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DEVELOPMENT OF EXPERTISE IN FERTILIZER PLANT OPERATIONS

DP/IND/85/006

REPUBLIC OF INDIA

Technical Report: Report on the Visit to India*

Prepared for the Government of the Republic of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of David G. Hooper
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United Nations Industrial Development Organization
Vienna

MADRAS FERTILISERS LIMITED

REPORT ON VISIT OF D G HOOPER ON BEHALF OF UNIDO

TO MFL, INDIA TO DISCUSS

WATER TECHNOLOGY MANAGEMENT

MARCH 8 - 10 1988

CONTENTS

This report contains the basic conclusions reached regarding the Water Technology aspects of MFL operation at Madras and more detailed notes on some of the discussions and key questions put forward by MFL personnel.

CONCLUSIONS

1. On the whole the system is operating well and there are few failures of the boiler and cooling system.

2. Regular failures of the synthesis gas compressor turbine may involve some design problems but deposits suggest less than adequate steam purity. Investigations into steam purity should be carried out to ascertain the reason for carry over.

3. High levels of caustic and chloride in the boiler water are traced to a probable shortage of cation resin in the mixed bed. The resin interface should be set up accurately.

4. A further way of reducing caustic (and hence reducing TDS and possibly improving steam purity) is to dose neutralising amines. It is concluded that this could be done and the checks necessary to prove this are highlighted.

5. The future water supplies to the site are being reviewed. The likely choice is tertiary treated sewage effluent. This is a matter of fundamental importance to the site as a whole and resources should be allocated to resolving the complex issues which cannot be accomplished by discussion alone.

6. The choice of cooling water inhibitor is under environmental pressure. Technically it is far better to retain chromate - especially if future water quality (see 5) deteriorates. Non chromate programmes are likely to be both 2-3 times more expensive and less effective.

1.0 PRE TREATMENT AREA

1.1 Intermediate Storage

The supply of well water would normally be expected to be clear but by putting it into open ponds, weed and algae have become established and fish and other animals have colonised them. This necessitates frequent cleaning and chemical dosing was discussed as a way of controlling the problems. This is likely to cause further problems (equipment purchase, maintenance, control and operation plus detrimental effects to the demin plant and boiler). It is recommended that covering the tank to exclude the light is the best solution. This will have the added benefit of considerably reducing evaporation losses.

1.1 Cold Lime Softening

The water at MFL lends itself well to cold lime softening (CLS) due to its high hardness and high alkalinity. The high proportion of magnesium hardness is likely to cause some problems in as much as $Mg(OH)_2$ - the form in which it is precipitated - tends to form a light gelatinous floc which can be difficult to settle. For this reason control needs to be particularly good or excessive turbidity will occur.

There is no reliable and effective on line instrumentation for monitoring and controlling the performance of such softeners. Turbidity meters can be bought but they foul quickly and drift such that the measurement is better done manually. For true control of CLS units the relationship between alkalinity and hardness must be monitored. No successful on line instruments exist to do this. For example, in a properly softened water, the following conditions should normally be fulfilled.

i)   The total alkalinity must exceed the residual hardness

ii) The caustic alkalinity must exceed the residual magnesium hardness

iii) The carbonate alkalinity must exceed the residual calcium hardness

To fully control turbidity in the MFL water it is expected that a coagulant would have to be used eg. sodium aluminate or ferric sulphate or an anionic or non-ionic poly electrolyte. Correct pH control at pH >10 should leave no residual coagulant. Lab tests would be needed to find the best coagulant and its optimum dose, as over dosing can be as ineffective as underdosing.

Discussions covered the recovery of boiler blowdown by returning it to the CLS plant. My belief is that this is a good idea although I have no practical experience of it. References refer to potential problems in CLS plants in British ambient conditions but the hot lime/sodium phosphate process is used where temperatures of $90^{\circ}C$ and excess caustic alkalinity to give pH> 10.5 produce excellent quality waters. A few laboratory tests would quickly indicate any potential problems at MFL.

It is recommended that these are carried out as it is an excellent way of saving water and energy although a maximum temperature of 40°C is recommended for water fed to a Type II anion exchange resin (60°C for a Type I)

1.3 Post Precipitation Exit CLS

Post precipitation is a common problem in CLS units often due to the occurance of supersaturated solutions of $CaCO_3$ or $Mg(OH)_2$. This is usually due to departures from the equilibrium of the simple chemical reactions. Precipitation shculd be as rapid as possible but this may be hindered by certain organics eg. from sewage or levels of phosphate (see above). The rate of formation of the precipitates can be increased by the following means:-

i)   Increasing the temperatures, which speeds crystallisation and reduces the solubility of the precipitates.

ii) Using an excess of the reagents to reduce solubility

iii) Mixing the reagents well with the water

iv) Stirring or agitating the water to bring super saturated solution to the solid surfaces

v)   Bringing the water into contact with preformed particles of precipitate or grains of sand which can act as nuclei for the precipitation

Due to the complexities of approaching equilibrium there is no way if specifying minimum levels in the outlet which will cause post precipitation. The plants own experimental results are of the most use.

1.4 Dust Problem with Powdered Lime

The use of powdered lime for softening is common and the better the quality the fewer the problems with preparing suspensions. Dust can always be a problem but its solution is the logistics of handling the bags. Lime should be lifted in bags and dropped a short distance from above into the water. It should not be lifted, loose, from below.

1.5 Disposal of CLS Sludge

The disposal of softener sludge is a perennial problem to all CLS operators. Mixing with spent HCl from the demin plant is a good idea to neutralise the acid and solubilise some of the sudge but there is no convenient use for such a sludge.

2.0 DEMINERALISATION AREA

2.1 On Line Instruments

Operation of the demin plant directly effects the life and economics (blow down) of the boilers. As such it is vitally important that it operates reliably to produce the correct quantity of water at the correct quality at all times. To enable this it is important that on line instruments at the outlets of the working vessels are in commission. The minimum requirement in my opinion would be conductivity exit the anion and mixed bed and silica analysis exit the mixed bed. The use of sodium or pH meters are useful but there is no convenient way or real need to monitor for other specific ions eg chloride.

A sodium monitor exit the cation (or a pH and conductivity meter exit the anion) will indicate when a cation unit is exhausted or there is high slip from the bed. High sodium slip will lead to excessive caustic in the boiler or overloading of the mixed bed and will significantly reduce the operating capacity of a type II anion exchange resin by causing early silica break through (partial regeneration on line).

2.2 Resin Life

Cation resin should last many years and will probably never need to be fully replaced. A certain amount of attrition will occur or resin loss through mechanical damage to the vessels, which will need to be made good but otherwise there should be no need to replace it. Failure of units to operate is usually due to :

i) Mechanical loss of resin (irreversible).

ii) Failure of addition of acid

iii) Consumption of acid by some other material eg excessive carryover of floc from the CLS plant or filter failure.

Anion resins, however, do lose their chemical activity over a period and will need regular replacement. Organic materials or high temperatures (>40 degree C) both cause this. The main cause is reversion of quaternary ammonium groups to tertiary groups on the resin matrix. This results in early silica breakthrough and hence reduced operating capacity. A lab test for total capacity will show little change from new resin but the weak base capacity will have increased by the same amount that the strong base capacity has decreased. The resin could continue to operate as a weak base resin if required but its ability to remove silica is irreversibly lost.

A further factor governing the rate of degradation is the inherent quality of the resin in the first place. There are several suppliers of resin available but the choice of resin is too important to be based on simple price alone as sudden resin failure could mean the complete closure of the complex. Penal guarantees should be sought from suppliers in terms of free extra resin/free recharge or money back terms if a replacement resin does not match, say, the practical performance of a resin that was satisfactory to the plant. This will not totally safeguard against failure but it will promote better technical discussions and understanding of the risk. For example, it is better to buy a resin that is 20% more expensive if it will last 40% longer.

2.3 Failure of Laterals

Discussions were held on the possible causes and remedies for the frequent failure of laterals and internals in the exchange units. The most frequent causes are :

i)   Compaction of the resin due to excessive time on line, high fines content or accumulation of dirt such that on back washing the resin lifts as a plug with a piston effect to break internals.

ii)   Water hammer due to fast valve operation or mixtures of gas and water being in a pipe.

iii) Incorrect flow patterns eg putting high full bed backwashes through control laterals instead of top internals.

Occasionally the solution is to provide more engineering support to the laterals, but usually it is to lessen dirt (improve water quality or improve backwashing efficiency) or review all valve sequence operations eg in mixed bed operation no backwash should ever come out of the central laterals.

2.4 Chemical Regeneration - Ejectors versus Pumps

Both systems are used but the only problem with ejectors is a susceptibility to increased back pressure. They are simpler, require less maintenance than pumps; their performance rarely varies once set up and they require no pressure relief devices downstream involving corrosive liquids. In general, ejectors are preferred.

2.5 Resin Vessel Charging

Portable ejectors can also be used for this duty. The resin can be added to a small tank to which there is a flow of good quality water. Simultaneously the ejector is used to empty the tank. The fluidised resin will transfer and can be directed to an exchange vessel 20 cubic metres of resin can easily be transferred in an hour. Centrifugal pumps should never be used to transfer resin.

2.6 Materials for Handling HCL Regenerant

Glass reinforced plastic (GRP) or mild steel rubber lined equipment is widely used. Fuming of the acid is a problem and in my experience fume scrubbers rarely work unless grossly oversized. The vapour causes excessive external corrosion to local equipment. GRP or plastic coated pipes will limit this or frequent painting.

See also Boiler Area - Caustic and Chloride level in the boiler Section 3.3.

3 BOILER AREA

3.1 Alternatives to Hydrazine

Hydrazine chemically scavenges the residual oxygen from a mechanical deaerator and it, or an alternative must ALWAYS be used. There are several alternatives eg di-ethyl hydroxylamine, methyl-ethyl ketoxime, carbohydrazide, pyrogallols, hydroquinones, erythorbic acid and sulphites. Much debate has been initiated by sellers of the above regarding the toxicity and carcinogenicity of hydrazine and therefore the need to use (their) alternative. The latest evidence is very strongly that hydrazine is not carcinogenic to man. It is, like many other chemicals, toxic and should be handled with care but it is the cheapest and best tried of all those available for boilers such as those at MFL and in my opinion should be retained.

3.2 Blowdown Management

In principle, demin water should have only traces of ions in it and the chemistry should be dictated by the dosing at the plant. Thus, for a constant feed water quality, blow down rate and boiler load, no change should occur in any parameter eg P-alkalinity should not rise. Subtle, almost unmeasurable changes in feed quality eg ammonia from condensate or sodium leakage from the demin plant will cause changes. There is a danger that the boiler never reaches equilibrium from the last change and if adjustments are too frequent the boiler will never reach steady state. It is recommended that, emergencies excepted, blowdown is set at approximately 2% as a continuous rate and is not adjusted.

If parameters such as Fhosphate, TDS or alkalinity start to drift too high, then reduce the chemical dosing to bring them under control. Increasing blow down due to excessive dosing is not sensible practice.

3.3 Caustic & Chloride Levels in the Boilers

The caustic levels appeared very high and by modern standards are considered excessive. Caustic is dosed into the common demin water to raise its pH>8.5 to protect the boiler feed systems and tri-sodium phosphate is dosed to each individual boiler drum. Some dosing of the feedwater is undoubtedly required to protect the economisers and fed heat systems but the use of caustic can be questioned.

