corrosivity of the environment seems to be completely controlled by the concentration of residual chlorine in the pulp suspension. The severest attacks occur, in the form of crevice and pitting corrosion, in the gas phase above the suspension. In recovery boiler scrubbers, corrosion is caused by the acid solutions which are a result of absorption of certain gas components in a chloride containing scrubbing liqour. The severest conditions exist at the gas inlet where hydrogen chloride and sulfur trioxide are preferably absorbed.

A field test, performed in a C stage washer, shows that 6Mo stainless steel Avesta 254 SMO is considerably more resistant than the highest alloyed conventional stainless steels. Very little corrosion occured even in the gas phase and in the presence of high amounts of residual chlorine. Under extreme conditions, e.g. on hot shower pipes and in the presence of very high residual chlorine levels, even the most resistant metallic materials can be attacked. In such as position rapid corrosion has occurred also on 254 SMO.

A great number of industrial applications, in bleach plant washers as well as recovery boiler scrubbers, show that Avesta 254 SMO can be successfully used under conditions where conventional stainless steels have failed.

Introduction

In the pulp and paper industry corrosion problems exist in many places. Quite often the problems can be solved simply by choosing a more highly alloyed material. In some cases, this measure might be doubtful from an economical point of view, especially if expensive materials like titanium or nickel base alloys are the alternatives. However, during the last ten years several highly alloyed stainless steels have been developed. These steels which have an excellent corrosion resistance and a reasonable price, often fill the wide gap between the conventional stainless steels and the exotic alloys.

If we confine ourselves to the parts of the pulp and paper plant where wet corrosion is the major problem there are two applications where even the best conventional stainless steels may have a marginal resistance and where great amounts of stainless steel are used. These applications are the filter washers in the bleach plant and the recovery boiler scrubber. The intention with this paper is to discuss the corrosion conditions existing in these parts of the plant and to show how one of the new, highly alloyed stainless steels has reduced existing problems.

The name of the steel is Avesta 254 SMO and its chemical composition is 20Cr, 18Ni, 6.1Mo, 0.7Cu and 0.2N. The steel is included in eleven ASTM standards for sheet, plate, bar, forgings, welded and seamless pipes under the designation UNS S31254. Avesta 254 SMO has a good weldability and is available in plate thicknesses up to 50 mm and as castings.

Corrosion Conditions

Bleach plant washers

In the bleach plant washers and in the filtrate system, stainless steels of type 316 L and 317 L are used extensively (1, 2). Corrosion problems are numerous, especially in the chlorine (C) and chlorine dioxide (D) stages, where the environment consists of an acidic and strongly oxidizing chloride solution, ideal for promoting localized corrosion. The conditions existing in C and D stage washers will be discussed below.

Stainless steel in C and D washers

In a filter washer, the construction material is exposed to two different environments, i.e. a liquid phase (pulp suspension) and a gas phase above the pulp suspension. In both the C and D stage the gas phase is generally more corrosive (1,3,4) although there are exceptions in the D stage (5). Alternate dry/wet exposure, such as with filter drums, results in less corrosion than either liquid or gas phase exposure (5). Corrosion seems to be less severe in the D stage than in the C stage (4, 5), but the liquid phase of the D stage is sometimes more corrosive than that of the C stage (6, 7).

The predominant types of corrosion are pitting and crevice corrosion, but the risk for crevice corrosion is appreciably higher (8, 9). The propagation rate of an already established attack is considered almost constant by some investigators (6) while stop and go propagation has been suggested by others (9,10,11). However, the latter mode seems unlikely since repassivation of a propagating attack requires very low corrosion potentials, which can hardly be reached without external measures taken (8, 12). On the other hand, if crevice corrosion occurs under fiber deposits the attacks would stop if the deposits are removed.

Influence of environmental parameters

In most corrosive solutions pH, chloride concentration and temperature have a decisive effect on the degree of pitting and crevice corrosion. However, in bleach plant washers these parameters are of secondary importance (5,6,10) although some influence has been noticed on type 316 L exposed to liquid phase (7).

It has long been known that the residual chlorine concentration has great influence on the corrosion of stainless steel in C and D stage washers (8,13). It has been suggested that as long as the residual chlorine is kept at a low level, the composition of the pulp suspension is of minor importance (3). For steels of type 316 L and 317 L a maximum of 10-25 ppm is recommended in both C and D stage washers in order to avoid corrosion in gas as well as liquid phase (4, 5, 8, 12). Of course, more highly alloyed materials can resist higher residual chlorine values.

Protective measures

As is always the case with stainless steels clean surfaces have the best corrosion resistance. In practice, intermittent cleaning with water spray has been very effective in reducing corrosion on the inlet box above the pulp suspension (14).

It is evident that a close control of the residual chlorine level is necessary in order to reduce corrosion in washers made of type 316 L and 317 L If the bleaching reactions are permitted to go to completition, little residual chlorine can be expected in the bleached stock. If this is not possible, the residual chlorine can be chemically reduced by a reductant. In practice, controlled addition of sulfur dioxide (antichlor) to the pulp suspension leaving the D-towers has been successfully used for many years (13) and the positive effect of antichlor has been confirmed in several field tests (3,4, 5, 11, 15). From the corrosion point of view, antichlor should be just as effective in C-stage washers and it is also used in some Swedish bleach plants (16).

The effect of sulfur dioxide is increased if pH is simultaneously increased (15). Alkalization alone also reduces corrosion in the D stage, at least if pH is increased to minimum 6(5) or 8(15). In the D stage, the pH range 3.5-5 should be avoided since any attack will produce great amounts of solid corrosion products which stimulate further attack. In more acid solutions, these corrosion products will dissolve, and in more alkaline solutions localized corrosion is reduced (5). An alkaline filtrate from a D stage, where sulfur dioxide antichlor is not employed, should not be used as wash water in the C stage. In such a filtrate, residual chlorine exists as non corrosive sodium chlorite and in the acid, oxidizing C-stage environment corrosive chlorine dioxide is regenerated (13, 17).

Sulfur dioxide antichlor is effective because the corrosion potential of the stainless steel is lowered below the critical crevice and pitting corrosion potentials. Thus antichlor provides chemical cathodic protection of the filter washers. Of course, electrochemical cathodic protection is also possible and has been successfully used for protection of filter drums in washers where the vat is made of non metallic material (4, 18, 19, 20). However, while antichlor is effective in all parts of the filter, the gas phase included, electrochemical cathodic protection only affects the parts exposed to the liquid phase.

A successful result of electrochemical cathodic protection depends on an even distribution of the protection current. This is especially true for acid environments. If the current density is too high, the potential of the stainless steel will enter the region where active uniform corrosion occurs while too low current densities do not prevent crevice and pitting corrosion (4, 19, 20). An even current distribution is difficult to accomplish if the geometry of the structure to be protected is complex. Simultaneous protection of drum and vat, both made of stainless steel, has not, therefore, been without problems (4). However, the effective potential range is much wider if highly alloyed stainless steels are used instead of type 316 L and 317 L (21). On the other hand, the best of these highly alloyed stainless steels will be sufficiently resistant in most applications, gas phase exposure included, even in the absence of cathodic protection (3, 5, 6).

Recovery boiler scrubbers

Effect of gas components

The flue gases formed when burning evaporated, spent cooking liquor in the recovery boiler contain valuable process chemicals which have to be recovered. Therefore a recovery unit is an integrated part of a kraft as well as of a sulfite plant. As a final stage, the recovery units are often equipped with wet scrubbers. During scrubbing, aggressive conditions occur due to the presence of sulfur dioxide, sulfur trioxide and hydrogen chloride in the gas. The composition of recovery boiler flue gases, and their corrosive effects, have been discussed in some detail in a recent publication (22).

When the gases enter the scrubber the temperature is normally 120-150°C. In the scrubber they are first quenched to the saturation temperature, which is 60-70°C. After quenching the main part of the sulfur dioxide content is absorbed in great amounts of scrubbing liquor which mostly consists of a neutral or slightly acidic sulfite-bisulfite mixture.

In a scrubber, the corrosion conditions are not the same in all parts. Especially severe conditions occur in the gas inlet where the gas is quenched. Since the absorption rates of hydrogen chloride and sulfur trioxide are much higher than that of sulfur dioxide, mainly the former compounds are absorbed in the quenching stage forming hydrochloric and sulfuric acid. The sulfuric acid forms a mist which is difficult to absorb in other media than concentrated sulfuric acid, and part of this mist passes through the scrubber.

The difference in solubility between hydrogen chloride and sulfur dioxide has been used to remove chlorides from the process streams in the plant. By using very small amounts of water during the quenching and by using a high gas velocity, 60% of the hydrogen chloride can be washed out without noticeable loss of sulfur dioxide (23).

In the section of the scrubber where sulfur dioxide is absorbed, the temperature is lower and the pH is higher than in the quenching stage. However, the chloride content of the scrubbing liquor can be quite high, especially if it is highly recirculated.

