Corrosion management in bleach plant

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In view of the complex nature of the pulp and paper industry, it is of extreme importance to give a serious consideration to the various unit processes and unit operations involved at various stages of the manufacturers of Pulp and Paper. The selection of equipment and processes has a direct bearing on the viability of the project; and to ensure competitiveness, the selection of materials of construction for various machines is of utmost significance.

Review of Bleaching Technology :

Since the dawn of Pulp & Paper Industry, chlorine has played a very important role in the bleaching of pulp. In the most elementary bleaching practices, H-H, or C-E-H sequences were incorporated. Later on sequences were modified and extended to C-E-H-H or C-E-H-E-D or C-E-D-E-D. Chlorine Dioxide has been found to be much more superior than chlorine in enhancing brightness without deteriorating pulp strength or reducing viscosity. Among the latest bleaching practices, short sequence bleaching is gaining much more importance, due to inherent advantages, the most common sequence is C/D-O/E-D.

The use of chlorine dioxide and chlorine together in the first stage has raised several problems in the selection of a suitable material of construction for washers, tower equipment and other auxiliary items. The use of nonmetals is possible but only in a limited way (e g. FRP/PVC for chemical mixers, piping etc.) Bleach washers require mechanically strong materials which can also withstand the action of corrosive atmosphere of chlorine, chlorides, Hydrochloric acid etc. etc.

Dorr-Oliver had carried out some pioneering work in this area, in search of a suitable and economically viable material of construction. Material science indicates Titanium, 1925 HMO and Hastelloy C-276, as highly satisfactory materials. However, among these materials, on the basis of initial cost of a bleach washer, 1925 HMo has been found to be quite satisfactory.

Mechanism of Corrosion :

Apart from mechanical strength, resistence to corrosion also plays an important role in the selection of material. In view of highly capital intensive nature of the industry, a life expectancy of 20-25 years is normally aimed at for key equipment items. Among the chemicals used in the processing of raw materials, Acidic, Alkaline, as well as oxidizing environments, both are encounteted. During pulping operation, materials are generally exposed to alkaline atmosphere, whereas in bleaching operation, acidic and highly corrosive environments are prevalent on account of the existence of Chlorine, Chlorine dioxide, Hypochlorite and Peroxide.

Following are the important parameters which cause corrosion at an accelerated pace :

	Parameter	Mechanism
1.	Temperature	The releation between Temperature and Corrosion is a logarithmic one. The rate of increase is very rapid. The rate increases 2-3 times for each 10°C rise. Hence temp. control very essential.
2.	pH	Most metals are highly susceptible to liquid solutions of low pH (i.e.

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Acidic environment). At low pH highly reducing conditions (in the absence of oxidizing agents) develop which are quite corrosive, even to superior grades of stainless steels enriched with Cr & Ni.

3. Aeration : Aeration leads to (dissolved) oxygen transfer at much higher rate and as such it increases corrosion.

4. Localized effect : Local variations in temp. and crevices result in formation of concentration cells which result is accelarated corrosion in the localized area.

5. Galvanic Cells : Even in the case of superior alloys, formation of Galvanic Cells, lead to sever "pitting" and "Crevica" Corrosion. "Passivation" of alloys can reduce corrosive attack by suppression of Galvanic Cell activity. 'Electro chemical Protection" is yet another means to prevent such corrosion.

With a view to understand the mechanism of corrosion, it is desirable to have a look at the "Galvanic Series of Metals & Alloys", as illustrated below :

Galvanic series of Metals & Alloys

(Corroded end—Anodic or least Noble)

Mg	)
Zn	)
Al	)
Cd	)
Mild Steel	)
Ni resist	)
50 : 50 Lead Tin Solder	)
18-8 304 SS (active)	)
18-8-3 316 SS (active)	)
Lead	)
Tin	)
Mun'z metal	) Corrosion Resistance
Nickel (active)	) Increasing
Inconcl	)
Cr	)
Silicon Bronze	)
Ni (Passive)	)
Monel 400	)
18-8.3 316 SS (Passive)	)
Silver	)
Graphite	)
Gold	)

(Protectek end—Cathodic or most noble)

As can be seen from the above, corrosion resistent metals or nobler metals are Cathodic, whereas metals susceptible to corrosion in a liquid phase are anodic.