The levels of chloride in the boiler are very high and it is understood that low pH is seen at the end of a mixed bed regeneration using HCL for the cation. It is believed that the interface of the cation and anion resins has dropped below the central laterals resulting in acid contacting some anion resin. This leads to high chloride leakage initially and probably low leakage throughout the cycle run. The remedy is to add extra cation resin until, on backwashing, the interface is visible in the mixed bed window at just below the lateral position. (Regeneration of the new sodium form cation resin will increase its volume by 7 - 10%). This should improve mixed bed regenerations, reduce rinse, reduce chloride leakage, reduce the level of caustic required and reduce caustic and chloride in the boiler. Until this is done, 2% blowdown may not be attainable due to excessive concentration effects.

3.4 Use of Amines

Alternatives to caustic include neutralising amines eg morpholine, cyclohexylamine or amino methyl propanol (AMP). These amines would protect the feed water system at the 5-10 ppm level and they would also pass out with the steam to be present in the condensate to minimise corrosion in the condensate recovery system. It is probable that traces of ammonia are currently in the condensate (breakdown of hydrazine, leaks from machines) and this will benefit the system by reducing mild steel pipe and steam trap corrosion. Copper alloy materials are potentially at risk from primary amines (eg cyclohexylamine, ammonia and AMP) although less so from secondary amines (eg morpholine). However, the key factor is the oxygen level in the condenser due to air ingress. Elemental copper is not soluble in the above amines but if oxygen is present a film of copper oxide rapidly forms and copper oxide is soluble in amine solutions. Thus to minimise corrosion on copper alloys the oxygen level needs to be low and the concentration of amine should be limited. For example, with ammonia <5ppm and oxygen <0.02 ppm practical experience shows no copper corrosion. (Ref : Butler and Ison. Corrosion and its Prevention in Water). Experience at Billingham shows that pH 8.5 with 10 ppm of morpholine at up to 4 ppm of oxygen did not corrode 70:30 Cu:Ni (NB the presence of organic acids depressed the pH. In theory 10 ppm morpholine should give pH 9.2).

It is suggested that checks are made on MFL condensate to ascertain oxygen and ammonia levels to see how they compare with this experience. The addition of morpholine would avoid caustic desing in the feed water, reduce cuastic in the boilers, positively protect the mild steel parts of the condensate system and subject to the above, not cause any problem in the admiralty brass condensers. When there is no cooling water leak and condensate is put directly back into the deaerator, some morpholine will be lost, but much of it will recycle around the system thus cutting costs. If the condensate is put through the condensate polishing unit the morpholine will be removed on the cation resin.

Combination of amines with differing characteristics can be used but are probably not justified a site the size of MFL (Billingham uses only morpholine). Under no circumstances should a blend containing a filming amine be used if the condensate is ever put to a condensate polishing unit as it will irreversibly foul the cation resin.

3.5 Boiler Water Specification

Past operating experience on a boiler system is a good guide for the quality of water which can be used as the decision is somewhat heuristic. However, my current thinking for a 600 psi, demin fed boiler is summarised in Table 1.

TABLE 1

ANALYTE	NORMAL RANGE	MAXIMUM
$Na_3 PO_4$	10 - 30 ppm	50
pH	9 - 10	10.5
N_2H_4	0.02 - 0.04 ppm	No upper limit
SiO_2	1 - 5 ppm	20 ppm
P-alkalinity	0 - 5 ppm	10 ppm
TDS	20 - 50 ppm	100 ppm
Fe	0.05 - 0.2 ppm	0.2 (Indication of problem)
Chloride	0 - 1 ppm	5 ppm

3.6 Deposits and Carryover into Steam Systems

Deposits can get into steam systems and into turbines in two
distinct and independent ways.

(i) True solubility in steam (steam volatility)

(ii) Gross carryover of droplets of boiler water.

In the former, the only species of relevance in a 600 psi system
is SiO2 as the others are 10^4 or more times less soluble.
Experience has shown that SiO2 levels of <0.02 ppm in steam give
few problems in turbines. To better this figure it is necessary
to stay below 20 ppm in a 600 psi boiler at pH 9-10. At pH 11 a
theoretical level of 30 ppm SiO2 could be tolerated and at pH
12.1 approx 50 ppm.

Gross carryover of boiler water would lead to dryout in the
superheater (particularly in the primary) and the passage of some
constituents to the turbine where they could be expected to cause
damage. It is understood that at least sodium, chloride,
phosphate and silica have been found on failed wheels in the syn
gas compressor.

Carryover is likely to be caused by :

(i) Broken or missing steam separators
(ii) Poorly designed steam drum or levels set incorrectly.
(iii)Fluctuating levels in the steam drum
(iv) Fluctuating steam production rates
(v) Foaming in the boiler
(vi) Pressure surges in the steam main

Once the material has carried into the turbine the only method of
on-line cleaning is to reduce load and run wet steam or
condensate through the machine. This will remove soluble salts,
including crack initiators such as caustic or chloride but will
rarely remove silica. The only way to remove silica is to remove
the turbine for mechanical cleaning.

4.0 COOLING WATER AREA

4.1 Choice of Inhibitor Programme

Discussion centered on the choice between chromate and non-chromate inhibitor systems.

Four factors can be identified in cooling systems. They are :

i)   Scaling-deposition of sparingly soluble salts eg CaCO3
ii) Corrosion-reversion of metal to oxide eg plant to rust
iii) Fouling deposition of amorphous solids
iv) Microbiological effects

All can occur simultaneously and one may cause another but all have to be controlled by the inhibitor programme. The current chromate phosphate regime coupled with chlorination is undisputedly recognised world wide as one of the best technical programmes available. The programme is relatively cheap, gives low corrosion rates, is virtually free from scaling; limits microbiological growth; can quickly recover from low pH upsets by extra dosing; can recover from high pH upsets by extra acid dosing to a reasonable extent; can tolerate high skin temperatures; can tolerate low velocities (with extra dosing); moderately tolerant of ammonia ingress; easily analysed; is not effected by over dosing. Its major problem is its toxicity.

The alternatives currently available include: phosphate; phosphonate; zinc; combined zinc phosphate and all organic treatments. None are such good inhibitors as chromate so all are run at higher pH to limit corrosion. At higher pH the other three fundamentals become major problems and extra precuations must be taken to limit this effect.

Polymers are used to stabilise scaling and fouling species eg Ca, PO4 and Zn. Whilst they work tolerably well within very highly defined limits of pH and temperatures, they fail unforgivingly with upsets to high pH eg ammonia ingress; can recover from low pH upsets only if monitored closely but will fail if the polymer to ion ratio is not correct when reverting to the normal pH; cannot tolerate high skin or bulk water temperatures; cannot tolerate low velocities; are not easily analysed; fail if overdosed. Their deposit forming tendency is much higher than chromate and they produce much higher fouling factors. The effectiveness of chlorine is much reduced due to the higher pH and the use of continuous chlorination to overcome. This results in degradation of many of the stabilising polymers. The need to use non-oxidising biocides increases costs and the loss of the anti fouling properties of chlorine necessitates the use of further polymers as extra dispersants. Suspended solids critically interfer with polymers (by adsorption) and side stream filtration is usually required to keep solids as low as possible. The necessity for accurate dosing requires reliable positive metering systems.

It is estimated in the UK that non-chromate systems will cost two to three times more to run as a revenue cost and lead to two to three times more failures plus loss of efficiency requiring more cleaning if not controlled perfectly.

It is strongly recommended that from a technical and commercial point of view, the political and environmental pressure to change from chromates is resisted as long as possible.

4.2 Use of Zinc or Phosphate as a Synergist to Chromate

UK experience is that zinc (a purely cathodic inhibitor) is preferred to ortho phosphate (anodic) or tripolyphosphate (cathodic) which yields $O-PO_4$ by hydrolysis. Low pH and high temperatures enhance reversion to $O-PO_4$ and increase the dangers of pitting. High pH leads to calcium phosphate scaling. See Betz Polymers. Zinc can tolerate low pH but is lost in high pH such as with ammonia leaks or locally at the point of addition of CLS water (pH 10.5). It is possible that this caused the problems to MFL when zinc sulphate was used earlier. These points illustrate that synergised chromate programmes are not immune to problems and technical effort is still required. The fact that zinc is still found occasionally today suggests major deposits were laid down and are gradually being redissolved.

4.3 Use of Betz Polymer

Data collected by MFL staff showing improving fouling factors on key exchangers since the introduction of the Betz 2020 Polymer are a strong indication of the benefits in using this expensive chemical. In the longer term this will improve efficiency and reduce maintenance and failures.

4.4 Cooling Water Specification

Acceptable levels of ammonia, chloride sulphate and calcium were discussed. In general terms ammonia is preferred as low as possible due to interference with pH control and chlorination. In practical terms, it is not a deciding factor in, say, shutting down a plant. Chloride is similarly preferred to be low as higher chloride increases general corrosion. However, from a stress corrosion point of view, if exchangers are fully flooded, levels up to 1000 ppm have not initiated SCC in European and UK chemical plants. Calcium sulphate, despite its theoretically low solubility, is rarely a problem in open evaporative cooling systems. The dominant factor is the calcium concentration and provided this is <800 ppm as $CaCO_3$ levels up to several thousand ppm of sulphate can be tolerated.

Table-2 is a suggested specification based on the available make up water:

TABLE 2

Analyte	Range	Maximum
pH	6.5 - 7.0	6.0-7.5 (with Betz 2020)
CrO4	25-35	No max. Min 20 ppm
0-PO4	1-5	10 (with Betz 2020)
Poly PO4	1-15	20 ppm
TDS	1000-3000	3000 ppm
Ca	300 - 600 ppm CaCO3	800 ppm CaCO3
Cl	900 - 1000 ppm	1000 ppm

4.5 Future Cooling Water Requirements

Due to shortage of water in the Madras area (the local government withheld supplies for several months last year causing a total shutdown), MFL are actively considering alternative supplies. They are :

i)   Sea water cooling through an intermediate plate exchangers.

ii) RO or desalination of low grade or sea water

iii) Tertiary treatment of sewage effluent.

Of these the sewage effluent appears commercially and politically most attractive. Several flow sheets have been proposed but there is insufficient experience in the world to resolve many of the questions and significant testing will be required to optimise the capital cost and ensure reliability.

It is possible that combined CLS with cationic polymers or other coagulants directly on the effluent from the percolating filter clarifier could yield sufficiently high quality water to feed demin plants and cooling systems. High chloride concentrations could prove a major problem and partial demineralisation may be required for cooling tower make up.

5.0   ACKNOWLEDGEMENTS

The technical discussions were held with personnel from the Technical Services and production units.

Particular thanks are acknowledged to Mr M Nagarajan and Mr M S Rajappa who organised the meetings, visits, transport and refreshments etc.

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F A C T

REPORT ON SECOND VISIT OF D G HOOPER ON BEHALF

OF UNIDO TO FERTILISERS AND CHEMICALS TRAVANCORE

LTD. INDIA TO DISCUSS WATER TECHNOLOGY MANAGEMENT

MARCH 17 - 19 1988

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FN276

1.   Summary and conclusions

Due to industrial action on 14-16 March 1988, the visit had to be cut
short. One and half days were spent at Cochin Division, one day at
Udyogamandal Division and half a day in writing this report. Such a
consensed timescale will inevitably show in the quality of the report
for which apologies are made.

