J. Mater. Environ. Sci. 4 (3) (2013) 420-425 *Sharma et al.*
ISSN : 2028-2508
CODEN: JMESCN

In Plant Test for Corrosion Investigations in Digester of a Paper Mill

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Received 29 Oct 2012; Revised 11 Jan 2013; Accepted 11 Jan 2013
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Abstract
In the Pulp and Paper mill Industry, Digester house is the main section and corrosion is a big problem in this section. The presence of sulfate, sulfide, and chloride in liquor and Silicone in steel produce the severe corrosion problem in digester. An In plant test of six month duration was done in the bottom part of a batch digester, made of mild steel of volume 85m^3. The wood chips are filled in the digester and cooking liquor is then charged keeping liquor to wood ratio as 1:2.8. Volume of cooking liquor inside the digester was kept between 37 to 42 m3.The cooking liquor consists of mainly sodium hydroxide (NaOH) (92 gpl as NaOH) and sodium sulfide (Na_2S) (22.4 gpl as NaOH) having pH ~13.2. Maximum temperature attained during the pulping process is 168^{0}C and it operates at a pressure of 6.2 Kg/Cm^2.The results showed that mild steel (MS) experiences highest corrosion rate while Duplex stainless steels experienced least corrosion rate. It is concluded that the bottom part of the digester is affected due to erosion as well as localized assisted corrosion and the bottom part can be constructed of duplex stainless steel without severe risk of corrosion.

Key Words: In Plant test, Paper Industry, Digester, Steels, Corrosion

1. Introduction :

Extensive corrosion is experienced by the process equipment and machinery items in different sections of paper mill. Digester house is one such section which is severely affected by corrosion. Carbon steel kraft digesters generally gave good service life up to 1935. Since then some undetermined changes have been found to cut the life to as little as 1-4 years. An extensive review by [1], about different aspects related to corrosion in digesters and its control has appeared in 1996. The cases of sudden failure of digesters due to corrosion have been reported in past [2, 3]. Interest about corrosion of digester can be gauged from reporting of large number of articles dealing with mill survey, in - plant tests, in-situ corrosion monitoring, inspection for digester etc. In the first ever reported mill survey [4], on corrosion problems in sulfate pulp mills, increased corrosion was observed due to presence of (i) Sulfide in liquor and (ii) Si in digester steel. A mill questionnaire by [5], found the corrosivity in kraft operations to have increased considerably between 40’s and 50’s. Another survey by [6], observed that ~75% of the digesters were 28-48 years old. Approximately 73% of the digesters had Stainless Steels weld overlay at-least some part of the digester. Mills with higher sulfidity were found to have higher corrosion. An inspection on corrosion in digester house [7], revealed uneven corrosion in digesters formed of 405 stainless alloys as lining material in approximate 5 years. The cause of this type of attack was related to hot plate boiling action. In yet another inspection, corrosion in kraft digester was observed to due to (i) high C and Si in killed steel (ii) circulation of gases and liquor impinging on the walls of digester (iii) change in chemical concentration. Similarly, in – plant tests have been conducted to investigate corrosion performance of the candidate materials. Thus in first ever reported in-plant test by [8], done on mild steel (MS) and MS-welds in sulfate mills showed (i) corrosion rate of MS varying from 28 to 138 mils per year (mpy) linearly with Si content, (ii) surface preparation and heat treatment affecting the degree of attack (iii) galvanic coupling, for the purpose of protective lining, of SS 347 or inconel with MS does increase corrosion of MS significantly. In another in-plant test by [9], C-steel and SS coupons were exposed to 6 kraft digesters. Corrosion rate of C-steel was very high while that of Stainless Steel (SS) was very low in all cases with no sign of localized corrosion. Duplex SS showed least corrosion. Cause of increased corrosion was found to be higher concentration of oxidizing chemicals e.g. thiosulfate and polysulfide etc. Similar conclusion has been drawn in test reports [10, 11], with regard to the dependence of the corrosivity of liquor on its composition. It has been argued that a higher concentration of polysulfides may show passivating effect. Addition of sulfur was suggested as means of reducing corrosion. In yet another in-plant test [12], corrosion rate for SS 304L and SS 316L have been measured at ~0.02 mm/year.

