

ON LINE CHEMICAL CLEANING OF CRITICAL HEAT EXCHANGERS FOR COOLING WATER DEPOSIT AND THEIR CONTROL TO SUSTAIN HIGH PRODUCTION LEVEL OF METHANOL. - AN EXPERIENCE AND CASE STUDY AT GNFC

Dr. R. K. Sharma, Mr. L. R. Patel & Mr. M. M. Bhatt.

GNFC, Bharuch, Gujrat

ABSTRACT

Deposit control is the most critical aspect of cooling water treatment because it is directly related to very purpose for a cooling system heat removal. Any deposit present in heat transfer surfaces impairs heat removal and there for reduces the efficiency of entire system.

Cooling water deposits are of two types - scales and fouling. Scales are hard dense, crystalline deposits formed by the precipitation of dissolved materials when their solubility have been exceeded due to change in conditions. Foulants form softer non crystalline deposits because suspended materials settle out or adhere to metal surfaces.

INTRODUCTION

Deposit control is the most critical aspect of cooling water treatment because it is directly related to very purpose for a cooling system heat removal. Any deposit present in heat transfer surfaces impairs heat removal and therefor reduces the efficiency of entire system. Unless deposition is properly controlled, it can negate the effectiveness of an expensive and well designed cooling water treatment and its system.

This direct effect on cooling efficiency has always required deposits control be an integrated part of cooling water treatment programs. The potential for deposition is increased by the trend to conserve water and the need to use more environmentally acceptable material for controlling corrosion and deposition. To conserve water higher cycles of concentration are being used, this increased the levels of scale forming or fouling material in the water. The need to use Non-toxic corrosion inhibitors is also increasing the potential for deposition. Since many of these less toxic corrosion inhibitors are more effective at high pH conditions, scaling potential is increased, while the effectiveness of many micro biocides is decreased. Meeting the need of these conflicting objectives, require a good, understanding of the effects and cause of deposition and their control by adopting new methodology like **on line chemical cleaning and its monitoring, to sustain high production level of the plant with out its shut down.** This paper deals with this subject.

EFFECT OF DEPOSITION

Deposits affect cooling system operation both directly/indirectly. Heat transfer can be reduced directly due to the insulating effect of a deposit as shown in Fig-1. Deposits have lower thermal conductivities than the metal wall of tube and there after act much like insulation to impair rapid heat transfer. Deposition can also reduce cooling because it restricts water flow, across heat exchangers and increase AP. Reduced heat transfer increases production loses due to reduced efficiency.

Deposits besides reducing cooling efficiency, can initiate leaks in the system by promoting localized corrosion. The phenomenon is described as under deposit corrosion.

COOLING WATER DEPOSITES AND THEIR CONTROL

The sources of potential deposits are as diverse as the effect of these deposits. Potential deposits can enter the cooling system through the make up water, from the air, through process contamination, as well as being formed within the system through corrosion. Make up water may contain both dissolved as well as suspended materials, which can forms deposits. The scrubbing action of a cooling tower can introduce considerable quantities of dissolved gases, dust, dirt and other particulates matter carried by the air. Process contaminants are as diverse as the number of products manufactured and may enter through leaks and plant upsets etc.

COOLING TOWER DEPOSITS ARE TWO. TYPES: SCALES AND FOULING.

A. Scales : Scales are hard, dense, crystalline deposits formed by the precipitation of dissolved materials when their solubilities are exceeded due to condition changes.

Calcium Carbonate is the most common scale in cooling water, whose solubility is very low about 13 ppm. Other common scales of cooling water are Calcium Sulfate, Calcium Phosphate, and Calcium Fluorides etc. Scale occurrence in cooling water system is observed as shown below in table 1.

Calcium Phosphate
Calcium Carbonate
Silica
Calcium Sulfate
Calcium Fluoride

Table 1

1. Calcium Phosphate scale : Calcium Phosphate has become leading form of scale, due to phosphate based corrosion inhibitor. When orthophosphate is present in the water, calcium phosphate scale is formed, inhibit heat transfer and lead to under deposit corrosion. The formation of $\text{Ca}_3(\text{PO}_4)_2$ scale is governed by the pH, Calcium and Phosphate concentration and temperature of recirculating water.