The follow up visit to FACT (Udyogamandal Division) was very
encouraging in that several of the earlier problems had been tackled
using the recommendations made at that visit. Even more encouraging
was that improvements appeared to be being obtained.

At Cochin Division, a series of problems were discussed including
pre-treatment, boiler water and cooling water programmes.

On the Caprolactam Plant; the commissioning approach used in new
plants was discussed eg. chemical cleaning and storage of equipment.
The subsequent boilers water treatment which would be required was
also discussed.

2.   Udyogamandal Division

2.1   Follow up to 1986 visit

This Division was visited in November 1986 and these
discussions were centered on the recommendations made in the
report of that visit and the progress FACT had made towards
implementing them. The following section should be read in
conjunction with that report.

2.1.1   Sulphuric Acid Plants

(Section 3, 1986 report)

New anion resin was installed in the plant and regular
manual silica analysis carried out on the exit water. The
beds are regenerated on a lower throughput and silica levels
of 0.02ppm have been typical up to a maximum of 0.2ppm with
a maximum of 20ppm in the boiler water. Tri-Sodium
phosphate is now dosed into the feed water to raise its pH
to 8.0 Typical boiler water figures have been as in Table
1.

TABLE 1

Analyte	Typical	1986 Specification
Phosphate as PO_4 ppm	30-35	20-40
Silica as SiO_2 ppm	20	2-40
		(2-10 normal)
pH	10.0-10.5	9.5-10.5
Iron as Fe ppm	0.1	0.2
TDS as ppm	100-150	35-100

No further failures have occurred which is very encouraging.
No chemical cleaning has been carried out nor is envisaged.

2.1.2   <u>Ammonia Plants</u>

(Section 4, 1986 Report)

The demineralised plant is no longer over-run. Since 1986 a
sample of deposit from the Flue Gas Boiler (FBG) has been
analysed. It was found to be mainly hydro-xyapatite and
iron. Calcium Phosphates should not be present in a DM
water fed plant and it is believed this has occurred due to
break through from the DM plant either through the earlier
mentioned over-runs or, more probably at times of major
upsets due to high salinity water ingressing the lagoons.
Whatever the cause, the requirement is still for the boiler
to be chemically cleaned. Chemical cleaning companies have
been approached but the concept had been for them to obtain
samples at the next planned shutdown with a view to cleaning
it in the following shutdown. It is recommended that this
programme is accelerated and the job carried out as soon as
possible based on the samples obtained so far.

2.1.3   <u>Cooling system</u>

(Section 5, 1986 Report)

In 1986 the absence of soluble zinc was highlighted as a key
reason why the cooling water programmes were not working
effectively. The site has instituted more regular dosing of
agents in a move towards reliable continuous dosing, and has
managed to attain levels of all the inhibitors in solution
as indicated in Table 2.

TABLE 2

Typical cooling water analysis

Analyte	Typical	1986 Specification
pH	6.5-6.7	6.5-7.2
CrO_4 ppm	20-25	20-30
Soluble Zn ppm	1- 2	1- 2
Total Zn ppm		1- 5
$MetaPO_4$ ppm	10-15	10-20
$OrthoPO_4$ ppm		5

Plant personnel considered that they were getting less
failures and less fouling of exchangers since implementing
these values.

There was still a tendency on the reform ammonia plant for
bacterial oxidation of ammonia to cause pH excursions down
to 5.5 which biocide dosing still controlled. The composite
ammonia plant system has had a side stream filter unit
installed since 1986. No data on its efficiency was
available.

2.1.4 Analytic.l Control

(Section 7, 1986 Report)

Investment had been made to purchase millivolt meters and
electrodes for pH analysis and an atomic absorption
spectrophotometer as suggested. These were in regular use
to provide the quality of analysis required for such a site.

2.2 Pre-treatment plant at Udyogamandal

See Section 4.1 where the comments on the Cochin Division
plant are of relevance in terms of start up and operation.

The new Dorr Oliver plant was not visited for lack of time,
but plant personnel explained that it was not working. Dorr
Oliver did not seem to be able to commission it and were
claiming that the current good quality of water was
incapable of being clarified. Jar test carried out by FACT
personnel indicated an optimum pH of 6.2-6.4 but Dorr Oliver
was insisting on 7.0-7.2. The following comments are
relevant:

i   The water is good at the present time, making
     clarification particularly difficult.

ii) The optimum pH for alum clarification is normally pH
     6-6.5. Higher or lower pH's will yield less floc and
     lighter (more difficult to settle) floc.

iii) Operating at pH 6-6.5 yields water corrosive to
     concrete and mild steel. To overcome this, higher
     grade concrete or coatings must be specified.

iv) No floc blanket had been established.

It would appear that there is a reluctance by Dorr Oliver to
operate at lower, more optimal pH's. Their pH has produced
little floc of poor settling characteristics making it
difficult or impossible to create a sludge blanket. This
has led to a failure of the plant to meet silica, iron,
aluminium or suspended solids specifications. The use of a
lower pH should improve all these characteristics but will
certainly lead to at least corrosion of the mild steel
scraper and pipework.

Alternative approaches which could be tested include:

i)   Use of polyelectrolytes
ii) Use of ferric rather than alum salts
iii) Use of aluminate

2.3 Choice of volatile Amine for Boiler Dosing

Discussion covered the choice between morpholine and
cyclohexylamine for boiler dosing (morpholine is imported)
cyclohexylamine is indigenously produced).

The key differences are that, while cyclohexylamine is a stronger base, it is more volatile than morpholine and therfore lost to the steam, more quickly. However, in condensation (as opposed to evaporation) the first formed condensate will not be alkaline so amine will dissolve and ionise. Once ionised it cannot volatilise but can act as a base. Up to pH 9 cyclohexylamine is 98% ionised. At pH9, morpholine is 18.6% ionised. Thus at the low pressure for the condensing turbine on the Udyogamandal captive power plant, it is possible that cyclohexylamine should work as well, if not better than morpholine. Table 3 gives some values.

TABLE 3

Quantities of Amine required

Amine	Pure Water	CO_2 containing H_2O
Morpholine	4 ppm for pH 9	2 ppm/ppm CO_2 for pH 7.4
Cyclohexyalamine	1 ppm for pH 9	2.3 ppm/ppm CO_2 for pH 8.1

It is recommended that trials are carried out with cyclohexylamine.

3. **CAPROLACTAM PLANT**

Discussions were held with construction/commissioning personnel on the caprolactam project.

3.1 **Commissioning Procedures for Water Using Equipment**

It is recommended that boiler systems are pre-commission chemically cleaned. This removes any debris from fabrication and construction and any rusting following pressure testing procedures. For pressure testing demineralised water can be used for stainless steel equipment but ammonia (50ppm) and/or hydrazine (200ppm) should be added for carbon steel equipment.

The general programme for a pre-commission chemical clean would be as follows:-

i)   Set up an external pumping and water storage system capable of overcoming system pressure drops to generate flushing velocities 1.5m/s. Three system volumes of water are required for flushing. Carry out flushing until clear.

ii)   Degrease. Heat to 80-90°C. Circulate alkali for 12 hours (tri-sodium phosphate at 1000ppm for light grease, 3% NAOH plus 1% $KMnO_4$ for bitumen coatings etc.)

iii) Drain and carry out high velocity flushing.

iv) Heat to 70°C. Add HCL to give 4-5% with inhibitor
Rodine 213. Circulate at velocities of maximum 1.0
m/s. Analyses for Fe and free acid. Fe 1.5% HCL 3%
when

 iron levels are stable (3-6 hours) drain.

v) Fill with 0.1% citric acid. Circulate for 30 minutes.

vi) Drain and carry out high velocity flushing

vii) Heat to 50°C. Add 0.5% citric acid. Circulate for 30
minutes.

viii) Add ammonia to give a pH 9.5

ix) Add 0.5% sodium nitrite. Circulate for 2 hours.

x) Drain and rinse free of nitrite. Final flush with
50ppm ammonia in demineralised water.

A key consideration in chemical cleaning is that chemicals are
flowing in all parts of the system. La Mont boilers are
particularly susceptible to partial flow and some techniques to
prove flow in each of the passes is required. The following have
been used:-

i) Radio-isotope pulse velocity technique

ii) Doppler meters

iii) Temperature monitoring

The best technique is the use of radio isotope. This should be
done before and after the clean to prove all is well.

Chemical cleaning can be carried out on steam mains rather than
steam blowing but this requires the use of hydrofluoric acid and
different welding specificiations at erection.

Insufficient time was available to fully discuss this technique.

Cooling water system should be flushed clear of debris and
pretreated with a solution of 1000ppm of trisodium phosphate by
circulating for several days. This should then be replaced with
water containing the normal levels of the inhibitor programme of
choice.

The boiler and steam system were briefly described but no
detailed flowsheets were available. From the description it
would appear to be important that a volatile amine is added to
boiler feedwater at the captive power plant. This will condition
the steam for all its uses and safeguard the equipment which uses
condensate directly as feed water. The choice would normally be
between morpholine or cyclohexylamine. See section 2.3. It is
suggested cyclohexylamine is tried.

4. COCHIN DIVISION

4.1 Clarifloculator operation

Poor floc formation has been seen and carryover of floc into the downstream pressure sand filters and cation units. During discussion it emerged that no floc blanket had ever been established and this is probably the root cause of the problems.

The water quality through the seasons is very variable and this variability will effect the ease with which coagulation and clarification can be carried out. Alum floc is always a fairly light one and the better the quality of the raw water the lighter the floc will be.

To aid the removal of the floc it is necessary to create as large a particle as possible. Slow mixing in the central chamber enhances this (too high a mixer speed will sheer the floc and defeat the objective). The floc passes downwards, with the flow of water and then radially outwards and upwards to the launder. Gravity causes the particle to fall but the upward flow causes it to rise. The rise rate in m/h ie. m^3/m^2h-m^3 flow per m^2 of surface are in one hour) must be less than the free fall rate of the particle or it (the floc) will be washed out as carryover. If a considerable amount of floc is kept in suspension in the radial chamber the medium size particles will collide and form much larger aggregates which will settle faster. Higher rise rates (flow rates for a fixed surface area) can then be attained still keeping the "floc blanket" suspended or fluidised. The dense nature of the blanket enhances the capture of newly formed floc, so, once a blanket has been established design flow rates can be attained and the new, light floc is trapped in the old, denser blanket. At this stage some of the floc blanket will need to be purged.
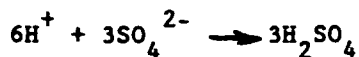
It can be seen that this is quite a delicate balance and clarifloculators do not tolerate rapid changes in flow rate, pH (effects solubility of floc) or temperature.

At start up, low flow rates and/or recirculating the sludge is required to establish a blanket as quickly as possible. This could take anywhere between 1-3 weeks.