With a view to enhance production of paper with better pulp quality and reduce pollutants in their stream, the process of cooking of wood chips has undergone marked changes. Thus digesters now operate at increasingly higher temperature and use cooking liquors having higher sulfidity. These liquors also have higher concentration of other sulfur compounds namely thiosulfate, polysulfide which along with increased amount of Cl^- enhance corrosion attack on digester material. Accordingly, instance of severe corrosion attack in the form of caustic cracking and higher metal loss assisted with water, pitting and crevice corrosion have been reported in recent years by [6, 13-18]. In this changed scenario, it was thought appropriate, to conduct an in-plant corrosion test for investigating the performance of materials normally used in kraft digesters. Based on a report [19], on the experiences of digesters fabricated of duplex Stainless steel, coupons of several newly developed duplex steels were also considered for the present test. Incidentally, the present reported test appears to be the second ever in-plant test performed in the digester of mills in South/South East Asia.

2. Details of In-Plant Test :

2.1. Paper Mill and Conditions in Digester :

The in-plant test was done in the batch digester of a paper mill namely Star Paper Mill Limited, Saharanpur which uses 80% poplar and 20% eucalyptus as raw material for making printing/writing and packaging grade paper. The digester used in the in–plant study has a capacity of 85 m^3 and it is constructed of mild steel. The wood chips are filled in the digester and cooking liquor is then charged keeping liquor to wood ratio as 1:2.8. Volume of cooking liquor inside the digester is kept between 37 to 42 m^3. The cooking liquor consists of mainly NaOH (92 gpl as NaOH) and Na_2S (22.4 gpl as NaOH) having pH ~13.2. Maximum temperature attained during the pulping process is 168^0C and it operates at a pressure of 6.2 Kg/Cm^2.

2.2. Materials :

The selection of materials for the in-plant test was done on the basis of their current utilization and their possible applications in future for constructing the digester and related allied machinery in pulp and paper industry. While mild steel have been used as the basic material of construction, SS304L and SS316L have been suggested for cladding or weld overlaying the digester requiring refurbishment as a result of enhanced corrosion attack. Of late, newly developed duplex Stainless steels have been suggested to be the prospective material of construction for digesters by [18] because of their better corrosion resistance not only against localized attack but also against caustic stress corrosion cracking (an important factor in digester corrosion). Consequently, following materials were considered for the in-plant test: mild steel, austenitic SS 304L and SS 316L, duplex Stainless Steels 2205 and LDX. The stainless steel samples were supplied courtesy M/S Avesta AB, Sweden along with their chemical analysis Table-1 and mechanical properties Table-2.

2.3. Exposure of Coupons :

For exposure in digester, duplicate coupons, including autogenously welded part, of stainless steel of size 6cmx6cm and thickness varying between 2-4mm along with mild steel coupon of 4cmx4cm and thickness 5mm were fixed in a rack formed of SS-316 rods and plates .The coupons were cleaned using emery paper from coarse to fine up to 800 grit on a polishing machine .These cleaned and acetone degreased coupons were weighed and their surface area was measured prior to putting for the test. Serrated washers were used while mounting the coupons. After this the test rack was welded in a digester in bottom part (Fig 1). The test rack was kept in this position for duration of six months after which coupons were removed for the analysis of corrosion attack. During this period, the pulping liquor was analyzed weekly for its chemical constituents following SCAN procedure [20-22]. The chemical analysis of various chemicals found in pulping white liquor, on the basis of average values, is given in Table-3

Table 1 : Composition of Steel Plate Samples

Alloy	C	Si	Mn	P	S	Cr	Ni	Mo
MS	0.18	0.04	1.66	-	-	-	-	-
SS304L	0.036	0.44	1.84	0.024	0.001	18.11	8.01	0.26
SS316L	0.019	0.50	1.11	0.027	0.002	17.43	11.26	2.03
SS2205	0.022	0.35	1.47	0.02	0.001	22.13	5.55	3.16
LDX	0.024	0.69	5.07	0.017	-	21.36	1.49	0.30

Table 2 : Mechanical Properties of Steels

Grade	Proof Strength (N/mm^2)	Tensile Strength (N/mm^2)	Elongation (%)
SS 304L	276	616	62
SS 316L	276	575	61
SS 2205	636	712	40
LDX	-	-	-

