APPLIED CHEMISTRY DIVISION
PROGRESS REPORT
FOR THE PERIOD 1990 - 1992
Edited by
S. R. Bharadwaj, Kamal Kishore and V. Ramshesh

1993
GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

APPLIED CHEMISTRY DIVISION
PROGRESS REPORT
FOR THE PERIOD 1990 - 1992
Edited by
S.R. Bharadwaj, Kamal Kishore and V. Ramshesh
Applied Chemistry Division

BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA
1993
<table>
<thead>
<tr>
<th>Item</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Security classification:</strong></td>
<td>Unclassified</td>
</tr>
<tr>
<td><strong>Distribution:</strong></td>
<td>External</td>
</tr>
<tr>
<td><strong>Report status:</strong></td>
<td>New</td>
</tr>
<tr>
<td><strong>Series:</strong></td>
<td>BARC External</td>
</tr>
<tr>
<td><strong>Report type:</strong></td>
<td>Progress Report</td>
</tr>
<tr>
<td><strong>Report No.:</strong></td>
<td>BARC/1993/P/005</td>
</tr>
<tr>
<td><strong>Title and subtitle:</strong></td>
<td>Applied Chemistry Division progress report for the period 1990-1992</td>
</tr>
<tr>
<td><strong>Collation:</strong></td>
<td>234 p., tabs., figs., appendices</td>
</tr>
<tr>
<td><strong>Project No.:</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Personal author(s):</strong></td>
<td>S.R. Bharadwaj, Kamal Kishore, V. Ramshesh (eds.)</td>
</tr>
<tr>
<td><strong>Affiliation of author(s):</strong></td>
<td>Applied Chemistry Division, Bhabha Atomic Research Centre, Bombay</td>
</tr>
<tr>
<td><strong>Corporate author(s):</strong></td>
<td>Bhabha Atomic Research Centre, Bombay - 400 085</td>
</tr>
<tr>
<td><strong>Originating unit:</strong></td>
<td>Applied Chemistry Division, BARC, Bombay</td>
</tr>
<tr>
<td><strong>Sponsor(s) Name:</strong></td>
<td>Department of Atomic Energy</td>
</tr>
<tr>
<td><strong>Type:</strong></td>
<td>Government</td>
</tr>
<tr>
<td><strong>Date of submission:</strong></td>
<td>July 1993</td>
</tr>
<tr>
<td><strong>Publication/Issue date:</strong></td>
<td>August 1993</td>
</tr>
</tbody>
</table>

contd...(ii)
The report covers the research and development (R&D) activities of the Applied Chemistry Division for the period January 1990 to December, 1992. R & D programmes of the Division are formulated to study the chemical aspects related to nuclear power plants and heavy water plants. The Division also gives consultancy to DAE units and outside agencies on water chemistry problems. The thrust areas of the Division's R & D programmes are: decontamination of nuclear facilities, metal water interaction of the materials used in PHT system, chemistry of soluble poisons, biofouling and its control in cooling water circuits, and treatment of cooling waters. Other major R & D activities are in the areas of: solid state reactions and high temperature thermodynamics, primary coolant water chemistry, speciation studies in metal amine systems, high temperature aqueous radiation chemistry. The Division was engaged in studies in novel areas such as dental implants, remote sealing of pipes in MS pipes, and cold fusion. The Division also designed and fabricated instruments like the Knudsen cell mass spectrometer, calorimeters and developed required softwares. All these R&D activities are reported in the form of individual summaries. A list of publication from the Division and a list of the staff members of the Division are given at the end of the report.

Keywords/Descriptors: DECONTAMINATION; RADIATION CHEMISTRY; RADIOLYSIS; CALORIMETERS; MASS SPECTROMETERS; COLD FUSION; PHWR TYPE REACTORS; BWR TYPE REACTORS; WATER CHEMISTRY; FOULING; CORROSION; BARC; RESEARCH PROGRAMS; PROGRESS REPORT; COMPLEXES; CHEMICAL PREPARATION; REACTOR COOLING SYSTEMS; NUCLEAR POISONS; SOLIDS; CHEMICAL REACTIONS; CRYSTAL STRUCTURE; THERMODYNAMIC PROPERTIES; EXPERIMENTAL DATA
FOREWORD

I have great pleasure in bringing out this report covering the activities of the Applied Chemistry Division for the period January 1990 to December 1992. In this period, the Division has contributed significantly to the R & D programmes on chemistry aspects related to Nuclear Power Stations. Important contributions were also made in basic research in the fields of radiation chemistry, complex chemistry, solid state reactions and high temperature thermodynamics. Consultancy services were rendered to nuclear and thermal power stations, heavy water plants and other organisations on various water chemistry problems. The Division also took active part in the training programmes of the centre.