Increasing the alum dosage will not create a heavier floc although it will create more. Aluminium salt in solution should not occur provided the pH is maintained at the correct level. In a low alkalinity water such as Cochin, adding excess alum is likely to significantly decrease the pH and increase aluminium solubility. The control of lime addition is critical. The optimum is usually in the region of pH 6.0-6.5

4.2 Effect of Clarifloculator on Anion Resin in Demineralisation Plant

When alum is added, hydrolysis occurs to produce and precipitate aluminium hydroxide according to:-

$$Al_2(SO_4)_3 \longrightarrow 2AR^{3+} + 3SO_4^{2-}$$

$$6H_2O \longrightarrow 6H^+ + 6OH^-$$

$$2Al^{3+} + 6OH^- \longrightarrow 2Al(OH)_3$$

$$6H^+ + 3SO_4^{2-} \longrightarrow 3H_2SO_4$$
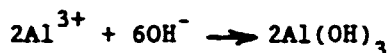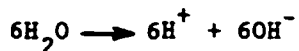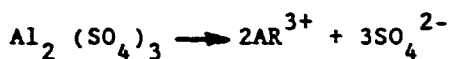
The sulphate has to be removed from the water by the anion resin. Therefore dosing alum directly increases the anion loading and shortens its run length while having no effect on the cation loading. (H^+ ions are not exchanges). Nothing can be done about this.

4.3 Boiler Water pH Control

Cochin have found difficulty in obtaining the specified pH 9.5-10.0 whilst obeying the maximum specification of 5ppm phosphate.

This is to be expected when using tri-sodium phosphate and my recommendations would be to operate at pH9.0-9.2 which is approximately what 5ppm phosphate will produce. It is not recommended to add caustic to raise the pH. The addition of morpholine would show no effect in the boiler water as the maximum pH obtainable with moderate levels of morpholine (up to 15ppm) is pH 9.2

4.4 Dissolved Oxygen Exit Dearators

Levels of 0.014 ppm O_2 against 0.007 ppm have been seen despite maintaining design conditions. World experience is that this is not unusual. Provided an excess of hydrazine is added to the feedwater eg. 0.2 ppm N_2H_4, no damage will result.

4.5 Cooling Water Treatment - PDIL study

PDIL were commissioned to make recommendations for treating the cooling system at Cochin (Ref.No.CRW/D(2) dated 21.4.87). Although my interpretation of some of the detail of the report and my final choice would be different, their general approach cannot be faulted. Where I do believe points of detail are important however, is in the final control parameters specified and analytical requirements.

PDIL have given no specifications for orthophosphate alkilinity or turbidity so it seems strange to ask for them to be measured.

They have not specified the form of zinc analysis in terms of total, or soluble. Both figures are required for correct control of such a programme. Only soluble zinc gives corrosion protection.

PDIL have specified a pH7.5-8.5. At such a pH nearly all the zinc will be lost as hydroxide or phosphate in the absence of a zinc stabilising polymer. Such a pH, on Cochin water will require the addition of alkali.

The best programme for Cochin would undoubtably be zinc chromate although I believe a phosphate or zinc/phosphate programme would be second best.

From the data supplied by PDIL I would put forward the following suggested specifications for their choice:-

TABLE 4

Suggested Non-Chromate cooling water specification

Analyte	Normal range	Min	Max
pH	6.8 - 7.4	6.5	7.5
Total hardness	60 - 80	50	200
Chloride			100
Total suspended solids	5 - 10		20
Organophosphorate	10 - 15	5	20
Meta-phosphate	5 - 10	5	15
Ortho-phosphate	1 - 5	1	5
Total zinc	2 - 5	2	2 ppm more than solZn
Soluble zinc	2 - 5	2	

N.B. Zinc chromate is still, technically, the best treatment and given a free technical choice this should be preferred to the following specifications.

TABLE 5

Analyte	Range	Min	Max
pH	6.5-7.2	6.5	7.5
Total Hardness	60-80		200
Chloride			200
Total suspended solids	5-20		50
Total zinc	5- 7	2	2 ppm more than solZn
Soluble zinc	5- 7	2	
Chromate	25-35	1	10 .

4.6 Corrosion in Heat Exchangers

Despite low general corrosion rates as measured on remote sensors, key exchangers have been failing. The discussion highlighted the role of velocity and heat flux on failure rates. Low velocities and high heat flux both speed failures independent of measured bulk water characteristics.

4.7 Drinking water filter

Much discussion was held on the poor performance of the new slow sand filters for producing drinking water to the Cochin township and plant (Short runs + poor quality). No firm conclusions could be drawn in the time but the following points may be relevant.

      i) Being open to the light encourages algae growth and will cause short run.

     ii) Backwashing filters will remove dirt but the quality of water produced for some time after a backwash will be poor.

    iii) The solids in the raw water are high. Short runs could be expected with very fine sand.

    iv) Using the existing pressure filters in a roughing duty may improve the output.

5.   ACKNOWLEDGEMENTS

Many people were involved in the discussions but my special thanks go to Mr Narasimhan for arranging accommodation etc. at the difficult time of the strike and to Mr Joseph who accompanied us throughout our visit to FACT.

FN276

GUJARAT NARMADA VALLEY FERTILIZERS COMPANY LIMITED

REPORT ON VISIT OF MR.D.G. HOOPER ON BEHALF OF UNIDO

TO G.N.F.C. LTD., BHARUCH (INDIA) TO DISCUSS

WATER TECHNOLOGY MANAGEMENT

MARCH 20 - 25, 1988

C O N T E N T S

1. SUMMARY AND CONCLUSIONS :

1. The G.N.F.C. Complex is relatively new but quite old enough to be showing problems from potential errors 'in water management. Very few problems have been identified and this is an unspoken testament to the skill and dedication of the managers and work force.

2. No fertiliser complex will work unless it has water of the correct quality in the correct quantity and the first step in producing that water is the pretreatment stage. This is obviously working well and is one of the key reasons why there are so few subsequent problems. Of the four clariflocculators. I have seen in India it is the only one which is being managed properly and which is working as it should.

3. Due to the good operation of the pre-treatment plant there are no major problems on the demineralisation plants or boilers.

4. Occasional depressions in Boiler pH may be due to organics in the feed water. The plant approach of careful, limited addition of caustic to regain pH control is considered the best solution and is discussed.

5. If suspected corrosion in steam lines carrying two phase flow is confirmed, it is recommended that alternative amines to ammonia are used for boiler dosing. There is nothing to be gained in changing any parameters if no problems are identified as the current regime is sensible and the cheapest possible.

6. Chemical cleaning is commended as a powerful tool for preventive maintenance and renovating fouled equipment. It is one which must only be used with great care and attention to detail but is one that GNFC could use to its benefit as the plants naturally age. Provisional methods are discussed.

7. The cooling systems have provided most problems in the past and one or two exchangers still foul unacceptably. The root cause is the design of those exchangers. No minor changes to the water management will stop the fouling. Possible options are discussed.

2. BACKGROUND TO G.N.F.C.

G.N.F.C. is a new company based at Bharuch, about 70 kms south of Baroda. It was started in 1978 and the plants commissioned in 1981/82. About 1800 people are employed on site.

The company operators :

A 1350 Te/d single stream ammonia plant based on fuel oil by the Texaco partial oxidation process, obtaining its oxygen and nitrogen from a Lind air separation unit;

- an 1800 te/d single stream Urea Plant from M/s. Snamprogetti;
- a 60 Te/d loop to make Methanol by the ICI process from the Ammonia Plant synthesis gas.
- a 2.5 Te/d batch process Butachlor (pesticide) Plant;
- a 25 MW Captive Power Plant
- Associated demineralisation, condensate recovery and Efflu-
  Treatment Plant.

The company is currently very bouyant enjoying high plant utilisation rates, high profits and impressive capital investment both in chemical plants and in diversification. These include Formic Acid, Nitrophosphate (granulation), Printed Circuit Board (electronics) and Motor Scooter production.

2.1 General Water Aspects :

The site plus township requires approximately 35-40,000 M^3/ day of raw water. Some 60% is make up for cooling duties with the rest going as process water, demineralisation and drinking water. (See Fig. 1). The site has two sources of water for security of supply. One is the Narmada River 14 kms away from where it is pumped to the site reservoirs. The other is from the River Tapti which is dammed 80 kms from Bharuch Canals bring the water to a specially constructed reservoir holding 1.3 million M^3 from where it is pumped the final 11 kms to the two site reservoirs which hold 1,60,000 M^3.

All the water is pre-treated by chlorination (1 ppm) and clariflocculation with alum followed by filtration and storage before being taken to individual plants or for further chlorination and drinking.

Typical analyses of the site water are given in Table-1.

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FIGURE 1.

GNFC ORIGINAL WATER BALANCE

RAW WATER FROM URBMC :

wer
Narmada Abstraction

Main Reservoir

Supply to site reservoir
8.5 to 9 MGD (say 8.75MGD)

Supply to Bharuch
Municipality 2 MGD

Losses due to seepage
and evaporation

Raw Water Treatment Plant
8.75 MGD

Losses due to evaporation
and seepage

Filtered water storage
Tank to 8.4 MGD

Effluent to Treatment
Plant 0.35 MGD

SG Plant for
Ash Slurry
2 MGD

Cooling Tower
Make-up
4.0 MGD

DM Plant
Make-up
1.2 MGD

Service Water
0.75 MGD

Drinking water
0.45 MGD

Ash pond
as 10%
Ash
Slurry

Evaporation
& drift
loss 3.3.
MGD

Blow
down
to ETP
0.7 MGD

DM Water to
deaerator
1 MGD

Effluent
to ETP
0.2 MGD

Storm water
channel/sewage
pits.

Steam to various
users

Boiler
Blow-down
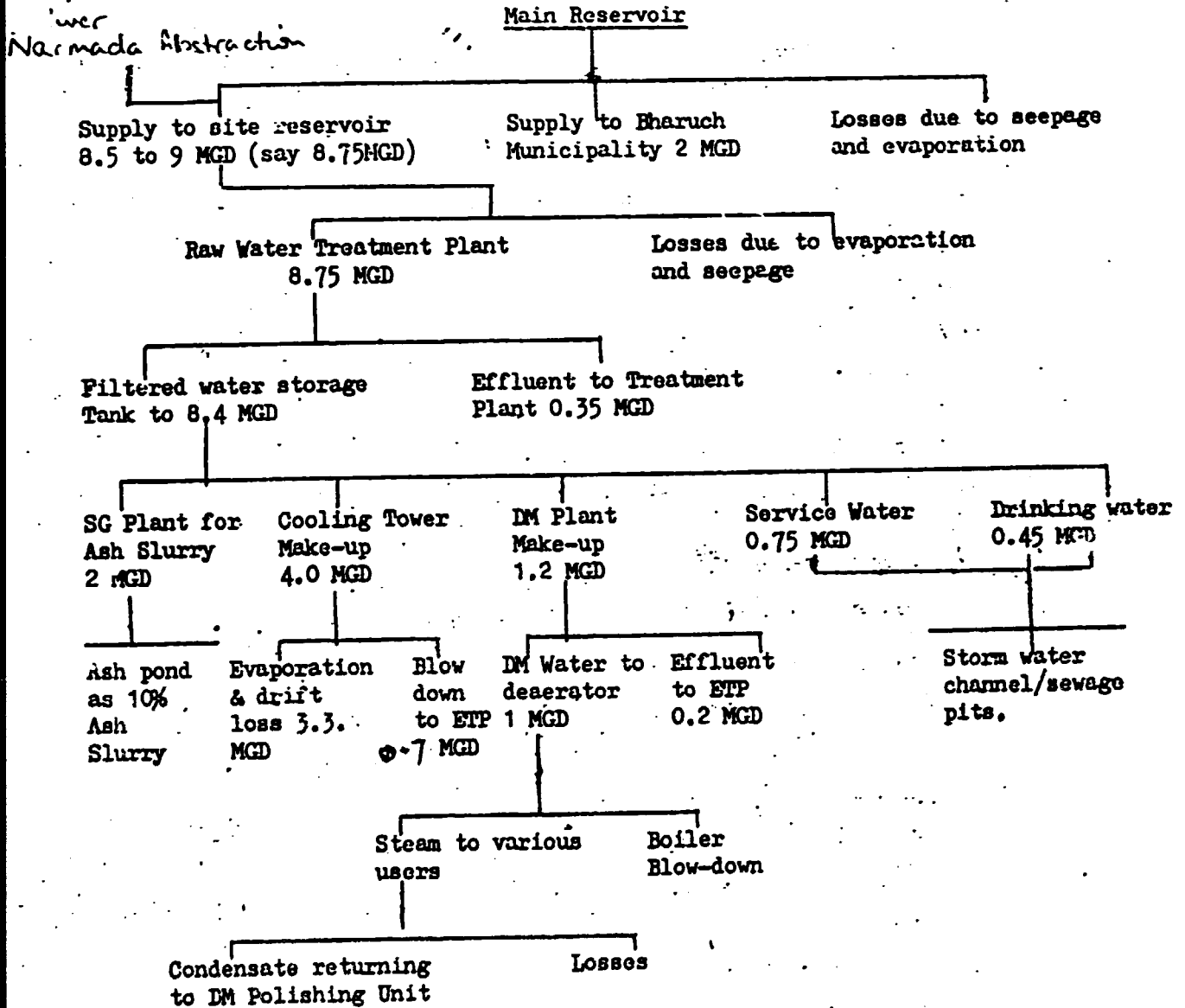
Condensate returning
to DM Polishing Unit

