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CORROSION CONTROL IN FERTILIZER INDUSTRY

INDIA

DP/IND/85/006/11-03

Technical Report: Project Findings and Recommendations*

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

Based on the work of C.P. Dillon
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ABSTRACT

Problems of corrosion control by suitable materials selection and related methods (e.g. protective coatings, inhibition, electrochemical techniques, improved design) are discussed for four (4) fertilizer and chemical plants in the Cochin and Bombay areas of India.

Specific problems are discussed in a variety of operations, such as production of sulfuric acid, ammonium sulfate, ammonium chloride, phosphoric acid, ammonium phosphate, nitric acid, ammonia, urea, etc. Problems in associated plant utilities (e.g. steam generation, cooling water) are also discussed. Protection against external corrosion by polluted tropical marine atmospheres is a special problem.

General recommendations for improved technical education, professional development and improved communications are provided. Detailed specific recommendations of a technical nature are made in the problem areas described for particular operating units.

INTRODUCTION

During the month of February 1987, the author and his counterpart visited various fertilizer and chemical plants in Cochin and Bombay, India, in partial fulfillment of UNIDO Project DP/IND/85/006/11-03.

The purpose of the project is to upgrade existing expertise and skills at selected plants through training and consultancy. The duties defined for the project included, but were not limited to, the following.

1. To assess the corrosion problems in each of the plants and study the methods that have been used to control corrosion.
2. To study some specific corrosion problems of the plants and make recommendations.
3. To assist the Fertilizer units in improving and developing newer techniques in corrosion monitoring and protection.
4. To prepare a final report, based on the findings of the mission, giving recommendations on further action which might be taken.

In support of this project, the author and his counterpart, Mr. M.P. Gupta of Projects & Development India Limited, visited the Fertilizers and Chemicals Travancore Limited (FACT) plants at Udyogamandal and Ambalamedu, Cochin, during the period 1987 February 5th through 15th, the Rashtriya Chemicals and Fertilizer (RCF) plants in Trombay and Thal during the period 1987 February 16th through 24th, and aided in presentation of a Corrosion Seminar at Gujarat State Fertilizer and Chemical Company in Baroda on 1987 February 21.

Our general and specific recommendations are summarized in the following section and the details of the mission are reported in the appropriate chapters, plant by plant.

RECOMMENDATIONS

It is evident that there is in India an adequate basic understanding of corrosion and materials technology in certain quarters (e.g. PDIL itself and among other metallurgical and engineering staff). However, these knowledgeable people are relatively small in number, isolated from each other by distance and lack of contact, and do not yet communicate effectively either vertically (i.e. from plant operations and maintenance to design engineering) or horizontally (i.e. between plants within the same company; between companies).

There is little opportunity to control the materials selection in new design provided from technical resources outside India. Even in indigenous operations, the responsible parties seem often to be hampered by administrative policies which effectively restrict them to native materials and products as they attempt to resolve the corrosion problems in their operating plants, where indigenous products often have proven inadequate. There is little opportunity to utilize materials of advanced technology but foreign origin, such as high performance stainless steels, titanium alloys or advanced nonmetallic materials (e.g. perfluoralkoxy resins) or composite materials. It is also evident that there has been insufficient thought in the area of the economics of materials selection in terms of cost effectiveness based on the annual cost of the Present Worth (after taxes) of the alternative installations.

An area of major concern is external deterioration of metals and concrete due to lack of control of atmospheric pollution (e.g. ammonia and acid fumes) and inadequate painting specifications, procedures and maintenance.

In light of these observations during our plant visitations to Fertilizers and Chemicals Travacore Limited, Rashtriya Chemicals and Fertilizers Limited and the Gujarat State Fertilizer and Chemicals Company, we have the following recommendations.

General Recommendations

1. Establish a permanent working relationship between the corrosion/metallurgical staff at PDIL and the various chemical and fertilizer companies, in which relationship PDIL would effectively supervise the education and training of plant personnel and the execution of plant exercises in corrosion testing and failure analysis.

2. Increase the staffing at company level to include trained corrosion engineers for each company (and the larger plants).

3. Provide professional training by short courses or seminars in materials selection for and maintenance of chemical plants, including the areas of water treatment, paints and coatings, and electrochemical techniques (e.g. cathodic protection, anodic protection). In-plant corrosion testing and monitoring should be emphasized, as opposed to laboratory techniques.

4. Increase the opportunities for professional development of senior staff by funding their participation in international meetings, especially the annual NACE conference (USA). Attendance every 3-5 years is considered essential, both to keep abreast of technological advances and to establish professional contacts which constitute an advisory resource.

5. Encourage industry-wide and intra-company meetings to discuss common problems of a non-proprietary and non-competitive nature (e.g. cooling water, maintenance painting, cathodic protection, advances in stainless steels and other corrosion-resistant alloys, use of plastics in corrosion control, corrosion-resistant bolting and hardware, etc.).

6. With the advice of a select committee from various industrial organizations, establish some sort of distribution point which might provide adequate amounts of sheet, plate, pipe and tube, etc., in various high performance materials, in an effort to facilitate expeditious maintenance or refurbishing in critical services.

Details of our discussions and recommendations are provided in the text proper, but a summary of specific recommendations in important areas is as follows.

Specific Recommendations

1. Atmospheric Corrosion

To minimize corrosion in industrial marine atmospheres, every effort should be made to minimize polluting emissions. Because some industrial contamination will inevitably occur, high priority must be given to proper painting and painting maintenance of good quality industrial coatings. Reinforcing bar ("Rebar") for concrete should be epoxy-coated before installation in these plants. Both steel and stainless steel insulated structures should be coated appropriately before insulation is installed.

2. Utility Systems

2.1 Steam Generation

Although boiler feedwater treatment appears to be adequate, contamination of return condensate occurs by ingress of oxygen or carbon dioxide from operating units. The appropriate use of filming amines (e.g. octadecylamine) and/or neutralizing amines (e.g. morpholine) needs to be further developed.

2.2 Cooling Water

The mineral salt content of the available waters is low enough that non-chromate inhibition (to minimize environmental concerns) is feasible. However, successful treatment will require more attention to biocidal treatment and sludge/silt removal than is presently evident.

3. Sulfuric Acid Converters

Appropriate measures must be developed to control corrosion/iron contamination in the reactor outlet piping (e.g. by strip-lining) and to minimize acid attack in the gas/gas exchangers (e.g. by "safe-ending" with high performance alloys or by retubing in the same).

4. Phosphoric Acid Systems

Corrosivity of phosphate rock digestion systems tends to be unpredictable because of erosion/abrasion and the influence of contaminants such as ferric, chloride and fluoride ions. Low carbon Type 316 (S31603) is generally inadequate and the use of high performance stainless steel alloys must be systematically explored and cost/benefit analyses conducted.

5. Nitric/Phosphoric Systems

Corrosivity of nitric acid is affected by contaminants (e.g. chlorides, fluorides) and even by accretion of corrosion products (e.g. Cr VI). Improved life of equipment can be sought through the use of higher chromium alloys (e.g. 25% Cr) than the conventional 18-8 alloys such as S30403, S32100 and S34700. Cost/benefit analyses must be conducted, but it is evident that current leaks and pollution call for swift remedial action.

6. Ammonia Systems

Safety in ammonia systems requires regular hydrotesting and ultrasonic or other sophisticated non-destructive examination of liquid ammonia tanks to verify successful inhibition against stress corrosion cracking. There are also areas where ammonium carbamate can form, due to ingress of carbon dioxide, and in which areas higher alloys than carbon steel may be required.

7. Urea Plants

Corrosion in urea synthesis is always due to ammonium carbamate. The successful use of materials of construction is related to the maintenance of passivating conditions, usually through injection of air or oxygen to the reactor. If Urea-grade S31603 is not suitable, higher alloyed austenitic stainless steels (or even titanium or zirconium) must be employed. Selective corrosion of welds can be controlled by welding with a richer alloy rather than a matching electrode (e.g. N08904 or N08028 for welding S31603).

These specific recommendations are discussed in more detail under appropriate sections of the chapters devoted to the individual plant locations.

The key to improved production reliability and maintenance cost reductions by the corrosion control measures suggested lies primarily in more effective communications (e.g. between plant operations and design; between plants; between companies) and only secondarily in technical advances. Existing indigenous technology, if carefully developed, expanded and utilized, should be adequate to this purpose. However, optimizing performance may require use of some imported materials.

I - FACT, Udyogamandal

On arrival at the Fertilizers and Chemicals Travacore, Ltd., (FACT) plant in Cochin, my counterpart, Mr. M.P. Gupta of Project & Development India, Ltd., and I met with the General Manager, Mr. P.R. Srinavasan, and Mr. P. Ramakrishna, Chief Superintendent of Technical Services. We discussed our proposed schedule and procedure. We agreed that Mr. Ramakrishna would schedule our meetings with selected plant personnel for our projected stay of approximately ten days, based on the subject matter presented in a memorandum to Mr. J.K. Sondhi, National Project Director of PDIL on 1986 September 17.

A. Sulfuric Acid Plant

Sulfuric acid is manufactured by oxidation of sulfur to sulfur dioxide, catalytic conversion to sulfur trioxide, and absorption of the latter compound in strong acid.