Corrosion considerations

The corrosion conditions discussed above indicate that most types of corrosion are possible in a recovery boiler scrubber. In the quenching and chloride removal stage, uniform corrosion might be caused by hot and strongly acidic chloride solutions. In the main scrubber, conditions should be milder but crevice and pitting corrosion might be caused by the weakly acidic or neutral scrubbing liquor.

Due to relatively low temperatures and relatively low chloride concentrations, stress corrosion cracking is not a big problem. However, if there are hot surfaces, a dilute chloride solution might be evaporated by local boiling. The acidic concentrated solution thus formed considerably increases the risk for stress corrosion cracking. Hot surfaces may exist in dry-wet zones in the quenching stage and in the heat exchangers sometimes used for reheating the stack gas.

If hot, unscrubbed flue gas is used for reheating, dew point corrosion, caused by sulfur trioxide, might be a problem e.g. in the stack. Any sulfuric acid mist passing through the scrubber will contribute to this problem.

Field tests

Bleach plants

Several field test programs covering many metallic materials have been carried out in North American and Scandinavian pulp and paper industry in recent years (1, 3-7, 9, 10). The most common way has been to expose test racks containing nonwelded or welded coupons for various lengths of time in C and D stage washers. The influence of environmental conditions on the performance of the tested stainless steels has been described previously in this paper.

The overall results indicate that type 316 L and 317 L give a poor performance in these tests. Also Alloy 904L shows limited resistance in many cases. Austenitic stainless steels containing 6 % Mo, as for example Avesta 254 SMO, and some superferritics are the only stainless steels that can give an acceptable performance.

Test in a chlorination washer

Avesta has conducted field tests in a chlorination stage in connection with a complete replacement of the filter washer. The old filter washer consisted of a type 316 filter drum and tile vat, while the new unit was fabricated entirely out of 254 SMO.

Test samples of size 500x130x3 mm were made of the four different stainless steels listed in Table 1, and contained a vertical overlay weld and a horizontal butt weld (see Figure 2). Both welds were made applying manual metal arc (MMA) welding. The filler metals used for the conventional steels were of approximately the same composition as the base metal.

Table 1: Stainless steels tested in field exposures

Grade	Cmax	Si	Mn	Cr	Mi	Mo	Others
AISI 316 L	0.03	0.5	1.5	17	12	2.7	-
Type 317 M	0.05	0.5	1.5	17	14	4.3	-
Alloy 904L	0.02	0.5	1.5	20	25	4.5	1.5Cu
254 SMO	0.02	0.4	0.5	20	18	6.1	0.2N.0.7Cu

As regards 254 SMO, this was the case in the first exposure. However, in the later exposures a nickel base overalloyed filler metal Avesta P12, containing 60Ni, 21 Cr, 9Mo and 2Nb was utilized. This welding consumable is recommended by Avesta in all cases where post weld heat treatment is not carried out. After welding, the samples were pickled. The test racks were made of titanium and the samples were insulated from metal-to-metal contact by teflon spacers. During the test the racks were partly submerged in the incoming pulp suspension in the inlet box thus exposing the samples both to the gas and liquid phase of the washer.

The first exposure (A) was performed in the old washer for 21 months. The tests in the new washer where divided into two periods which extended for 84 (exposure B) and 56 (exposure C) days respectively. In the second period (C), evacuation of the atmosphere under the filter hood was increased by a factor of about 3. One test rack was exposed for 140 days (exposure D), the sum of exposures B and C.

The environmental conditions during exposure A are not known in detail. During the later exposures (B-D) in the new unit, however, analysis of the liquid as well as the gas phase was made. The chlorine content of the gas was obtained by bubbling a measured volume of gas through a bottle containing a solution of potassium iodide. The amount of iodine formed was analyzed by iodometric titration.

The main part of the equipment used to collect condensate from the gas phase was a laboratory glass condenser cooled with water of about 10°C. The condensate was collected outside the filter washer.

The results are shown in table 2, where the values for exposures B and C represent the first 48 hours of each period.

Table 2: Environmental conditions in C-stage filter

Parameter/ location	Exposure A	B		C	
Liquid phase **Temp.°C**	**Av.**	**Av.**	**min-max**	**Av.**	**min-max**
Inlet box	20	27	24-29	21	16-24
Filtrate		29	26-31	24	20-27
Shower w. I	50	65	63-66	70	68-74
Shower w. II		58	56-60	56	54-58
pH					
Inlet box	1.8	1.6	1.5-1.7	1.9	1.8-1.9
Filtrate		1.6	1.5-1.6	1.9	1.8-2.0
Shower w. I		6.7	6.5-6.9	6.5	6.2-6.7
Shower w. II		11.0	10.7-11.4	11.1	10.7-11.6
Cl_2, ppm					
Inlet box	60	94	28-227	140	50-340
Filtrate		73	18-178	93	14-234
Cl^-, ppm					
Inlet box	1000	1340	1150-1470	1230	1120-1300
Filtrate		1270	1040-1400	1110	1000-1200
Gas phase **Temp. °C**					
Shower pipes		39	37-40	35	28-40
Gas outlet		52	50-54	41	41-41
pH (condensate)					
Shower pipes		2.6	2.6-2.9	2.7	2.6-2.7
Gas outlet		2.5	2.4-2.6	2.3	2.2-2.3
Cl_2, mg/Nm^3					
Shower pipes		1340	250-2880	550	60-1250
Gas outlet		2460	340-2550	430	350-520

The major differences between exposure A and exposures B and C are the higher temperature of the shower water and the higher level of residual chlorine in the inlet box in the latter exposures. As the stock from the bleaching tower is diluted by the filtrate, the pulp suspension in the inlet box reaches a higher temperature too because of the increased shower water temperature. The lower temperatures in the inlet box and in the filtrate in exposure C depend on colder incoming stock. The variation of the residual chlorine level during exposure A was not reported.

The increased evacuation (exposure C) seems to have resulted in lower residual chlorine and temperature in the gas phase. However, the chlorine content in the liquid phase is higher in exposure C than in exposure B. According to amperometric measurements during the entire exposure periods, the residual chlorine content in the inlet box exceeded approximately 200 ppm 5% of the total time in exposure B and 13% of the time in exposure C. Short peaks of approximately 500 ppm have occurred in both exposures B and C.

The pH value in the gas condensates is somewhat higher than in the liquid. One analysis of the chloride content in the condensate during exposure B gave a value of 100 ppm.

The results of the corrosion tests are summarized in Figure 1, which follows an evaluation method used by other workers. The corrosion performance is divided into three categories; good, moderate and poor with depths of attack <0.1 mm, 0.1-0.5 mm and >0.5mm respectively. Perforation of the sample is indicated by "P". In addition to the crevices formed between the samples and the teflon spacers, deposits of fibres also gave rise to areas of crevicing, particularly on the side of the sample facing the wall of the inlet box. Hence it was difficult to separate pitting from crevice corrosion.

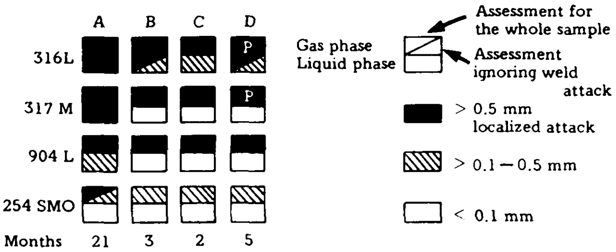

Figure 1
Corrosion assessments of samples exposed in a C-stage washer

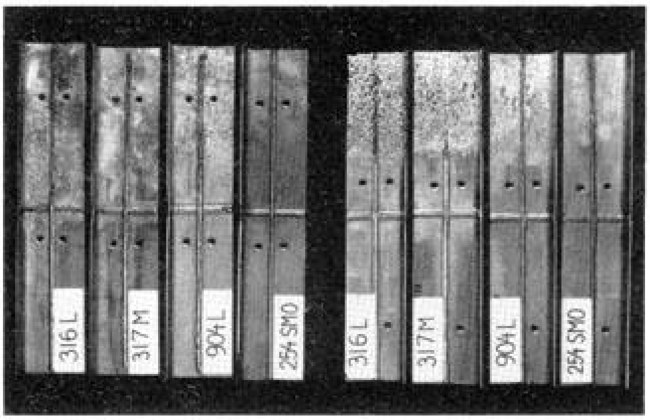

Figure 2
Test samples of exposures A (left) and D (right)

Discussion of results

The gas phase is evidently much more aggressive than the liquid phase, as demonstrated in Figure 1. This is also illustrated in Figure 2, where the entire samples after exposures A and D are shown. In the gas phase, the whole surface of the conventional steels is attacked while in the liquid phase only a few attacks exceed 0.5 mm in depth.

It can also be concluded that at least the gas phase has become more corrosive in the new unit, as both type 316 L and 317 M were perforated by corrosion after only 5 months of exposure. If the maximum propagation rates of localized corrosion attack in exposure B and C are calculated, this corresponds to approximately 10 mm/year. Obviously, in this test, the propagation rate is almost constant. The maximum corrosion rates for type 316L and 317M in the exposure for 21 months are 1.5 and 1.0 mm/year respectively.