Galvanic Corrosion is the corrosion rate above normal, associated with the flow of current to a less active metal (Cathodic) in contact with a more active metal (Anodic). In the same environment.

Coupling two metals widely apart in this series, generally will provide accelerated attack on the more active metal. Protective oxide films and other effects, however, very often tend to reduce galvanic corrosion.

Potential difference leading to galvanic type cells can also be set up on a single metal by difference in temp, velocity or concentrations.

It has also been observed that relative differences in the surface areas of two metals at a junction also play an important role in the corrosion.

e.g

(a) Steel rivet in a rivetted joint (steel plate) — Rivet gets corroded

(b) Steel rivet in a copper plate — Rivet corrodes faster

(c) Copper rivet in a steel plate — Rivet corrodes slower

Special Properties of certain materials of construction

Iron : It withstands anhydrous acids and concentrated solutions of some acids but is attacked by dilute aqueous solutions. It resists alkaline solutions with the exception of very hot highly concentrated solutions.

Nickel : It possesses the characterisitics of a seminoble metal. It is acted upon by dilute acids with relative slowness, so that it can be used, frequently, at a fairly low pH. It resists concentrated caustic solutions very well.

Stainless Steels : These are alloys of Chromium—Iron-Nickel and belong to the solid solutions type of alloys, when they are properly heat treated. segregation takes place, and become susceptible to electrolysis. The resistance of stainless steels to acids increases with Nickel content.

Following catagories have special resistance to certain corrosive atmosphere.

			Resists
i)	317 SS	: 18-20 Cr, 14 Ni, 3-4 Mo, balance Fe & 0.1% C	Moist SO_2 Moist Nitrous gases
ii)	Hastelloy C	: 14 Cr, 58 Ni, 17 Mo, 5W, 6 Fe	Moist SO_2, Nitrous gases, Hydrochloric acid vapour, moist chlorine etc.
iii)	Illeum G	: 55-60 Ni, 18-24, Cr, 5-7 Mo, 4-8 Fe 1-8 Cu	Mosit Nitrous gases, moist Hydrofluoric acid vapours,

In the last few years, substantial technological developments have taken place and depending on the metellurgical properties, various Catagories of stainless steels have been classified under three basic categories, namely;

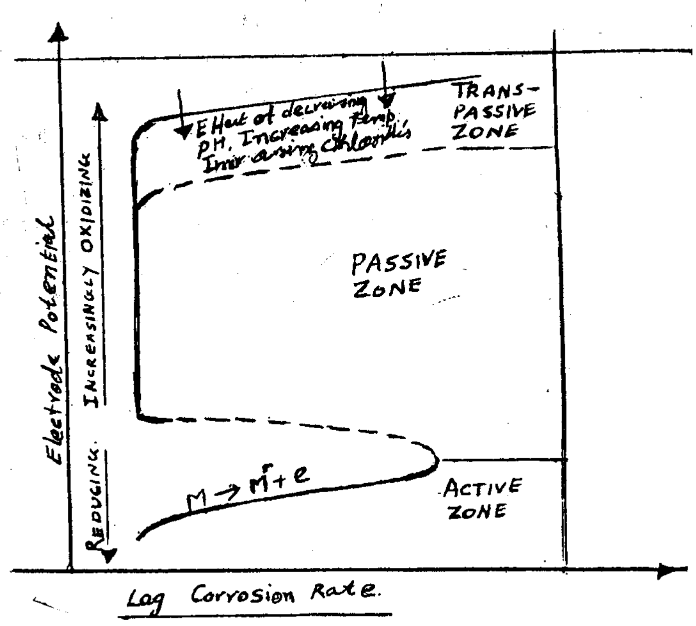
a) Austenitic b) Ferritic c) Duplex

Typical chemical compositions of certain varieties under each category are given below ;