In reactor related programmes, chemical decontamination of PHWRs and BWRs was the major area of investigation; besides, several other aspects such as chemistry of soluble chemical poisons for PHWRs, diffusion and migration behaviour of corrosion and fission product species in pressure tube and steam generator tube materials, biofouling and biocorrosion in power plant cooling systems etc. were also investigated.

In the field of radiation chemistry, radiolysis of N₂-water systems, effects of radiation on components of decontaminant formulations and pulse radiolysis studies on a number of technologically important compounds such as corrosion inhibitors, drugs etc. were carried out.

There is growing evidence to suggest that the specific toxic effects of aluminium on terrestrial and aquatic organisms are related to its chemical identity. Hence studies on characterization of aluminium complexes with various organic ligands were initiated.
Copper being a major constituent of steam generator alloys, studies on its speciation with a number of amines having potential as AVT (All Volatile Treatment) reagents were carried out.

The use of metal bifluorides of the general formula, $\text{MHF}_2$ where $M = \text{NH}_4$, Li, Na, K and Rb to fluorinate a variety of inorganic compounds such as vanadates, binary oxides and high $T_c$ oxides and also metals and alloys has been demonstrated by studying a number of such solid state reactions. A very interesting outcome of this work is the observation that even grinding together the two reactants is not required to bring about the reaction at room temperature; by merely keeping in contact the two reactant solids at room temperature, the reaction commences by the formation of a crystalline product layer at the interface.

Knowledge of thermodynamic properties of fission products and their chemical interactions with the fuel and the clad are important in predicting the long term integrity of the nuclear fuel under irradiation. Therefore, several experimental investigations and evaluations on systems containing fission product elements such as Cs, Mo, Zr, Pd and Te were undertaken to obtain reliable thermodynamic data on a wide variety of compounds involving fission products and the fuel. Setting up of the thermodynamic database for Pd and Te was another important activity in this field.

Studies were undertaken in novel areas such as dental implants for the BARC hospital, remote sealing of pipes in MS pipes and in the then frontline area of "cold fusion".

Several new instruments were designed and fabricated viz., the Knudsen cell mass spectrometric system, the thermogravimetric
assembly for transpiration experiments, DSC for heat capacity measurements and computer controlled DTA apparatus. Several softwares were developed by the scientists of the Division: (i) software for retrieval of powder XRD data from JCPDS database, (ii) expert system for secondary side water chemistry monitoring in PHWRs, (iii) a basic program for processing electrochemical data and (iv) a d-Base program for computerization of indents placed with DPS.

On the human resources development front, the staff members of the Division continued to take active part in teaching various courses of the BARC Training School and also participated in the selection programmes of the Training School.

The expertise available in the Division in the areas of water chemistry related to the primary and secondary side of nuclear power reactors and the cooling water aspects of these and other industrial plants is often sought by other DAE units. One of the principal agencies through which this is channelised is the Committee on Steam and Water Chemistry (COSWAC), of which the Chairman and Member-Secretary are from this Division.

Analytical support was given to Korba Super Thermal Power Station and FBTR. Besides, a total of 1328 samples were analysed by various techniques such as TG, DTA, DSC, XRD etc. These services were rendered to various units of BARC/DAE and other institutions such as the universities.

The list of publications from the Division (given at the end of this report) includes 108 papers published in journals, 91 papers presented at various conferences/symposia, 8 reports, 7 Ph.D theses, 20 invited talks and 9 articles in books; this speaks about the quantum of work done during this period. A separate volume containing the reprints of the papers published
is being brought out by the editors.

The report in the present form would not have been possible but for the hard work put in by the editors in collating the contributions from the individual scientists, and I am very thankful to them. No less has been the role of the individual scientists, not only because their contributions have been noteworthy, but they have also helped a great deal by providing the necessary information in the format as required by the editors for both of which I am very grateful.

I hope, this report will give the readers a brief account of the spectrum of activities in which the scientists of Applied Chemistry Division are engaged.