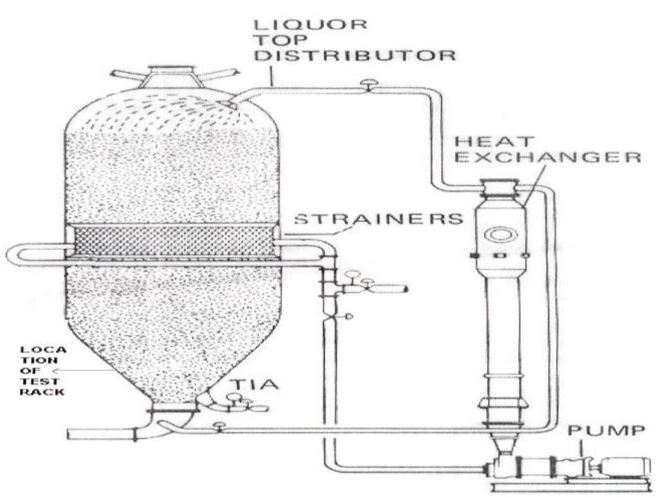

Fig. 1 : Kraft batch Digester with Location of Test RacK

Table 3 : Chemical Composition of White Pulping Liquor

Chemicals	Composition
pH	13.2
Sulfidity	~20.0%
NaOH (Sodium Hydroxide)	90.5±0.5gpl
Na_2S (Sodium Sulfide)	23.1±0.4 gpl
S_x^{2-} (Poly Sulfides)	0.06±0.019 gpl
$Na_2S_2O_3$ (Sodium Thiosulfate)	2.45±0.9 gpl
Na_2CO_3 (Sodium Carbonate)	18.3±2.0 gpl
Cl^- (Chloride)	1.49±0.35 gpl

2.4. *Evaluation of Corrosion Attack* **:**

The corroded coupons, after removing them from the test rack, were cleaned initially mechanically and later chemically using cleaning solution of 50 gpl $SnCl_2$ +20 gpl $SbCl_3$ in concentrated HCl, as per ASTM guidelines. The cleaned coupons were weighed and their corrosion rate was calculated. These coupons were also analyzed for any localized attack namely pitting, crevice corrosion and weld related attacks using metallurgical microscope (Reichert Jung, USA).The results of the analysis are given in Table-4.

Table 4 : Corrosion Attack on the Steels Coupons

Grade	Corrosion Rate (mils per year)	Localized Corrosion Maximum Pit Depth (mm)	Crevice Corrosion Maximum Pit Depth (mm)
MS	6.83	*NMA	1.36
SS 304L	0.023	0.105	0.97
SS 316L	0.008	0.078	0.73
SS 2205	0.004	0.002	0.003
LDX	0.005	**NVA	**NVA

*NMA – No Measurable Attack, **NVA- No Visible Attack

3. Results and Analysis :

The cooking liquor of the mill has a sulfidity of ~20%. This is the sulfidity usually observed in Indian mills. However, it is much lesser than that observed in mills of USA, Canada and Scandinavia etc. (~40% or so). Polysulfide and thiosulfate content is also lesser in the mill under report. Higher sulfidity, polysulfides and thiosulfates have been indicated to be the factors responsible for higher corrosivity of the cooking liquor. The corroded coupons show uniform corrosion. Pitting is observed significantly in some cases while in others no visible attack is observed .Crevice corrosion is also observed on the coupons. A comparison of corrosion attack on different materials indicates uniform corrosion of less degree even in case of mild steel Table-4. The degree of pitting attack in case of SS 304L and SS 316L is within the limit of acceptability [23], for a material of construction.

Maximum corrosion rate is experienced by mild steel followed by SS 304L, SS 316L and duplex stainless steels. Thus mild steel show least resistance from the standpoint of uniform corrosion. Duplex stainless steels show lesser corrosion rate in comparison to the austenitic stainless steels, in accordance with earlier observation by [9] and [24]. Their better resistance, in digester liquor, can be attributed to the higher amount of Cr and N in all the two of them 2205 and LDX as compared to 304L and 316L. Whereas Cr provides protection against corrosion by forming stable $Cr(OH)_3$ layer at higher pH, Mo has not been considered for imparting corrosion resistance since it dissolves as MoO_4^{2-} at these pH, Normally resistance against corrosion attack (including pitting), in

acidic chloride environments is estimated on the basis of pitting resistance equivalent number (PREN) [25]. It is however not applicable and may give misleading result if applied to alkaline environments of the digesters.
Uniform corrosion is observable on mild steel samples. Pitting is observed in case of SS 304L and SS 316L whereas the duplex stainless steels do not show any visible attack. SS 304L is observed to be lesser resistant against pitting in comparison to SS 316L. As indicated in above paragraph, for alkaline pH as in digester, Cr and N in Stainless Steels appear to be more important than Mo in providing the corrosion resistance. Probably this may result into development of new duplex stainless steels, without Mo, having equivalent mechanical properties and resistance against localized corrosion. Such steels are also likely to be cost effective. It may be noted here that higher proof strength, comparable ductility and better resistance against localized corrosion and cracking (due to lesser Ni content) of duplex Stainless steels in comparison to SS 316L is slowly but surely turning duplex stainless steels as the preferable material in comparison to the conventional SS 316L in case of digesters [19].