Alloy	Chemical Composition (Wt %)							Remarks
	Cr	Ni	Mn	C	N	Si	Mo	
Austenitic								
316 L	16	13	1.6	0.03	—	0.1	2.3	) Excellent for welded
317 L	18	14	1.9	0.02	—	0 5	3.2	) construction tough and
Carpenter 20 Cb-3	20	33	0 3	0.04	—	0.4	2.4	) ductile. Pitting and
Sandvik 2RK65	20	25	1.8	0.02	—	0.5	4 5	) Crevice Corrosion
Haynes H2OM	22	26	0.8	0.03	—	0.6	4.2	) Resistance increase
Cronifer 1925 C	20	25	1·4	0.02	—	0 4	4.8	) with Molybedenum
Cronifer 1925 HMO	21	25	1 3	0 02	0 14	0.3	5.9	) content
Ferritic								
29—4	29	0.1	0 1	0.003	0.01	0.1	4 0	) not as easy to weld) as Austenitics, and
NYBY MONIT	25	4.0	0.3	0 02	0 01	0.2	4.0	) prone to embrittlement) when thick sections
E-Brite 26-1	26	0.5	0 3	0.01	—	0.3	1.1	) are welded-
Duplex								
Uddeholm 744 LN	25	6 2	1.7	0.025	0.17	0.4	1.5	) Relatively good wel-) dability and excellent) resistance to chloride) stress corrosion
Sandvik 3RE60	18	4.7	0 2	0 02	—	—	2.7	) cracking Overall) corrosion resistance) not as good as most) resistant Austenitics.

Annexure 1

SCHEMATIC DIAGRAM OF THE CHARACTERISTIC RELATIONSHIP BETWEEN ELECTRODE POTENTIAL AND THE CORROSION RATE OF STAINLESS STEELS.



Stainless steels from all three groups depend on a self protective, passivating surface film to prevent corrosion. The specific resistance of this film depends on Mo content. Acceptable corrosion resistance in any environment depends both on the stability of the film and its ability to reform when it is ruptured or penetrated.

In Annexure I, a chart is shown, indicating the relationship between the oxidizing power of the environment (or the potential) and the corrosion rate of stainless steels.

In the bleach plant operation, higher chloride levels, higher temperatures, and lower pH are the major agents for reducing the magnitude of the passive region, because they each reduce the stability of the passive film.

It has been observed that, in most of the cases, for stainless steel, localized corrosion "*Pitting or Crevice Corrosion*" associated with transpassive behaviour, comes into play. However, they may under go general corrosion in strongly reducing (very acidic) environments. Certain heat treatments in austenitic stainless steels lead to intergranular corrosion, due to stress corrosion cracking, in neutral and acidic, chloride containing solutions.

As already stated earlier, 1925 HMo has been found to be very satisfactory material of construction for stainless steel Bleach washer required for installation in Multistage Bleach plant for stage like C, D/C and D.

Chemical composition and mechanical properties of this material (1925 HMo) are given below :-

Chemical Composition of 1925 hMo (produced by V. D. M.)

Cr	19-21%	C	0.02% max
Ni	24-26	Mn	2.0
Mo	6-7	P	0.03
Cu	0.5-1.0	S	0.01
N	0.18 - 0.25	Fe	Balance

Mechanical Properties of 1925 H Mo

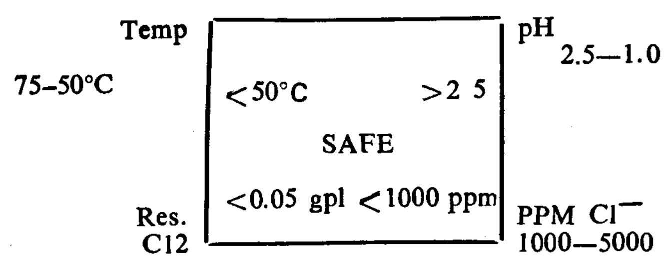
Tensile N/mm² (Ksi)	Yield 0.2% N/mm² (Ksi)	Elongation %
600/800 or (87/116)	300 or (44)	35

To determine the relative resistance of an alloy, extensive laboratory testing is needed, by the determination of "Critical Pitting Temperature" (CPT) and "Critical Crevice Temperature (CCT) in 10% Ferric Chloride solutions. Following is a summary of the test data for certain grades of stainless steel alloys.

