Polymers in handling corrosion by bleach plant chemicals

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ABSTRACT

In this paper various polymeric materials such as polyolefins, PVC, natural and synthetic rubbers, polyesters, epoxies and composites based on them have been evaluated for their performance based on physical and mechanical properties, chemical resistance and thermal behaviour to handle bleach plant chemicals, mainly chlorine, alkali, hypochlorite and acids which are widely used in paper industry. The data collected in the laboratory and those gathered from user industries form the basis of this review.

INTRODUCTION

Any industry using chemicals to carry out processes needs a constant vigil on its structure and equipment for repairs and replacement due to corrosion. Pulp and paper industry throughout the world uses a large share of its maintenance expeness to combat and prevent corrosion.[1-12] The search for alternate materials which could reduce or prevent corrorsion has now brought a large number of materials which can minimise the corrosion losses at an affordable cost.[13-20] Sections of the plant using bleach chemicals such as caustic soda, chlorine and mineral acid cause for more severe corrosion of equipments and structures than any other unit and pose formidable problems to reduce contamination of products and material losses. This paper reviews the availability of polymeric materials, their properties and performance in chemical environments to combat corrosion in equipments handling bleach chemicals. The information is based on data from literature and the laboratory experience over the years in handling these chemicals with an eye on the aspects of their ability to corrode mild steel and its control by alternatives[21].

CORROSION PREVENTION METHODS

Corrosion is defined as destruction of a metal by chemical or electrochemical reaction with its environment.

The most widely used structural material mild steel is vulnerable to corrosion. Its electrode potential —0.44V is such that it is oxidised to ions in presence of oxygen and water through galvanic currents. Oxygen is converted to hydroxyl ions which form the ferrous hydroxide and other rust products. May factors notable temperature, chemical reactions, pH, stresses on the part, adherence of oxide films and flow rates of solutions affect the severity and rates of corrosion.

The methods available to inhibit corrosion are as follows.

(1) Coating of material to prevent access of water, chemicals and oxygen to the surface. Unfortunately, defects in the coatings are major cause of failure in this method.

(2) Galvanising of Iron with Zinc which protects Iron against atmospheric corrosion. The method fails in chemical environments.

(3) Cathodic protection using a sacrificial anode such as Magnesium which can protect till its own depletion.

(4) Use of inhibitors particularly in aqueous soluotions which remove oxygen and other ions which accelerate corrosion reaction of Iron.

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(5) Lining, covering or use of corrosion resistant materials.

METALS AS MATERIALS OF CONSTRUCTION (MOC)

Metals are undisputably the best MOC as far as strength, load bearing properties, abrasion and high temperature use is concerned. But most of these fail in the corrosive environmant because these are affected by electrochemical forces generated in contact with the chemicals. Corrosion rates of some commonly used metals and alloys are given in Table—1.[17,22] As compared to cast Iron, Lead, Aluminium and Nickel based alloys have a very low rates of atmospheric corrosion at ambient temperature and low relative humidity. The behaviour towards acids and alkalis is, however, different for different metals. Cast Iron, Lead, Aluminium Monel and even Stainless Steel are unsuitable to handle 10-20% of hydrochloric acid. Only Hastelloy can withstand this acid though the severity of attack increases with high concentration and temperature of acid. In low cost metals, only Cast Iron can withstand alkali. Stainless Steel and Nickel based alloys are ideally suited to handle caustic soda solutions. Chromium-Nickel (18/8) steels perform best under oxidising conditions since the chemical resistance depends on the oxide film on the surface of the alloy. Reducing conditions and the chloride ions destroy this film and bring a rapid attack which is very severe in stressed parts causing stress corrosion cracking.

The same oxide film performance is responsible for exceptionally good corrosion resistance of Titanium. It is not attacked by solutions of sodium chlorate, chlorite and hypochlorite. It shows no pitting corrosion in aqueous solutions of matal chlorides and can resist 27% HCl at 35°C. The cost is very high. The best to handle boiling HCl and corrosive liquids is Tantalum which is costlier than Titanium[19],