Losses

TABLE : 1   Typical Values for GNFC Site Water :

Analyte	Unit	Raw Water	Pretreated Water	Ammonia Condens.	Urea Condens.	Demin. Water
pH		7.9-8.5	7.1-7.4	9.1	9.0	6.8-7.0
Conductivity	uS/cm	230-310	275-360	19	17	
Turbidity	NTU	5-17*	1 - 2			
Total Solids	mg/l	150-290*	160-200			
TDS	mg/l	140-270	10-190			
Suspended Solids	mg/l	8-20*	6-10			
P-Alkalinity	mgCaCo3/l	0-15	Nil			
n-Alkalinity	"	100-160	90-110			
Total Hardness	"	100-130	100-130			
Ca	"	50-70	50-70			Nil
Mg	"	30-60	30-60			
Cl	"	20-23	20-23	<0.05	<0.05	
So4	"	10-12	12-20			
K	"	2.5	--			
Na	"	77	--	<0.10	<0.10	
Soluble SiO2	mg/l	11-18	13-17	0.066	<0.02	<0.015
Colloidal SiO2	"	--	--			
Fe	"	--	--	<0.02	<0.02	
KMNO4 Value	mgO2/l	1-2	1-2	1.4	0.97	
NH3	mg/l			2.5	2.2	

*   Excluding the monsoon period.

3. **WATER STORAGE RESERVOIRS AND PUMPS :**

At the reservoir receiving Tapti water via the canals at Gadkhol
village, a weir has been constructed with a depth guage for read-
ings to be taken manually for estimation of flow and preparation
of invoices to GNFC. The weir lip has been constructed below the
top water level desired for the reservior so the weir is often
flooded and although there may be no flow, GNFC are invoiced as
if the reading indicated full, forward flow.

There is no reliable instrument that will operate remotely to
give the required indication from the currently constructed
flume. A hand held turbine meter temporarily installed to a fixed
fitting could be used when the flume is flooded.

Vast amounts of silt have been carried into the reservoir. The
scale of the problem is such that a dredger would be needed to
carry out the desilting if water were left in the reservoir.   The
best method would be to drain it and remove the silt mechanically
(in India that would mean, literally, manually or "womannually").

At the abstraction point on the Narmada, silt accummulation at
the base of the suction wells has caused problems. The problem is
one of the mechanical design of the pumps or civil design of the
well and is outside my expertise.

4. **PRE-TREATMENT PLANT :**

A single clariflocculator treats the full flow of water and was
working well when visited. 50 ppm alum was used at pH 7.2. Some
floc was carrying over and the plant personnel described how it
was difficult to operate the plant with low inlet turbidities as
occurred at this time of year. They wanted to use a polyelectro-
lyte to improve matters but had not been able to find one which
was approved for use for drinking water applications.

I believe some polymers have been accepted for such a use but I
have no details of them. Enquiries will be made on my return to
England.

The use of a polyelectrolyte will not increase the load to the
ion exchange resins. Indeed, it might even reduce it because
lower amounts of alum might be possible although pH adjustment
would still be required. Gross overdoping of the polymer could
lead to carry through to the ion exchange resin units which may
cause problems and experiments would need to be carried out on
resins with the chosen agent.

5. DEMINERALISATION PLANT AND WATER STORAGE :

The site runs a three stream semi-automatic plant comprising: Activated Carbon Filters : sodium sulphite dosing : counter current, strong cation units regenerated with Hcl : Weak Base Anion : degassers : strong base anion units regenerated thorough fare to the weak base with caustic and mixed bed units.

Problems have included organic fouling and resin fines causing nozzle blockages. The inclusion of activated carbon and weak anion resins has been to reduce the problems with organics.

5.1 Resin Problems :

The loss of operating capacity on the cation resin and reducing water regain (moisture content) are indicative of some type of fouling but further, detailed chemical analysis would be required to understand this as it is unknown in my experience for this to occur on cation resins altohugh quite common on anion resins.

The prcblem of fines production, again from the cation resins in particular, is not particularly experienced in the UK with resins from the major suppliers. It does, however, appear to be a problem in India as Madras Fertilizers Ltd. suffered similar problems. The only time it is seen in the UK is with poor quality resin which tends to be used in non-critical applications e.g. domestic softening or non-regenerable units. Discussions should be held with the suppliers to see if they have any comments.

5.2 Material of Construction :

Discussions were held on the choice of material for acid and caustic lines. In the UK, concentrated caustic ($\sim$ 48%) is handled in stress relieved carbon steel while dilute caustic (4%) is handled in stainless steel or rubber lined mild steel. Concentrated hydrochloric acid (28 - 35%) is handled in glass re-enforced plastic (GRP) or polythene containers and in GRP or rubber lined mild steel pipes while dilute acid (< 7%) is handled in rubber lined mild steel pipes.

The treated condensate from the Urea Plant is stored in a rubber lined tank at 80 DegC. The lining has frequently blistered and become detached from the tank wall necessitating repairs. Such a repair was occuring at the time of the visit and the material was inspected. The advice of a materials expert should be sought for confirmation, but in my experience the material did not appear unduly degraded or softened. It showed the symptoms of not having been applied and/or cured correctly as it was showing patchy adhesion to the metal. The problem was only found on the sides of the tank and not on the floor.

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5.3 New Types of Ion Exchange Resin :

Conventionally, in India, polystyrene based resins‚have been used for anion resins. Resins based on acrylic matrices are now available worldwide and these resins show appreciable advantages in capacity and resistence to organic fouling. They do, however, have the disadvantages of being more expensive, having a higher pressure drop and an upper temperature limitation of 30 DegC. I will send copies of data sheets on my return to England.

There are no such new developments in the production of cation resins.

6. BOILER PLANT :

There are three, 180 Te/Hr, coal fired boilers. Normally two are on line and one on standby generating at 105 Bar and exporting superheated steam at 510 DegC and 96 Bar.

Discussion highlighted that some early corrosion problems had occured in the downcomers but this had been overcome by remarking the expanded joints. Occasional tube failures had occurred but these were believed to be more associated with fireside, soot blowing operations than any water chemistry problem.

6.1 pH Control :

The major problem experienced had been unexplained drops in pH in the boiler water which appeared to occur periodically.

The demineralised water (DM) was deaerated and dosed with hydrazine and ammonia to give a pH 9.1 - 9.2 and tri-sodium phosphate to give 5 - 10 ppm as PO4 and pH 9.0 - 9.2 in the boiler. The chloride level was measured at ~ 0.02 ppm in the boiler.

On at least two occasions in the last three years and for a period of a couple of months around April to May the boiler pH had dropped to as low as pH 8.2 while the feed water remained at pH 9.1 and the chloride at ~ 0.02 ppm. Tri-sodium phosphate was increased to 15 -20 ppm as PO4 but this did not raise the pH. Caustic was added and the pH re-established at normal levels.

Due to the seasonal although irregular, nature of the phenomen plus the fact that it effected both boilers simultaneously, it was concluded that it was a feed water quality problem. It was probably due to the nature of the organic in the water at that time of the year. Optimisation of the pre-treatment plant e.g. slight change in alum dose or pH might improve the situation, as might the future use of a polyelectrolyte, but this is in no way predictable.

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The important point was to raise the pH as quickly as possible by first trying hi̇ ̇ ̇ r phosphate levels or using caustic i.e. exactly what pl. ̇ personnel did.

There is a slight danger in adding caustic that the adjustment will go too far and lead to alkaline corrosion. Although there is little danger of being able to overdose sufficiently to cause gross effects, if there are points of local concentration, due to departure from conditions of necieate boiling, even minute amounts of free caustic in the bulk water can cause failure.

On the current information available regarding the GNFC boilers, the risk of corrosion from a depressed pH appears to be much higher than the risk of caustic corrosion by additon of free sodium hydroxide to elevate the pH to ~ 9.0. The use of trisodium phosphate alone, over the past few years, will almost certainly have resulted in a little free caustic being in the boiler water. This is because tri-sodium phosphate, in a dry out zone, yields an incongruent salt with a sodium to phosphate ratio of ~ 2.8:1 the residual "0.2" being as free caustic. That no failure has occured is good evidence of no dry out mechanism and an indicator that a few ppm of caustic could probably be tolerated quite safely.

6.2 Hydrazine or Alternatives :

Discussions covered the choice of oxygen scavengers and whether hydrazine, catalysed hydrazine or some other agent was best.

Technically hydrazine works very well and is the cheapest of all the alternatives. Questions have been raised regarding its toxicity, carcinogenicity and speed of operation. Un-doubtedly it does have a degree of toxicity and, like every other chemical, it should be handled with due care. However, no evidence has been found of any carcinogenic effect to man and this argument should be discounted. In terms of its speed of operation, laboratory data suggest that at feed water temperature the reaction between hydrazine and oxygen can take many minutes which is clearly unacceptable to boiler operators. However, practical experience shows that the removal of oxygen is very rapid and no oxygen pitting has been found in economisers receiving oxygenated water dosed only seconds before with hydrazine. It is believed the reason for this is the following :

1) $N_2H_4 + O_2 = 2H_2O + N_2$
     is very slow, but
2) $4Fe + 3O_2 = 2Fe_2O_3$
     is very fast, as is
3) $6Fe_2O_3 + N_2H_4 = 4Fe_3O_4 + 2H_2O + N_2$
     which rapidly yields the required magnetite to protect boilers. Also

4) $4Fe_3O_4 + O_2 = 6Fe_2O_3$

occurs rapidly, but in the presence of hydrazine, (3) takes place and the destruction of oxygen is effectively catalysed by the boiler itself. There is thus no reason to pay a salesman for a catalyst when your own boiler will do it for you.

6.3 Alkalising Amines :

Ammonia is currently used as it is cheap, available and apparently effective. However, some corrosion has been seen in parts of the steam/condensate system where two phase flow is occurring.