Alloys	CPT	CCT
316 L SS	15°C	10°C
317 L SS	28°C	10°C
904 L SS	45°C	25°C
1925 H Mo	65°C	50°C
C-276	95°C	85°C

In U.S.A. it is a common practice to develop a suitable "OPERATING PARAMETER BOX" (based on actual test data on the selected material of construction) to ensure that the equipment would not corrode, provided all process parameteres are kept within the Box.

Following is such a "Box" for 1925h Mo.



In actual practice, it does happen, that one or two parameters can not be maintained with in the box, all the time, and as such additional measures in the form of "Electrochemical protection" could be provided. A patented Electrochemical protection system reduce corrosion by maintaining potential in the passive region.

Water Reuse (Recycling of filtrates) and Selection of Superior Alloys :

It has almost become mandatory to close the loop within the mill, with a view to attain the ideal situation of Zero discharge. In a pulp mill (equipped with recovery) the maximum quantity of effluent (with high BOD & COD) originates from the Bleach Plant. If the Bleach Plant is designed to recycle filtrate from the succeeding stages to preceling stages, it would be necessary to give a serious thought to the selection of materials for all the bleach washers : because in that case

Annexure—II

TABLE 1—WELDING PRACTICES

Material	Plate Thickness mm	Filler Metal Diam mm	Cr-Ni0—Mo%	Process	Post Weld Cleaning
Type 316L	3.19	3.18	17-12-2.5	SMA	S.S.W.B.
Type 317L	3.18	3.18	19-13-3.5	SMA	S.S.W.B.
Type 317LM	3.43	N.R.	22-60-9	GTAW	S.S.W.B.
Type 317X	3.18	N.R.	19-15-5.5	GTAW	S.S.W.B.
NITRONIC 50-1	3.18	3.97	21-12.5-2	SMA	GSP
NITRONIC 50-2	3.18	3.97	22-60-9	SMA	GSP
Jessop 700	3.18	N.R.	22-60-9	SMA	S.S.W.B.
Uddeholm 904L	3	N.R.	21-25-4.6	SMA	PICKLED
Avesta 254SLX	3	3.2	20-25-4.5	SMA	W.B.
Avesta 254SMO	3	3.2	22-60-9	SMA	W.B.
AL-6X	3.18	A	—	GTAW	NONE
Sanicro 28	3	1.6	27-31-4	OTAW	S.S.W.B.
Carpenter 20Mo6	3.18	1.6	22-6-9	GTAW	S.S.W.B.
INCOLOY 825	3.18	N.R.	22-41-3	GTAW	N.R.
HASTELLOY G	3.18	1.0	22-40-6.5	GTAW	N.R.
HASTELLLOY G3	3.18	1.0	23-44-7	GTAW	N.R.
INCONEL 625	3.18	NR	22-60-9	GTAW	N.R.
HASTELLOY C 276	3.18	1.0	15-55-16	GTAW	N.R.
E-BRITE	3-18	A	—	GTAW	NONE
Crucible SC-1	3.18	N.R.	26-2-3	GTAW	S.S.W.B,
NYBY MONIT	3.18	0.8	25-4-4	GTAW	N.R.
Uddcholm 44LN	3	3.25	23-9-3.0	SMA	PICKLED
Schomac 30-2	3	1.6	30-0.2-2	GTAW	S.S.W.B.
AL 29-4	3.18	A	—	GTAW	NONE
AL 29-4-2	3.18	A	—	GTAW	NONE
Titanium Grade 2	3.18	N.R.	Ti	GTAW	W·B,
Titanium Code 12	3.18	N.R.	Ti	GTAW	W.B.