TABLE—1

Corrosion Rates of Common Metals and Alloys

S. No.	Material	Atmospheric Corrosion ambient T mm/year	Medium	Temp. °C	Corrosion rate mm/year
1	Cast iron	0.13	(a) 15% HCl	30	>1.25
			(b) 10% NaOH	30	<0.05
2	Lead	0.007	(a) 30% HCl	30	>1.25
			(b) 10% NaOH	30	>1 25
3	Aluminium	<0.003	(a) 15% HCl	30	>1 28
			(b) 10% NaOH	30	>1 28
4	Monel	<0.0015	(a) 20% HCl	30	>1.25
			(b) 30% NaOH	125	<0 05
5	Hastelloy--B	<0.0025	(a) 20% HCl	125	<0.5
			(b) 20% NaOH	125	<00 5
6	Stainless Steel 18/8	Almost Nil	(a) 10% HCl	30	>1.25
			(b) 20% NaOH	150	<0.5
7	Stainless Steel 316	Almost Nil	(a) 10% HCl	30	>1.25
			(b) 20% NaOH	150	<0.5
8	Titanium	<0.001	(a) 20% HCl	30	<0.02
			(b) 30% NaOH	30	<0.02

POLYMERS AS MOC

Polymers as a class are made of covalently linked carbon atoms and are not affected by electrochemical forces causing corrosion. These are ideal materials to handle corrosive fluids (Table 2). The materials have combination of properties such as strength, flexibility, low thermal and electrical conductivity, low density (thus resulting in very high strength-weight ratios), transparency and colourability, easier methods of fabrication as compared to metals and modifiable to improve strength and chemical resistance with reinforcing fibres. However, their severe limitation is low limits of operating temperature and rapid fall of strength properties with increase in temperature. Unlike metals these fail by either swelling or cracks arising due to effect of oxidation, sunlight, radiation or hydrolysis in Chemical environment [23-26].

The merits and limitations of using these materials in handling caustic, chlorine and other corrosive fluids is discussed under the following groups.

RUBBERS

These are the weakest polymers in strength but have a high flexibility and abrasion resistance. Natural rubber gives very strong vulcanisates (Table 3) and offers a good chemical resistance to both acids and alkalies at temperatures from ambient to 70°C. It is resistant to both dry and wet chlorine gas but can not resist sulphuric acid and hypochlorite solution. It also offers the low cost alternative to handle (Table 4) chlorine chemicals and is therefore widely used as lining materials for pumps, valves and storage tanks[27].

TABLE—2

Corrosion Resistance of Some Plastics to Common Chemicals

S. No.	Polymer	HCl 10%	HCl 30%	NaOH Conc.	H_2SO_4 50%	Cl_2 gas dry	Cl_2 gas wet	Hypo. chlorite
1	Polyethylene (HDPE)	G	G	G	G	F	P	G
2	Polypropylene	G	G	G	G	F	P	G
3	Polyvinyl-chloride	G	G	G	G	F	P	G
4	ABS	G	G	G	G	G	G	F
5	Natural rubber	G	G	G	F	G	G	P
6	Chloroprene rubber	G	G	G	F	F	P	F
7	Hypalon	G	G	G	F	F	P	G
8	Polyesters (GRP)	G	G	P	G	G	F	F
9	Epoxies (GRP)	G	G	G	G	G	P	F
10	Polyvinylidene fluoride	G	G	G	G	G	G	G

G—Good. F—Fair. P—Poor

Temperature—ambient

TABLE—3

Strength Properties of Plastics
(S. No. refer to materials in Table 2)

S. No.	Elastic modulus $10 \times MN/m^2$	Tensile strength MN/m^2	Compressive strength MN/m^2	Maxium service temp. °C
1	50 — 100	8 — 40	16 — 18	100
2	100 — 150	30 — 40	60 — 70	140
3	100 — 200	20 — 55	50 — 90	110
4	136 — 240	40 — 50	40 — 70	95
5	0.1 — 0.2	27 — 35	——	105
6	0.2 — 0 3	15 — 25	——	110
7	0.1 — 0.3	15 — 18	——	120
8	500 — 750	30 — 70	90 — 260	220
9	100 — 900	20 — 110	100 — 150	120
10	100 — 180	20 — 50	15 — 18	130

TABLE—4

Cost Ratio of Various Materials of Construction
(Typical for 100 mm diameter fabricated pipes)