P.N. Moorthy
Head, Applied Chemistry Division
"What is there in preparing a Progress Report of a Division?" one may ask. After all, the contributors will write their portions, Head of the Division will approve them and the editors have only to compile these. If only life were so simple and things work so well -- then there would be no need for editors and a report can be produced in no time.

In actual practice there are several BUTS besides the IFS. Collecting the contributions from everyone is only the first task. This involves gently reminding them that their contribution is important. Then getting these approved by Head of the Division can be challenging depending on the exactness demanded by the latter. In this case the drafts after revision by the Head had to be referred back to the contributors and this sequence was followed a couple of times! Then came the final stage of arranging the report and this went through several permutations and combinations.

All these operations require several skills -- considerable degree of interpersonal interactions, tact and, of course, tight rope walking; the editors should have the capacity to please everyone (or at least not displease anyone). And they should have infinite patience! If we could cope up with all these it was because of the goodwill shown by all our colleagues and the encouraging attitude of the Head of the Division. Words are inadequate to express our debt of gratitude to one and all. We can only say, 'THANK YOU FOR ALL THE HELP'.

Finally the Report is with you. We would be obliged for a feedback -- so that we can judge our own worth.

(S.R. Bharadwaj)  (Kamal Kishore)  (V. Ramshesh)
## CONTENTS AT A GLANCE

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOREWORD</td>
<td>(i)</td>
</tr>
<tr>
<td>EDITOR'S PAGE</td>
<td>(v)</td>
</tr>
<tr>
<td>1 REACTOR RELATED PROGRAMMES</td>
<td>1 - 59</td>
</tr>
<tr>
<td>2 RADIATION CHEMISTRY</td>
<td>60 - 74</td>
</tr>
<tr>
<td>3 COMPLEX CHEMISTRY</td>
<td>75 - 82</td>
</tr>
<tr>
<td>4 SOLID STATE CHEMICAL REACTIONS</td>
<td>83 - 96</td>
</tr>
<tr>
<td>5 STRUCTURE, THERMODYNAMICS AND THERMOCHEMISTRY</td>
<td>97 - 115</td>
</tr>
<tr>
<td>6 BIOFOULING, BIOCORROSION AND CHEMISTRY OF COOLING WATER SYSTEMS</td>
<td>116 - 124</td>
</tr>
<tr>
<td>7 NOVEL AREAS</td>
<td>125 - 129</td>
</tr>
<tr>
<td>8 INSTRUMENTATION AND SOFTWARE DEVELOPMENT</td>
<td>130 - 137</td>
</tr>
<tr>
<td>9 HUMAN RESOURCE DEVELOPMENT</td>
<td>138 - 146</td>
</tr>
<tr>
<td>10 CONSULTANCY AND REPORTS</td>
<td>147 - 158</td>
</tr>
<tr>
<td>11 SERVICE ANALYSES</td>
<td>159 - 162</td>
</tr>
<tr>
<td>12 PUBLICATIONS</td>
<td>163 - 206</td>
</tr>
<tr>
<td>13 APPENDICES</td>
<td>207 - 217</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS

1. **REACTOR RELATED PROGRAMMES**

   1.1 **Decontamination of PHWRs**
      
      1.1.1 Feasibility study of chemical decontamination of PHT system of MAFS
      
      1.1.2 Corrosion compatibility studies in the decontamination formulation
      
      1.1.3 Electrochemical study of compatibility of decontaminant formulations with PHT system materials
      
      1.1.4 Compositional characteristics of magnetite synthesised from aqueous solutions at temperatures upto 523 K
      
      1.1.5 Kinetics of metal oxide dissolution from the point of view of chemical decontamination
      
      1.1.6 Ion exchange studies relating to the development of decontamination processes
      
      1.1.7 Development of analytical procedures for estimation of various constituents of the decontaminant formulation
      
      1.1.8 Dissolution of magnetite in decontaminant formulations and the effect of gamma irradiation on their efficacy
      
      1.1.9 Effect of corrosion inhibitors on the corrosion rate of carbon steel in EAC decontaminant formulation
      
      1.1.10 Methodology of decontaminant formulation preparation
      
   1.2 **Decontamination of BWRs**
      
      1.2.1 Polarographic studies on $\text{VO}_3^-$ ion

   (vii)
1.2.2 Electrochemical preparation of LOMI formulation
1.2.3 Vanadium estimation
1.2.4 Decontamination studies on coupons from TAPS clean-up recirculation system