A — AUTOGENOUS
SMA — SHIELDED METAL ARC
GTAW — GAS TUNGSTEN ARC WELD
GSP — GLASS SHOT PEENED
N.R. — NOT REPORTED
S.S.W.B. — STAINLESS STEEL WIRE BRUSH

Annexure II

TABLE 2

ENVIRONMENTAL DATA

	C, D/C Stage								D Stage								H Stage		
Mill	AA	BB	CC	DD	EE	FF	GG	JJ	AA	AA	CC	DD	EE	FF	GG	JJ	DD	JJ	CC
Test Rack Nos.	1,3	5,6	7,8	15,25	18,20	21,22	27,28	37,38	32,33	31,34	9,12	13,26	17,19	23,24	29,30	35,36	14,16	39,40	10,11
Stage	D/C	C	C	C	D/C	C	D/C	D/C	D_1	D_2	D_1	D	D_2	D	D_1	D_2	H	H	H
Environment-Vat																			
pH																			
Av. of Daily Min.	1.9	1.4	2.0(1)	2.0	2.0	1.6	1.4	2.1(1)	3.4	3.1	6.5(1)	5.5	5.2	6.7	2.1	3.3	7.5	9.1	9.5(1)
Av. of Daily max.	2.4	1.6		2.7	2.2	2.2	2.2		4.1	3.7		7.0	5.8	7.7	3.5	5.5	9.5	10.7	
Residual g/l																			
Av. of Daily Max.	0.016	0.050	0.030(1)	0.050	0.015	0.027	0.148	0.320	0.062	0.035	N.R.	0.008	0.030	0.011	0.181	0.064	.058	1.023	N.R.
Av. of Daily Min.	0.006	0.010		0.008	0.001	0.002	0.013	0.061	0.003	0.003		0.001	0.003	0.003	0.020	0.004	.005	.180	N.A.
Temperature-F																			
Av. of Daily Max.	137	114	105(1)	98	103	103	138	109(1)	151	176	150	169	155	166	157	128(1)	132	88(1)	110(1)
Chloride-ppm																			
Av. for Exposure Period	5500	3500	1100	1000	1500	1900	1500	1400	1700	5600	Low	750	500	1000	1800	1550	2000	2453	Low

(1) Average for Exposure Period
N.R. Not Reported

Annexure—II

TABLE 3—CREVICE CORROSION

Number of Specimens—
Max. Depth in mils any of 4 crevices sites

Base Metal Material	16—C Stage			16—D Stage			6—II Stage		
	<5	6-20	>20	<5	6-20	>20	<5	6-20	>20
316L	3	7	6	3	5	8	3	2	1
317L	3	11	2	3	11	2	4	1	1
317LM	4	11	1	7	6	3	3	1	2
317X	10	5	1	11	4	1	5	—	1
N-50-1	4	11	1	5	6	5	3	1	2
N-50-2	4	11	1	6	5	5	3	1	2
JS-700	8	8	—	6	6	4	4	1	1
UHB-904L	8	8	—	6	5	5	3	2	1
254 SLX	6	10	—	2	6	8	2	3	1
254 SMO	15	1	—	8	5	3	A	—	—
AL-6X	8	8	—	3	10	3	3	3	—
Sanicro 28	9	7	—	7	7	2	3	1	2
Carp. 20Mo-6	14	2	—	15	1	—	A	—	—
INCOLOY 825	9	7	—	7	5	4	4	1	1
HASTELLOY G	A	—	—	14	1	1	A	—	—
HASTELLOY G-3	A	—	—	13	3	—	A	—	=
INCONEL 625	A	—	—	A	—	—	A	—	—
HASTELLOY C-276	A	—	—	A	—	—	A	—	—
E-BRITE	—	15	1	—	10	6	4	2	—
Crucible SC-1	14	2	—	15	1	—	A	—	—
MONIT	11	5	—	6	9	1	A	—	—
UHB-44LN	3	13	—	2	10	4	3	1	2
Schomac 30-2	A	—	—	14	2	—	A	—	—
AL 29-4	14	2	—	11	5	—	A	—	—
AL 29-4-2	12	4	—	5	11	—	A	—	—
Ti-Gr2	A	—	—	A	—	—	A	—	—
Ti 12	A	—	—	A	—	—	A	—	—