Comparison with Other In-Plant Tests :
Findings of the present in-plant test could be compared with those of Swedish test [9], only because the other test relate to different aspects of material performance [8], and third test by [12], is related to continuous digester. Comparisons of the results reveal the following. In general, the Swedish mills (having a sulfidity of ~40%) show a higher corrosion rate of mild steels (1.7-5.9 gm/m^2 .cook with an average of 3.3 gm/m^2 cook). The amount of silicon in the tested mild steel varies between 0.06 - 0.1 %. In the present test, mild steel shows lesser corrosion rate (~0.74 gm/m^2.cook, considering ~ 500 cooks in the test duration of 6 months). This could be due to lesser Si content (~0.4%) in the mild steel and less (~20%) sulfidity in the digester liquor. Both these factors have been suggested to affect corrosion rate in the manner as observed here, [9] and [26]. Lesser sulfidity probably is also responsible for lower corrosion rates in case of stainless steels as compared to those in Swedish mill. Like the case of Swedish mill, mild steel shows uniform attack. Pitting is observed on SS-304L (max. pit depth ~ 105 µm and average pit depth ~ 71 µm) and 316L (max. ~78 µm and average 59 µm) coupons. The steel coupons show less crevice attack. Lesser crevice attack could be due to highly alkaline nature of the digester liquor.

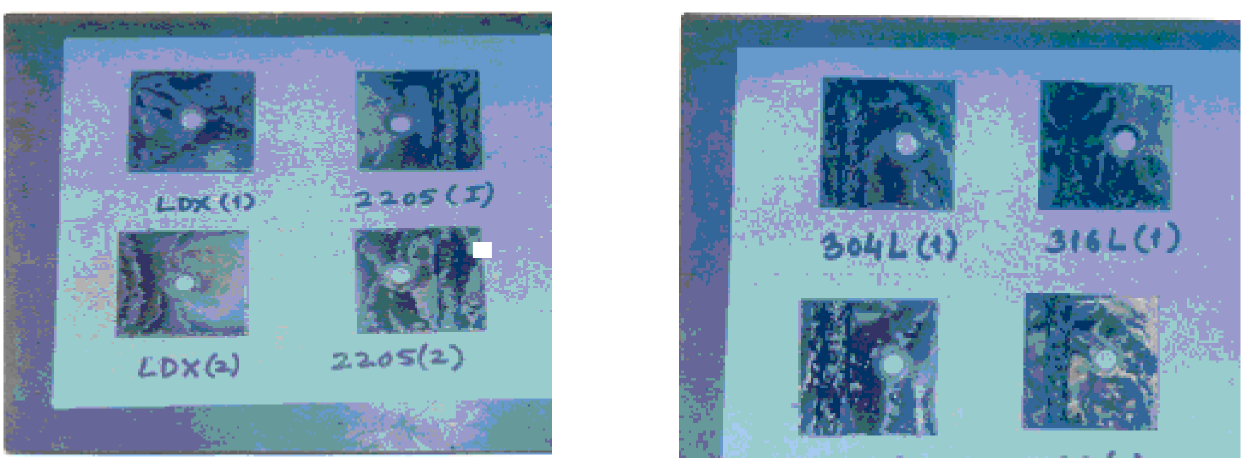

Fig. 2: Test Coupons After removal from Digester

Conclusion

An overall view of the corrosion attack indicates that all the materials, excluding mild steel, tested have sufficient corrosion resistance in the tested media. However, since the liquor composition is likely to change in future so as to have higher sulfidity, thiosulfate, chloride and polysulfide content because of advantages associated with high sulfide pulping, it is likely that austenitic stainless steels SS304L and SS316L will no more be considered suitable and one may have to opt for duplex stainless steels 2205 or LDX. This aspect needs to be checked in laboratory prepared solutions using long term immersion and electrochemical tests on various steels. Secondly, the part of digester that is affected most by corrosion reactions is due to erosion assisted corrosion and this part is the bottom cone of digester. The present in-plant test seems to support this hypothesis as bottom part (where the rack of coupons was fixed) of the materials experience corrosion and erosion. This test, therefore, also seems to indicate that with the present liquor and the process conditions, the bottom part of the digester can be constructed of duplex steel without severe risk of corrosion.

Acknowledgements: The authors are thankful to Chairman, Prof. Kamal Ghansala, Director Research, Prof. Ankush Mittal, Graphic Era University, Directors THDC, SPML and Professor A.K. Singh IIT Roorkee for providing necessary facilities and valuable suggestions to complete this work.

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