The application of PBTC + HEDP polymer have reduced calcium phosphate deposits. They have performed well with Ca^{++} levels up to 450 ppm as CaCO_3 with total phosphate 10-18 ppm as PO_4^{3-} The copolymers of poly melates and poly acrylates have exhibited good calcium phosphate scale control.

2. **Calcium Carbonate:** Calcium carbonate is the most common scale. Fig. 2 shows the relation ship of temperature to the solubility of calcium carbonate. The calcium carbonate deposition is influenced by pH, Calcium and alkalinity level in cooling water.

Several new phosphonates are providing exceptional control to calcium carbonate scale, because most of these polymers act as crystal modifier. Outstanding among these is one known as Phosphono- butane-tricarboxylic acid (PBTC). The use of 50:50 PBTC: HEDP, with 3-5 ppm level is found effective under severe scaling conditions. The blend has enabled our system to tolerate the calcium hardness up to 450 - 500 ppm, with total hardness up to 900 - 1000 ppm level, in circulating cooling water in different plants at GNFC.

3. **Calcium sulfate:** - Specially sulfate ions replaces alkalinity when sulfuric acid is fed to cooling water system to control system pH, but sulfate scale poses limited solubility, exhibit serious problem to cooling water system operation, since its solubility decreases as temperature increases *(Fig. 2). Sulfate scale control has been achieved by charging the polymer like poly aoylate / poly acrylamide at 2-3 ppm level in cooling water containing 500 ppm calcium as calcium carbonate.

4. **Silicate scales :** - High operating cycle of concentration based on silica and the rising use of reclaimed water are accountable for high silica levels in circulating cooling water. The formation of silicates can be prevented by limiting silica levels in circulating water max. up to 150 ppm as SiO_2 , although precise limit is dependent to make up water SiO_2 with respect to the operation of cooling tower on high cycle of concentration based on silica.

To prevent magnesium silicate deposition, magnesium and silica concentrations are controlled, so that the following solubility product is not exceeded.

$$(\text{Mg, ppm as CaCO}_3) \times (\text{SiO}_2, \text{ ppm as SiO}_2) \text{ is } < 40,000$$

New treatment (ter polymers) has been developed to increase silica solubilities attainable in cooling water system.

B. FOULING : - Foullants form softer non-crystalline deposits because of suspended materials settle out or adhere to metal surfaces. Silica besides being scale is also one of the common foulants. Fouling with materials high in silica is common because suspended solids, mud, slit and dirt are common in most surface water. The extent of fouling from sediments in circulating water is a result of the time afforded the particle to settle. Since cooling water basins, water boxes and shell side flow area involve appreciable holding times as a result of their size and the low velocities through them, the settling of sediments remains extensive, in above areas.

Polymers of high molecular weight (300,000 to 15 million) at doses level of 0.5 to 1.0 mg/lit. are commonly used. They attract fine foulant particles on to polymeric chain, forming large puffy particles that are easily removed from heat exchangers surfaces. Non-toxic low foaming wetting agents such as poly oxyalkylane have provided improved control on gelatinous and oil base foulants.

Functional mechanism of organophosphonate / polymer in reduction of scale & fouling in cooling water

Organophosphonates are one of the best deposit control agents. The Threshold and crystal distortion property of these compounds interferes with nucleation of hardness of crystals causing much higher levels of hardness to stay in solution. When scales are formed they are distorted that they are non-adherent and form very soft sludge.

Phosphonates also provides excellent control of hydrated ferric oxides deposits, which are formed as a result of corrosion. They adsorb on the particle surfaces and reduce the attraction forces between individual iron particles. The sequestering ability of phosphonate enables it to control heavy metals (Fe,Cu, Zn) deposits. Phosphonates also help to disperse suspended particles.

Low molecular weight polycarboxylic polymers also exhibit threshold and crystal distortion property. When used in conjunction with organophosphonate, poly phosphate and zinc, they aid in corrosion inhibition / deflocculation, dispersion and crystal distortion, leading to soft scale.