1.3 Soluble chemical poisons for PHWRs
1.3.1 Studies on gadolinium nitrate for possible use as chemical poison in NPRs
1.3.2 Stability of Gd(NO₃)₃ solution under moderator system conditions
1.3.3 Aspects of boron chemistry

1.4 Mass transport behaviour of corrosion and fission product species in pressure tube and SG materials
1.4.1 Studies on the migration and segregation of activated corrosion and erosion products in steam generator tube materials
1.4.2 Mass transport studies of iron in pressure tube material
1.4.3 Studies on the release of gaseous and volatile fission products from 'SIMFUEL'

1.5 Water chemistry studies
1.5.1 Comparative study of hydrazine and dichromate treatments
1.5.2 Studies on different corrosion inhibitor formulations

1.6 Work related to nuclear power stations
1.6.1 Hot conditioning evaluation of primary heat transport system surfaces of NAPP-2 and KAPP-1
1.6.2 Modified hot conditioning (With reference to future NPRs)
1.6.3 Evaluation of coolant sea water for TAPP - 3 & 4

(viii)
1.6.4 The zinc addition approach to radiation field reduction in nuclear power reactors

1.7 Other aspects

1.7.1 High temperature pH measurement
1.7.2 Copper speciation in MAPS moderator system
1.7.3 Behaviour of iodine species in chemical environments relevant to nuclear applications
1.7.4 Chemical speciation of iodine in MAPS PHT system
1.7.5 Particle size and Zeta potential measurements on metal oxides
1.7.6 Simulation loop (SIMLOOP) for decontamination studies
1.7.7 High temperature – high pressure loop
1.7.8 Biofouling test facility

2. RADIATION CHEMISTRY

2.1 Radiolysis in nitrogen-water systems
2.2 Radiation degradation of EDTA, ascorbic acid and citric acid
2.3 Pulse radiolysis studies
2.3.1 Phenyl thiourea
2.3.2 Diethyl thiourea
2.3.3 Thiosemicarbazide
2.3.4 Dipheny1carbazide
2.3.5 2-Mercapto benzimidazole
2.3.6 5-Amino tetrazole
2.3.7 Benzotriazole
2.3.8 Pyridinols
2.3.9 3-Hexyn-1-ol
2.3.10 Tetracycline
2.3.11 Sulpha drugs

(ix)
2.3.12 Aromatic sulphoxides 72
2.3.13 Picolinic acid 73
2.3.14 Benzidine 73
2.4 Studies on triplets of some biphenyl derivatives 74

3. COMPLEX CHEMISTRY 75

3.1 Studies on aluminium chelates with some organic ligands 75
3.1.1 Aminopolycarboxylic acids 75
3.1.2 Malic acid 76
3.1.3 Orthodihydroxy phenols and aromatic ortho-hydroxy carboxylic acids 76
3.2 Characterization of aluminium complexes in tea extract 77
3.3 Copper speciation studies 78
3.3.1 3-Methoxy propylamine(MPA), 1-Dimethylamino 2-Propanol(DMAP), Dimethylamino Ethanol(DMAE) and Piperidine(PIP) 79
3.3.2 2-Amino 2-methyl propanol(AMP), Diethylamino ethanol(DEAE) and Methyl pyrrolidine(MPy) 80
3.3.3 ESR and uv-visible spectroscopic studies of Cu-amine complexes 81

4. SOLID STATE CHEMICAL REACTIONS 83

4.1 Fluorination of oxides of iron by ammonium hydrogen fluoride 84
4.2 Solid state reactions between metal bifluorides and vanadates 85
4.3 Interfacial reaction between ammonium bifluoride and binary oxides at room temperature 88
4.4 Solid state reaction at room temperature between $\alpha$-naphthol and 1,4 naphthoquinone
4.5 Reaction between $\mathrm{NH}_4\mathrm{HF}_2$ and metallic Al, Ni and Cr
4.6 Superconducting materials: preparation, characterization and thermal studies
4.7 Preparation of other rare earth analogues of $\mathrm{YBa}_2\mathrm{F}_7$
4.8 Oxygen loading and its effect on $T_c$ and other properties of fluorinated 123 oxide
4.9 Preparation of electron superconductor $\mathrm{Nd}_2\mathrm{CuO}_4-x\mathrm{F}_x$
4.10 Preparation and characterization of $\mathrm{ZrMo}_2\mathrm{O}_8$
4.11 Preparation and characterization of cesium uranates
4.12 Solid state synthesis of cesium molybdates
4.13 Reaction of boric acid with cesium iodide