The higher gas phase corrosivity in exposures B-D compared to that of exposure A is most likely due to the increased chlorine level in the inlet box.

The improved evacuation of the washer atmosphere did apparently not change the aggressiveness of the gas phase since exposures B and C roughly produced the same extent of attack. One possible reason could be that the observed decrease in gase phase chlorine content was not sufficient to reduce the corrosion rate. Another explanation is that the gas phase analysis made might not reflect the environmental conditions in the wet films existing on the steel surfaces. The pH and chloride content of the analyzed condensates do not indicate any severe corrosivity. However, this condensation occurred at a temperature which is very low compared to that of the test specimens. This might influence the composition of the condensates.

The ratings of the four tested alloys are similar in all exposures. Types 316 L and 317 M have been subjected to severe corrosion attacks. Although less corroded, Alloy 904L also showed limited resistance in the aggressive gas phase.

The high molybdenum stainless steel Avesta 254 SMO has a superior performance in comparison with the other steels tested. In contrast to the other alloys, the parts exposed to the liquid did not show any sign of attack. In the 21 month gas phase exposure, pitting occurred in the weld metal. As the composition of the weld metal in this sample was the same as for the base metal, this result is not surprising considering the earlier tests performed by other workers (5). In the gas phase exposures, where the recommended overalloyed filler metals were used (B-D), localized attacks did not ocur on 254 SMO. However, as can be seen in Figure 3, a superficial etching attack, similar to that of uniform corrosion, has taken place. This explains the reported moderate performance in Figure 1.

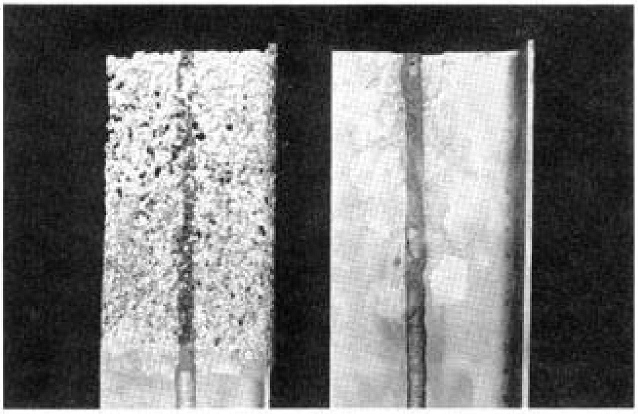

Figure 3
Parts after exposure to gas phase for 140 days. Type 316 L (left) and 254 SMO (right)

Recovery boiler scrubbers

Few field tests in recovery boiler scrubbers have been published. However, as the corrosion conditions are essentially the same in other flue gas desulfurizer scrubber systems, considerations regarding alloy performance in these systems can be utilized for pulp and paper industry (22). In a comprehensive study by International Nickel (24), a large number of corrosion test spools have been exposed in various scrubbing systems. In these tests ratings for general corrosion and pitting corrosion clearly show the beneficial influence of molybdenum on corrosion resistance.

As described in a previous paper (22), the Swedish Corrosion Institute has performed field tests in recovery boiler scrubbers in Sweden. These tests too showed the positive effect of molybdenum on the alloy performance, and in the most corrosive locations, sufficient corrosion resistance is obtained only with alloys containing a minimum of 6% molybdenum.

Applications

Avesta 254 SMO has been widely used in the pulp and paper industry since 1977. A number of references from bleach plants and recovery boiler scrubbers (installed 1977-83*) are listed in Appendix 1 (page 8). In addition to the list, more than 10 filter washer drums are under fabrication and will be installed within a year. Also in other areas of the pulp and paper industry, the high corrosion resistance of Avesta 254 SMO has been utilized. Interesting examples are: absorption stage packings in tall oil distillation, piping for residual acid from chlorine dioxide plants and crystallizers for chlorate production. Avesta 254 SMO is also used in many flue gas scrubbers in metallurgical and chemical industry.

Below a few examples of experiences with Avesta 254 SMO are presented in more detail.

Experiences in bleach plants

D stage filter washer

The filter washer was originally made of type 316 L steel. The inlet box and the vat were perforated by pitting after six years in areas exposed to the liquid as well as the gas phase. These parts were therefore lined with Avesta 254 SMO.

The composition of the liquid in the inlet box has been measured as follows:

	min	max
Cl^-	180	250 ppm
Cl_2	2.5 (6.1)	3.6 (110) ppm
pH	2.9	3.8
Temp.	72	77°C

The figures in parentheses represent values measured before automatic adjustment of pH was installed. Earlier, pH was manually adjusted with sodium hydroxide, and varied from 2.9 to 11.9. Addition of antichlor (sulfur dioxide) is controlled by redox measurements. Since the redox potential caused by a certain amount of residual chlorine is lower at higher pH values there will be no antichlor added if the environment becomes alkaline, not even if the amount of residual chlorine is high. When pH drops again there will temporarily exist high concentration of residual chlorine.

The filter washer has been inspected on several occasions. A few small areas with shallow pits and light etching were observed at the first inspection. The etching has the same appearence as the corrosion observed on the 254 SMO specimens from the field test, as shown in Figure 3. The attacks were all located in areas exposed to the gas phase. The very same attacks, without any changes, were observed at the later inspections. No apparent propagation had occurred. The most probable explanation is that the corrosion was initiated during the period when the residual chlorine content could be higher. Later, when pH was automatically adjusted and the chlorine content was kept at a lower level, the corrosion stopped. In this filter washer U profiles which regulate the flow of pulp suspension between inlet box and vat are still made of type 316 L steel. These parts which are mostly exposed to the liquid phase show extensive pitting.

C/D stage filter washer

Type 317 L steel was originally used in this filter washer, but the steel was perforated by pitting within 9 months and extensive repairs of the inlet box and the vat were necessary. Alloy 904 L was used for these repairs, but this steel too suffered pitting within one year and had to be replaced step by step within 15 to 30 months. For these later repairs Avesta 254 SMO was used.

Analysis of the liquid in the inlet box has given the following result:

Cl^-	1200 ppm
Cl_2	20-150ppm
pH	2.0
Temp. (tower)	22-30°C
Temp. (Shower water)	60-65°C

At the latest inspection, when Avesta 254 SMO had been in service for about 6 years, only very light etching could be seen in some limited areas exposed to the gas phase. The depth of attack was too small to be measured.

C stage filter washer

This is the unit where the previously described corrosion tests were performed. The old washer drum was made of type 316 with a service life of approximately 20 years. The environmental conditions reported in Table 2 (exposure A) represent an average of the values during the last few years. These data indicate lower residual chlorine level and lower temperature of the shower water than for the new washer.

In the new unit, Avesta 254 SMO is used in the inlet box, vat, drum and shower pipes. The corrosive environment in the new washer is presented under exposures B and C in Table 2. These data were collected during comparatively short periods, however. During the service time so far, about 18 months, excursions in residual chlorine up to 950 ppm have been observed.

As in the field tests a moderate etching attack has occurred under fiber deposits in some gas phase exposed areas of the inlet box and the vat. The parts exposed to the liquid, and also the drum, show no signs of corrosion.

The shower pipes, however, show very rapid corrosion. It is known from experience that shower pipes have a very exposed position due to the corrosive atmosphere on the outside and the high temperature, obtained from the hot shower water. For example, even shower pipes of titanium with a water temperature of 85°C have failed in D-stage filter washers (25).

Experiences in scrubbers

Spray tower type scrubber in a kraft pulp mill

The scrubber is used forcleaning flue gases from the kraft recovery boiler. Originally, the entire scrubber was made of type 316 steel, but the lower section was rapidly corroded. The washing liquid at the bottom of the quenching stage has the following composition:

Total S	3100-8200 ppm
Cl^-	2800-4600 ppm
Temp.	70°C
pH	7

The liquid is continuously neutralized with sodium hydroxide. Probably dry-wet conditions have prevailed in certain areas, thus contributing to the corrosion.

A new lower section made of Avesta 254 SMO was installed six years ago. Some time later droplet separators and other internal parts in the same steel grade were installed. Disregarding very light attacks on one droplet separator, no corrosion has been reported.

Packed-bed type scrubber in a sulfite mill

The scrubber type contains a quenching stage in the lower part and an absorption stage in the upper part. An earlier scrubber, made entirely in type 317 L steel, was severely corroded after one year. After four years of frequent repairs the entire scrubber was replaced by a new unit with the internal parts in the absorption stage made of Avesta 254 SMO.

The composition of the incoming gas is:

H_2O	33-35%	H_2S	50 ppm
CO_2	15-16%	HCI	74 ppm
SO_2	6000 ppm	Na_2SO_4	80 mg/Nm^3

In the first stage, the sodium sulfate and some 65% of the hydrogen chloride are washed out. The sulfur dioxide is absorbed in a sulfite-bisulfite mixture in the absorption stage. The resulting liquor is slightly acidic, and has a temperature of maximum 80°C. All steel parts in the absorption stage are in excellent condition after more than three years in service.