The problem may be one of design due, simply, to excessively high velocities but problems have been seen in two phase flow where low pH of the liquid phase occurs because the majority of the base is in the steam phase. Ammonia is particularly volatile and changing to a less volatile base has worked in several nuclear power stations around the world e.g. Wylfa and Oldbury in the UK.

The amines which could be used include morpholine, cyclohexylamine and amino methyl propanol (AMP). The effect of any of these on copper alloys will be less than Ammonia although all of them could cause corrosion in the presence of oxygen. No corrosion has been seen in systems with oxygen <0.02 ppm and Ammonia <5 ppm (Ref. Butler and Ison. Corrosion and its prevention in waters. Published by Leonard Hill, 1966). It is suggested that, if corrosion is confirmed in the two phase condensate piping, one of the other amines is tried. It should be added as a direct replacement for Ammonia at the same point. The exact quantity required should be ascertained by trial but sufficient to give pH >8.5 in the feed and condensate should be added. It is expected that 5 - 10 ppm of amine would be required.

6.4 Reuse of Condensate as Boiler Feed Water (BFW) :

Currently power plant condensate is fed directly back to the deareator as BFW but the Urea and Ammonia plant condensates are treated in separate polishing plants consisting of cation and mixed bed units.

Provided the condensate is within specification i.e. similar levels of contaminants to the DM Water, there is no reason why they should not go back directly as BFW. However, if plant blowdown is added, it will not meet such a specification due to the presence of silica, chlorides, sodium and phosphate and it will have to be polished. The danger of sudden contamination e.g. oil break through becomes a much more acute risk if no polishing is being carried out although the polishing plant is not designed to remove oil and should not be used in any attempt to do such a job.

6.5 Chemical Cleaning :

The necessity for cleaning boilers fed on good quality demineralised water was discussed and the recommendation was made that it was good, preventive maintenance to carry out a chemical clean after 8 or 9 years to return the boiler to an "as new" status removing any excessive magnetite film and debris.

It was strongly emphasised that the engineering aspects of carrying out a chemical clean were probably more important than the choice of chemicals and attention to detail at all stages was paramount.

The outline philosophy of a chemical clean would be as follows :

1. Identify and physically isolate all potential "dead legs" in the system where chemicals must not be allowed to ingress.

2. Isolate all plant pumps and set up an external pumping system capable of overcoming all pressure drops to yield flushing velocities of 1.5 m/s minimum in all parts of job (ingenuity with "Direction Control" adaptors or the use of "gas lift" in some natural circulation boilers will be needed).

3. Leak test the system.

4. Flush each part of the system at a minimum of 1.5 m/s using three times the volume of water of that part of the system.

5. Carry out a degrease (if required) by heating to 90 DegC and adding the chosen chemicals. Maintain heat if required for upto 12 hours.

6. Flush each part of the system at a minimum of 1.5 m/s using three times the volume of water of that part of the system.

7. Fill and heat to the required temperature (60 DegC for H.F., 80 DegC for HCL, 90 DegC for citric acid).

8. Add acid to required strength (1% for HF, 5% for HCL, 3% for citric) complete with inhibitor at 0.1 - 0.2% circulate at velocities <1 m/s.

9. Circulate until foulant (usually Fe) reaches a plateau concentration (approx. 1 hour for HF, 6 hours for HCL, 3-12 hours for citric). DO NOT HEAT during this stage, even if the temperature falls significantly.

10.   Drain acid and refill with 0.1% citric acid solution.

11.   Flush each part of the system at a minimum of 1.5 m/s
      using three times the volume of water of that part of
      the system.

12.   Fill and heat to 60 DegC.

13.   Add 0.5 - 1.0% citric acid with no inhibitor.
      Circulate for 60 minutes or until no more iron dissolves.

14.   Add sufficient ammonium hydroxide to give pH >9.5.

15.   Add 0.5 - 1.0% sodium nitrite and circulate for 2 - 4
      hours.

16.   Drain and flush at velocities < 1 m/s.

This will produce a clean, passive surface which will be
stable for 48 - 72 hours. Undertake a storage procedure if
the boiler will not be recommissioned within this time.

Increasingly hydrofluoric acid is replacing other acids as
the main agent. Its advantages are :

i)   The inhibitors work well with it giving exceptionally
      low corrosion rates.
ii)   It dissolves iron oxides very well rather than loosening
      deposits.
iii) It works quickly.
iv)   It dissolves silica as well as iron.
v)   It can be used on stainless steels.
vi)   It can be used at lower concentrations.
vii) It can be used at lower temperatures.

Its disadvantages are :

i)   It cannot be used on calcium deposits.
ii)   It cannot be used on high titanium alloys.
iii) It is a particularly hazardous chemical to handle.

6.6   OnLine Chloride Analysers :

Such instruments exist for boiler applications in the range
of 1 - 100 ppb and for cooling water in the range of 1 - 100
ppm. They are highly sophisticated and require considerable
maintenance with the ones for cooling water being
particularly prone to fouling and drift. I will send
some data sheets on my return to England.

7. COOLING SYSTEMS :

7.1 Cooling System Specification :

The three main cooling systems (Ammonia, Urea and Captive Power Plant(CPP)) are dosed with an inhouse developed blend according to Table 2.

TABLE 2 :   Cooling Water Specification :

Analyte	Specification
Inorganic phosphate*	10 ppm
Ortho Phosphate	<5 ppm
Organophosphate+	10 - 15 ppm
Zinc	0.5 - 1 ppm
pH	7.5 - 8.0
Dispersant for calcium phosphate	

* Added as sodium hexametaphosphate.
\+ Added as HEDP

The role of each of the constituents of the programme was discussed and the limits to which they could be exposed.

The polyphosphate is essentially added as a cathodic corrosion inhibitor but high temperatures and high pH values cause reversion to orthophosphate which leads, in turn to the deposition of zinc and calcium phosphates. As a rule of thumb, bulk temperatures should be kept below 50 DegC and the pH around 7 or slightly below to minimise O - PO4 reversion.

HEDP acts slightly as a cathodic corrosion inhibitor but principally as an inhibitor of calcium carbonate scales. At high pH (Say >pH 8 or so) it becomes less effective and at lower pH values it is less necessary as a scale inhibitor as the solubility of calcium carbonate increases so much.

Zinc acts as a cathodic corrosion inhibitor but only if it is present as soluble zinc ions. At the cathode zinc ions are precipitated by the high local pH generated by the reduction of oxygen.

$$5) \quad 2H_2O + O_2 + 4e = 4 OH^-$$
$$6) \quad 2Zn^{++} + 4 OH^- = 2 Zn(OH)_2$$
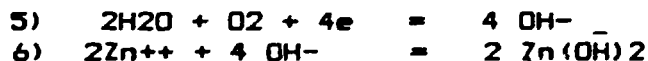
This produces a film of zinc hydroxide which limits the contact of the metal surface with oxygen and stifles the cathodic reaction. 1-2 ppm Zn++ in solution is required to do this. At pH >7.5 very little zinc remains in solution - especially in the presence of orthophosphate. At 60 DegC with 3 ppm orthophosphate only 0.2 - 0.3 ppm of zinc will

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remain in solution. In the absence of phosphate approx. 1 ppm zinc will remain under the same conditions. At 50 DegC, in the absence of phosphate, 2 ppm soluble zinc could be expected at pH 7.5. Any zinc which is precipitated as the hydroxide or phosphate will have no anticorrosive properties but will lead to fouling and possible under deposit corrosion mechanisms.

From the above, it can be seen that pH, in particular, plays a vital role in the synergy of the inhibitors. For this reason the specified range of pH 7.5 - 8.0 is believed to be too high and it is recommended that a pH nearer 7.0 is adopted with a range of pH 7.0 - 7.5 to minimise scaling of the exchangers and to give corrosion protection to the carbon steel pipe work.

7.2 Microbiological Control :

Chlorination to yield 0.5 ppm free chlorine at the tower top was effectively keeping control on the ammonia and urea plants although very variable amounts of chlorine were consumed and monthly peaks of sulphate reducing bacteria (SRB) were observed ! SRB's only grow in anaerobic conditions e.g. in deposits but they are not killed by oxygen. A normal standard adopted in the UK to indicate unacceptable levels would be 1000/100 ml. Chlorine will kill SRB's but only if it can penetrate through the deposits to reach them. Non oxidising biocides may diffuse through some deposits more quickly but methylene bisthiocyanates are not very effective against any bacteria at pH >7.5 and chlorinated phenols are very slow acting (>>12 hours) so these could not always be relied upon to control SRB's under the current conditions at GNFC. These statements can be explained by considering the following points which were discussed in the meetings.

Bacteria exist in large populations so their elimination by biosides can be represented statistically. Figure 2 represents the kill effect of three biocides. They kill at different rates (slope of line) and therefore take differing times to achieve the same final result. (i) kills more quickly than (ii) which is quickers than (iii)
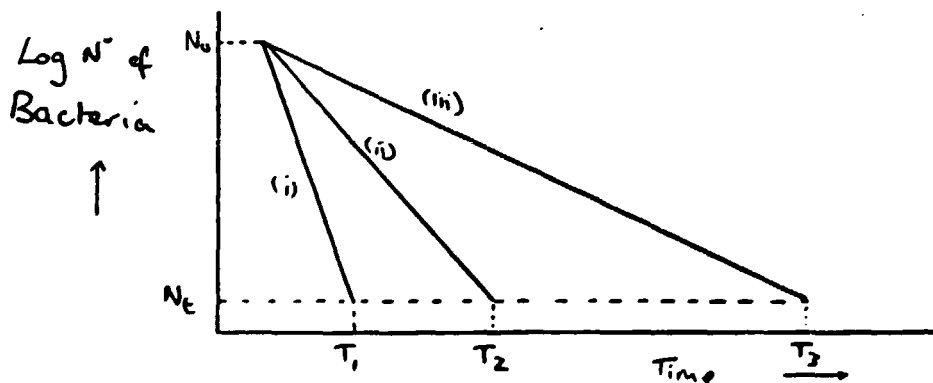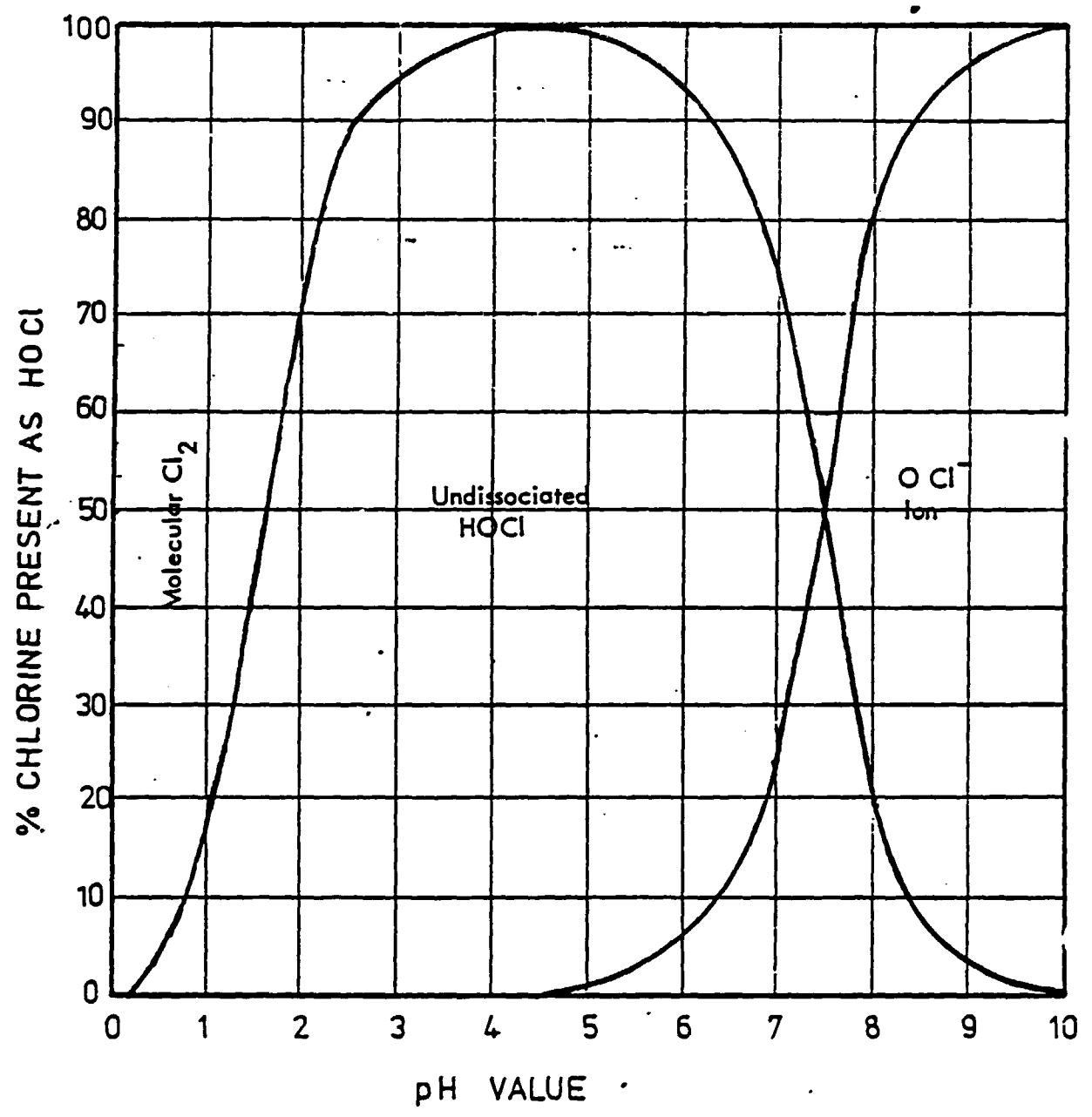
FIGURE 2 :   Graph of kill rates of differing biocides