5. STRUCTURE, THERMODYNAMICS AND THERMOCHEMISTRY

5.1 X-ray crystal structure determination of platinum complexes
5.1.1 $[\text{PtMe}(\eta^2-\text{Ph}_2\text{ppy})(\text{Ph}_2\text{ppy})][\text{BPh}_4]$
5.1.2 $[\text{PtMe}_3(\text{SSPPPh}_2)]_2$
5.1.3 $[\text{PtMe}_3(\text{py})\text{SSPPPh}_2]$
5.2 Setting up of the Cambridge Crystallographic Data Base
5.3 Cambridge Crystallographic Database searches
5.4 Analysis of hydrogen bonding in compounds containing carboxyl and amino acid groups
5.5 Thermodynamic properties and thermochemical behaviour of nuclear materials
5.5.1 Standard free energy of formation of $\mathrm{ZrMo}_2\mathrm{O}_8$ and $\mathrm{HfMo}_2\mathrm{O}_8$
5.5.2 Thermodynamic data for pure palladium
5.5.3 Chemical state of palladium in the nuclear fuel cycle and the binary phase diagrams of palladium

5.5.4 Critical evaluation of the binary phase diagrams of platinum group metals

5.5.5 Thermodynamic investigations on Pd-Pt alloys

5.5.6 Correlation between thermodynamic properties and atomic orbital overlaps in noble metal alloys

5.5.7 Thermodynamic database for Te bearing species in Me-Te and Me-Te-O systems

5.5.8 The chromium-tellurium system

5.5.9 Thermodynamic calculations using the SOLGASMIX-PV program

5.6 Thermochemical investigations

5.6.1 Thermogravimetric and dilatometric studies on pure and doped ceramic superconducting materials

5.6.2 High temperature X-ray powder diffractometric studies on Bi$_2$CaSr$_2$Cu$_2$O$_x$

5.6.3 Thermal studies on Li$_2$O.5B$_2$O$_3$.10H$_2$O

5.6.4 Studies in the pseudo-binary system Li$_2$O-B$_2$O$_3$

6. BIOPOUFLING, BIOCORROSION AND CHEMISTRY OF COOLING WATER SYSTEMS

6.1 Macrofouling control

6.2 Macrofouling ecology

6.3 Chlorination of cooling water

6.4 Biofilm characterization

6.5 Biocorrosion in FBTR service water system

6.6 Exopolymer production and bacterial adhesion

6.7 Diatom fouling in the coastal waters of Kalpakkam
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8</td>
<td>Studies related to RAPS and FBTR</td>
<td>123</td>
</tr>
<tr>
<td>6.8.1</td>
<td>RAPS cooling water</td>
<td>123</td>
</tr>
<tr>
<td>6.8.2</td>
<td>FBTR service water</td>
<td>124</td>
</tr>
<tr>
<td>7.</td>
<td>NOVEL AREAS</td>
<td>125</td>
</tr>
<tr>
<td>7.1</td>
<td>Dental implants for BARC Hospital</td>
<td>125</td>
</tr>
<tr>
<td>7.2</td>
<td>Remote sealing of holes in mild steel pipes</td>
<td>126</td>
</tr>
<tr>
<td>7.3</td>
<td>Studies on &quot;Cold Fusion&quot;</td>
<td>127</td>
</tr>
<tr>
<td>8.</td>
<td>INSTRUMENTATION AND SOFTWARE DEVELOPMENT</td>
<td>130</td>
</tr>
<tr>
<td>8.1</td>
<td>Knudsen cell mass spectrometric system</td>
<td>130</td>
</tr>
<tr>
<td>8.2</td>
<td>Thermogravimetric assembly for transpiration experiments</td>
<td>130</td>
</tr>
<tr>
<td>8.3</td>
<td>Heat capacity measurements of solids by differential scanning calorimeter (DSC)</td>
<td>132</td>
</tr>
<tr>
<td>8.4</td>
<td>Computer controlled differential thermal analysis (DTA) assembly</td>
<td>134</td>
</tr>
<tr>
<td>8.5</td>
<td>Fabrication of sample assembly for differential scanning calorimeter</td>
<td>134</td>
</tr>
<tr>
<td>8.6</td>
<td>Software for retrieval of powder XRD data from JCPDS database</td>
<td>135</td>
</tr>
<tr>
<td>8.7</td>
<td>Expert system for secondary side water chemistry monitoring in pressurised heavy water reactors</td>
<td>135</td>
</tr>
<tr>
<td>8.8</td>
<td>A basic program for processing electrochemical data</td>
<td>136</td>
</tr>
<tr>
<td>8.9</td>
<td>Computerisation of indents placed with Directorate of Purchase and Stores</td>
<td>137</td>
</tr>
<tr>
<td>9.</td>
<td>HUMAN RESOURCE DEVELOPMENT</td>
<td>138</td>
</tr>
<tr>
<td>9.1</td>
<td>Training School</td>
<td>138</td>
</tr>
<tr>
<td>9.2</td>
<td>Other Training Programmes</td>
<td>139</td>
</tr>
<tr>
<td>9.3</td>
<td>Training undergone by staff members</td>
<td>140</td>
</tr>
</tbody>
</table>
9.4 Deputations 141
9.5 Seminars 142