Conclusions

1. Corrosion tests in a C-stage washer show that the highly alloyed stainless steel Avesta 254 SMO is considerably more resistant than conventional stainless steels.
2. The corrosion tests also show that the gas phase is much more corrosive than the liquid phase although the latter is aggressive enough to attack conventional stainless steels.
3. The composition of condensates taken from the gas phase in the C-stage washer cannot explain its higher corrosivity.
4. The concentration of residual chlorine in the liquid phase seems to control the corrosivity of both the liquid and the gas phase in C stage as well as D stage washers.
5. Practical experience from many applications of Avesta 254 SMO in bleach plant washers and recovery boiler scrubbers show that this grade is resistant to environments where conventional stainless steels have failed.

Acknowledgement

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Presented at Fourth International Symposium on Corrosion in the Pulp & Paper Industry, Stockholm May 30-June 2,1983.

* Note: An updated list of references as of January 1988, covering some 60 installations of 254 SMO in pulp bleach plants, can be aquired from Avesta AB, S-774 01 Avesta, Sweden.

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Appendix 1 Reference List of Avesta 254 SMO in Pulp & Paper Industry, Bleach Plants

End user	Mill/Country	Stage	Equipment	Installed
Fiskeby	Skärblacka, SWEDEN	C/D, D	Washer vats	Jan /77
Kopparfors	Norrsundet, SWEDEN	C/D, D	Dandy rolls	Jun /77
Leykam-Mürztaler	Gratkorn, AUSTRIA	D	Pulp pipes	Jan /78
Pölser Zellulose	Pööls, AUSTRIA	C	Washer vats	Aug /79
Södra Skogsägarna	Mönsterås, SWEDEN	C/D, D	Washer vats	Oct /79
Abitibi	Smooth Rock Falls, CANADA	C	Washer drum	May /80
Celbi	Figueira da Foz, PORTUGAL	C	Washer drum	Fall /80
G.E.C.	Cell. d'Aquitaine, FRANCE	C	Washer drum	Sep /80
SCA	Östrand, SWEDEN	D	2 washer drums	Dec /80
Severoceske Papirny	Steti, CSSR	C	Screen unit, diffuser	Dec /80
Billerud	Skoghall, SWEDEN	C	Ion exchange column	Dec /80
G.E.C.	Cell. d'Ardennes, BELGIUM	C	Washer drum	/81
Södra Skogsägarna	Mörrum, SWEDEN	C	Washer drum + vat	May /81
Canadian Forest Products	Port Mellon, CANADA	C	Washer drum	Aug /81
St. Anne-Nackawic	Nackawic, CANADA	D	Washer drum	Oct /81
Crown Zellerbach	Elk Falls, CANADA	C	Washer drum	Oct /81
C.I.P. Inc.	Latuque, CANADA	C/D	Washer drum	Mar /83
Recovery boiler scrubbers				
Iggesund	Iggesund, SWEDEN	Kraft	Scrubber body	Sep /77
Fiskeby	Skärblacka, SWEDEN	Kraft	Venturi	Nov /78
Korsnäs-Marma	Gävle, SWEDEN	Kraft	Gas inlet	Jun /79
Leykam-Mürztaler	Gratkorn, AUSTRIA	Sulfite	Venturi	Jun /79
Rauma-Repola	Rauma, FINLAND	Sulfite	Int. components	Nov /79

Field Tests with Metallic Materials in Finnish, Norwegian and Swedish Bleach Plants

by
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Summary

Welded test coupons of nine stainless steels and one nickel-base alloy have been exposed in the C, D/C, H and D stage washers of 17 conventional bleach plants and in the D/C and D stages of one displacement bleach plant. An assessment is made of the relative corrosion resistance of the materials tested and the results are correlated with the corrosive environments. In order to improve the understanding of the gas phase corrosion in the chlorination stage washers and to permit its monitoring, a special pH and redox cell was developed. The maintaining of a constant low residual chlorine concentration in the liquid phase of the filter washers, however, is considered to be the best measure for counteracting both gas and liquid phase corrosion. Suitable threshold values for the residual chlorine concentration in the chlorination and chlorine dioxide stage washers are discussed.

Introduction

A joint Nordic project "Corrosion protection in the pulp industry" undertaken by the research organisations of the Finnish, Norweigan and Swedish paper and pulp industries and the Swedish Corrosion Institute has recently been completed. The aim of the project has been to study the corrosion problems encountered in bleach plant filter washers and to suggest countermeasures against them. The project comprised the following subprojects:

1. A survey of the corrosion and the environment
2. Field tests with metallic materials
3. Field tests with glass-fibre-reinforced polyesters
4. Laboratory studies in simulated chlorine and chlorine dioxide environments
5. Full scale applications of cathodic protection
6. Full scale tests on polarometric control of the residual chlorine concentration.

The present report is an abbreviated version of the Swedish final report on subproject No 2. Readers who are interested in greater detail concerning experimental procedure, environmental variables and results are referred to the final report on the whole project (1).

Experimental procedure

Test coupons of nine stainless steels and one nickel alloy have been exposed in 17 conventional bleach plant filter washers and in one displacement bleach plant. The tests, which were generally of about six months' duration, have been made in the chlorination, chlorine dioxide and hypochlorite stages in conventional bleach plants and the chlorination and chlorine dioxide stages in the displacement bleach plant.

The tests were made with welded test coupons, sized 60X60 mm, of the same type as described earlier (2). Table 1 shows the various materials tested.

Table 1: Chemical composition of the test materials.

	%by weight						Micro-
Materials	C	Cr	Ni	Mo	Cu	N	structure
SS 2343 (type 316)	.036	17.0	11.4	2.6	0.3	.053	Austenitic
SS 2562 (type 904L)	.009	19.8	24.9	4.4	1.5	.039	
Sandvik Sanicro 28	.018	26.9	31.7	3.4	1.0	.023	
Avesta 254 SMO	.014	20.1	18.0	6.1	.8	.204	
Cabot Hastelloy G	.033	22.1	44.3	6.2	1.8	-	
Nyby-Uddeholm MONIT**	.013	25.0	4.0	4.0	-	.010+Ti	Ferritic
Allegheny 29-4	.003	29.6	-	4.0	-	.012	
Allegheny E-Brite	.002	25.9	-	1.0	-	.006	
Nyby-Uddeholm 44 LN**	.026	24.4	5.9	1.5	-	.250	Ferritic-austenitic
Sandvik SAF 2205	.018	22.2	5.5	3.0	-	.140	

The thickness of the initial sheet was generally 3 mm, with the exception of the ferritic steels Allegheny 29-4 and E-Brite which were delivered in the form of 1.6 mm sheet. The material was tested as delivered, cold-rolled and pickled or bright-annealed. After welding, which was generally done by MMA (except the ferritic steels MONIT, 29-4 and E-Brite which were TIG-welded), the welds were cleaned with pickling paste. The filler metals, which were selected on the basis of the sheet suppliers' recommendations, are shown in Table 2.

Table 2. Filler metals and methods of welding

Parent metal	Welding method	Filler metal	
		Designation***	Diam., mm
SS 2343	MMA	832 SKR AC/DC	2.5
SS 2562	MMA	254 SLX AC/DC	2.5
Sanicro 28	MMA	NiCro 31-27 basic	2.5
254 SMO	MMA	P 12 basic	2.5
Hastelloy G	MMA	Hast G rutile	2.4
MONIT	TIG	wire	2.0
29-4	TIG	sheet strip	1.6X3.0
E-Brite	TIG	sheet strip	1.6X3.0
44LN	MMA	453 S AC/DC	2.5
SAF 2205	MMA	Arosta 4462 rutile	2.5

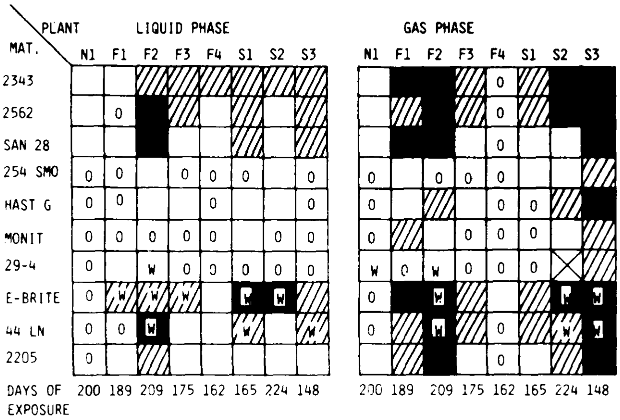
In the course of the tests regular analyses have been made of the environmental parameters of significance for corrosion - residual chlorine (in some cases also with redox potential measurements), chloride, pH and temperature - partly by the plants' own staff and partly by researchers of the Swedish Corrosion Institute. In some cases the redox potential in the liquid phase of the washers was recorded for up to two months. Especial interest has been devoted to establishing the pH and redox potential of the gaseous phase condensates.