Leading scale control agent and methods are shown in Table 2.

Agent	CONTROL ACTION		
	Solubilization	Dispersion	Crystal modification
Phosphonate			
HEDP/AMP	Primary	-	-
PBTC	Primary	Moderate	-
Polvacrylate Copolymers			
Acrylate / maleate	Slight	Moderate	Primary
Acrylate/acrylamide	Primary	Moderate	Slight
Ter Polymer			
Maleate/Acrylate/sulfonate	Slight	Slight	Primary
Acrylate/Acrylamide/sulfonate	Slight	Moderate	Primary

Table 2

ONLINE CHEMICAL CLEANING AND ITS GAIN :-

On line chemical cleaning of E-405 (Reactor gas condenser) and E 509 (Refining column condenser) was done first time in GNFC on 15th Sept. 2000 and subsequently done on 30th Nov. 2000 and 1st Feb. 2001. Sulfamic acid was used with anticorrosive material and pH of the recirculating water was brought down to 2.8 - 4.0 for about 2 hrs.

The acid cleaning was followed by flushing the heat exchangers with low molecular weight polymer along with biodispersent to remove any available loose scale / fouling, either in tube side or shell side.

On completion of chemical cleaning the cooling water equipments & piping were passivated with double dose of treatment chemicals charged.

During chemical cleaning the Turbidity of E 405 out let shot up to 77 NTU and E 509 out let Shot up to 61 NTU. The E405 & E509 out let pH and Turbidity is shown in Fig. 3 & Fig. 4. The turbidity observed high due to removal of scale of Mg, Zn, Fe phosphate etc. The total hardness of circulating water has gone up from 360 ppm to 500 ppm, total solids from 916 ppm to 1620 ppm, Fe from 0.44 ppm to 1.28 ppm. The water analysis before, during chemical cleaning and after passivation is shown in Table-3. The relationship of

Zn, Mg & P₀₄ is shown in Fig 5 & 6 for E405 & E509 heat exchangers, which were responsible for poor heat transfer and limiting the plant, load, resulting in low productivity of methanol. On their successful cleaning plant production has gone up. The condenser and refining column data before and after chemicals cleaning are placed in Table-4. These data shows the effectiveness of on line chemical cleaning of deposits of scale on shell sides of E405 and tube sides of E509.

ADVANTAGES OF ON LINE CHEMICAL CLEANING

1. Plant shut down has been averted.
2. Production of methanol has gone up by 5 to 6 MT / day, as shown in Fig. 7.
3. The reactor gas condenser (E 405) cooling water out let temperature has gone down from 54 to 49°C i.e. 5°C, which enhance gas processing capacity of exchanger.
4. E 509 refining column condenser pressure dropped from 0.94 bars to 0.41 bars on 30th November cleaning and was hold there. The %valve opening of cooling water reduced from 100 to 26 %, hence the refining column efficiency has gone up to process more crude methanol.
5. The return header cooling water temperature increased by 1°C, which indicates high heat recovery with circulating cooling water rate of 3500M³/Hr.
6. Commercial gain, due to in-house technical development & its execution.

The details of chemical cleaning, with removal of different type of scales and foulants, with variation in cooling water pH and application of low molecular weight polymer with biodispersent to ensure the control of scale and biofouling with planned dose of corrosion & scale inhibitor to overcome the corrosion & scale formation and to sustain high production of methanol, without plant shut down, is over all theme of this paper.

ACKNOWLEDGEMENT

The authors are thankful to GNFC management for allowing to carryout on line cleaning of critical heat exchangers like E405 / E509 and MeOH II plant operation group members and M/s. Chembond chemicals personnel for their valuable support in making on line chemical cleaning successful.