10. CONSULTANCY AND REPORTS 147

10.1 Work through COSWAC 147
10.2 Work directly for the Operating Power Stations 150
  10.2.1 Tarapur Atomic Power Station 150
  10.2.2 Rajasthan Atomic Power Station 150
  10.2.3 Narora Atomic Power Station 150
  10.2.4 Kakrapar Atomic Power Station 151
10.3 Senior Level Task Force for MAPS Decontamination 152
10.4 NPC-BARC Collaboration Committee 152
10.5 500 MW(e) PHWRs 152
10.6 FBTR/ IGCAR 152
  10.6.1 Condenser cooling and service water system of FBTR 152
  10.6.2 FBTR Task Force on service water system of FBTR 153
  10.6.3 Steam-water system of FBTR 153
  10.6.4 Chilled water system of IGCAR 154
10.7 Consultancy to Heavy Water Plants 154
  10.7.1 HWP Manuguru 154
  10.7.2 HWP Kota 155
  10.7.3 HWP Thal 155
  10.7.4 General 155
10.8 Work in relation to Bureau of Indian Standards (BIS) 156
10.9 Work in relation to International Atomic Energy Agency (IAEA) 156
10.10 Work in relation to International Association for Properties of Water and Steam (IAPWS) 157
10.11 Work in relation to Board of Research in Nuclear Sciences (BRNS) 157
10.12 Quarterly and Annual Reports 158
10.13 Official Language Implementation Committee 158

(xiv)
11. SERVICE ANALYSES

11.1 Performance evaluation of Condensate Polishing Unit of Korba Super Thermal Power Station (KSTPS) 159
11.2 Analytical support to PBTR 160
11.3 Sample analyses 160
11.4 Other Services 160

12. PUBLICATIONS 163

13. APPENDICES 207

Appendix I Objectives and thrust areas 207
Appendix II Plan Projects 210
Appendix III Staff Chart 217
1. REACTOR RELATED PROGRAMMES

Radiation field control on out of core surfaces in the primary coolant circuit of nuclear reactors is of relevance in the context of economics of operation, plant life extension, plant reliability and safety. Short term reduction in the radiation level is effectively achieved by decontamination which may have to be repeatedly performed to bring down radiation field during the lifetime of a reactor. For the decontamination on an operating nuclear power plant, process employing dilute chemical formulation is generally employed from the following considerations: minimum corrosion damage to system components, reasonably high decontamination factors (DF), waste accumulation in compact solid matrix, only modest hardware requirements and low man-rem expenditure during the decontamination operation. The chemical process involved in decontamination removes the protective oxide coating completely, and hence the radioactivity incorporated in the oxide film over a period of a few years also gets removed. Depending upon the type of water cooled reactor, materials of construction and water chemistry during operation the chemical process needed for decontamination requires to be optimised. Sometimes, it could even be a two stage process.

The development of decontamination technology addresses itself to the following aspects: (i) Efficiency and kinetics of oxide dissolution, (ii) General and specific material compatibility, (iii) Removal and consolidation of waste (metals, radioactivity and organics) and (iv) Engineering interface for chemical addition, reaction system adaptability and auxiliary purification circuit.
1.1 **Decontamination of PHWRs**

The Indian PHWRs are characterised by high radiation fields around boiler and feeder cabinets due to thick deposits on carbon steel (CS) feeders and headers and fairly large surface area of monel tubes used in the steam generators (SG). Chemical decontamination of such systems is therefore to be tailored for oxides of Fe on CS surfaces and for oxides of Ni, Cu and Fe on SG tubes. Due to highly improved fuel design, very little fuel failures occur and defective fuel gets expelled from the core through on-line refuelling. Hence, the dominant deposited radioactivity in PHWRs is due to Co-60 and Co-58 and other activated corrosion products.