The specimen-holders with plane crevice-creating teflon gaskets between the individual test coupons have also been described earlier (2). The specimen-holders in the conventional bleach plant washers' liquid phase were placed in the inlet vats, whereas the gas phase holders had been suspended under the lowest spray pipes. In the displacement bleach plant there were special test vessels of reinforced plastic placed in by-pass pipes. The specimen-holders were exposed entirely in liquid phase in the latter.

Results

The results are illustrated graphically in Figure 1 for the chlorination stages, Figure 2 for the chlorine dioxide stages, Figure 3 for the hypochlorite stages and Figure 4 for the various locations in the displacement bleach plant. The maximum depth of crevice corrosion and/or pitting measured after the exposure times reported in the diagrams is presented by means of the following symbols:

🄾	No localized attack
☐	Depth of localized attack <0.1 mm
▨	Depth of localized attack 0.1-0.5 mm
■	Depth of localized attack >0.5 mm
W	Attack most marked in weld or HAZ
S	Stress corrosion cracking
☒	No exposure



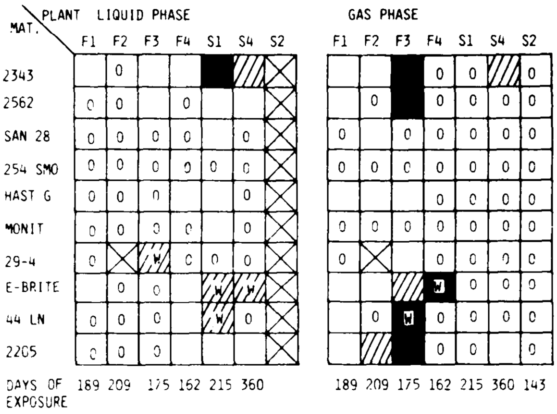
LIQUID PHASE

MAT. \ PLANT	N1	F1	F2	F3	F4	S1	S2	S3
2343	☐	☐	▨	▨	▨	▨	▨	▨
2562	☐	0	■	▨	☐	▨	☐	▨
SAN 28	☐	☐	■	☐	☐	▨	☐	▨
254 SMO	0	0	☐	0	0	0	☐	0
HAST G	0	0	☐	☐	0	☐	☐	0
MONIT	0	0	0	0	0	☐	0	0
29-4	0	☐	W	0	0	0	0	0
E-BRITE	0	▨ W	▨ W	▨ W	☐	■ W	■ W	▨
44 LN	0	0	■ W	☐	☐	▨ W	☐	▨ W
2205	0	☐	▨	☐	☐	☐	☐	☐
DAYS OF EXPOSURE	200	189	209	175	162	165	224	148

GAS PHASE

MAT. \ PLANT	N1	F1	F2	F3	F4	S1	S2	S3
2343	☐	■	■	▨	0	▨	■	■
2562	☐	▨	■	▨	0	▨	■	■
SAN 28	☐	■	■	☐	0	☐	☐	■
254 SMO	0	☐	0	0	0	☐	☐	▨
HAST G	0	☐	▨	☐	0	0	▨	■
MONIT	0	▨	☐	0	0	0	☐	▨
29-4	W	0	W	0	0	0	☒	▨
E-BRITE	0	■	■ W	▨	☐	▨	■ W	■ W
44 LN	0	▨	■ W	▨	0	▨	▨ W	■ W
2205	☐	▨	■	☐	0	☐	▨	■
DAYS OF EXPOSURE	200	189	209	175	162	165	224	148

Figure 1
Maximum depth of crevice corrosion and/or pitting in the chlorination stage washers. N1 is a pure C stage, the others are combined D/C or C+D stages.



LIQUID PHASE

MAT. \ PLANT	F1	F2	F3	F4	S1	S4	S2
2343	☐	0	☐	☐	■	▨	☒
2562	0	0	☐	0	☐	☐	☒
SAN 28	0	0	0	0	☐	0	☒
254 SMO	0	0	0	0	0	0	☒
HAST G	0	0	0	☐	☐	0	☒
MONIT	0	0	0	0	☐	0	☒
29-4	0	☒	▨ W	0	0	0	☒
E-BRITE	☐	0	0	☐	▨ W	▨ W	☒
44 LN	0	0	0	☐	▨ W	0	☒
2205	0	0	0	☐	☐	☐	☒
DAYS OF EXPOSURE	189	209	175	162	215	360	

GAS PHASE

MAT. \ PLANT	F1	F2	F3	F4	S1	S4	S2
2343	☐	☐	■	0	0	▨	0
2562	☐	0	■	0	0	0	0
SAN 28	0	☐	0	0	0	0	0
254 SMO	0	0	0	0	0	0	0
HAST G	☐	☐	☐	0	0	0	0
MONIT	0	0	0	0	0	0	0
29-4	0	☒	☐	0	0	0	0
E-BRITE	☐	☐	▨	■ W	0	0	0
44 LN	☐	0	■ W	0	0	0	0
2205	☐	▨	■	0	0	☐	0
DAYS OF EXPOSURE	189	209	175	162	215	360	143

Figure 2
Maximum depth of crevice corrosion and/or pitting in the chlorine dioxide stage washers.

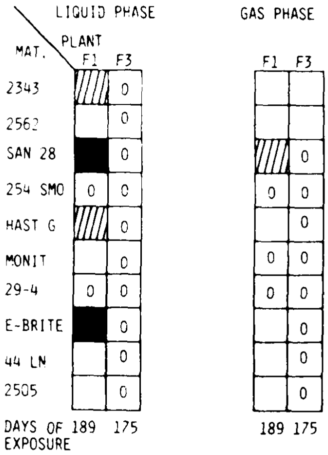


Figure 3
Maximum depth of crevice corrosion and/or pitting in the hypochlorite stage washers.

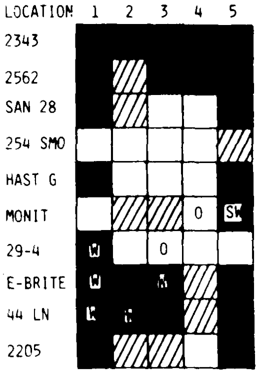


Figure 4
Maximum depth of crevice corrosion and/or pitting in the displacement bleach plant. The environments of the five locations are listed in Table 3. Time of exposure 210 days.

Table 3: Corrosion environments in the displacement bleach plant.

Location	Max. Cl_2 g/l	Max. Cl- g/i	Min. pH	Max. temp. °C
1. D/C mixers	1.3	9.5	1.3	58
2. D/C extraction liquor	.1	9.5	1.2	63
3. D_1 extraction liquor	.9	4.1	2.1	73
4. D_2 extraction liquor	.8	3.2	2.5	82
5. D_2 displacement liquor	2.8	3.5	1.8	62

From these diagrams it can be easily seen how the different materials have withstood localized attack in the respective bleaching stages. If a material is to be regarded as acceptable for practical use, the depth of localized attack after half a year of operation should reasonably not exceed 0.1 mm. This criterion is generally fulfilled by the following materials in the bleaching environments listed:

Liquid phase of chlorination stage washers
254 SMO, MONIT, 29-4 and Hastelloy G

Gas phase of chlorine dioxide washers
254 SMO, Sanicro 28, MONIT, 29-4 and Hastelloy G

Liquid phase of chlorine dioxide washers
Type 904 L, 254 SMO, Sanicro 28, MONIT, SAF 2205 and Hastelloy G

Gas phase of chlorine dioxide washers
254 SMO, Sanicro 28, MONIT, 29-4 and Hastelloy G

Liquid phase of hypochlorite washers
Type 904 L, 254 SMO, MONIT, 29-4,44 LN and SAF 2205

Gas phase of hypochlorite washers
All materials tested with the exception of one specimen of Sanicro 28 with a crevice corrosion depth of 0.2 mm.

Chlorine and chlorine dioxide stages of displacement plant, liquid phase
254 SMO with the exception of displacement liquor in the D stage and 29-4 with the exception of liquor from the D/C mixers.

Discussion

Relative corrosion resistance

It is generally recognized that the resistance of chromium nickel alloys to localized attack in a chloride environment improves the greater their contents of chromium and molybdenum. On the basis of electrochemical determination of the pitting potentials of different steels it has been found that molybdenum is about 3 times as beneficial as chromium in this respect. This has been expressed by the equation

$$PRE=1 \cdot \%Cr + 3.3 \cdot \%Mo$$

where PRE is a pitting or crevice corrosion resistance equivalent which should be as high as possible if the resistance to initiation of localized attack in a chloride environment is to be the best possible (3).

Some researchers have put forward the view that also the nitrogen content in the steel has a positive effect, especially in molybdenum-alloyed steels (4,5). According to Herbsleb the contribution of nitrogen to the pitting resistance equivalent is as much as $30 \cdot \%N$.