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Figure 3

EQUILIBRIUM DIAGRAM FOR $Cl_2 \rightleftharpoons HOCl \rightleftharpoons OCl^-$
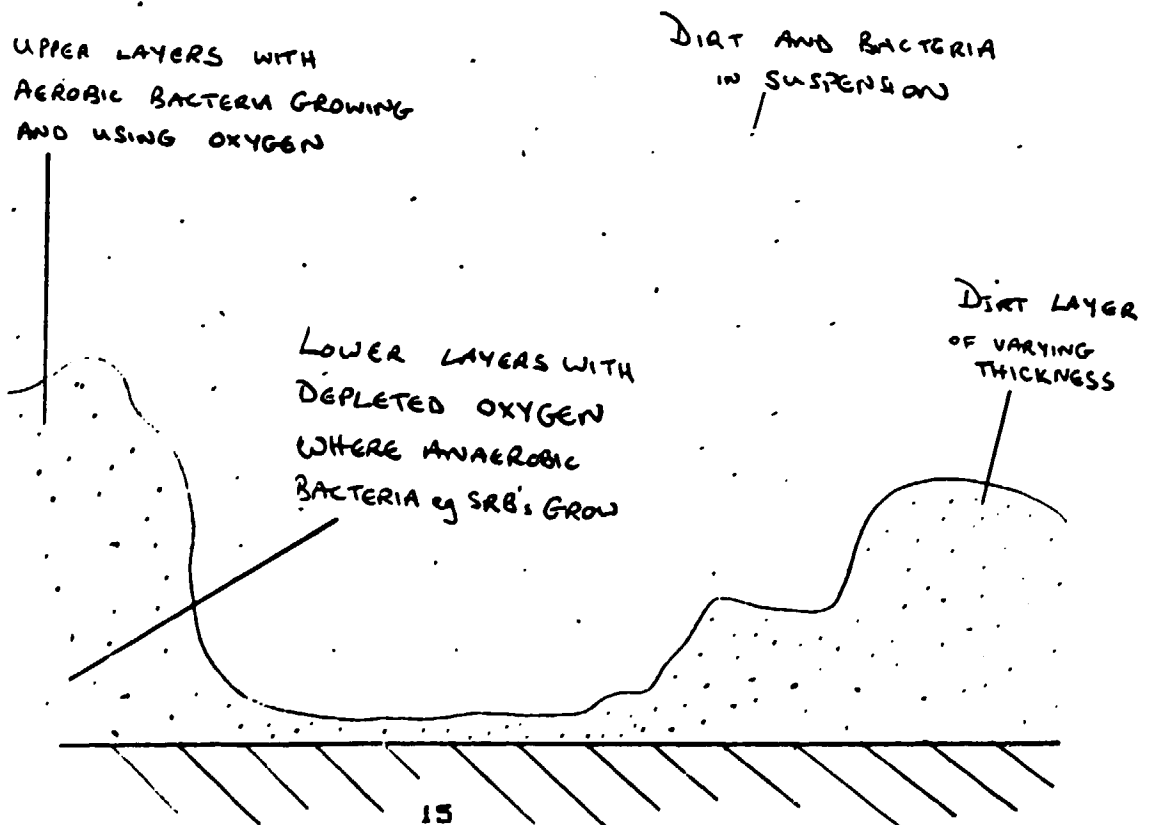
Each biocide would be equally as effective after time T3 but only biocide (i) would be effective at T1. (i) and (ii) would be equally effective after T2 but (iii) would be less effective.

Hypochlorous acid (HOCL) is very effective with a kill time of approx. 1 minute while hypochlorite ion (OCL) has a kill time of approx. 100 minutes. Thus the form in which chlorine (Cl2) is present in the water is very important in terms of dose timing e.g. shock versus continuous. Figure 3 shows the equilibrium diagram for the chlorine in water system. It shows that, at pH 7.5 to 8.0 the chlorine is 50   80% in the OCLform and will therefore need a longer contact time to be effective. Even at pH 7.0 to7.5 it is still about 20   50% in the OCL form.

In the presence of ammonia, chlorine forms chloramines which are not detectable as free chlorine, are not as toxic and are very volatile so they are easily lost to the atmosphere when the water goes over the tower. This has the effect of considerably increasing the chlorine usage to maintain the same free chlorine residual.

In real systems, debris will always occur. on metal surfaces as indicated in figure 4.

FIGURE 4 :   Situation on metal surface in a cooling System

UPPER LAYERS WITH
AEROBIC BACTERIA GROWING
AND USING OXYGEN

DIRT AND BACTERIA
IN SUSPENSION

LOWER LAYERS WITH
DEPLETED OXYGEN
WHERE ANAEROBIC
BACTERIA eg SRB's GROW

DIRT LAYER
OF VARYING
THICKNESS

A biocide will easily come into contact with suspended bacteria and kill them, but bacteria within the dirt layers are partially protected as the biocide has to diffuse through this dirt. Some of the biocide, especially an oxidising biocide, may be consumed and never reach the bacteria at a sufficient concentration for a sufficient length of time to kill them.

Thus, shock chlorination can sometimes fail due to the presence of dirt levels while continuous chlorination can control the situation. SRB levels are a good indication of the degree of control of deposits and biocide dosing and should be used as an indicator of the efficiency of micro-biological control.

7.3   Urea Plant Cooling System :

Typical analyses of the circulating water are shown in Table 3. Most of the plant exchangers are stainless steel and although deposits are seen in many exchangers only one is causing real problems. This is the E7 exchanger and typical analyses are shown in Table 4 (E7 is the Medium Pressure Condenser).

The deposit is largely calcium phosphate. The high loss on ignition could be due to the presence of calcium carbonate or organics. The process side temperature is 140 DegC and high water temperatures up to 62 DegC have been seen. Scaling of this exchanger causes regular plant shutdowns.

TABLE 3   Typical Cooling Water Analysis :

Date			24/10/1987
Time		Standard	
pH		7.5-8.0	8.0
Free Chlorine		0.50.7ppm	0.5
Conductivity		<1500 mphos	1085
Total Solid		600 ppm	774
Hardness			
	Ca	150 ppm	236
	Mg	100 ppm	124
	Total	250 ppm	360
Chloride		120 ppm	78
Fe		2 ppm	0.10
Phosphate			
Ortho		35 ppm	3.1
Poly		1015 ppm	1.7
Organo		10 ppm	11.5
Turbidity		<10	10.0
Zinc		1 ppm	0.48
Silica		<80 ppm	62

Dropping the pH of the circulating water, as discussed above, will help the E7 exchanger but with such extreme conditions it is doubtful if any of the normal cooling water chemical regimes could safeguard it for a reasonable period (say a year to each major shutdown). The danger of calcium scale is very high and can only be avoided by reducing or eliminating calcium from the cooling water.

The make up to the urea tower is between 80 - 120 M^3/Hr and the cost of providing this as demineralised water would be very high. Use of the urea hydrolyser effluent would lead to high microbial growth due to its residual ammonia and urea which would be very expensive, if not impossible, to control.

One option discussed was to provide a small, dedicated cooling system for the E7 exchanger. This could be made up with DM Water and simple dosing with sodium carbonate to give pH >8.0 would give a satisfactory regime to avoid corrosion in the carbon steel pipework. In the absence of specific inhibitor the chlorides should be kept as low as possible and I would suggest a value of 5 ppm (say max. 10 ppm). Sodium nitrite at 500 - 1000 ppm at pH >8.0 could be used in which case chloride levels would be less important, but microbial reversion of nitrite to nitrate can be a problem necessitating the frequent use of expensive, non-oxidising biocides e.g. chlorinated phenols or quaternary ammonium compounds.

TABLE 4   Typical Analyses of E-7 Scale - 1/3/1988

Sr No.	Test	Unit	Results
1)	Loss of Ignition at 900 DegC.	%by wt.	29.58
2)	Acid insoluble	"	12.03
3)	Silica as Sio2	"	10.22
4)	Aluminium as Al2O3	"	04.03
5)	Iron as Fe2O3	"	04.15
6)	Calcium as CaO	"	16.45
7)	Magnesium as MgO	"	02.83
8)	Zinc as ZnO	"	01.00
9)	Chromium as Cr2O3	"	00.04
10)	Phosphate as PO4	"	29.64
11)	Titanium as TiO2	"	00.13
12)	Chloride as Cl-	"	00.01
13)	Sulphate as SO4	"	00.11
14)	Carbonate as CO3	"	00.74

Remarks : Results are reported on Dry Basis.

8.. EFFLUENT TREATMENT :

SNFC operate a sophisticated and highly integrated effluent recovery, treatment and disposal/reuse programme. It is by far the largest and most impressive I have seen and the figures on water savings speak for themselves e.g. the 2 MGD shown in Fig. 1 as going to the Steam Generating (SG) Plant for ash slurrying is now totally supplied by reusing various effluents. (2 MGD = 9000 M^3/Day or 380 M^3/Hr).