REFERENCES

1. Sharma R.K., Patel L.R. & Bhatt M.M. : "Monitoring & Evaluation of cooling water of NP Complex plant, based on improved inhouse treatment"; *Indian Fertilizer Scene Annual 2000-2001*.
2. "The role of organophosphates in cooling water treatment ." D.J.Banerjee; vol. 4, No.3 ,1981, corrosion & maintance.
3. "Principles of Industrial water treatment." Drew chemical corporation.
4. "Scale & Deposits control in cooling water systems." Jeffery R. Townsend, 1978, Drew Chemical Corporation.

Analysis report of MeOH II Cooling Water during on line chemical cleaning of the E405 / E509 exchangers by sulfamic acid (HSO_3NH_2) on 01/02/2001.

No	Test	Unit	Result						
			Before	E-405 O/H01/2/01)				E-509	Basin
			01/2/01	15:45	16:00	16:35	16:45	16:45	11:30
1	P'	-	7.0	2.9	2.7	3.6	2.8	3.1	7.1
2	Conductivity	p. mhos/cm	1118	1519	1642	1467	1660	1380	1164
3	Turbidity	NTU	22	61	61	66	77	61	43
4	Total alkalinity as CaCO ₃	PPM	46	-	-	-	-	-	56
5	Total Hardness as CaCO ₃	PPM	360	500	490	500	500	490	428
6	Calcium Hardness as	PPM	234	260	250	250	260	250	228
7	Magnesium Hardness as CaCO ₃	PPM	126	240	240	250	240	240	200
8	Iron as Fe	PPM	0.44	0.91	1.17	1.01	1.28	1.01	0.63
9	Chlorides as Cl	PPM	188	200	200	200	200	200	154
10	Free Chlorine	PPM	0.5	nil	nil	nil	nil	nil	0.5
11	Silica as SiO ₂	PPM	56	53	55	56	56	57	57
12	Ortho Phosphate as PO ₄	PPM	2.7	6.1	7.0	8.3	7.5	7.1	11.8
13	Poly Phosphate as PC>4	PPM	1.9	3.8	3.5	3.9	3.6	3.8	5.7
14	Organo Phosphate as PO ₄	PPM	3.0	3.8	4.2	7.3	7.1	5.5	8.2
15	Zinc as Zn	PPM	0.8	2.14	2.00	2.43	2.29	2.20	2.32
16	Ammonia as NH ₃	PPM	-	nt	nt	1.0	2.0	2.0	8.1
17	Sulfate as SO ₄	PPM	-	250	225	200	175	188	275
18	Total Solids	PPM	916	1424	1498	1492	1620	1296	1202
19	Total dissolved solids	PPM	-	1360	1434	1420	1540	1232	1158
20	Total suspended solids	PPM	-	64	64	72	80	64	44

Table 3

DATE	E 405		E-509	
	I/L temp.	O/L temp.	Press	% Valve open
27-01 01	103	52	0.41	52
28-01 01	103	52	0.41	50
29-01 01	103	53	0.41	62
30 01-01	103	53	0.51	100
31-01-01	102	53	0.51	94
01-02-01	103	54	0.46	100
02 02-01	102	51	0.41	29
03-02-01	102	51	0.41	30
04-02-01	102	49	0.41	19
05 02-01	101	49	0.41	25
06-02 01	102	48	0.41	24
07-02-01	102	48	0.40	27
08-02 01	102	48	0.42	24
09-02-01	104	48	0.41	25
10-02-01	102	48	0.41	26
11-02-01	103	51	0.41	43
12-02-01	102	49	0.41	31
13-02-01	101	48	0.41	26
14-02-01	104	50	0.41	25
15-02-01	102	50	0.41	26
16-02-01	102	49	0.42	26
17-02-01	102	49	0.42	24
18-02-01	103	51	0.41	39
19-02-01	104	54	0.42	47
20-02-01	104	52	0.42	50
21-02-01	103	52	0.41	41
22-02 01	102	49	0.40	27
23-02-01	100	49	0.42	22
24-02 01	102	50	0.42	59
25-02-01	102	51	0.42	59
26-02 01	102	51	0.42	57
27-02-01	101	51	0.42	53
28-02-01	100	47	0.42	26