1.1.1 **Feasibility study of chemical decontamination of PHT system of MAPS**

(S.V. Narasimhan and P.N. Moorthy)

In order to develop a dilute chemical decontamination technology suited to Indian PHWRs based on the results of laboratory experiments carried out in the Division employing mixtures of reductant, complexant and organic acid and in-situ regeneration of the complexant the P&I diagrams of the PHT system and the purification circuit of MAPS were studied. The total quantity of oxide to be removed was estimated to be \( \approx 200 \) kg based on the extrapolated growth rate of \( \text{Fe}_3\text{O}_4 \) on CS. A very conservative upper limit estimate for radioactivity incorporated in this oxide is the equivalent of 500 Curies of Co-60. The total flow needed for purification i.e., reagent regeneration during decontamination was estimated to be between 1200-1500 lpm for MAPS. As facility for achieving this flow does not exist, it was decided to use both the pressure pumps to get an average flow of 1000 lpm. The present ion exchange (IX) columns at MAPS are not designed for handling this high flow. Also sufficient
quantity of IX resin cannot be accommodated in the existing primary coolant purification IX columns. Hence, the complete purification circuit was redesigned to meet this requirement. This consists of 6 cation exchange columns and 4 mixed bed columns. Each column is about 700 mm in dia and about 1.4 m resin height. The columns are made of carbon steel coated with epoxy and have a resin volume of 520 l. The layout is such that the two columns can be valved in parallel while two more can be added in series for each branch. A schematic diagram of the column as well as the layout of the purification circuit is given in Figs.1.1.1a and 1.1.1b. The individual columns are shielded by lead for containing 85 Ci of $^{60}$Co uniformly distributed over the resin volume such that the surface dose of each column will not be allowed to exceed 200 mR/hr. The total weight of the column has been kept below 10 tons due to handling constraints and the shields have been designed such that they can be opened easily at the bottom and the columns disposed of in tile holes. A procedure for sequential valving in of cation and mixed bed column has been worked out. Criteria for column change over and termination of the process are also evolved.

The chemicals will be added as solids through four of the existing 100 l capacity ion exchange columns from the MAPS additional purification circuit. Detailed analytical procedures for the determination of individual and total organics, iron, and radioactivity in solution were formulated and tested. A scheme for performance monitoring by way of chemical and radiochemical analysis and radiation field measurements at 25 locations by portable monitors has also been evolved. Separate procedures for chemical addition and deuteration and dedeuteration of the IX resins have been worked out. A feasibility report dealing with all these aspects and the laboratory data supporting the efficacy of the formulation for carrying out decontamination at MAPS has been prepared and submitted to NPC.
Fig 1.1.1(a)
Design of Shielded Ion Exchange Column (for decontamination)
Fig1.1.1.(b) Additional Purification circuit for decontamination
Corrosion compatibility studies in the decontamination formulation

The relative rates of oxide dissolution and base metal corrosion play an important role in determining the efficiency of a decontamination process. The general corrosion of carbon steel (CS) is important as it has a higher corrosion rate even in a weakly acidic medium existing in dilute chemical decontamination (DCD) formulations. Hence the corrosion compatibility behaviour of the construction materials of the PHT system of PHWRs particularly CS was systematically studied in the decontaminating formulations.

Compatibility studies were carried out on carbon steel in formulations based on (i) oxalic acid and (ii) ascorbic acid. Components of decontamination formulations viz., EDTA (1.25 mM), citric acid (2.5 mM), ascorbic acid (2.5 mM) and oxalic acid (2.5 mM) were tested individually as well as in the form of binary and ternary mixtures in deaerated solutions for their corrosiveness with special emphasis on specific attack. The observations were:

(a) There was no pitting type of attack due to any of these components and their mixtures (optical microscopic examination).

(b) Ascorbic acid based formulations showed 20-30% higher corrosion rate as compared to oxalic acid based formulations.