Discussions were held on possible reuse of the urea hydrolyser effluent as cooling water make up but this was not recommended due to the danger of initiating uncontrollable microbiological problems.

Discussions were held on the use of Reverse Osmosis (RO) to treat cooling tower blow down prior to returning it to the filtered water tanks. In my experience, high calcium and organic containing waters lead to high rejection flows (i.e. less make) and rapid fouling of the membranes requiring high maintenance and frequent replacement (in the order of two to ten times the claims of the supplier). The only way to find the true commercial viability would be to conduct trials. In the UK, it could be expected that a supplier would cooperate for a nominal cost or give free of charge use of his equipment.

9. ACKNOWLEDGEMENTS :

The technical discussions were held with personnel from the Water Treatment Area, Performance Monitoring Group, Ammonia Production, Urea Production, Power Plant Operation and Laboratory in a pleasant positive and professional manner.

My particular thanks go to Mr.V.S.Joshi who organised the meetings, visits, transport and refreshment and ensured all ran smoothly.

INDIAN FARMERS FERTILISER COOPERATIVE LTD.

REPORT ON VISIT

OF

MR D G HOOPER ON

BEHALF OF UNIDO TO IFFCO, PHULPUR, INDIA

TO DISCUSS WATER TECHNOLOGY MANAGEMENT

MARCH 28-30, 1988

CONTENTS

1. <u>Summary and conclusions</u>

    a.   The IFFCO Phulpur complex is relatively new but quite old enough to be showing problems from errors in water management. Very few problems have been identified and this is proof of the care and dedication of the managers and workforce.

    b.   For optimum (technical and economic) control of boiler water it is recommended that blowdown is continuous and apart from emergencies, not varied. Adjustments to boiler water parameters eg. PH, Phosphate, TDS can then best be effected by altered dosing.

    c.   Turbine deposits have been seen intermittently and this is concluded to be due to priming in upset condition. The nature of the deposits should be further studied for indications of other potential problems.

    d.   The use of a zinc chromate cooling water programme is giving a reliability factor to the plants which might easily be overlooked and it is emphasised that this benefit should not be forgotton or lightly given away.

2.   <u>BACKGROUND TO IFFCO</u>

The IFFCO site visited was at Phulpur, near Allahabad and the plants under discussion were commissioned in 1981. The site employs just under 800 people.

The plant consists of:-

    a.   900te/d single steam Kellogg ammonia plant based on Naphtha

    b.   1300te/d urea plant from Snamprogeti

    c.   12.5 MW captive power plant (CPP) coal fired

    d.   associated demineralisation, condensate recovery and effluent treatment plants.

2.1   <u>General Water Aspects</u>

The site plus township requires about 12-1300m^3/h and all the water is supplied from several borewells on the IFFCO site to a 16,000m^3 covered storage tank. Drinking water is led direct to the township (no treatment at all, not even chlorine) boiler feed water is made in demineralisation plant, cooling tower make up is pretreated in a cold lime softening (CLS) plant. Some blowdown from the cooling tower is also recycled via the CLS plant but the rest is treated in a chromate removal plant (acid plus ferrous sulphate followed by alkaline precipitation of chrome (iii) hydroxide).

Typical analysis of the site water are given in table I.

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Table 1.

Typical values for IFFCO Site Waters

Analyte	Unit	Raw Water	Pre-treated Waters	Cooling Waters	Denim Waters
pH		7.5	10.5-10.8	6.4-6.6	6.5-7.0
TDS		540-650			
Cl	MgCaCO$_3$/l	23-57		200	
SO$_4$	"	26-57		1000	
m-Alkalinity	"	424	∟ 156		
p-alkalinity	"	nil	20		
Total hardness	"	348	80		
Mg hardness	"	188	40	400	
Ca hardness	"	160	40	400	
Na	"	214			
SiO$_2$	Mg/l	16-25		150	∟ 0.01
Fe	"	0.04-0.06			
CrO$_4$	"			30	
Zn	"			2-4	
PO$_4$	"			5-8	
HEDP	mgPO$_4$/l			15-20	
Turbidity	NTU	∟ 5	∟ 5		
Conductivity	µs/cm				∟ 0.4

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3. PRETREATMENT AREA

The CLS plant was working extremely well when visited although plant personnel indicated a number of modifications they had to implement to ensure this eg. commissioning of ejectors and launder. .: handle lime slurries because of unreliable pumps and scaling of pipelines. No particular problems existed on the plant aother than the universal one of disposal of the sludge.

The demineralisation (DM) plant consisted of four streams of weak cation: counter-current strong cation regenerated thoroughfare with hydrochloric acid: degasser: weak anion: strong anion regenerated thoroughfare with caustic: Mixed bed.

Normally a degasser would be placed after a weak anion exchanger to improve a weak base resin's capacity. Discussions could not clarify why the above order has been selected.

Problems had been encountered with the integrity of the middle laterals in the strong cation unit which had repeatedly broken during water hold down, counter-current regeneration,. This had resulted in significant outage time and lost resin. The plant has made modifications to the piping to include resin traps in the line between the strong and weak cation and this had prevented further resin loss. Few breakages had occured recently. No problem of fines generation was experienced in the cation resin in contrast to the expe iences at MFL and GNFC.

The Co-currently, thoroughfare regenerated anion units had presented no problems.

The plant had been modified to use ejectors for regeneration instead of the original pump systems which had proved unreliable. Fume from the hydrochloric acid storage tanks has been a problem but scrubber systems had been fitted. Although these used a reasonable amount of water, they were working well and had significantly reduced external corrosion of adjacent plant. The system was mild steel rubber lined.

4. BOILER PLANT

The CCP received treated process condensate from the ammonia plant. This was treated by stripping followed by cation exchange and steam stripping. No analyses had been carried out but it was expected that up to 50ppm of methanol could be present and discussions covered the effect this might have on the CCP's $110kg/cm^2$ boilers.

UK experience suggests that considerably less than 50ppm of methanol will be present (12ppm is typical of one ICI plant) but traces of chloride from the cation exchanges may be present plus residual ammonia and carbon dioxide. The CCP doses hydrazine, cyclohexylamine and trisodium phosphate to the boiler and this should cope with all the other contaminants at their likely levels. Some of the methanol will pass into the steam and some of that will be partially degraded to water and carbon dioxide. None of these components will cause major problems in any of the IFFCO uses of the steam. However, some of the methanol will probably be degraded to e elemental carbon

on the heat transfer surfaces. This will lead to thick layers of mixtures of magnetite, carbon and other trace elements possibly effecting heat transfer and potentially leading to concentration sites by wick boiling. Cleaning of the boilers is recommended periodically (say 8-10 years). In fact, such cleaning would be recommended independent of the presence of methanol as it is good preventative maintenance on all heat flux boilers.

Some deposits have been found on turbines and detailed discussions of the control parameters were held.

The plant had been dosing hydrazine and cyclohexylamine continuously but had been blowing down and dosing phosphate intermittently to control pH, silica and phosphate levels. The specification for silica was 1ppm max but the plant did not exceed 0.5ppm. It was recommended that ALL dosing and purging should be carried out on a continuous basis for optimum control. In fact, a purge should be set, say, at approximately 2%, of the steam rate and, except in emergencies, it should not be altered. If sodium phosphate levels became high, the dosing should be reduced slightly with the same, fixed blowdown. This will gradually bring the phosphate down without upsetting the silica level control or wasting money in excessive blowdown. If the phosphate is low, dosing should be increased slightly.

The deposits on the turbine had not been fully analysed but only showed approximately 5% by weight as SiO_2. This suggests gross carryover of boiler water eg. at pressure upsets when the boilers would prime. Fuller analyses of the deposit should be made to troubleshoot for other problems. For example, value of 31% for loss on ignition was quoted which is difficult to explain in terms of the known chemistry of the system. There is no phenomena of Silica not being analysable in a 110kg/cm^2 boiler but being present to cause turbine deposits. Non-detected collodial Silica present in the feedwaters would be converted to soluble Silica under boiler conditions and be detected.

5. COOLING SYSTEMS

The three main cooling systems (ammonia, urea and CPP) were all dosed with an in-house blend of zinc sulphate, sodium dichromate, sodium hexametaphosphate, HEDP, sulphuric acid for PH and chlorine for microbiological control, non-oxidizing biocides such as quaternary ammonium compounds and methylene-bis-isothiocyanates ('MBT') were used when required depending on microbiological analyses.

Without doubt, a zinc/chromate/phosphate system is the best technical programme to minimise corrosion, scaling and fouling. The choice and management of this regime is directly the reason for so few cooling water problems and the use of carbon steel exchangers.

Although the chromate removal system is working well there is still the problem of disposal of the final chroma (III) rich sludge. Alternative technologies such as ion exchange methods are discussed in the literature and a few full sized units have been installed in the USA but I have no practical experience of them. I will send references to these on my return to the UK.

Inspection of the heat exchangers and cooling tower pond have shown very little in the way of microbiological deposits. Routine monitoring of total viable count has shown around 10^5 counts/ml. which would normally be thought of as moderately high but no data was available on the type of bacteria eg. slime forming types such as Pseudomonas Spp or Fravobacteria Spp or non troublesome types. Specific analysis was carried out for sulphate reducing bacteria (SRB) but these numbers are moderately low and tie in well with the inspection eg. 50/100ml in the make-up and 500-900/10ml in the circulating water. A typical standard in the UK to indicate potential trouble would be a count of 1000/100ml. It should be noted that at a concentration factor of 8 with, say 50/100ml in the make up the above standard could be raised to 1400 to 1500/100ml for the same margin.

Discussion covered the need to combine supplementary biocides with chlorine and their frequency. From a technical point of view chlorine should be able to control all situations alone. However, the presence of ammonia reduces its' efficiency and levels below 0.5ppm are not sufficient for full control. IFFCO chooses to dose at 0.1-0.3ppm residual chlorine and higher levels would considerably increase the chloride level in the cooling water which was preferred at approximately 200ppm. Latest reviews show that levels up to 1000ppm have not initiated stress corrosion cracking in UK and European chemical plants.

If supplementary biocides are preferred they should only be used when required eg. if microbiological growth is not kept at a steady level by chlorine or the SRB numbers increase substantially (indicating deposits in the system and loss of control in those deposits.)

The presence of SRB in make-up water to the cooling towers is a little surprising as none would be expected in a borehole water. Discussions confirmed that there were none in the direct borehole supply but water exit the storage tank contained the SRB. This indicates deposits in the tank or on the walls. I knew of no health risk directly from SRB but it indicates that contamination has entered the tank and aerobic bacteria must also have been introduced. They will be capable of growing near the surface of the water ("wind and water" areas) and could cause more problems. Some consideration should be given to mechanically cleaning this tank and or disinfecting the water before it is drunk.

6. ACKNOWLEDGEMENTS

Discussions were held with many personnel but my particular thanks to Mr B K Bansal who organised all the necessary details to make such a visit successful.

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TSD/MTS/88/0238   25 March 1988

Sub: <u>Industrial Water Treatment</u>

Enclosed is the report of Mr D G Hooper, the UNIDO Consultant on Water
Management. Mr D G Hooper held discussions with the concerned personnel of
all Divisions from 17-19 March. This is put up for favour of information.

K JOHN JOSEPH
MTS

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To: Mr Hooper

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