Table 4

INSULATION EFFECT OF A DEPOSIT

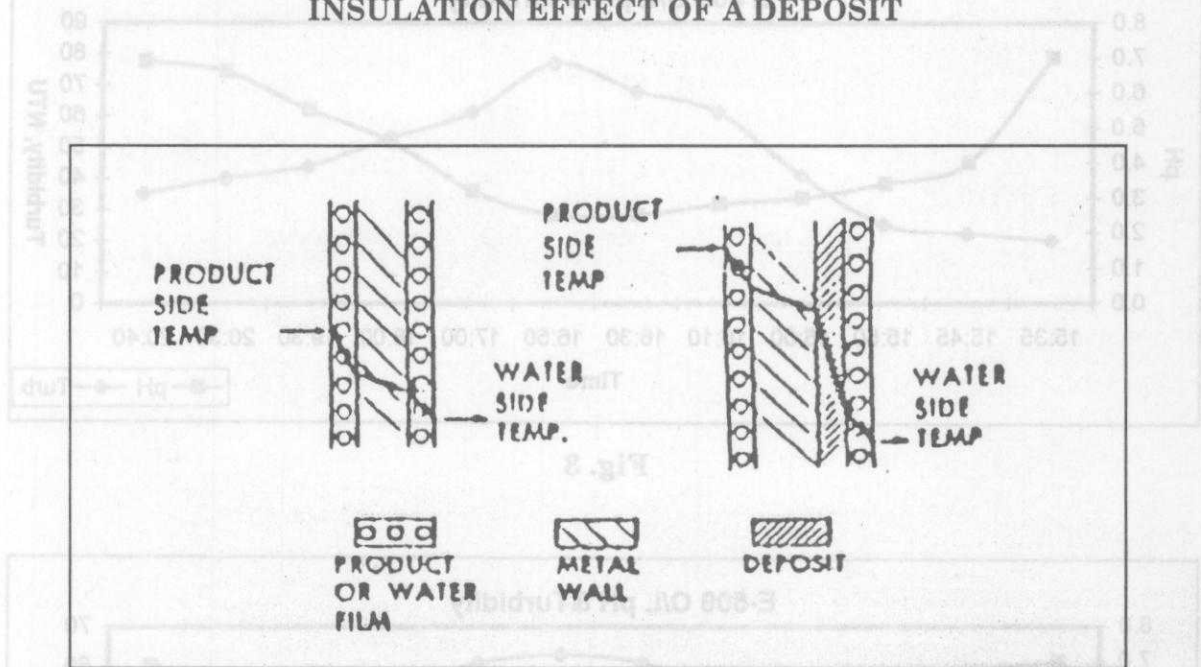


Fig. 1

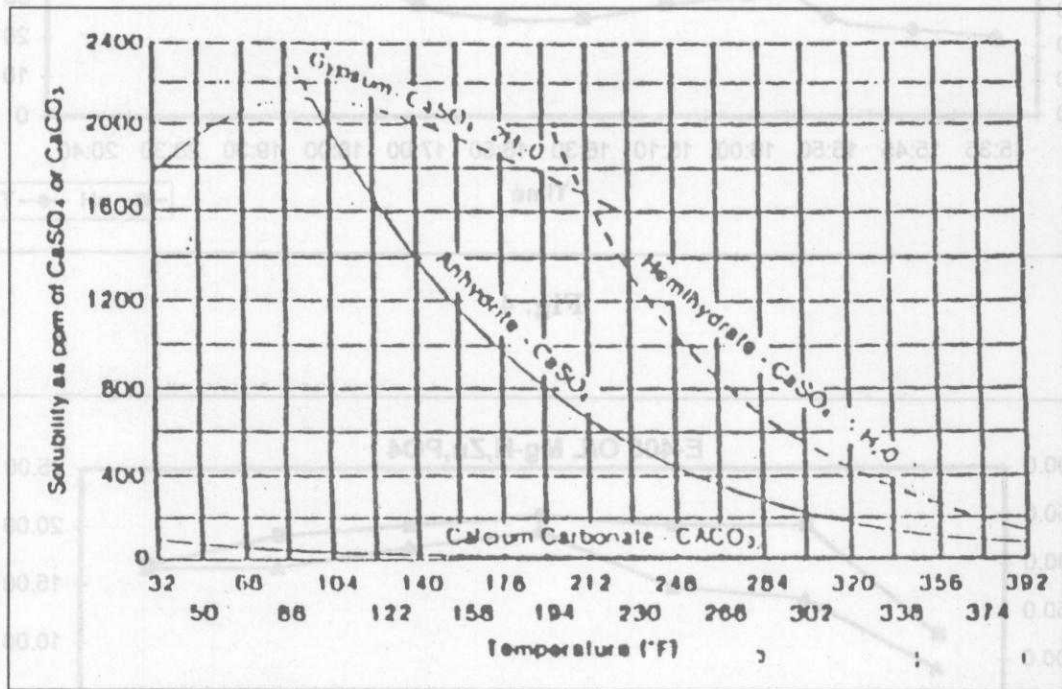


Fig. 2

Comparison of solubilities of calcium sulfate and calcium carbonate solubility in equilibrium with normal carbon dioxide content of the system