Apart from some minor deviations, which may be partly explained by the depth of corrosion being just below or above one of the three group limits for localized attack, the results of the field tests accord fairly closely with the ranking expected on the basis of the pitting resistance equivalents, especially if the effect of nitrogen is taken into account.

Some exceptions from this rule should, however, be touched upon. MONIT, for example, despite relatively low pitting resistance equivalent, 38.5, has largely exhibited as good corrosion resistance as 254 SMO with pitting resistance equivalent 46.2 and 29-4 with 43.2. On the other hand Hastelloy G, despite its high pitting resistance equivalent of 42.8, does not appear to be entirely of the same class as the three latter materials, either in the gas phase of the chlorination stages or in the displacement plant. Sanicro 28, too, exhibits a lower corrosion resistance than expected on the basis of its high pitting resistance equivalent. Judging by these results one would be tempted to ascribe to an elevated nickel content a negative effect on the resistance to localized attack. The good corrosion resistance of Hastelloy C-276 in bleach plant environments shows that this disadvantage can be counteracted by a sufficiently high molybdenum content.

One valuable result is that weld metal of 254 SMO did not suffer localized attack more than the parent metal, as was the case in an earlier study (2). The reason is that this time the steel was welded with the over-alloyed filler P12, with a molybdenum content of 9%, that is now recommended by the manufacturer. Good results with the P12 filler metal have also been reported by Garner (7).

In the most aggressive locations of the displacement bleach plant the weld metal of P12 suffered some general corrosion, most likely of a transpassive nature. Similar attacks were also found in the steels with the highest chromium contents, i.e. Sanicro 28, MONIT and 29-4. In the latter, however, the general attack was evenly distributed between weld and parent metal.

More severe, localized attack in weld metal or HAZ than in parent metal occurred otherwise only in the entirely ferritic steels E-Brite and 29-4 and in the ferritic-austenitic steel 44 LN. No such tendencies, on the other hand, were observed in the entirely ferritic steel MONIT - apart from the unexpected stress corrosion cracking in the chlorine dioxide stage of the displacement plant - or in the ferritic-austenitic steel SAF 2205.

Correlation between corrosion and environment

The effect of the corrosion environment, e.g. the differences in depth of localized attack on exposure to liquid and gas phase, has already received some consideration in the discussion of the results (page 10). In the sequel an attempt will be made to correlate in greater detail the corrosion environment with the depth of localized attack.

The chlorination stages

As earlier noted, the corrosion has generally been more serious in gas than in liquid phase, which accords also with the information obtained from the bleach plant survey which was included in the project.

In the Swedish chlorination stages the residual chlorine concentrations have normally been around 60 mg/l with max. values up to 450 mg/l. In the corresponding Finnish washers the mean values have seldom exceeded 10 mg/l and the max. values 100 mg/l. The corrosion has nevertheless been of the same order of magnitude in the two countries with the exception of the Finnish F4 bleach line where the residual chlorine concentration was constantly below 10 mg/l. One explanation of this would seem to be the roughly 10°C higher temperature in the Finnish washers compared with the Swedish. A direct consequence hereof is that the threshold value of 25 mg/l indicated at an earlier study in Swedish bleach plants is not generally valid (2).

In the only Norwegian chlorination stage studied - this was also the only pure C stage - the residual chlorine concentration was max. 20 mg/l and the corrosion negligable.

To study what causes the high gas phase corrosion in the combined C+D stages, determinations were first made of residual chlorine, chloride, pH and redox potential in condensed, evacuated gas phase from the washers. As these analyses showed a wide scatter, however, at the same time as the actual sampling procedure was questioned, it was decided to attempt to develop a special cell for in situ measurements in condensate, Figure 5.

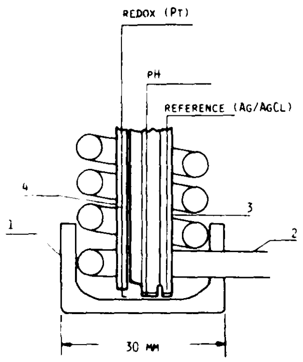


Figure 5
Sketch showing the principle of the cell for pH and redox potential measurements in condensate.

1. Teflon cup
2. Water-cooled coil
3. The combination electrode
4. The Pt electrode

The cell is built up around a standard combination electrode of the type used for pH measurements on human skin. The electrode is placed vertically with its flat end in a small Teflon cup and surrounded by a water-cooled spiral coil. In the condensate collecting in the cup the pH is measured by the combination electrode and the redox potential by means of a platinum electrode and the reference electrode of the combination electrode. (Ag/AgCl in 3M KCl).

Measurements have been made with the aforementioned type of cell in Swedish bleach plants in three C+ D stages, one C stage and five D stages. In the gas phase condensate of the chlorination stages were measured redox potentials between +800 and +1130 mV/SCE and pH between 1.3 and 2.0. Pronounced gas phase corrosion was found in all these chlorination stage washers. In the D stage washers the redox potential was seldom higher than +360 mV/SCE and the pH varied between 2.6 and 3.3. No corrosion occurred in these washers.

It is remarkable, however, that the values measured in the gas phase of the C and C+D filters do not differ appreciably from those in the liquid phase although the corrosion in the gas phase is generally more severe than in the liquid phase. This indicates an inhibitor action of some non-volatile component in the liquid phase or a higher buffering capacity of the latter.

It is probable that the type of cell described could find practical use for monitoring of the corrosive gas phase environment in bleach plants. Another method, of course, is to control the residual chlorine concentration in the liquid phase by measurement of the redox potential or more exactly by means of polarimetry. Both procedures have been used for the monitoring of the bleaching process. As far as is known, however, no applications have been made with the primary aim of reducing corrosion. The Finnish plant F4, however, which for environmental reasons applied strict monitoring of residual chlorine (<10 mg Cl_2/l), has succeeded also in preventing corrosion (8).

The chlorine dioxide stages

In the liquid phase of conventional bleach plants corrosion has arisen on moderately alloyed stainless steels in the Swedish bleach lines with mean residual chlorine concentrations between 90 and 100 mg/l and max. concentrations up to 300 mg/l, but not in the Finnish with mean concentrations around 5 mg/l and max. concentrations up to 70 mg/l.

In gas phase the corrosion is, in general, moderate with the exception of the Finnish plant F3. The high corrosion in this stage has been explained, however, by excess addition of SO_2 (8). In an earlier bleaching plant study severe corrosion had arisen in the gas phase of a D washer in a Swedish sulphite plant (2). In the present project there was no exposure of corrosion coupons in this plant. On the other hand the gas phase environment was analysed and found to be harmless. The reason for this is believed to be the change from manual to automatic monitoring of the residual chlorine concentration.

The conclusion from the exposure of materials and environmental analyses in the D stages is that their corrosivity is usually lower than that of the C+ D stages. With residual chlorine concentrations below 10 mg/l even type 316 steel seems to be able to withstand corrosion of practical significance. This value must not, however, be regarded as a threshold. Earlier tests indicate that the same threshold value of 25 mg/l as was proposed for the chlorination stages should also be applicable for the D stages (2).

The results of exposure in liquid and gas phase of the D washers appear to accord closely with those of the laboratory experiments concerning corrosion in liquid and gas phase presented by Ahlers (1).

The hypochlorite stages

From Table 3 showing the depth of localized corrosion in the H stage washers, it is evident that corrosion is moderate. In one of the two Finnish bleach plants, however, the corrosion is more severe, at the same time as the residual chlorine concentration exhibits higher values and the pH of the solution is rather lower. This applies to the liquid phase in the washers. In the gas phase the corrosion has in both cases been very low. This result accords closely with the practical experience from these two plants. The answers from other bleaching plants to a questionnaire indicate that the maintenance of a high pH, 10.0-11.0, is the most important corrosion-prevention measure in the H stages (1).

The *displacement bleach plant*

Table 3 shows the corrosion environments in the five locations in the displacement bleach plant in which test coupons were exposed. Owing to their generally extremely high residual chlorine concentration these environments are known to be very corrosive to all other metallic materials than titanium, which is also reflected in the results presented in Figure 4. 254 SMO and 29-4, i.e. the special steels with the highest Cr and Mo contents, have best withstood also this very aggressive environment.

Table 3: Corrosion environments in the displacement bleach plant.

Location	Max. Cl_2 g/i	Max. Cl^- g/i	Min. pH	Max. temp. °C
1. D/C mixers	1.3	9.5	1.3	58
2. D/C extraction liquor	.1	9.5	1.2	63
3. D_1 extraction liquor	.9	4.1	2.1	73
4. D_2 extraction liquor	.8	3.2	2.5	82
5. D_2 displacement liquor	2.8	3.5	1.8	62

Conclusions

The following conclusions may be drawn from the corrosion tests and the environmental analyses in different bleaching plant environments:

- In the chlorination stage of the displacement bleach plant the high-alloy austenitic stainless steel 254 SMO exhibited very good corrosion resistance compared with the other materials tested. The same applies to the ferritic stainless steel 29-4 in the chlorine dioxide stage of the same plant. They can, however, not generally be regarded as sufficiently corrosion-resistant to be used as substitutes for titanium in the displacement plant.