Initially, the problem areas cited were the carbon steel gas ducts to the converter, cast iron cooler pipes, and external corrosion. In further discussions, problems were reported with traces of acid in molten sulfur, leakage of brick-lined steel vessels after about ten years' service, cracking of carbon steel expansion joints, contamination of the catalyst beds with iron salts, localized corrosion of gas/gas heat exchangers by condensed acids, early failure of steel ductwork at excessive temperatures (i.e. above 500 C) and quality control problems with the spun-cast iron cooler pipes.

a. Steel Ductwork

We suggested lining or weld-overlaying the steel ductwork over the catalyst bed with high alloy stainless steel (e.g. UNS N08904, N08020)* as aluminum-sprayed ("metallized") coatings have not been successful in this service. (It should be noted here that the use of better and more resistant materials seems to be limited by a policy which greatly favors indigenous, as opposed to imported, materials.)

*See Table I (Annex II) for Unified Numbering System Alloy Designations

b. Gas:Gas Exchangers

We discouraged the proposed installation of hot-dip aluminum coated steel tubing in this application. While such aluminum-coated materials are used for high-temperature sulfur dioxide applications, they do not resist sulfur trioxide condensed as sulfuric acid.

Where steel is subjected to temperatures above 430 C, 1.05 Cr-.05 Mo alloys should be employed to resist high temperature metallurgical changes (e.g. "spheroidization" of graphite).

c. Cast Iron Pipe

Although ductile cast iron is preferred for strong acid piping, it is not an indigenous material. Mr. Gupta explained the necessary quality control measures required for good grey cast iron quality in centrifugally cast pipe at the foundry.

Other problems were discussed in minor detail. It appears that the substitution of higher alloy materials (e.g. N08020) in these services would require both policy decisions re imported materials and economic appraisal of the current maintenance/production loss costs vs. the benefits from the more expensive alloys. Technical literature was provided as copies of personal file material (viz. "Recommended Practice for Handling and Storage of Concentrated Sulfuric Acid at Ambient Temperature", "Materials of Construction for Handling Sulfuric Acid") and of the NiDI Bulletin CEB-1 on

"Corrosion Resistance of Nickel-Containing Alloys in Sulfuric Acid or Related Compounds".

B. Ammonium Sulfate Plant

Ammonium sulfate is manufactured by the direct reaction of anhydrous ammonia with sulfuric acid. The preliminary report indicated problems with the acid feed piping to the reactors in the mother liquor system, and assorted weld-repair problems. In discussions with plant personnel, four specific problem areas were defined.

a. Reaction Feed System

In the reaction system acid feed loop, the injection piping (which projects into the recirculation piping) is S31600, externally sheathed in Teflon PTFE. This injection pipe is gradually corroded internally, due to an exothermic reaction between the acid feed and the process stream. We recommended installing a slightly larger pipe section, with both an external PTFE sheath to protect it from the abrasive slurry and an internal PTFE liner of interference fit to resist the corrosion in the exotherm area. An alternative high alloy material (i.e. N08020) is not indigenous in wrought form, although equivalent castings (i.e. ACI CN7M; Alloy 20) are available.

In the reaction product, which has been diluted with steam condensate, S31600 piping of smaller diameter has developed numerous leaks in the weld areas. This piping carries 40% ammonium sulfate and mother liquor having a free acid content of 2-3 grams/liter at a temperature of approximately 70-75 C. An S31603 low-carbon grade would be preferred, but a section of the S31600 pipe weld should be removed for metallurgical examination, as there are several possible corrosion mechanisms besides intergranular corrosion. A high alloy rod (e.g. N08904) in a full-penetration weldment would be preferred for maximum integrity.

b. Crystallizer Cone

Cracking has occurred in internal components of the crystallizer cone after about 10 years' service. This is apparently due to mechanical fatigue (rather than stress corrosion cracking) as the cracks are reported to be readily amenable to weld repair (i.e. there is no attendant "running" of the cracks during welding). Every attempt should be made to minimize vibration in the cone, but major design or materials changes are probably not warranted.

c. Sulfuric Acid Feed

Corrosion is reported in the steel piping between the sulfuric acid feed tank and the cast Alloy 20 (CN7M) pump. The tank discharge nozzle should have a stainless steel insert liner installed, and the steel piping section should be replaced with S30403 or grey cast iron (see "Recommended Practice...").

C. Carbon Slurry Piping

Attempts to handle a 0.2% carbon slurry in demineralized water from the scrubber on the CO/Hydrogen system to waste disposal have resulted in corrosion of 4" Schedule 40 steel pipe within two years' time. An examination was recommended to identify various aspects of erosion-corrosion and/or acid corrosion by carbon dioxide or other species. A proper water-sampling procedure was described and an analysis for pH vs. Total Acidity was recommended.

D. Ammonium Chloride Plant

Ammonium chloride is made by direct reaction of anhydrous ammonia with hydrogen chloride. Water is added subsequently to maintain a constant liquid level in the reactor/evaporator, and the product is subsequently centrifuged from the resulting evaporated slurry. The original inquiries related primarily to external corrosion of vessels and piping. In subsequent discussions, three process-related problems were raised.

a. Reactor

The Ebonite (i.e. hard rubber) lining in the reactor fails periodically, apparently from poor workmanship primarily but aggravated by the combination of vacuum conditions and the operating temperature of about 70 C. Brick-lining is under consideration and is recommended to refurbish existing vessels against an acid pH condition in the liquid phase. For new construction, "wall-papering" (i.e. lining with very thin sheets of alloy material) in N06985 (Alloy G-3) should be investigated vs. rubber lining. The feasibility of applying a corrosion-resistant coating internally should be explored.

b. Slurry Piping

S31603 piping of 2-3" diameter, installed to feed the ammonium chloride slurry to the centrifuge has been failing, mainly at the welds. In some cases, pinholes have been observed in the parent metal. The cause of the failures will have to be verified by metallurgical examination but are most probably due to chloride stress corrosion cracking. Thermal stress relief of the pipe, in the fabricator's shop) at about 900 C, with a slow cool, should be considered. A loose internal high density polyethylene (HDPE) lining may be feasible. Corrosion inhibition of both SCC and chloride pitting (see c. below) might be achieved by injection of about 80 ppm of catalyzed 20% hydrazine. Alternatively, replacement of a high performance stainless steel may be required.

c. Centrifuge

An S31603 centrifuge is failing by chloride pitting after about four years' service, while its perforated screens suffer erosion and abrasion. As previously indicated, oxygen scavenging may eliminate the pitting. Eroded screens might be replaced with S15700, a molybdenum-bearing precipitation-hardening stainless steel. For new equipment, we would suggest purchase of the machine in a high performance austenitic alloy (e.g. S31254, N08904, N08028), if possible.

External corrosion of steel from general corrosion in the ammonium chloride plant, as well as of stainless steel from external stress corrosion cracking (ESCC), is best effected by application of heavy-duty catalyzed epoxy (or other suitable) coatings.

E. Superphosphate Plant

The only problem reported in this process is corrosion of lead-lined steel tanks and lead piping by corrosion in 67% sulfuric acid at about 80 C. This may be due to exceeding the limiting concentration/temperature parameters for lead, as well as velocity and turbulence effects (i.e. erosion-corrosion).

F. Phosphoric Acid/Ammonium Phosphate

Phosphoric acid is manufactured by the wet process (i.e. digestion of phosphate rock by sulfuric acid). Ammonium phosphate is made by reaction of anhydrous ammonia with phosphoric acid and sulfuric acid. Originally, it was reported that there were no specific current problems other than necessary maintenance repair of rubber linings. Further discussion revealed problems with the rubber covering on the agitator shaft and erosion-corrosion or abrasion of pumps.

It must be understood that the corrosivity of the reaction mixture of calcium phosphate rock with sulfuric acid is determined by the amount and concentration of contaminants (e.g. ferric ions, Fe III; fluoride; chlorides) in an unpredictable manner. The phosphate rock currently digested contains about 4% fluorides but only a few hundred parts per million (ppm) of chlorides. The corrosive action is resisted by a cast version of N08904 (i.e. CV9) and by N08020 (i.e. CN7M), the latter being used for pumps.

a. Agitators

Rubber-covered agitator blades of HV9 are resistant, but the rubber sleeve over the carbon steel agitator shaft fails at intervals, exposing the substrate steel to corrosion and torsional breakage. We recommended an N08904, N08026 or N06625 weld overlay on the shaft, before rubber-sheathing, to minimize corrosion (and possible hydrogen embrittlement) when localized damage of the rubber sheathing occurs.

b. Slurry Pumps

For the slurry pumps, an experimental installation of N08028 was recommended. It appears that N08904 is probably not more resistant than the N08020 currently employed, in which alloy failures are reported in as little as three months.

c. Acid Injection

Corrosion of an S31603 sulfuric acid injection pipe is apparently due to the dilution exotherm. It has already been replaced with a PFTE pipe, which should be totally resistant.

d. HF Scrubber

The teakwood hydrofluoric acid scrubber is reportedly satisfactory. HDPE and other HF-resistant plastics are suitable alternative materials.

A Sandvik Steel Company paper, "Metallic Tubular Phosphoric Acid Evaporators: Corrosion Performance and Plant Experience," by M. Tyrell, was provided. We noted, however, that the documented superiority reported for N08028 is contradicted by other published technical papers, reflecting the unpredictability of corrosion determined by contaminants.

G. Oil Gasification

In this process, naphtha is oxidized with steam and the steam is reduced, forming carbon monoxide and hydrogen. The carbon monoxide is subsequently oxidized to carbon dioxide. The preliminary report had indicated no problems but further discussions revealed four major concerns.

a. Oil/Steam Preheater

In the preheater, erosion of steel coils occurs within three years' time, reportedly due to the erosive action of carbon particles recycled in the process. Since it apparently is not feasible to eliminate this condition by more complete oxidation, replacement with S30400 piping may be a solution. It was suggested that an experimental installation of an S30400 piping segment be made, joining the stainless to the steel with an N06600-type electrode, to determine whether such a materials change would be cost-effective. It is probable, but not certain, that S30400 would be more erosion- and/or abrasion-resistant than steel in this application.

We also discussed further the erosion-corrosion of steel piping in the waste stream (cf. C. above). A water analysis has been requested, to include chloride analysis as well as pH and Total Acidity, to determine whether S30400 might be considered for replacement, or whether plastic (e.g. FRP, HDPE, PVC) might be recommended.

b. High Pressure Scrubber

In the high pressure water scrubber, in which carbon dioxide is partially removed from hydrogen, the steel vessel and aluminum trays are resistant. However, the steel tails piping (viz. 18" pipe of 0.5" wall thickness) had about a five-year life. A bronze pump has suffered only minor corrosion in 18 years. For various reasons (e.g. adverse effects of chromates on bronze under acidic conditions; galvanic effects of aluminum liners), there is probably no cost-effective alternative to steel, since the pressure is too great for FRP. However, it would be worthwhile to check on possible use of a light-gauge stainless liner.

c. MEA System

A conventional 15% monoethanolamine (MEA) acid gas removal system is used to remove the last vestiges of carbon dioxide from hydrogen. S30400 tubes are employed in the solution heat exchanger before the stripping still, as well as in the reboiler. The impeller of the circulating pump is also stainless steel. Corrosion of the steel absorber tails piping and the pump volute is reported after ten years' service. We reviewed the suggested operating conditions for such systems (e.g. the maximum recommended mol ratio of carbon dioxide:MEA is 0.3 vs. the reported 0.4), the possible formation of heat-stable (and corrosive) degradation products, and the use of vanadate-based corrosion inhibitors. However, there appear to be no serious concerns as the system is currently operated.

Lastly, better painting systems (e.g. epoxy-based) in lieu of alkyd or oleoresinous paints, which latter deteriorate rapidly in the presence of ammonia releases, should be investigated. Serious external corrosion was reported on steel equipment and structures which had suffered damage to the paint systems.

H. Tonnage Oxygen

The air separation and gas separation units are cryogenic operations involving the production of liquid oxygen. Materials (e.g. copper, aluminum and austenitic stainless steels) are selected for their good low-temperature impact properties.

A. Air Separation

In the air separation unit, a copper "Y" connection failed after about 15 years' service, apparently due to work-hardening by cyclic pressure at the operating temperature of - 180 C. We concurred in a replacement in S30400, which has superior mechanical properties at low temperature.

b. Gas Separation

In the gas separation unit, gas:gas plate-and-frame aluminum heat exchangers have developed weld leaks after 15-20 years. Argon-shielded repair welds are not holding. The defects are probably due to thermal cycling in service. Replacement in kind is recommended. There has been some corrosion of aluminum equipment due to entrainment of trace amounts of caustic, but it is believed that the proposed new cyclone separator will eliminate this problem.

c. External Corrosion

As always in cryogenic plant, there is significant corrosion of steel items subject to thawing of rime ice from atmospheric condensation. Conventional painting systems will not withstand this type of atmospheric exposure. Recommendations for an appropriate heavy-duty industrial coating should be solicited. It should be noted that the heavy-duty catalyzed epoxy coatings require a white metal surface for application (as by sandblasting) which poses problems in maintenance painting in some areas. Coatings which can be applied over hand-prepared surfaces (e.g. aluminum-pigmented water-cured urethanes or other suitable systems) may be required.

I. Ammonia Plant

The preliminary report had been that only external corrosion of steel equipment was of concern in and around the ammonia plant. However, six other topics arose in further discussion.

a. Naphtha Piping

Pitting corrosion of 2" Schedule 80 steel pipe has occurred in scrubbed naphtha service after some 15 years' service at 150 C. This may be due to disruption of otherwise protective sulfide films (formed by traces of hydrogen sulfide), due to contamination with organo-lead compounds in the naphtha. There are no economical alternative materials of construction.

b. Ammonia Recovery Column

The steel Raschig ring packing in the ammonia recovery column suffers corrosion in the 10% ammonia/water solution, which is heated by steam injection to 200 C at 24 atmospheres pressure. Customarily, extra packing is added to the top of the column (to replace that lost by corrosion) during a simple outage that involves no lost production. We believe the corrosion to be due to traces of carbon dioxide, from the steam or other modes of ingress, forming traces of ammonium carbamate (a common problem in ammonia recovery systems). We suggested that the operating people explore the use of stainless steel packing of any available grade, subject to a cost/benefit analysis.

c. Ammonia Pipeline

An ammonia vapor pipeline about 1 kilometer long is suffering random pinhole leaks after about 10 years' service. There appears to be no consistent pattern related to welds, bends or fittings. Either ammonia stress corrosion cracking or some type of carbamate corrosion may be involved. When possible, a metal segment should be trepanned for metallurgical examination. A copy of a paper, "A Review of Stress Corrosion Cracking of Carbon Steel in Ammonia" (A. Loginow, MATERIALS PERFORMANCE, December 1986), was provided for information purposes.

Cracking is also reported to occur in cold ammonia piping after some 5 years' service. Again, a metallurgical examination would be required to differentiate such possible failure mechanisms as fatigue, stress corrosion cracking or a nil ductility transition temperature brittle failure.

d. Converter Cooler

A cooler on the ammonia converter outlet consists of 1.05 inch, .38" wall steel pipe, cooled by water spray. Ammonia at 270 C is on the inlet process side. After 5 years' service, the return bends (which are not copiously rinsed, compared to the coils themselves) have been severely corroded. Only a protective barrier (e.g. metallized aluminum; aluminum-pigmented silicone coating) can alleviate this condition. The economics of such protection should be further explored.

e. External Corrosion

High pressure piping suffers external corrosion underneath the piping clamps, apparently by oxygen concentration cell corrosion of the poorly painted pipe. An improved coating system should be employed, in conjunction with a bituminous tape wrap (to exclude moisture) and galvanized steel clamps, whose zinc coating should afford a measure of cathodic protection.

J. Plant Utilities

a. Steam

The technology of boiler feedwater and boiler blow-down treatment is beyond the scope of this study. However, we note that waste heat boilers, as in the ammonia plant, have suffered corrosion in the section between the preheater and the boiler. Tentatively, we ascribe this to breakthrough of traces of oxygen, despite the prescribed hydrazine treatment. A recent change to catalyzed hydrazine (to accelerate reaction with dissolved oxygen) should minimize the possibility of further corrosion.

b. Water

The subject of plant cooling water, various problems with which were described in the initial correspondence, was not raised directly during our plant call. However, the subject was discussed at length with Mr. Gupta. We reviewed the report by Mr. D.G. Hooper of ICI, the UNIDO expert who had specifically addressed this problem area.

We are practically in total agreement with Mr. Hooper's findings that the basic chemistry (i.e. mineral content) of the makeup and circulating (i.e. cycle) water is amenable to corrosion inhibition by either chromate-polyphosphate-zinc or by organic inhibitors, and that the current ineffectiveness of the chromate treatment relates to turbidity, contamination and inadequate control of the inhibitor additions.

In order to bring the cycle water system to a condition amenable to corrosion and scale inhibition, chemical cleaning, inhibitor pretreatment, more sophisticated treating techniques and a proper corrosion control study and evaluation would be required. This would require local implementation by a competent junior engineer or laboratory technician, at least, under suitable technical supervision.

Unless the system is thoroughly cleaned and kept free of biomasses and other insoluble materials which prevent free access of the treatment to the steel surface, changes in inhibitor concentration or type will be of no avail.

II - FACT, Ambalamedu

There had been no prior definition of problems for the FACT plant at Ambalamedu, as there had been at Udyogamandal. However, the department operations (and some of their problems) were known to Mr. Gupta. During the period 1987 February 11 through 14, discussions were held with interested plant personnel, as available.

A. Ammonia Plant

In discussions with Technical Service and operating personnel, two areas of interest developed.

a. Combustion Air Preheater

This item is a vertical carbon steel tube-and shell heat exchanger in which hot gases at about 400 C heat ambient air entering at the bottom on the tube-side. The 1" tubes of 2 mm wall thickness have corroded through from the cooled process side after about 4 years' service. Our discussion concluded that this is probably due to condensation of wet hydrogen sulfide plus oxygenated sulfur-based acids. It appears impractical to neutralize these acidic species under the operating conditions. We recommended "safe-ending" replacement tubes by welding a short length of S30403 tube to the steel tubes, using a machined socket-fit and an S31003 seal-weld for the bimetallic joint. We recommended against a suggested steam-injection to the shell-side, fearing corrosion of carbon steel and possible polythionic corrosion effects on stainless steel.

b. Ammonia/Carbon Dioxide

We explained the lesser-known ramifications of the ammonium carbamate reaction, especially the reversible relations between ammonia, carbon dioxide and water. Although the ammonia and ammonium carbonates are essentially noncorrosive, ammonium carbamate is formed at least in small amounts whenever ammonia and carbon dioxide are present. Corrosion of steel, S41000, S30403, S31603 and even of higher alloys may ensue, depending upon specific conditions of temperature, pressure and oxidizing capacity of the environment.

B. Urea Plant

There were three problems raised by Urea Plant personnel.

a. Reactor

A conventional S31603 plate lining is employed in the reactor, in which ammonia and carbon dioxide are reacted at elevated pressure in the presence of 1000-2000 ppm of oxygen (added by air injection). During some 14 years of service, preferential corrosion of the welds has been observed, although this is not perceived as a serious problem. We recommended repair with a high performance molybdenum-bearing rod (e.g. S31254, N08904 or similar material) rather than with a matching composition electrode. A new reactor is fabricated from a "Urea grade" alloy (i.e. of higher minimum molybdenum content than conventional S31603, plus small amounts of titanium as stabilizer). We discussed the background of stainless alloy development, the specific roles of alloying constituents, the effect of ferrite content and of segregation in welds, etc. Modern alloys for urea reactors include not only the special variety of S31603 but also the high performance duplex and austenitic alloys, as well as titanium and zirconium.

b. Gasket

The plant is experiencing problems with flat aluminum gaskets of 99.5%+ purity (presumably UNS A91100) due to cold-flow and permanent deformation. We suggested that a metallurgist specializing in aluminum alloys be contacted concerning the possible use of A93003, A95154, A96063 or other alloys of resistance equivalent to A91100 but having superior strength and elasticity.

c. Gas Holder

The carbon dioxide Gas Holder tank is a concentric steel compartment riding by buoyancy in an outer steel tank filled with water. The steel in the annular space was not coated and is undergoing corrosion by the sealing water. Thirteen years old, it is inspected annually for policy reasons as well as corrosion considerations. The bottom is externally protected by mastic and the concrete pad. The inside, except for the annular space, is epoxy coated. We recommended application of a suitable immersion coating during the March 1987 shut-down, and additions of a suitable corrosion inhibitor (e.g. polyphosphonate) to the seal-water. At a later date, if deemed necessary, zinc sacrificial anodes could be installed to augment the coating protection.

C. Sulfuric Acid Plant

Problems with iron contamination in the top of the converter are analogous to those reported for Udyogamandal. The conventional problems with materials selection for tanks, piping, valves and pumps were discussed, and we provided the same reference material as at Udyogamandal. Three specific plant problems were discussed.

a. Absorption Tower

Problems have developed with this tower, where a double course of acid-proof brick has been applied over a proprietary rubber lining ("Rhepanol"). It is not possible to make an accurate diagnosis of the problem at this remove. The parameters for acid concentration and temperature at which a lead lining as membrane might provide improved performance should be investigated.

b. Acid Storage Tank

A concentrated sulfuric acid tank developed major hydrogen blistering after about ten years' service, due to "laminations" (i.e. manganese sulfide inclusions) in the plate. We described the mechanism of blistering by nascent hydrogen, suggested the use of shear-wave ultrasonic inspection to verify the quality of plate in this and similar tanks, and concurred in their use of external reinforcing to assure the ability of the tank to withstand hydraulic head pressure. We suggested installation of desiccating vents on all such tanks to prevent ingress of atmospheric moisture.

c. Acid Coolers

There is severe water/atmospheric corrosion of steel bolting in the flanges of the water-sprayed cast iron coolers. Bolt failures then permit flange separation, gasket leakage and further acid attack. We described the development of corrosion-resistant bolting for severe atmospheric exposures. Use of galvanized steel bolts is recommended as a first approach. More resistant bolting may prove necessary (e.g. hot-dip aluminized; polyimide/PTFE-coated). We hope specialty threaded fasteners will become available from an indigenous source in the future. Use of 18-8 bolts (e.g. S30300) for half the flange fasteners might also be a cost-effective solution. We also discussed the use of ASTM A242 "Weathering Steels" for structural applications. A Japanese-made auxiliary boiler may have been provided in such a low-alloy steel.

D. Nitro-Phosphate

a. Reactor

The sole process-related problem in this unit is the preferential attack of an S31603 vessel at the liquid level. This vessel replaced a brick/rubber-lined steel vessel which had proven unsatisfactory. (The process liquor is a phosphoric acid/sulfuric acid mixture containing 2-3% fluoride, at 120 C.) Apparently, the vessel wall is locally thinned, ultimately developing a through-wall crack due to mechanical weakening. The cracks have been successfully patch-repaired by welding. We suggested an internal strip-lining with one of the high performance alloys (e.g. N08904, N08028). We advised against a proposed brick lining, because of the high coefficient of thermal expansion of the austenitic stainless steels. Localized corrosion of the sulfuric acid injection pipe can be remedied by the substitution of PTFE, as previously described.

b. Phosphoric Acid Tanks

Failures of rubber-lined phosphoric acid tanks are evidently due to poor quality control by the manufacturer or to adhesive deterioration at high tropical ambient temperatures. We suggested appraisal of glass-reinforced plastic (GTRP) tanks for this service, as they are reportedly used successfully in other countries.

c. Fuel Oil Tank

This tank is maintained at 70 C and has suffered corrosion on the underside of the steel roof, apparently due to ingress of atmospheric air and humidity, possibly aggravated by traces of hydrogen sulfide. A desiccating air-vent should minimize this problem.

d. External Corrosion

We reiterated our position that control of air pollution, good maintenance painting procedures, and the use of heavy-duty epoxy coatings are the answer to the external corrosion problems described. Wet insulation is particularly corrosive, and steel vessels should be epoxy-coated prior to insulation. The proposed use of concrete to prevent atmospheric corrosion of steel structures will work only in the absence of acidic pollution and is heavily dependent upon proper density and depth of "cover." Steel to be concrete-covered should also be epoxy-coated, although the sophistication of the coating system is less critical than for boldly exposed structures. Concrete over "Rebar" or other steel internals will crack due to the pressure of rust products accumulated in tropical industrial atmospheres, unless the internal steel is coated or otherwise protected (e.g. as by cathodic protection of steel rebar in bridges). Aluminum-coated steel would be superior to galvanized steel in marine environments and in the lee of cooling towers, but not against acid pollution. GTRP grating and structural members are useful against atmospheric corrosion where safety considerations allow them to be used.

E. Ammonia/Phosphate Plant

a. Digesters

In the digesters, erosion-corrosion problems are cited with the HV9 (N08904) agitator blades. We are unable to recommend a suitable hard-facing material (the nickel-cobalt-chromium-base alloys lack molybdenum for corrosion resistance to this mixture), but suggested trial installations of N08028 or N06985. Rubber-coated N08904 blades have reportedly been successfully used at Udyogamandal.

b. HF Scrubber

Fan blades in the HF scrubber have proven unsatisfactory in the original rubber-coated steel construction. We concurred in the proposed use of S31603 blades coated with a chlorsulfonated polyethylene.

c. Digesters

There was prolonged discussion of failure of 98% sulfuric acid feed piping. S31603 had been replaced with N08904, which also failed. Another acid injection pipe (4" OD by 6') was fabricated by Dow Chemical Company in PTFE-over-S31603 construction, but the PTFE separated from the alloy substrate and obstructed flow. A change in the vapor piping discharge has permitted better removal of corrosive vapors, and an N08904-type proprietary alloy (2RK65) is now apparently satisfactory.

F. Plant Utilities

a. Steam

1. We discussed boiler water treatment for the 800 psi boilers, which currently use trisodium phosphate for alkalinity control. Some carbon dioxide gains entry in returned condensate. Neutralizing amines may be employed for control of carbon dioxide corrosion, while filming amines would be used where oxygen ingress has occurred. We also discussed the problem of copper contamination of boiler feedwater, emphasizing that cementation (i.e. copper plating on steel) poses a galvanic corrosion problem only under wet, air-contaminated shutdown conditions.

2. The auxiliary boiler in the ammonia plant has suffered four corrosion failures on the outside of the first stage economizer after five years' prior trouble-free service. The fuel oil contains 0.8% sulfur, plus vanadium compounds which catalyze

the formation of sulfur trioxide. The plant diagnosis, based on inspection and chemical analyses, indicates corrosion by condensation of sulfuric acid. We concurred in the proposed addition of a proprietary potassium nitrate compound to the combustion products, which is intended to tie up sulfuric acid-type products while liberating innocuous oxides of nitrogen.

3. The seal-welds in the carbon steel feedwater heaters are failing in the first exchanger primarily. We described the proper sequence of "drifting in," seal-welding, testing and rolling-in of replacement tubes, and the use of S31003 rod for completion of the weld (for added resistance to carbonic acid weeping from the hot gas side).

4. In the naphtha-fired heater, coil failures have been experienced in the 1.05 Cr-.05 Mo coils, apparently by excessive temperatures and attendant creep-rupture. The plant proposes to replace the affected coils with stainless steel pipe. We suggested the use of either S32100 or S34700 for optimum strength and oxidation resistance, but warned of the problem of differential thermal expansion between the steel and the austenitic materials. It would seem that a redesign is indicated.

b. Cooling Water

1. The lake water from the canal, diluted by rainfall, is somewhat lower in mineral content than the river water at Udyogamandal. The extraneous contamination at Ambalamedu arises from ammonia processes, rather than from phosphate rock. Specific ammonia-metabolizing bacteria aggravate the formation of biomasses. The plant has considered dropping the chromate-polyphosphate-zinc treatment in favor of a polyphosphate-zinc inhibitor. We emphasized that the system must be effectively cleaned before inhibition can be achieved. We recommended continuation of chlorination for maintenance biocidal treatment, supplementary biocides to prevent evolution of chlorine-resistant

strains, and concurred in the proposed weekly injection of a proprietary biocide specific for nitrifying bacteria. We recommended against continued addition of 5 ppm chromate as being potentially dangerous from the standpoint of pitting attack.

2. We reiterated our position that the mineral content of the water itself is readily amenable to corrosion inhibition by either chromate-based inhibitors (which are being phased out due to environmental concerns) or non-chromate treatments. It is essential, however, that the system be free of bio-masses (i.e. algae, slime, fungus), silt, mud, etc., prior to treatment for corrosion inhibition.

3. There is interest in a "Zero Blowdown" (ZBD) operation, with an eye towards water conservation. Normally, cooling tower systems are operated at 4-6 cycles of concentration to optimize water savings and ease of chemical treatment. Operation at higher cycles usually does not effect water conservation (by reduced blowdown) commensurate with the increased mineral content of the cycle water and attendant corrosion and scaling problems. However, a softened make-up can be concentrated without blowdown, providing the resulting chloride level is amenable to corrosion inhibition. The term "ZBD" is a misnomer, as there is sufficient windage in a mechanical-draught tower that concentration stabilizes at about 20-22 cycles, even with no deliberate blowdown. In the Cochin surface waters, with not more than 20 ppm chloride in the make-up, a cycle water at 22 cycles would contain less than 500 ppm chloride. This is a level still amenable to non-chromate inhibition, provided the water is at a pH appropriate to the hardness. It may not even be necessary to soften the make-up (although this is easily done), as pH control may be the only requirement. As stated previously, the system must be kept clean, free of bio-masses, silt, etc., by biocidal treatment, side-stream filtration, polyelectrolyte additions, etc.

4. We also discussed the effects of chloride content of cooling water on the 18-8 stainless steels (i.e. S30400, etc.). Potable water, with its restricted mineral content (e.g. 400 ppm chloride maximum by international standards) can be used for hydrotesting, distillation column start-ups, etc., but must be thoroughly drained before operations commence. Very low-chloride water (e.g. less than 25 ppm) is stipulated only for such critical applications as nuclear power installations. The practical limit for 18-8 condenser tubes is about 1500 ppm, when water is on the tube-side. With water on the shell-side, about 1000 ppm is a reasonable limit, but provision must be made to vent the tubesheet continuously (which simultaneously cools it by flushing and prevents formation of a vapor space). In either case, the exchanger design should be such that the tube-wall temperatures do not exceed 60 C.

5. A water supply in the phosphoric acid area is contaminated with acidic species from the barometric condensers, and has corroded the cast iron volute and phosphor bronze impeller of the large circulating pump. (The piping is rubber-lined to resist attack.) A 15% nickel cast iron volute (F41000) and S31600 impeller was used for replacement. The impeller is satisfactory, but the alloy cast iron is still being corroded (which is indicative of the severity of the acid contamination). We suggested either an all-S31603 pump or neutralization of the water on a continuous basis. Either an electrical resistance probe or a polarization probe might be used to monitor and control the neutralization.

6. There was intended to be installed at a remote location a seawater-cooled ammonia condenser. This item was to be of carbon steel construction with a proprietary baked epoxy-phenolic coating ("Sako-Phen") on the seawater side of steel components, to resist seawater attack. However, the indigenous licensee has reportedly reneged on the job, as far as coating the ID of the tubes is concerned. We suggested utilizing S44660 (a

ferritic high performance stainless) or S31803 (a high performance duplex grade), either of which would resist seawater, while closely matching the thermal expansion of the steel components. Cathodic protection of the coated heads would be required, using special zinc or aluminum sacrificial anodes with routine replacement. A forthcoming publication of the Materials Technology Institute of the Chemical Process Industries, Inc., "Guidelines for Seawater-Cooled Tubular Heat Exchangers in the Chemical Process Industries" will be helpful, when available.

7. We made a general presentation on the Galvanic Series in seawater and the general subject of bimetallic corrosion, especially the role of dissolved oxygen as a cathodic depolarizer. Galvanic corrosion in a bimetallic couple will not proceed in the absence of dissolved oxygen (or some other cathodic depolarizer), because of polarization of the cathodic member of the couple.

c. Underground Piping

We emphasized that steel structures underground in soils of less than 10,000 ohm-cms. resistivity (less than 25,000 ohm-cms. for explosive gases) should be cathodically protected. Coating alone, without C.P., is very dangerous, as galvanic corrosion or stray D.C. current corrosion ("Electrolysis") will focus corrosion at defects ("holidays") in the coating. The additional cost of a C.P. system, either by galvanic sacrificial anodes or by an impressed current system, is negligible compared with the installed cost of the coated buried lines.

III - RCF, Trombay

On arrival at the Rashtriya Chemicals & Fertilizers, Ltd. plant in Chembur, Bombay, we met with Mr. U.M. Nayak, General Manager, and Mr. P.N. Mehrotra, Chief Engineer (Corrosion, NDT & Inspection). A schedule was arranged for the various operating departments during the week of 1987 February 16. Mr. Nayak had supplied PDIL with a preliminary listing of plant problems. He also requested that we visit the new plant in Thal on February 23-24.

A. Ammonia Plant

a. Converter Heat Exchanger

There is unexplained cracking of S32100 tubes in this gas-to-gas exchanger. Photographs taken by the plant have the appearance of a creep rupture failure, but the reported temperature of 500 C is too low for this. It may be due to nitriding effects or to lack of stabilization head treatment of the S32100. A detailed metallurgical examination is recommended.

b. MEA Absorber

The preliminary information had high-lighted a problem with pinhole perforations in the monoethanolamine (MEA) absorber after 22 years' service. This may be due to stress corrosion cracking of the ASTM A-285 steel vessel, which had never been stress-relieved, due to incursions of gaseous contaminants (e.g. CO, HCN) or to caustic or sodium carbonate contamination of the system. The vessel should be thoroughly inspected by shear-wave ultrasonic examination to determine whether the cracking extends above the liquid level. The proposed lining with S30403 is in accord with our thinking, provided the mechanical safety of the absorber is first ascertained. The system is operating within recommended parameters, and no other problems are reported.

Nevertheless, with this length of service, replacement with a stress-relieved A516 vessel might be a preferred approach.

c. Carbon Dioxide Cooler

The shell-side of the cooler has been severely corroded, due to carbonic acid attack, within 1½ years' service. We concurred in an S30403 replacement.

d. Ammonia Storage Tanks

We discussed the safety aspects of liquid ammonia storage tanks. A summary review of this topic has been published in the December 1986 issue of Materials Performance. Copies can be obtained from PDIL. Ultrasonic techniques, magnetic particle inspection and acoustic emission are used to determine whether stress corrosion cracking has occurred. Hydrostatic testing, which poses some problems due to local soil subsidence, constitutes only a strength test. Frequency of hydrostatic testing should follow schedules established by industrial safety standards. Oxygen scavenging (e.g. by hydrazine additions) is an additional possible corrosion control measure.

e. External Corrosion

The usual problems were reported with external coatings in a marine environment complicated by ammonia fumes harmful to ordinary paint systems. We reiterated our proposal that PDIL provide expert consultation on epoxy paints and other possible systems (e.g. those applicable over hand-prepared surfaces). We discussed the use of zinc-pigmented paints, emphasizing that they pose no hazard to carbon steel. Possible hazards to austenitic stainless steels arise only when welding zinc-contaminated surfaces (which hazard can be prevented by a dilute nitric acid wash prior to welding).

B. Urea Plant

a. Carbamate Condenser

This item has been the major problem. Urea-grade S31603 was replaced with a proprietary alloy (2RE69) more or less equivalent to N08904, which is still not entirely satisfactory. We suggested investigation of other high performance grades of up to 6% molybdenum content, although even these may not be an improvement.

b. Stripper Heat Exchanger

A second problem is erosion-corrosion of titanium tubes in the exchanger at the slurry inlet end of the stripper. 2RE69 ferrules also suffer erosion-corrosion. It was indicated that some operators are considering the use of bimetallic tubes (i.e. thin-gauge zirconium within an outer heavier-walled high performance stainless steel).

c. Vapor Lines

Here, polymeric derivatives of urea form solid deposits, which have been removed by tedious hand-cleaning. High pressure water lancing was suggested, although chemical cleaning with a 5% urea solution is also feasible.

d. Iron Oxide Deposits

Where such deposits clog stainless tubes or piping, we suggested professional chemical cleaning, using inhibited sulfamic acid plus ammonium bifluoride and/or ethylene diamine tetraacetate as a chelating agent. The acid cleaning should be followed by passivation with 10-15% nitric acid at 65 C.

e. Flange Corrosion

Crevice corrosion in S31603 flanges with metallic gaskets is due to oxygen concentration cell attack. It can be alleviated by a weld overlay of N08904 or N08020 on the flange faces.

C. Methanol Plant

a. MEA Stripping Still

Severe corrosion is reported in the reboiler of this carbon dioxide stripping still. This has developed over about a thirteen year period and may or may not reflect currently increased corrosion. Field corrosion tests are recommended. The operating parameters were reviewed, and the use of a sodium vanadate/potassium antimony tartrate inhibitor considered. Strip-lining with stainless steel might not be effective, as active/passive corrosion even of S31603 has been encountered in similar systems.

b. MEA Interchanger

Corrosion and degradation products accumulate on the lean (shell) side of the MEA solution interchanger and have resisted steam-cleaning, even when a window was cut in the shell. Corrosion products and mill-scale, as well as magnetite formed by hydrolysis of iron carbonates, should be amenable to inhibited HCl cleaning, if ammonium bifluoride is added to the acid. (Only slight improvement in heat transfer had been observed after acid cleaning without the ammonium bifluoride addition.)

c. Converter

Cracking of the 5 Cr-.05 Mo steel tubes and tubesheet has been reported in the converter. This may be a carbon monoxide-carbon dioxide-water vapor cracking which is reported in the literature. In this department, the cycle water should be treated with a non-chromate inhibitor (the system has already been cleaned) because vapor leaks of the methanol products to the water side reduce chromate and permit corrosion from the water side. Attempts to maintain chromate levels result in overtreatment. Analysis of the deposits show them to be mostly tricalcium phosphate/complex calcium phosphate plus iron phosphates.

d. Reformers

Mr. Gupta discussed inspection of HK-40 reformer tubes by in situ metallography, ultrasonics and magnetic permeability measurements, as well as electronic calipering for distension caused by creep.

D. Sulfuric Acid Plant

a. Leaf Filters

The 200 mesh 36 SWG S31603 screens in the leaf filters for molten sulfur suffer corrosion failures. This is thought to be due to chloride contamination rather than an acid effect, because ammonia is injected to neutralize acid species and because there is no reported corrosion of associated galvanized hardware. The combination of ammonium polysulfides and chlorides suggest the need for a high performance grade, such as N08904 or N08020. A PTFE screen would also be suitable.

b. Acid Coolers

Corrosion failures occur in the cast iron 98% acid coolers, as at other locations. Plate exchangers of N10276, or S31603 coolers with anodic protection, may ultimately be required. We reviewed the problems of quality control of cast iron pipe, as discussed at other locations and previously described.

c. Waste Heat Boilers

We reiterated our recommendations for proper procedures for seal-welding tubes to tubesheets, because this unit also reports failure in the seal-welded joints of the waste heat boilers.

d. Converter Piping

We reiterated our position on aluminum metallizing as being good in sulfur dioxide but susceptible to sulfur trioxide attack. S31603 is the preferred liner for converter piping, as previously described. However, alonized (hot-dip aluminum) tubes may be worth trying in the gas/gas exchanger, where carbon steel is failing after 3-4 years' service. Such aluminum-coated tubes are reportedly performing in similar service, probably due to successful mist elimination. Otherwise, safe-ending with high performance alloys, or retubing with the same, may be necessary.

e. Weak Sulfuric Acid Tank

Failure of lead cooling coils in the 67% acid tank is most prevalent at the water-line. Wrapping with PTFE tape or clamping with PTFE sleeves was suggested. It might be advisable to scavenge the .05% nitric acid contamination by sodium sulfite additions. Tantalum-plated coils, silicon iron (F47003) bayonet exchangers or PTFE exchangers would also be suitable for cooling the dilute acid. Generally, polypropylene or rubber-lining should resist the acid once it is cooled for storage.

f. Strong Acid Tanks

Desiccating vents were recommended to minimize reported vapor-phase corrosion of these tanks.

E. Nitrophosphate

a. Reactors

There are a series of seventeen reactors, each S31603 reactor having twin legs containing agitators. The 34 cast 316L (i.e. CF3M; J92800) agitators suffer high rates of erosion-corrosion, particularly in the early, more acidic, stages where phosphate rock is treated with nitric acid and diammonium phosphate or phosphoric acid. It is impossible to predict the relative merits of high performance alloys (e.g. HV9 or N08904; N08028), but they should be tried experimentally and a cost/benefit analysis made.

A newer modification proposes to employ only 3 reactors of S31603 and agitators of a German composition (DIN 1.4500), according to a Finnish design. Mr. Gupta is to ascertain the composition of the alloy, as to whether or not it contains molybdenum and, if so, whether in adequate amounts. The new reactors will have S31603 cooling coils, and we warned against leaving water stagnant in the coils, as pitting would ensue. High performance coils (e.g. S31254, N08904) would be more reliable.

b. Scrubber

A GRTP scrubber is reported to have suffered erosion thinning after 5-6 years' service. It may have been chemically attacked by oxides of nitrogen in the gases at 70 C. We discussed relining with polypropylene, chlorsulfonated polyethylene or fluorinated plastics (e.g. PVDF, FEP, PFA).

c. Blowers

Blowers and fans in this unit become imbalanced due to accumulation of dust/silt deposits. After some discussion, we concluded that only a high-baked phenolic coating might be suitable for anti-stick protection.

F. Phosphoric Acid Plant

a. Digesters

A general discussion was conducted which reviewed the metallurgy of stainless steels, the use of S31603 in phosphoric acid digesters, and the development of high performance stainless steels and nickel-based alloys for such service. The high alloys show different ratings in different systems, as the oxidizing capacity of the liquors varies with the kind and concentration of contaminants (e.g. fluorides, chlorides and ferric or other cations).

b. Heat Exchangers

Graphite heat exchangers in this unit have suffered blockage and brittle failures. A replacement exchanger, using N08028 tubes in an N08904 tubesheet, has failed in 2-3 months. Only the alloy N06985 remains to be tried as a possible alternative to graphite. A block-type exchanger in graphite would be less susceptible to breakage than the tube-and-shell design.

c. Pumps

It was reported that an alloy cast iron (30 Cr-2 Mo) had proven successful in other phosphoric acid plants. We expressed strong reservations about using other than high performance austenitic alloys, but concurred in a trial installation.

G. Civil Engineering

a. Concrete

We discussed various aspects of corrosion of concrete (e.g. acidic attack, soft water attack, sulfate corrosion), epoxy-coating of rebar for concrete, concrete applications over steel, and brick linings and their cements.

b. HDPE Piping

Reported failure of a welded HDPE pipe (handling a chalk slurry in very dilute phosphoric acid) after 6-8 years seems to be associated with the clamping arrangement. A possible redesign for thermal expansion control may be necessary to prevent cracking at the clamping points.

c. Rubber-Lined Piping

Troubles with rubber-lined piping for gypsum slurries were again discussed. Failures after 7-8 years' service may be due to poor quality control, but service temperature effects on adhesives, or chloride effects (formation of brittle rubber hydrochlorides), may be a factor.

d. External Corrosion

Plant problems with external corrosion due to polluted tropical marine atmospheres were again discussed. Solutions based on improved painting systems and maintenance procedures should be investigated.

H. Nitric Acid Plants

a. Reactor Heat Exchanger

The gas/gas exchanger on the outlet of the reactor is apparently under-designed, with an outlet temperature of about 450 C vs. the design temperature of 230 C. The seal-welded tubes and portions of the shell are undergoing corrosion by the process gas on the shell side. Retubing in a proprietary alloy such as 2RE10

(S31003) or N08800 was recommended in lieu of the S30403 currently used.

b. Absorber Coils

The cooling coils, which are circumferentially welded where they pass through the roof of the vessel, are apparently failing from the cooling water side, possibly due to water-borne deposits in this area. A change to N08800 pipe for the coil would be a solution, as would the use of chloride-free water (e.g. steam condensate). A metallurgical examination is recommended to differentiate stress corrosion cracking from mechanical fatigue and other possible mechanisms.

c. Ductwork

There is a pervasive problem with failures of S32100 process gas ductwork in the weld heat-affected zones. This may be due to improper alloy composition or to lack of a stabilizing anneal before fabrication. We reviewed the origins of 18-8 stainless steels and the development of both the stabilized (S32100 with Ti; S34700 with Cb) and low-carbon grades. The stabilized grades are susceptible to Knife-Line Attack and heat-treatment problems. In today's technology, S30403 is preferred for welded applications in services below 425 C.

d. Gas-Cooling Condenser

In this exchanger (water in the tubes), the top rows of tubes are failing from the shell side, possibly opposite the gas inlet nozzle. External water spray to minimize condensation was suggested, but poses risks of external stress corrosion cracking. We suggested installation of an impingement plate, if Borescope examination confirms the suspected areas of tube failures as opposite the gas inlet.

e. Absorption Tower

There is severe corrosion of bubble caps and trays in the bottom section. The annual replacement might be avoided either by installing valve trays or sieve trays, if the process engineers would permit this change. Otherwise, a higher alloy (e.g. S31003) may be cost effective. We emphasized that the next grade of materials after the 18-8 varieties was the 25% chromium, molybdenum-free alloy exemplified by S31003 and N08800.

f. Reactor Basket

The S31008 baskets suffer creep deformation in high temperature service after some period of time. Replacement in N06617 was recommended, because of its strength and amenability to repair.

g. BFW Preheaters

The stainless steel boiler feedwater preheaters have been severely corroded on the tube side at the cooled gas outlet. Tube ends, seal welds and tubesheet show severe localized attack. A 2RE10 or N08800 template or weld overlay would protect the tubesheet, while the tubes should be replaced with a 25% chromium alloy. Safe-ending would not be economical in this relatively small exchanger. In new design, an S30403 item might be resized to prevent condensation in the exchanger.

h. Chloride Limits

Chrloides in nitric acid cause evolution of nascent chlorine, which greatly complicates the corrosion picture in various parts of the system. Presently, the plant is trying to maintain 50 ppm chlorides maximum, per the vendor's recommendation. The limits of permissible chloride ion contamination should be investigated.

I. Concentrated Nitric Acid

a. Dehydration Tower

Concentrated acid is made by dehydrating the 67% product with 98% sulfuric acid. The lead-lined steel towers contain cast ceramic sections about 3" thick and 3' high, joined with blue asbestos packing impregnated with acid-resistant silicate-based cement. There is some failure to the ID glaze on the ceramic, and leaks in the cemented joints, with resultant corrosion of the subtrate metals and further parting of the ceramic sections. Mr. Dillon will provide the address of Dr. Robert Pierce, Ohio State University, an eminent authority in the field of ceramics and cements, for possible advice.

b. Storage Tanks

The aluminum storage tanks for red fuming nitric acid suffer corrosion of the vapor lines due to ingress of atmospheric moisture. Desiccating vents must be provided. Reference was made to Mr. Dillon's article in Corrosion magazine in the early 1950's on "Vapor Phase Corrosion of Type 347 and Al 1100 in Concentrated Nitric Acid", which should be available from PDIL.

J. Ammonium Nitrophosphate

a. Erosion/Abrasion

There are major erosion-corrosion or abrasion problems in the centrifuge, prilling tower, crystallizers and mixed nitric/phosphoric acid pumps. It is evident that the wear is too much for S31603 components. We discussed duplex alloys (e.g. S31200, S31803, S32550), precipitation-hardening grades (e.g. S17400, S17700), nitriding of the PH grades, and hard-facing with cobalt-chromium alloys (e.g. the Stellites). All these mechanical wear problems must be resolved by plant experimentation, as it is impossible to predict performance of the candidate materials. We did note that the cast 28 Cr-4 Mo-0.2 C cast alloy (reported as of potential interest in phosphoric acid digesters) had failed in 2 months in the acid pump application.

b. Absorbing Reactor

In the dissolution of phosphate rock in 60% nitric acid, there is vapor phase corrosion of S30403 due to evolution of HF and traces of chlorine. We recommended changing to S31603 on a trial basis. N08020 or N08825 might be even more resistant. N10276 has been used for nitric-HF service.

c. Vapor Lines

In the vapors off the prilling tower, as well as above the stored molten ammonium nitrate (all at 170 C, the melting point of the salt), there is localized attack on S30403. We theorize that this is due to decomposition of discrete salt particles, releasing nitric acid in situ. This would not occur in the liquid phase, because of mixing, or would not be enriched with Cr VI irons as are discrete particles in the vapor. High performance alloys may be required.

d. Phosphoric Acid Feed

The 2" S31603 piping which feeds 35% phosphoric acid to the reactor, has failed, due to traces of sulfuric acid and other contaminants. A PVC-lined GRTP piping replacement apparently failed mechanically, due to inadequate provision for thermal expansion. Redesign (or replacement in polypropylene) was recommended, or an N08904 system. Chlorsulfonated polyethylene or a fluorinated plastic was suggested to replace polypropylene vent piping, which failed in about 2 years by oxidation and embrittlement due to oxides of nitrogen.

K. Plant Utilities

a. Steam

1. We recommended use of chrome-molybdenum steels for steam service above 450 C; mechanisms of graphite spheroidization were reviewed.

2. Corrosion of steam condensate return lines is reported. Although the condensate is polished to remove iron and other solids before return to the boiler feedwater system, we suggested use of filming or neutralizing amines, as further studies might indicate.

3. Procedures for seal-welding waste heat boiler tube/tubesheet connections were reviewed in detail (as previously described).

b. Cooling Water

Some 2 kilometers of buried steel piping, which brings the master stream of water to the plant site, is undergoing both internal and external corrosion after 15-20 year service. There is failure of the external coating and localized attack due to acid spillage. We recommended a current demand test by a professional C.P. engineer, to determine the feasibility of cathodic protection. We also recommended use of lime additions in backfill after repairs, and a scheduled replacement in GTRP piping for the future.

IV - RCF, Thal

A brief visit was made to the new RCF plant at Thal (commissioned in October 1984) on 1987 February 23-24. We met with Mr. K. Krishan, Dy. General Manager, Dr. C. Chakrabarty and others (see appendices). A list of plant problems had been prepared but was not available in advance. This plant has only air separation, ammonia and urea facilities.

A. Urea Plant

a. Carbon Dioxide Interstage Cooler

This exchanger has cycle water on the shell side and was fabricated with steel baffles, although the tubes were S30400. The baffles have suffered enough galvanic corrosion in 2 years to permit the tubes to vibrate and fail by baffle wear. Ingress of carbon dioxide then aggravates steel corrosion. The baffles and tie-rods should be replaced with S30400. We concurred in a temporary fix to be effected by welding a stiffening rod between individual tubes and baffles. C.P. is not feasible because it is impossible to effect proper current distribution.

b. Carbamate Condenser

In this horizontal S31603 exchanger, the water level on the shell varies, permitting excessive temperatures in the top layers of tubes. Tube failures may be due to fatigue (from vibration), crevice corrosion or other mechanisms. A metallurgical examination must be made before further decisions can be made.

c. Ammonia Condenser

Ammonia leaks to the water side may be due to corrosion of steel by traces of carbamates. The seal welds may be defective. The proper welding procedures and sequence were described.

d. Carbamate Evaporator

The carbamate solution is evaporated within the tubes of this vertical exchanger,, by steam on the shell side. The Urea grade S31603 tubes suffer general thinning. If a proper oxidizing capacity cannot be maintained (e.g. by injection of air or hydrogen peroxide), higher alloys like N08904, N08028 or titanium may be required.

e. Benfield Solution

This is the 30% potassium carbonate solution used to absorb carbon dioxide from the syn-gas (in a manner analogous to an MEA system). It is "inhibited" with vanadium pentoxide.

1. Reportedly, the CF3M pump is suffering erosion, abrasion or corrosion in the 110 C solution. Since steel is reportedly unattacked, this may be active corrosion of the stainless, in which case a nickel cast iron (e.g. F41000, F43000) might be a better choice. Mr. Dillon will seek out other peoples' experience. There was considerable discussion of oxidizing inhibitors (e.g. various valence states of vanadium; possible use of nitrites) and whether S31603 might be active due to alkali or in the transpassive range (due to excess oxidants).

2. An uncoated underground steel tank in a concrete containment is used to collect spillage. It has failed by ingress of ground water to the tank bottom, through the concrete. We suggested installation of a smaller tank, well-coated on the exterior, to be installed inside the original.

B. Utilities

a. Steam

Excessive iron contamination present in the boiler feedwater (3:1 make-up:returned condens The major problem is turbine imbalance due to iron deposits. We discussed further sampling and analyses to determine the source (i.e. plant condensate, the hot condensate tank, make-up before the deaerator). Steel pipe handling softened water before the deaerator should be replaced in S30400. We believe cyclohexylamine/morpholine should be added to the make-up tank; not before. Use of filming amines vs. neutralizing amines was discussed, as was boiler treatment in general. A professional study should also be made to fine-tune the steam generation system.

b. Cooling Water

1. The good quality make-up water is currently treated with chromate-polyphosphate-zinc, with apparent success as indicated by coupon and polarization techniques. We again discussed non-chromate treatments as a possible alternative.

2. The subject of chloride limits for 18-8 was again reviewed. There should be no problem at 60 C maximum tube-wall temperature, provided no extraneous films are deposited and no evaporation is permitted.

C. Areas of Concern

Because of limited time for discussion, we provide the following check list for areas of concern, based on experience in plants in this sort of climate and terrain.

1. Survey the plant site for soil resistivity; provide C.P. for bare and for coated steel underground where less than 10,000 ohm-cm prevail (25,000 ohm-cm for explosive gases).

2. Maintenance Painting

   a. Inspect all structures and uninsulated piping and vessels for first signs of deterioration. Touch-up top-coat before primer is damaged. Watch areas in the lee of cooling towers, especially.

   b. Investigate coating systems compatible with hand-prepared surfaces (e.g. water-curing polyurethanes).

   c. Coat steel flanges on 18-8 stainless vessels (and piping 6" and over) against external stress-corrosion cracking.

3. Insulation

   a. Inspect and repair all weather barriers

   b. When re-insulating vessels or large piping, coat with epoxy before installing insulation on either steel or 18-8.

4. Cooling Water

   Review equipment records on all stainless steel water-cooled exchangers.

   a. Schedule replacement of all steel baffles, tie-rods and hardware, when water is on shell side.

   b. Check steel shell thickness now for original reading. Inspect on a 3-year basis. Schedule replacement as needed. GTRP shells may be substituted.

   c. When water is on the tube-side, do not coat heads (nor shells when water is on shell-side).

d. Check raw-water intake for corrosion rate on steel, if uncoated.

5. Threaded Fasteners

a. Replace steel bolts/nuts on working flanges (those opened regularly) with more resistant bolting (i.e. galvanized, aluminum-coated, polyimide/PTFE-coated) after determining cost/benefit ratio and availability.

b. For cryogenic bolting, use 18-8 or PH grades, not high strength bronzes.

6. Ammonia Storage

a. Inspect ammonia storage tanks by shear-wave U/S for stress corrosion cracking in liquid and vapor phases. Investigate use of oxygen scavengers (e.g. hydrazine).

b. Review ammonia recovery systems for carbamate attack. Replace steel with S4100 to 40 C, S30403 to 60 C, S31603 above 60 C.

7. Firewater

Check fire-control water piping in dead legs for attack by sulfate-reducing bacteria. Monitor storage tank for corrosion by air ingress; monitor coating performance in tank, applying C.P. if required.

V - Miscellany

Miscellaneous activities comprised discussions with my counterpart, Mr. Gupta, in his capacity as PDIL representative, on various subjects, and participation in the one-day workshop at Baroda on "Corrosion Control for Productivity".

A. Workshop

On 1987 February 20, we proceeded to Baroda, at the request of the Gujarat State Chemicals & Fertilizer Company, Ltd. We met with Dr. M.H. Mehta, Dy. Director, and Dr. G.H. Thanki, Group Leader of the Corrosion & Materials Laboratory.

On February 21, I gave the key-note address to an assembly of engineers and managers, emphasizing the economics of corrosion control, comparisons of alternatives by annual cost/present worth analysis, the forms of corrosion (recognition and prevention), and the role of communication (vertical and lateral) in corrosion control. There followed three other papers; Dr. Thanki's review of GSCF's decade of experience in corrosion control, Dr. Perumal's paper on case histories in industrial corrosion problems, and Dr. T. Raman's paper on modern corrosion monitoring techniques. We also toured the new corrosion and metallurgical laboratory facilities before concluding with a panel question and answer session.

B. PDIL

In addition to technical papers of potential interest to PDIL, I provided Mr. Gupta with copies of two books; the McGraw-Hill publication, "Corrosion Control in the Chemical Process Industries" by C.P. Dillon (1986) and the NACE publication, "Process Industry Corrosion- The Theory and Practice" (1986).

Subjects extraneous to the plant visits were also discussed with Mr. Gupta, including

a. Phosphorous trichloride storage and reaction problems.

b. Hydrogen sulfide corrosion in methanol scrubbing systems in coal gasification processes.

c. Corrosion in copper sulfate production.

d. Economic calculations for comparison of alternative corrosion control measures, annual cost of present worth discount cash flow.

Annex I

Attendance; FACT, Udyogamandal

Plant	Contact	Position
Sulfuric Acid	Mr. T.P.S. Nair	DyCP(A)
	Mr. Muraleedharan	Proc. Engr.
	Mr. Hemachandran	PM (Acid)
Ammon. Sulfate	Mr. Krishnamachari	DySP(S)
Ammon. Chloride	Mr. Kochukkrishnan	MPG
Superphosphate	Mr. C.J. Sarasan	AM(T,S)
	Mr. P.P. Sunny	PE(S)
	Mr. P.K.V. Pillai	PM(S)
	Mr. Kulathu Iyer	PM (SAC)
	Mr. K. Rama Varma	PE(P)
Phosphoric Acid	Mr. Krishnamachari	DyCSP(S)
Phosphate	Mr. Mohankumar	PM(P)
Tonnox/OG Plant	Mr. Chackochan	Engr (TS)
	Mr. Jose Jacob	PM(OG)
	Mr. S. Parameswaran	APM(Tonnox)
	Mr. Job Joseph	Addl PM
Ammonia Plants	Mr. John Davis	PM(A)
	Mr. Madhava Menon	APM(CA)

Annex II

TABLE I

Alloy Designations & Composition

A. Aluminum

UNS No.	Common Name	Major Alloying Element
A91100	Al 1100	None (99.5%+)
A93003	Al 3003	Manganese
A95154	Al 5154	Magnesium
A96063	Al 6063	Magnesium, Silicon

B. Alloy Cast Irons

		Ni	Cu	Cr	Si	Fe
F41000	NiResist (I)	15	7	2	2	Bal.
F43000	Ductile D-2	20	--	2	2.5	Bal.
F47003	Duriron	--	--	--	14	Bal.

C. Nickel Alloys

		Ni	Cu	Cr	Fe	Mo	Other
NO6600	Alloy 600	76	--	15	8	--	---
NO6617	Alloy 617	52	.2	22	1 5	9	12.5 Co
N06625	Alloy 625	61	--	22	2.5	9	Cb/Ta
NO6985	Alloy G-3	45	2	22	20	7	Co,W,Cb,Ta
NO8020	Alloy 20Cb3	34	3	20	37	3	0.5 Cb
NO8026	Alloy 20-6M	34	3	20	34	6	
NO8028	Alloy 28	31	--	27	48	7	---
NO8800	Alloy 800	32	--	21	46	--	Ti, Al
NO8825	Alloy 825	41	2	21	30	3	Ti
NO8904	Alloy 904L	33	2	21	40	4	---
N10276	Alloy C276	55	--	16	6	16	W

TABLE I (Cont'd.)

D. Stainless Steels

Precip.	Hard.	Cr	Ni	Mo	Cu	C	Other
S15700	15-7Mo	15	7	3	--	.09	---
S17400	17-4PH	17	4	--	+	--	.07
S17700	17-7PH	17	7	--	--	.09	Al

E. Stainless Steels

Aust.		Cr	Ni	Mo	Cu	C	Other
S30300	303	18	9	--	--	.15	S,Se
S30400	304	18	9	--	--	.08	---
S30403	304L	19	10	--	--	.03	---
S31008	310	25	20	--	--	.08	---
S31003	310L	25	20	--	--	.03	---
S31600	316	17	13	3	--	.03	---
S31603	316L	17	12	3	--	.03	---
S32100	321	18	11	--	--	.08	Ti
S34700	347	18	12	--	--	.08	Cb/Ta

F. High Performance Stainless Steels

Ferritic		Cr	Ni	Mo	Cu	C	Other
S44660	Seacure	26	3	3	--	.025	N,Ti, Cb
Duplex							
S31803	2205	22	6	3	--	.03	N
S32550	255	26	6	3	2	.04	N
Austenitic							
S31254	254SMO	20	18	6	--	.02	---

Annex III

Attendance; FACT, Ambalamedu

Plant	Contact	Position
Ammonia	Mr. P.K. Achuthan	DyCSP(A)
	Mr. Balakrishnan	PM(A)
Urea	Mr. T.M. Rajan	PM(U)
Thermal	Mr. Sunny Mathew	PM(T)
NPK	Mr. Ramachandran	DyCSP(C)
	Mr. Sankaran	PM(NPK)
Sulfuric Acid	Mr. Elayidam	PM(SA)
	Mr. E.J. Joseph	PM(PA)

Annex IV

Attendance; RCF, Trombay

Plant	Contact	Position
	Mr. U.N. Nayak	General Manager
Ammonia	Mr. G.K. Diddee	DyGM
	Mr. H.K. Ghakkar	CM
	Mr. N.C. Bandophadhyay	OM
	Mr. K.G. Shridharan	Sr.PM
	Mr. H.S. Karangale	Sr.PE
Urea/Methanol	Mr. S.M. Ahmed	OM
	Mr. J.P. Chakravarti	CM
	Mr. R. Mandal	
	Mr. J.C. Sobti	OM
	Mr. S.K. Adchitre	PE
	Mr. O.P. Zanzaria	Sr.PM
	Mr. G.M. Pednekar	DyCE(M)
Sulfuric Acid/CNA	Mr. S.S. Agarwal	DyGM
	Mr. P.Y. Gurjar	GM
	Mr. S.K. Sirkar	APM
	Mr. D. Bhaskaran	PM
Suphala/Phosphoric	Mr. C.M. Garai	CM
	Mr. Bhatia	Sr.PM
	Mr. Handa	PE
	Mr. Bansal	APE
	Mr. D.K. Bhatta	Addl. CE
Phosphoric Acid	Mr. M.R. Duby	DyGM
	Mr. Bargale	DyCE
	Mr. Periwal	Sr.PE

ANNEX IV (Cont'd.)

	Mr. Krishnakumar	PM
	Mr. N.K. Banerjee	APM
Nitric Acid Plant	Mr. R.P. Juneja	OM
	Mr. K.K. Roy	DyCE
	Mr. M.P. Padukane	DyCE
	Mr. J.S. Bhalla	PM
	Mr. Y.P. Bhuchur	APM
	Mr. S.M. Sundaram	PM
ANP Plant	Mr. M.R. Duby	DyGM
	Mr. B.K. Chakrabarty	DyCE

Annex V

Attendance; RCF, Thal

Plant	Contact	Position
Urea	Mr. S.K. Dua	CM
	Mr. Nesri	DyCE
	Mr. S.K. Agarwal	DyCE
Ammonia	Mr. D. Deshmuhk	PM
Steam Generation	Mr. G.D. Sharma	CM
Water Treating	Mr. S. Shimpukade	DyCE
Laboratory	Dr. P.H. Ghate	DyCC
Tech. Service	Dr. C. Chakrabarty	Corr. Engr.