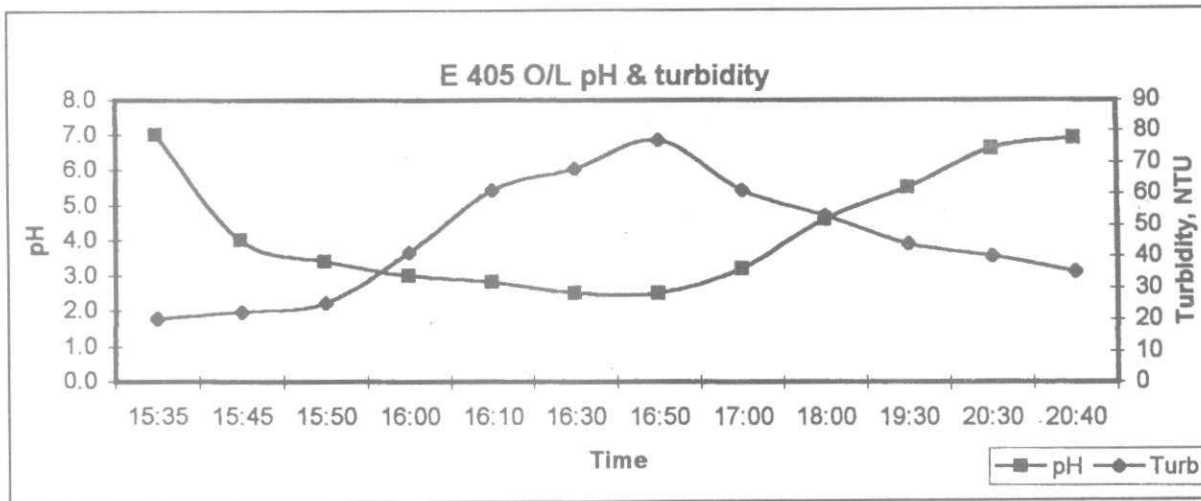


Fig. 3

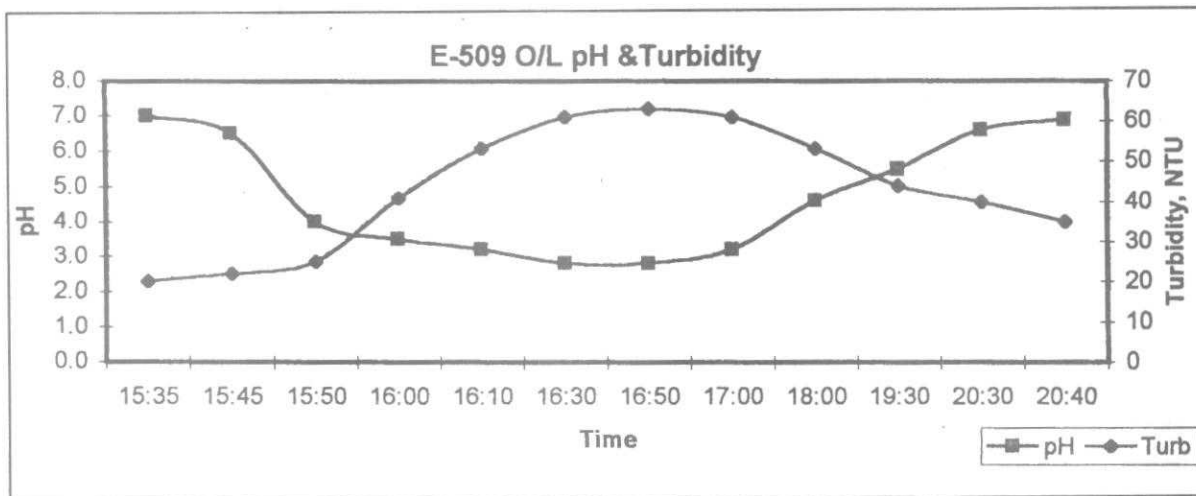


Fig. 4

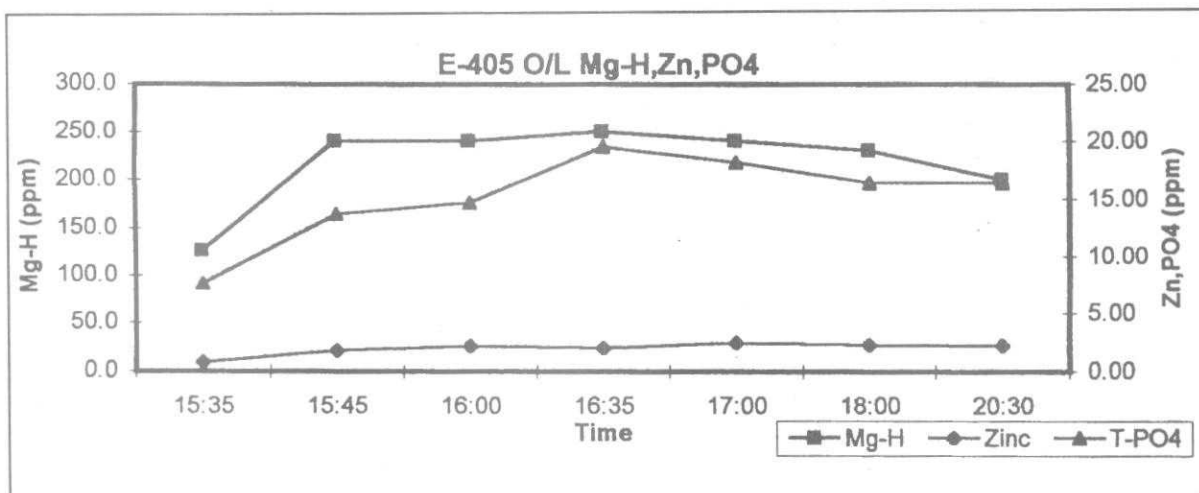


Fig. 5

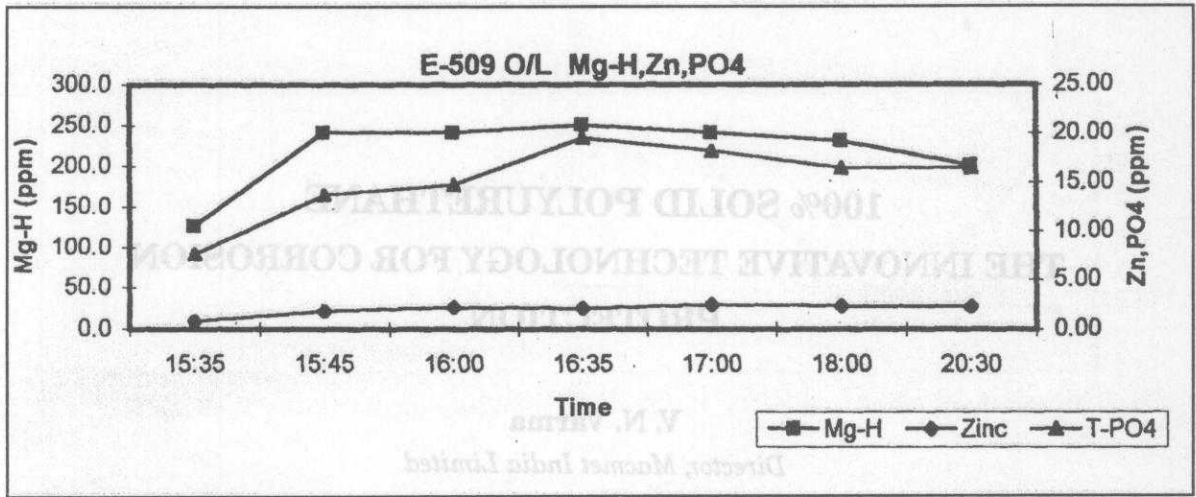


Fig. 6

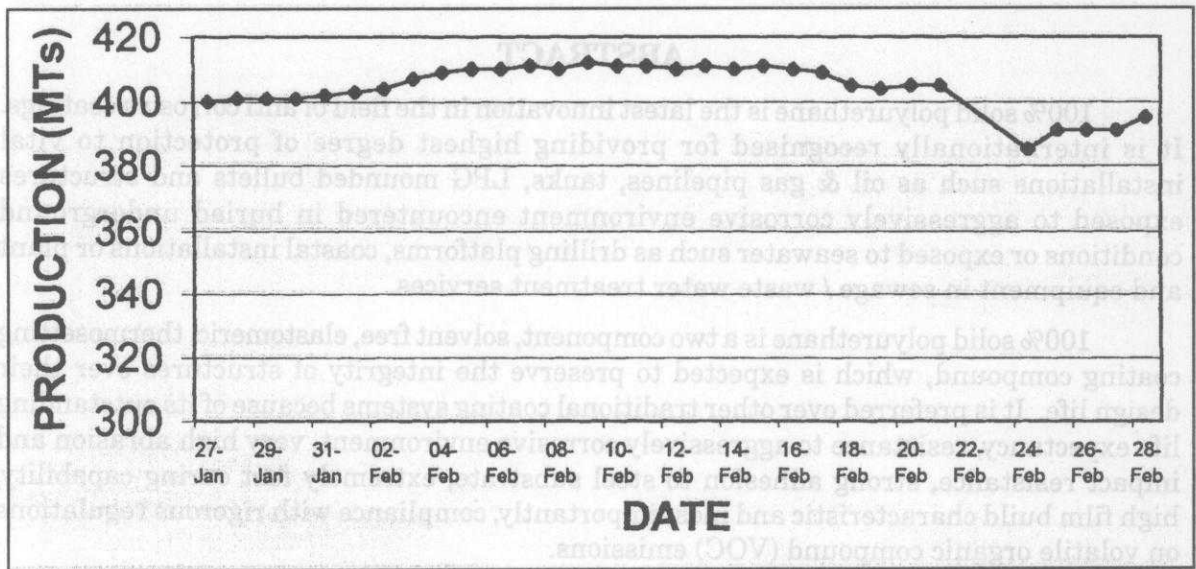


Fig. 7

In India, the concept of 100% solid polyurethane coating has come in only recently. Major oil and gas companies and reputed engineering consultants are now recommending its use to protect critical installations such as LPG rounded ballast, rehabilitated old pipelines where conventional coating have failed, field joint of cross country pipelines, internal linings of intake water pipelines in power plants, equipment employed in waste water treatment plants etc.

This paper discusses in depth the chemistry of 100% solid polyurethane, its properties & physical characteristics, equipment and application techniques as also the various advantages.

What is Polyurethane?

In its simplest chemistry, it is a product of reaction between two components viz. a polyol & an isocyanate. There are literally hundreds of different grades of polyols and thousands of isocyanates available to a polyurethane formulator to choose from, resulting in numerous permutations and combinations. Accordingly, properties of polyurethane vary from very soft and rubbery elastomers to tough and hard ceramic like systems. Polyurethanes also come in a wide variety of shapes and forms, such as: