SECTION II

CHAPTER 4

CORROSION STUDIES TO SELECT SUITABLE MATERIAL OF CONSTRUCTION

A) Corrosion studies to select material of construction for hot extraction of mixed salt with 36° Be bittern to recover potassium chloride and byproducts

B) Corrosion studies to select material of construction for the manufacture of potash alum from mixed salt

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CORROSION STUDY FOR SELECTION OF MATERIALS OF CONSTRUCTION

Materials of construction for the two processes developed for the utilisation of mixed salt to obtain potassium either as potassium chloride or as potash alum are discussed in this section.

1) Hot extraction of mixed salt to recover potassium chloride and byproducts

The process operations can be broadly divided under two categories namely 1) operations at elevated temperatures 2) operations at room temperature and at lower temperatures. Extraction of mixed salt with 36° Be bittern at 110°C, purification of impure potassium chloride also at 110°C and crystallisations of carnallite and pure potassium chloride are the operations carried out at elevated temperatures. Decomposition of carnallite, preparation of sel's mixts solution, saturation of epsom salt mother liquor with sodium chloride and crystallisations of epsom salt and sodium sulphate are carried out at room temperature or at lower temperatures.

The variety of equipments used for these purposes are (1) dissolvers or reaction vessels (2) filtration units (3) crystallisers (4) centrifuges and 5) driers. Besides these many auxiliary units such as crusher, elevators, hoppers, pumps, weighing machines and such other several small and big equipments are required for the production unit. In selection of material of construction many factors are taken into considerations such as initial cost, durability of equipments, cost of shut downs, period required for replacement or repairs and lastly the freedom of product contamination. Corrosion in addition to shortening the life of the equipment often gives off colours to the produced material which fetches less prices. It is equally important that the material of construction is indigenous and easily available. Marine salts are cheap and most of the recovery processes encounter many corrosion difficulties. The scope of selection of a suitable corrosion resistant material becomes limited, as the initial capital investment does not permit such considerations. The problem becomes more acute in extraction and crystallisation processes particularly where concentrated solutions containing corrosive salts are handled at elevated temperatures. Corrosion is also enhanced by abrasive action of the hard crystalline material on metallic surface where oxide films are removed and new surface is constantly exposed. Similar effect is produced on protected surfaces by surface coatings. Literature indicates (Table 90) variety of metals and alloys that can be used with different marine salts. Corrosion tests were carried out to find out suitable material of construction. Tests were undertaken to study whether these will resist corrosion under the severe experimental conditions.

The usual cheaper material of construction is mild steel and low carbon steel; however such materials are not able to combat corrosion by itself unless they are suitably protected by surface coatings or by cathodic protection. Monel metal is usually satisfactory and has become a standard material for use in contact with wet salt, brine and bittern. Stainless steel particularly alloyed with small amounts of molybdenum has proved excellent, because of its greater hardness and resistance to abrasion. However the use of these materials is often prohibitive in salt and byproduct industries as capital investment becomes large; most of them are not indigenously available and the end products are the cheap materials of commerce.

Laboratory experiments and pilot plant studies

Laboratory studies were carried out using glass beakers and metal and alloy pieces in the reaction mixture supported on glass hooks separated from each other at such a distance that during stirring the pieces were not touching each other. The pieces were tested for eight hours daily at 110°C. The volume of the reaction mixture was maintained by addition of water at intervals. The details of these tests are given in table 91. The results showed that copper stood better than certain alloys. Brass or bronze could be used for brazing and pumps. Stainless steel was equally suitable for mixed salt extraction.

A large sized dissolver of the following composition was fabricated to test corrosion resistance of the alloy (corresponding to EN 30).

Table 90 MATERIAL OF CONSTRUCTION (Standard data)

Concentration %	Chemical	Carbon steel	(14%Si) carbon steel	ASSI type 304 S.S	S.S 316	S.S 20	Al	Cu	Red Brass	Cupronickel	Silicon bronze	Al Bronze	Ni	Monel
10	$MgSO_4$	B	A	AB	AB	AB	B	AB'	AB	AB	AB	AB	AB	AB
20	Na_2SO_4	B	A	AB	AB	AB	A	AB	A	AB	AB	AB	A	A
30	$MgCl_2$	B	B	B^3	AB^3	AB	BC	AB	AB	AB	AB	AB	A	AB
10-20	KCl 100°F	B	AB	AB^2	AB^2	AB	C	AB	AB	AB	AB	AB	A	A
10-20	NaCl	AB	AB	AB^2	AB	AB	BC^2	AB	AB	AB	AB	AB	AB	AB
10	H_2SO_4	C	C	C	C	AB	C	B^1	B^1	B^1	AB^1	AB^1	C	AB^1
10	HCl	C	AB	C	C	C	C	C	C	C	B^1	C	BC	C

Corrosion resistance

A = very good

B = suitable

BC = acceptable

C = useless

Precautions

1) solution air free

2) pitting corrosion

3) stress corrosion

Table 91 TESTING OF METAL AND ALLOY PIECES IN REACTION MIXTURE CONTAINING MIXED SALT AND 36° Be BITTERN AT 110°C

Metal or alloy	Loss in weight in grams per 100 sq. cms.					
Time (hrs.)	24	40	64	120	240	360
Copper	0.025	0.080	0.089	Not taken	*	*
Brass	0.022	0.021	-	-	-	-
Bronze	-	0.132	0.179	-	-	-
Phosphor Bronze	-	0.109	0.168	-	-	-
Admirality brass	0.101	0.150	0.104	-	-	-
Mild steel	0.792	0.786	0.614	0.300	0.255	-
Low carbon steel	-	-	0.792	0.786	0.614 (168 hrs)	0.255 (280 hrs)
	-	-	-	-	0.300 (224 hrs)	-
Molybdenum steel	-	-	0.465	0.175	0.170 (160 hrs)	0.070 (280 hrs)
	-	-	-	-	0.06 (224 hrs)	-
Monel	-	-	0.045	0.079	0.324	0.472
Titanium stabilised steel	-	0.012	0.013	0.018	0.023	-
Stainless steel(305)	-	-	-	-	0.005	0.121
Hastelloy (C)	-	-	-	-	0.012	0.189

Alloy composition

Carbon	0.35 per cent
Molybdenum	0.40 "
Nickel	4.25 "
Chromium	1.2
Iron	Rest

The dissolver with 114 kg of mixed salt and 500 litres of bittern was used for pilot plant experiments. This material has been found to be very satisfactory in withstanding corrosion against hot solutions of 36° Be. Similarly copper coils utilised for heating reaction mixture instead of jacketted vessels were also satisfactory. Small dissolver units of 100 litres capacity were also fabricated from low carbon steel and mild steel to compare corrosion resistance of the material under exact experimental conditions. At elevated temperatures, carbon steel containing 14 per cent silicon, resisted corrosion better particularly if 2 to 3 per cent molybdenum was also present. Monel, copper and stainless steel was found equally suitable; stainless steel showed pitting corrosion at weak points. Pitting was more pronounced in case of saturated NaCl-KCl solution particularly during crystallisation of potassium chloride than with magnesium chloride solutions. Difficulties were experienced in repairing these points as local heating caused other weak centres which were severely attacked. Similarly attack was more pronounced at the surface layer than at the bottom. Copper coils were used for heating purposes and large vat type copper vessels were used as dissolver and crystallising units. Copper was found to be satisfactory for all the above purposes in magnesium chloride solutions. Copper screw conveyor was used for extraction of mixed salt instead of mild steel dissolvers. Little corrosion was observed when the screw conveyor was kept as such without washing after the experiments but in constant use the corrosion was much less. Copper could not be used for epsom salt and potassium chloride crystallising units. Corrosion of mild steel equipments used in sel's mixts solution tank, epsom salt and Glauber's salt crystallisers was also observed. But the attack was less severe than that in case of dissolvers at 110°C. Iron contamination with epsom salt and potassium chloride was negligible when crystallisers and centrifuges used were of stainless steel. Influence of inhibitors showed that potassium chromate (0.1 per cent) prevented the rate of corrosion of mild steel at 110°C to a remarkable degree. All the data revealed only one fact that costlier material of construction could only reduce the corrosion difficulties. The other alternative was to protect the surface of the metal by application of suitable paints. Epoxy paints which are resistant to chemical corrosion at higher temperature were supplied by following companies: (1) Shalimar Paints Ltd., (2) Addisons Paints and Chemicals Ltd., and (3) British Paints (India) Ltd., These paints were first applied to mild steel test pieces after proper cleaning as per instructions from the company. These pieces after proper curing period were tested in 36° Be bittern. The results were satisfactory. Hence miniature dissolvers, jacketted type with 100 litres capacity were fabricated from 1/8 inch thick mild steel plates. The exact particulars of the dissolvers were as follows.

Size 19"+ diameter, 23½"+ height, cone angle 30°
Heating surface 7.285 sq.ft., operated at 30 Psi.
Stirring speed 60 R.P.M, Power 0.25 H.P.

The dissolvers were cleaned by emery wheel grinding tool to a clean shining white metallic surface. Sand blasting recommended by the company was not possible and hence emery grinding was carried out. The exposed surface was immediately painted with a primer coat as per instructions supplied by the company. (Details are given in Table 92). The primer coat was allowed to dry for 24 hours at room temperature. The second coat of primer was given next day. The two primer coats were allowed to dry completely for three to four days. The finishing two coats were given with a time lag of 24 hours between two successive coats. The carefully painted vessels were allowed to cure for more than a week. The vessels were lagged and used for corrosion experiments. Every evening the vessels were emptied and cleaned with water to find out condition of the paint layer and other details. Next day a fresh batch was

Table 92 PROTECTION OF THE METAL SURFACE BY THE APPLICATION OF PAINTS

(Testing of paints at 110°C in presence of a reaction mixture containing mixed salt and 36° Be' bittern)

1) Company	Shalimar Ltd.	Addison Paints	British Paints
2) Paint layers	Shalimar epoxide chemical resistant paint No.2 red lead primer base 25/02. Shalimar chemical resistant No.2 red lead primer accelerator sample No.1501/4 ratio 2:1 base: accelerator	Primer i) Duratuff H.I.build primer off-white L.S.2571 ii) Hardner L.S. 25% for primer iii) Accelerator for primer iv) Flow control agent	Epilux No. 5 as primer epilux No.4 as finish coat
3) Total coats given	Two coats	Two coats of primer and two coats of enamel	Two coats of No.5. and two coats of No.4
4) Ratio of mixing	2:1 base:accelerator	Primer coat (200+200+10) g per litre Finish coat (200+200+10+20) g per litre Pot life 1 hr.	2:1 base:catalyst Pot life 1 hr.
5) Covering power	1689 sq. m. per litre	41 to 44 sq.ft. per litre or 35 to 38 sq.ft. per kg	6 to 7 sq.m. per litre
6) Vessels	Steam jacketted M.S.dissolver with all accessories.		
7) Surface treatment	Grinding of surface oxide layer with emery wheel grinding tool was done as sand blasting was not available		
8) Surface of vessel	1.161 sq.m.	1.161 sq. m.	1.161 sq.m
9) Colour change	slight colour change was observed in all cases		
10) Total hours run	500	700	700
11) Reaction mixture	Mixed salt and 36°Be bittern (ratio 1 kg:4.5L)		
12) Remarks:-	Surface damage 3 times due to bubble formation & pealing of colour. Repairing by re-painting (damage spot) was effective. Pealing was at the steam inlet.	No damage. Little damage was seen at the edges of the stirring assembly	No damage

started. Total time of stirring at 110°C per day was eight hours. The volume of the reaction mixture was maintained, by constant addition of water.

The reaction mixture contained four salts namely sodium, potassium, magnesium as chlorides and magnesium sulphate. The solution was saturated with all these salts at 110°C. The high chloride ion concentration together with sulphate and magnesium ion created the problem worst at elevated temperature. The pH of the reaction mixture was between 6 to 6.5 At higher temperature hydrochloric acid seemed to be liberated from magnesium chloride which was corrosive. Addison paint "Duratuff" remained in tact and no pealing of the colour or corrosion was seen even after 700 hours of continuous operation. Shalimar paint however showed bubble formation and pealing of the layer two to three times which was observed at various places during the 500 hours of run. The pealed off paint layer was removed; the metallic surface was cleaned with water and then with sand paper. A fresh coat of the primer and enamel was given as in previous case. The repairing work was carried out with the intention to find out whether such repairing was possible with big size vessels which would involve large investment for repainting the whole unit. The repaired paint layer was satisfactory. The British paint was also found satisfactory. The painted layer in each case was tested for minimum 500 hours of operation.

The results obtained on these small vessels were considered for the commercial plant. The results assessed on the commercial plant showed that the capital expenditure involved for suitable corrosion resistant material was too heavy. The application of epoxy paints to mild steel equipments such as dissolvers, crystallisers, hoppers proved to be satisfactory in solving the corrosion problem of the commercial plant. Alternatively mild steel equipments could be used for large scale units with a limited life of 5 years for equipments handled at 110°C and 8 to 10 years at low temperatures.

(2) <u>Manufacture of potash alum from mixed salt</u>

Mixed salt was treated with 35 per cent aluminium sulphate solution at 100°C. Most of the salts would go into solution and hot slurry was filtered hot to crystallise pure alum. The process was simple but corrosion problem was serious as the hot slurry was at 3 pH with little free sulphuric acid. The main reactions in the process are

(1) $2KCl + MgSO_4 = K_2SO_4 + MgCl_2$

(2) $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O = K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$

or

(3) $2KCl + MgSO_4 + Al_2(SO_4)_3 + 24\,H_2O = K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O + MgCl_2$

The reaction product magnesium chloride produced in the first reaction was corrosive. All the salts are corrosive pH of the solution is 2.5 to 3 and the presence of free acid and excess of chloride ion at 100°C make the corrosion problem very acute.

Laboratory experiments

In order to determine suitable material of construction corrosion studies of metals and alloys immersed in reaction mixture at 100°C were carried out and the results are presented in Table 93. Stainless steel 305, monel and titanium stabilised steels were found unsatisfactory. It was observed that the addition of 0.5 per cent (w/v) nitric acid decreased slightly the corrosion rate.

Table 93 Testing of corrosion of common metals in reaction with mixture at 110°C with and without addition of nitric acid.

No.	Metals	Without HNO_3 loss in weight in mg/sq.cm./hr	With 0.5% (w/v) addition of HNO_3 loss in weight in mg/sq.cm./hr
1	Copper	0.8683	0.5140
2	Brass	0.3500	0.2680
3	Adm.Brass	0.4190	0.1720
4	Monel	0.7235	0.5430
5	Stainless steel	10.0000	9.535
6	Lead	1.8560	...
7	Aluminium	0.5000	0.4890
8	Hestelloy (C)	0.1948	0.1538

As lead cannot be used in presence of excess of chloride ion concentration, for preparing pharmaceutical grade potash alum, complete data with lead and other alloys of lead were not tested. Admirality brass showed ~~that~~ low rate of corrosion in presence of 0.5 per cent nitric acid.

All the metals in Table 93 were tried under experimental conditions at 100°C and loss in weight was calculated as milligrams per square centimeter per hour. Laboratory data showed that all nickel based alloys including monel were unsuitable either for reaction vessel or for crystallisers. Granite stone flooring could be used. Live steam was used for heating the reaction mixture. For higher capacity plant, steam pipe lined with rubber or thick aluminium pipes could be used. Threaded porcelain pipes could also be successfully used for passing live steam. The choice of material of construction required was classified as follows.

i) Reaction vessel	i) Wood ii) Tanks prepared by using acid resistant bricks and acid proof cement.
ii) Stirrers	i) Wood ii) Live steam also produces sufficient agitation.
iii) Cooling tanks (Crystallisers)	i) Acid proof cement and brick tanks lined with glazed tiles. ii) Acid proof bricks for tanks channels and crystallisers. iii) Cement tanks with granite flooring. iv) Wooden vats.

iv) Filtration unit	i) M.S.sparkler or any other pressure filtration unit coated with suitable anti-corrosive paint.
	ii) Wooden plate and frame filter press.
v) Aluminium sulphate solution tanks	i) Acid resistant bricks and cement for tanks.
	ii) Wooden vats.
vi) Pumps	i) High silicon steel
	ii) Brass
	iii) Ebonite line pumps

Alum (aluminium sulphate) industries mainly use hard lead containing 6 per cent antimony for pipelines pumps and valves. However as the reaction mixture contained chloride and contamination by heavy metals in the final product was undesirable, the use of hard lead was out of question. Recently the use of high silicon iron for alum and aluminium sulphate industries had been suggested. High silicon iron was mainly used for valves and pumps. It was also recommended for resistant linings particularly for heating tanks, reaction vessels etc. High silicon steel coils are costly but are more suitable as the yield and quality could be easily controlled; Where condensation of steam inside the reaction mixture could be avoided. Durimet which showed low corrosion rate was comparable with hard lead. Durimet was suggested for shafts, stirrers and impellers. Bronzes were attacked slowly and w~~h~~ere used~~,~~ for fittings. Rubber was satisfactory with usual limitations such as strength and temperature. Polyster glass laminates for reaction vessels and crystallisers were recommended and were also recently available in the country.

For pilot plant experiments wooden vats were used for preparing aluminium sulphate solution as well as for heating the reaction mixture or even for crystallisation of alum. M.S. sparkler pressure filter laboratory model (8 - 3) was used which was coated inside with epoxy No. 4 anticorrosive paint. The paint was satisfactory and no corrosion was observed in the unit. The pumps used were brass lined with neoprene or brass impellers (centrifugal type pumps). Crystallisation of alum was carried out in acid resistant cement tanks lined with glazed tiles (porcelain tiles). Potash alum produced on pilot plant scale operations was crystal clear and satisfied the pharmaceutical specifications.