S. No.	Material	Cost ratio
1	Carbon steel	1.00
2	Aluminium	1 47
3	Rubber lined steel	1.48
4	Polypropylene lined steel	1.50
5	Stainless steel 316	3 00
6	Monel	3 95
7	Hastelloy B	5.02
8	Titanium	6.58
9	PVC lined steel	1.50
10	ABS lined	2.00
11	Chloroprene lined steel	2 50
12	Hypalon lined	3.00
13	GRP polyestpr	1.30
14	GRP epoxy	1.80
15	Polyvinylidene fluoride	4 00

THERMOPLASTICS

Polyethylene (HDPE) is the low cost thermoplastic which is easily available for fabrication of pipes, flanges etc. and as lining material. A lined pipe has an advantage over a plastic pipe as it can withstand higher pressures and has as good mechanical strength as the steel exterior. However, there are limitations on size (not more than 250mm dia) due to fabrication problems. A good method of fabrication is to extrude plastic liner in the form of a tube and insert the tube with a close fitting in a pre-fabricated steel pipe. Thermoplasticity of these materials facilitate the softening and good bonding between the substrate and the lining. HDPE is a tough and flexible lining material widely used to line fractured or corroded cast Iron and cement pipes. It is a good material to handle acids, alkalies and hypochlorite. It becomes stiffer with increasing density (0 92-0.96) and suffers from environmental stress cracking. Polypropylene has higher strength, rigidity and elevated temperature performance than HDPE in almost similar chemical environment.

Unplasticised PVC is a low cost material to handle acids, alkalies and salt solutions. It is extensively used for process piping, water drainage and effluent disposal. It becomes unexpectedly brittle at low temperatures and is liable to crack when water expands on freezing.

ABS has good tensile and impact strength and an overall good chemical resistance. It can be used to handle even wet chlorine gas in addition to mineral acids and alkalies where it is inferior to unplasticised PVC[28].

Polyvinylidene fluoride is an outstanding thermoplastic in terms of corrosion and abrasion resistance. It has poor bonding qualities. PVDF lined steel can safely be used in corrosive environments upto 130°C. It can withstand concentrated acids and 50% NaOH solution, liquid chlorine and wet chlorine gas which are all highly corrosive, upto 100°C. The cost of the lining is very high[29].

THERMOSETTS

The important materials of this class are Phenol Formaldehyde resins, polyesters and epoxy resins. The latter two are widely used as glass reinforced plastics (GRP) and have excellent strength, impact strength, abrasion and corrosion resistance. Being low viscosity liquids in the beginning these are more suitable for fibre reinforcement than thermoplastics. These have good overall chemical resistance, smooth surface finish and do not require any maintenance, However, the strength reduces in the prolonged use, as stress concentration is build up over the years. One limitation is that liquid pressure exceeding 5 to 20 bars are rarely applied or advisable for GRP vessels and pipes respectively[30,31]. Because of their low cost, these lining are very popular to handle corrosive chemicals. The corrosion resistance is highly dependent on chemical constituents of resins. For example, Bisphenol-A based polyester resins are superior to phthalic acid propylene glycol based resins. Diglycidyl ether of Bisphenol-A are most common epoxy resins. Similarly the type of glass used being C or E and its form whether stands, mat or glass cloth affects the strength and chemical resistance of GRP.

GRP based on polyesters have been used for 10% HCl at 65°C for upto 10 years without any adverse effect[30]. Higher HCl concentration (35%) has however been reported to cause blisters on the FRP due to diffusion of acid and its reaction with the E glass. FRP lining has a wide range of applications in pulp and paper industry such as for tanks and pipes of bleach chemicals, alum, white water, black liquor and waste liquor. The epoxy based FRP are superior to those based on polyesters in handling alkaline liquors[35]. Polyesters however, are better than epoxies in high temperature (> 120°) applications.

Except digesters for pulp where temperatures are too high for any plastic application, other auxiliary vessels such as liquor make up tank, spent liquor storage, sodium chlorate storage, green liquor storage, beater lining and agitator lining are some of the areas in which plastics linings will offer distinct advantage

CONCLUSIONS

The polymeric materials such as rubbers, thermoplatic or thermosetts can offer cost effective solutions to handle corrosive fluids and environment in pulp and paper plants.

These materials can be used in the form of moulded or fabricated pipes, tanks or fittings or as lining materials in steel or concrete structures, Their use as binder material in various paints for corrosion protection of mild steel is already well established. A proper and timely application of these materials can greatly help to minimise losses due to corrosion,

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