NOTE : 1 mil=0·025 mm
A=All
—=Zero

Annexure - II

TABLE 4

RESISTANCE OF BASE METAL, CREVICED AREA, WELD METAL AND HAZ BY STAGE

Base Metal Material	C, D/C Stage				D Stage				H Stage			
	Base Metal	Crevice	Weld Metal	HAZ	Base Metal	Crevice	Weld Metal	HAZ	Base Metal	Crevice	weld Metal	HAZ
316 L	3	3	2	3	3	3	3	3	2	2	3	3
317 L	2	2	3	3	3	2	3	3	1	2	3	2
317 LM	2	2	1	2	3	3	3	3	1	3	1	1
317 X	1	2	3	3	3	2	3	3	1	2	3	1
N-50-1	2	2	2	1	3	3	3	3	1	3	3	2
N-50-2	2	2	1	2	3	3	1	3	2	3	1	2
JS-700	1	2	1	1	3	3	1	2	1	2	1	1
UHB-904 L	1	2	1	2	3	3	2	2	1	2	1	1
254 SLX	2	2	2	2	3	3	3	3	1	2	3	1
254 SMO	2	1	1	1	2	3	1	2	1	1	1	1
AL-6X	1	2	1	1	3	3	2	2	1	2	1	1
Sanicro 28	1	2	1	1	3	2	3	2	1	3	1	1
Carp .20 Mo-6	1	1	1	1	1	1	1	1	1	1	1	1
INCOLOY 825	2	2	1	1	3	3	3	3	1	2	1	1
HASTELLOY G	1	1	1	1	1	2	1	1	1	1	1	1
HASTELLOY G-3	1	1	1	1	1	2	1	1	1	1	1	1
INCONEL 625	1	1	1	1	1	1	1	1	1	1	1	1
Hastelloy C-276	1	1	1	1	1	1	1	1	1	1	1	1
E-BRITE	2	2	2	3	3	3	3	3	1	2	3	3
Crucible SC-1	1	1	1	2	2	1	2	3	1	1	1	1
MONIT	1	2	1	2	3	2	2	2	1	1	1	1
UHB-44 LN	1	2	2	2	3	3	3	2	2	3	2	1
Schomac 30-2	1	1	1	1	2	1	1	1	1	1	1	1
AL 29-4	1	1	1	1	1	2	1	1	1	1	1	1
AL-29-4-2	1	2	1	1	2	2	1	1	1	1	1	1
Ti Gr2	1	1	1	1	1	1	1	1	1	1	1	1
Ti 12	1	1	1	1	1	1	1	1	1	1	1	1

NOTE : 1 = Superior
2 = Useful
3 = Unsatisfactory

corrosive filtrate originating from a succeeding chlorine dioxide stage would be used on Caustic extraction or a Hypo stage. Filtrate originating from "D" stage would invariably contain corrosive chemicals such as residual chlorine, chlorides etc. and as such the Bleach Washer drum in a preceeding stage has to withstand the corrosive action of "Filtrate" from a succeeding stages. In view of the above, there is a tendency to go for short sequence bleaching iucluding Oxygen delignification and oxidative extraction stages. Some of the popular sequences are.

(1) O — C/D — O/E — D
(2) D/C — O/E — Dl — D2
(3) D/C — O/E — D
(4) D/C — O/E — H1 — H2

In case of (2 & (3) it would be necessary to select exotic materials of construction like, 904L or 254 SMO or 832 SLRN for all the Washers In case of (1), the first stage washer can be in 316 L SS; with all other stage washers in superior alloys like 904L, 832 SLRN etc.

The selection of Material of Construction, therefore plays an important role in the overall viability of the project; and it also influence the selection of a bleaching sequence and overall process design.

We have worked in close conjunction, with a leading Indian Mill in this regard, and have manufactured bleach washers in superior alloys like Avesta 832 SLRN for D/C and D stages

CONCLUSION :

While designing bleach plant, serious consideration has to be given to the following parameters.

(1) Desired characteristics of end product, e g Brightness, strength etc.

(2) Capital investment and recurring costs of chemicals

(3) Life expectancy and Susceptibility of materials of construction to corrosive attack by Cl2, Cl02 etc.

(4) Water management and recycling of effluent with a view to achieve the idealistic situation of Zero discharge.

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