- In the chlorination stages of the conventional bleaching plants none of the tested materials has in general exhibited sufficiently good corrosion resistance in gas phase. In liquid phase, on the other hand, in addition to the two aforementioned special steels, MONIT and Hastelloy G have throughout shown very good corrosion resistance.

- Since corrosion is due chiefly to the residual chlorine concentration in the washers' liquid phase, an effective monitoring of the latter should be the best measure for counteracting corrosion. Earlier field tests have indicated that an appropriate threshold value for the residual chlorine concentration in the chlorine stage when using type 316 steel would be about 25 mg/l. This applied, however, at operating temperatures of max. 30°C. The results from the present project in bleach washers working at about 40°C indicate that in them the residual chlorine concentration would need to be reduced to max. 10 mg/l.

- The corrosion environment in the chlorine dioxide washers has generally been considerably less aggressive than in the chlorination stages. The results do not contradict the earlier proposal of a threshold value for the residual chlorine concentration of 25 mg/l.

- The tests have comprised only two hypochlorite stages, so that no definite conclusions can be drawn concerning the corrosivity of this environment. The results, however, indicate very moderate corrosion on all materials at pH ≥10, which is also confirmed by practical experience reported in answer to the project questionnaire. No threshold value for residual chlorine can be indicated for this bleaching stage.

- A special cell for in situ measurement of the pH and redox potential of the gas phase condensates has been developed. It is not impossible that this cell, if further developed, may facilitate maintenance of the proposed threshold values for residual chlorine concentration in the chlorination stages.

- The weldments have generally exhibited as good resistance to localized attack as the parent metal. Certain ferritic steels, especially E-Brite, and one ferritic-austenitic steel, 44LN, however, were attacked preferentially in the weld metal and HAZ.

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Notes

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** The Nyby-Uddeholm steel grades mentioned in the tables now have Avesta designations:
44LN = Avesta 25-6-1 LN. MONIT is unchanged.

*** The previous Avesta welding filler metals also have new designations:
832 SKR = SKR
254 SLX = 904L
223 FAL = 2205

Field Experience in the Application of 254 SMO (S31254) in the Scandinavian Pulp and Paper Industry

by
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Abstract

Avesta 254 SMO (UNS S31254) has been extensively applied in paper mill bleach plants in Scandinavia. A review of twenty installations in operating mills indicates that S31254 has performed well as a remedy to corrosion problems of 316L, 317L, and 904L. S31254 is now regularly used in the construction of major bleach plant components. Corrosion performance has been good for periods now extending beyond eight years.

Introduction

Many factors have caused a trend toward increased corrosivity of bleach plant environments. These include the introduction of new processes and the modification of existing processes for increased production efficiency. There are also the needs to meet environmental protection regulations, to reduce maintenance costs and to provide for increased performance reliability. All of these changes are leading the engineer to select more corrosion resistant grades.

Many new grades have been suggested by stainless steel and alloy producers. Each of these new materials comes supported by some level of laboratory corrosion data. Such data are important to the engineer as a starting point. However, no laboratory test can fully simulate the complex operating cycle of a bleach plant. Therefore, there is a call for field or operating experience with a new material. Such documentation is often difficult to obtain because each user has only a relatively narrow view of the performance of various grades. Therefore, an effort has been made to survey many bleach plant engineers for their experience with S31254.

S31254 is a proprietary 6Mo austenitic stainless steel produced by Avesta AB. It is the extension of the common austenitic grades AISI type 316 (2-3Mo) and AISI type 317 (3-4Mo) to maximize pitting and crevice corrosion resistance. It has been thoroughly characterized and reported as to corrosion resistance and weldability (1-4). In the late 1970s it was introduced for bleach plant service.

In 1981, a summary of applications was published, encompassing twenty-two bleach plants and other paper mill service (5). There are now too many applications for an exhaustive catalog. This report updates experience up to eight years at several of these previous locations and provides references to more recent applications, thus indicative of increased confidence in its use.

Reference 1
(Reference 1.1 in the 1981 report (5))

The plant began operation in 1975. It utilizes a bleaching sequence and corresponding filters designated as shown:

Stages: CD-E-CD-E-D
Filters: F1 F3 F5

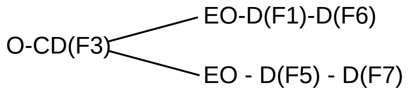
After only nine months of operation the plant observed severe pitting of 317L inlet boxes where exposed to gas phase, pitting at the bottom of the 317L vat for the third stage, and crevice corrosion of 316L blank discharge pipes. Inlet boxes F1 and F5 were partially lined with Alloy 904L (N08904) and 317 nozzles were replaced in kind within the first year. In 1977, F1 and F3 were given supplementary linings of S31254 and nozzles were replaced with 904L and S31254. In mid-1977, the 904L nozzles were observed to be pitted in all inlet boxes while the S31254 was unaffected. The 904L nozzles were replaced with S31254 in F1, F3, and F5. In 1978, the lining of F1 was supplemented by S31254. In 1978, the entire inlet box and the vat of the third stage was lined with S31254. New brackets of S31254 were installed in the shower and the sealing surfaces of the nozzles were lined with Hastelloy C-276. In 1979, the whole vat of the fifth stage was lined with S31254. No corrosion on any of the parts in S31254 has been observed.

The practice of lining areas suffering from pitting continued until the end of 1982 when all exposed parts of vats and inlet boxes had been covered with S31254. No further corrosion has been observed.

The corrosion environments in the inlet boxes were:

	F1	F3	F5
Cl^-	1300 ppm	800 ppm	300 ppm
Cl_2 res.	20-150 ppm	30 ppm	20 ppm
pH	2	2.3	2.3
temperature	22-30°C 72-86°F	45- 50°C 113-122°F	65- 75°C 149-167°F

The bleach plant was rebuilt in June, 1986, to utilize oxygen bleaching followed by two parallel lines as shown:



The designation EO refers to alkaline with oxygen addition. As shown in the diagram above, the existing filters were used in the new arrangement. Two new filters, F6 and F7, were constructed with drums and vats utilizing S31254. No environmental data are yet reported.

Reference 2

(Reference 1.21 in 1981 report (5))

The component is an ion exhange column for cleaning the effluent of the C-stage. It was installed in December, 1980. The operating environment is:

Cl^-	1600 ppm
Cl_2 residual	0 (controlled by SO_2)
pH	1.2
temperature	25°C (77°F)

The S31254 has performed well over this period with no incidents of corrosion being observed.

Reference 3

(Reference 1.5 in 1981 report (5))

The components are: (1) inlet box linings on the D/C, D1, and D2-stages; and (2) perforated sheet for the D/C stage. The bleaching sequence is D/C-E-D-E-D. The environment is:

	D/C	D1	D2
Cl^-	1020 ppm	440 ppm	190 ppm
Cl_2 res.	5 ppm	2 ppm	5 ppm
pH	2.0	2.7	3.5
temperature	42°C 108°F	60°C 140°F	70°C 158°F

The original construction of the inlet boxes used a 4.5Mo austenitic stainless steel, with a plastic coating on parts exposed to the gas phase. After one year the coating was detached and there was severe crevice corrosion. In June, 1977, the upper parts of the vats were lined with S31254. In December, 1977, crevice corrosion had occurred under deposits of pulp or resin in the gas phase region just above the liquid line. Attack was attributed to very high residual chlorine. The damage was repaired by welding and arrangements were made for improved washing down. The lining has been repaired several times since 1977, but the performance is considered economical and acceptable.

The perforated drum on the D/C-stage was installed in 1984 and has performed without incident.

Reference 4

(Reference 1.22 in 1981 report (5))

The components are nine filter drums on the C/D, D1, and D2-stage washers. The bleaching sequence and times of installation of S31254 are:

	C/D	- E -	D	- E -	D
line 1	1979		1980		1984
line 2	1984		1983		1980
line 3	1983		1983		1984

The environment is:

	Lines 1&2			Line 3		
	C/D	D1	D2	C/D	D1	D2
Cl^- ppm	1300	450	200	500	290	190
Cl_2 res, ppm	50	0	0	100	10	0
pH	1.8	3.0	3.5	2.5	3.0	3.5
temp. °C	30	70	75	30	65	70
°F	86	158	167	86	149	158

Type 316 drums suffered severe corrosion. Performance of the S31254 drums continues to be excellent for the drums installed in late 1980.

Reference 5

The components are pipes for handling recycle water from the D-stage filters. The bleaching sequence is C+D - E - D1 - E - D2. The environment is:

Cl^-	350 ppm
Cl_2 residual	not reported
pH	1.9-2.3
temperature	70-75°C (158-167°F)

Reinforced plastic failed by cracking and type 316 showed significant pitting and crevice corrosion within a few months of operation. S31254 was introduced in 1979 and used again for additional areas in 1984. No problems have been encountered with S31254.

Reference 6

(Reference 1.9 in 1981 report (5))

The components are vats in filter washers. The bleaching sequence and filter locations are C/D(F1) - E - D1(F2) - E - D2(F3). The environment is:

	F1	F2	F3
Cl^-	1000 ppm	300 ppm	300 ppm
Cl_2 res.	max 20 ppm	max 10 ppm	max 10 ppm
pH	2-3	3-4	3-4
temperature	40°C 104°F	60- 65°C 140-149°F	60- 65°C 140-149°F

The plant began operation in 1979. Drums were constructed of a 4.5Mo austentic stainless steel. Vats were S31254 in the portion exposed to the gas phase and the 4.5Mo grade elsewhere. Corrosion was observed in 1980 for the 4.5Mo grade in F1. The vat and inlet box of F1 were lined with S31254 in 1985. F2 and F3 have not suffered severe corrosion.

Reference 7

(Reference 1.4 in 1981 report (5))

The components are dandy rolls and vat linings for the C+D and D1-stage washers. The bleaching sequence is (C+D) - E - H - D1 - E - D2. The environment is:

	C+D	D1
Cl^-	2000 ppm	600 ppm
Cl_2 res.	100 ppm	15 ppm
pH	2.0	2.0
temperature	30°C (86°F)	55°C (131°F)

The dandy roll of the D1-stage first constructed with type 316L was destroyed by corrosion in about one year. The replacement roll of S31254 was installed in 1977. Inspection in 1978 indicated possible superficial corrosion but there has been no further development of corrosion and the equipment remains in service. S31254 dandy rolls were installed in the D2 and C+D stages in 1978 and 1979, respectively.

The original type 316 liner was penetrated in less than one year (3 mm, 0.120 in thickness). The vat was lined with S31254 in 1980 and no corrosion has been detected.

Reference 8

The components are two plate heat exchangers for cooling the effluent of the D1-filter, and the lining of the inlet box and shredder of the filter for the C-stage. The bleaching sequence is C - E - H - D1 - E - D2. The environment is:

	Plate heat exch process side	anger/C-stage /filter
Cl^-, ppm	200-300	500-1500
Cl_2 res., ppm	20-150	50- 100
pH	2-3	1.6-2.3
temperature	60°C (140°F)	30°C (85°F)

The S31254 plate heat exchangers were installed in 1979. After 2 years' service, there was slight etching attributable to attack by stagnant conditions. Construction was altered to permit back flushing during operations. No further attack has occurred since 1981.

The liner was originally 316 which corroded. S31254 was installed in 1981 and no corrosion has been observed.

Reference 9

The component is a filter drum in the D/C-stage. The bleaching sequence is D/C - E - H - D. The environment is:

Cl^-	500 ppm
Cl_2 residual	10 ppm
pH	2
temperature	28°C (82°F)

S31254 was installed in 1982 and the performance has been good.

Reference 10

The components are pipes from the mixer to the bleach tower in the new section. Experience has been good with S31254, with no corrosion being observed since the installation in 1982. The environmental conditions were not reported.

Reference 11

(Reference 1.16 in 1981 report (5))

The components are pipes between the mixer and the bleach tower for the D-stages. The pipe is 700 mm (27.6 in) diameter by 8 mm (0.315 in) in wall. The environment is not reported. A 4.5 Mo austenitic stainless steel was severely pitted within a few months of operation. S31254 was installed in the D1-stage in 1980 and in the D2-stage filter and in the D(2) in 1983. The S31254 has performed well, with some minor corrosion at the welds which were repaired.

Reference 12

The components are pipes before the mixer and between the mixer and the bleach tower (Rauma Repola process) in the D-stages, 600 mm (23.6 in) diameter by 5 m (200 in) length. The bleaching sequence is C - E - D1 - E - D2. The pipe was installed as new construction in 1983. The temperature is 70°C (158°F) but other characteristics of the environment are not reported. There has been no problem to date with the S31254.

Reference 13

The components are the pulp pipe from the mixer to the bleach tower (Rauma Repola process) and a filter vat and drum of solid S31254 construction. The bleaching sequence is C-E-D1-E-D2. The pipe was originally a 4.5Mo austenitic stainless steel which suffered severe corrosion within three years. S31254 was installed in 1981 and has performed satisfactorily since.

The vat and drum were originally 904L which has corroded. Replacement equipment with S31254 is now under construction. The environment for the vat and drum is:

Cl^-	1000 ppm
Cl_2 residual	10-20 ppm, excursions to 40 ppm
pH	1.5
temperature	55°C(131°F)

Reference 14

The component is the lining of a filter vat on the D/C-stage. The bleaching sequence is D/C-E-D-P-D. The environment is:

Cl^-	1400 ppm
Cl_2 residual	20 ppm
pH	1.5
temperature	not reported

A 4.5Mo austenitic stainless steel suffered corrosion. The S31254 was installed early in 1985. It has suffered slight attack at the gas-liquid boundary but no corrective action has been required.

Reference 15

The components are vats and drums of two filters as shown: C(F1) - E - D1(F3) - E - D. F1 was installed in 1981 and F3 was installed in 1985. The environments are:

	F1	F2
Cl^-	1000 ppm	350 ppm
Cl_2 res.	up to 117 ppm	max 10 ppm
pH	1.9	2.1
temperature	36°C (86°F)	65°C(149°F)

Spray nozzles and pipes of S31254 in F1 were severely corroded by very high chlorine content of the gas phase and resultant corrosive condensate, and were replaced by more highly alloyed material, not specified. Vats and drums of S31254 have performed satisfactorily.

Reference 16

The component is wire mesh used in the D2-stage filter washer. The bleaching sequence is D1 - E - HP (hydrogen peroxide) - D2. The environment is:

Cl^-	not reported
Cl_2 residual	20 ppm
pH	2-2.5
temperature	70°C (158°F)

Type 316 suffered corrosion and was replaced by S31254 in 1986.

Reference 17

The component is a filter drum in the C-stage of a pulp bleach plant. It was installed in July, 1986. The bleaching sequence is C-E-D-E-D. The environment is:

Cl^-	1100-1500 ppm
Cl_2 residual	12- 15 ppm
pH	2
temperature	35°C (95°F)

The drum had previously been type 316 which lasted about 10 years. The closing of systems to meet effluent regulations had increased the severity of the operating conditions leading to the upgrading.

Reference 18

The component is a tower rake in the D-stage washer. The bleaching sequence is HP (hydrogen peroxide) - D - HP. The environment is:

Cl^-	not reported
Cl_2 residual	less than 10 ppm
pH	2.5
temperature	70°C (158°F)

Type 316 was used in this service for almost ten years, but regularly required repairs. In July, 1986, S31254 replaced the type 316.

Reference 19

(Reference 1.13 in 1981 report (5))

The components are: (1) pipes between the mixer and the towers in the D-stages; and (2) spray nozzles in the D2 tower. The bleaching sequence is C/D - E - D1 - E - D2. The environments are:

	pipes	nozzles
Cl^-, ppm	600-700	200-250
Cl_2 res., ppm	0- 50	250
pH	5	5
temperature	60°C (140°F)	70°C (158°F)

S31254 was installed in the piping in the new plant in 1977. Some pitting corrosion was observed in welds in 1978, but the problem was determined to be incorrect filler material. The welds were repaired with the appropriately alloyed filler and no further corrosion has been observed.

The nozzles were originally Type 316L with min 2.5 Mo. These nozzles failed by pitting corrosion and were replaced by S31254, but the time of the installation is not reported. No problems have been observed for the S31254 nozzles.

Reference 20

The components are: (1) doctor blades in the C/D stage filter washer; and (2) plate heat exchangers for filtrate cooling in the D-stage. The bleaching sequence is C/D - E - H - D. The environments are:

	C/D	D
Cl^-	(see discussion)	
Cl_2 residual	30 ppm	0 (killed by SO_2)
pH	2	2.8-3.0
temperature	20-25°C	40- 60°C
	68-77°F	104-140°F

The plant was reconstructed in 1985. Prior to reconstruction, the chloride concentrations were 1300 ppm and 900 ppm for the C/D and D-stages, respectively. No new data is reported. The doctor blades were originally type 316L with min 2.5 Mo which suffered corrosion and were replaced during the reconstruction. The plate heat exchangers were also originally type 316L with min 2.5 Mo. One was replaced with S31254 in 1984, and two were replaced in 1985 during the reconstruction. No corrosion of the S31254 has been observed.

Summary

S31254 has been extensively applied in the severely corrosive areas of paper mill bleach plants. Initially it was used to upgrade materials selection after the common grades such as type 316L, type 317L, and alloy 904L had failed by corrosion. Experience in such applications, now exceeding eight years in some cases, has been excellent. Based on this experience, S31254 is now being specified both for maintenance replacement in problem areas and for new construction. The operating engineer now has a considerable body of field performance data on which to base his selection of S31254 as a versatile and cost effective material of construction in the bleach plant.

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