(c) Ascorbic acid based formulations did not leave any significant precipitate on the metal surface whereas oxalic acid based formulations left a thick crystalline deposit of ferrous oxalate on the coupons which apparently reduced the base metal loss.
a) **Compatibility studies in EAC formulation**

Compatibility studies in a formulation containing EDTA: ascorbic acid: citric acid (EAC 4:3:3; 1 g/l) were carried out at 85°C on carbon steel as well as other construction materials. Carbon steel corrosion in the above formulation under regenerating condition at 85°C in an inert atmosphere with the volume to surface (V/S) ratio the same as in the PHT systems of PHWRs (4.7 cm) was found to increase with regeneration rate. The corrosion rates were 0.46, 0.79 and 1.03 μm/hr. respectively at 3 different flow rates of 6.8, 11.5 and 23 ml/min. When the V/S ratio was increased to 20 cm, the corrosion rate rose to 3.5 μm/hr and it became independent of flow rate.

Corrosion rates of fresh carbon steel spirals at V/S = 4.7 cm in EDTA (1.4 mM) and in citric acid (1.4 mM) were found to be 0.69 and 0.65 μm/hr. respectively. This indicates that base metal corrosion is largely dependent on the total H⁺ activity in the formulation and not on the nature of the ligand. The corrosion rate for monel and zircaloy-2 were found to be less than 0.01 μm/hr. Corrosion rate of CS specimens coated with 1-2 μm Fe₃O₄ were also investigated. Such thin films did not reduce the corrosion rate of CS over the wide range of experimental conditions investigated, viz., for V/S ratio in the range of 4.7 to 20 cm, total concentration of formulation 0.2 to 1.0 g/l and temperature 50 to 85°C, the general corrosion rate was between 0.35 to 3.5 μm/hr.

Gamma irradiated EAC formulations did not show enhanced CS corrosion rate indicating that the chemical nature of radiolytic products did not enhance corrosion. Irradiated formulation after purification by mixed bed ion exchanger was used for the formation of magnetite film at pH 10 and 225°C. A uniform coating of 1-2 μm thick Fe₃O₄ was observed on CS after 12 days exposure;
zircaloy corrosion rate and the total H$_2$ pickup was the same as that observed with DM water adjusted to pH 10 with LiOH. No adverse hydriding was observed.

Some of the minor components of PHT system construction materials viz., asbestos, neoprene "O" ring, rubber diaphragm, rubber hose, teflon, Buna-N, nylon, flexitolic gasket, aluminium bronze and SS 410 were exposed to the EAC formulation at 85°C for 8 hours. None of the above materials except flexitolic gasket showed any weight loss. In the case of flexitolic gasket, there was a weight loss of about 1.7%.

b) Effect of Fe(III) EDTA on carbon steel corrosion

Experiments carried out to ascertain the influence of Fe(III) EDTA in the EAC formulation on carbon steel corrosion showed that corrosion rate increased with increasing concentration of Fe(III) EDTA. It was also observed that the concentration of Fe(III) EDTA gradually decreased with time in the presence of a coupon indicating the reduction of Fe(III) EDTA by carbon steel. The observed increase in the corrosion rate does not however, correspond to the amount of Fe(III) EDTA reduced, showing thereby that in the cathodic reaction of the base metal corrosion process, Fe(III) EDTA competes with the H$^+$ ion for the electron released. It can be summarised that the EAC formulation has acceptable corrosion rates on the various major and minor PHT system construction materials even in the absence of a corrosion inhibitor.

c) Evaluation of efficiency of corrosion inhibitors

In order to choose a suitable corrosion inhibitor for the EOC (EDTA, Oxalic acid, Citric Acid, 4:3:3, 1g/l) formulation a few corrosion inhibitors viz., (i) 1,2,3-benzotriazole, (ii) 3-hexyn-
1-ol, (iii) 5-hexyn-1-ol, (iv) 4-methyl thiophenol, (v) O-thiocresol (vi) N, N-diethyl thiourea and (vii) formaldehyde were tested for their efficacy in inhibiting the base metal corrosion in this formulation. Diethyl thiourea was found to be the best inhibitor with inhibition efficiency of 92% whereas all the other inhibitors exhibited a much lower reduction in corrosion rate (about 50%).

(*Ph.D Student, University of Madras)

1.1.3 Electrochemical study of compatibility of decontan4nant formulations with PHT system materials

(B. Yuvaraju, C.K. Vinaykumar, G. Venkateswaran and P.N. Moorthy)

Electrochemical experiments based on Tafel plots, linear polarisation, potentiodynamic anodic polarisation and time dependence of open-circuit potential of various primary heat transport system structural materials used in PHWRs have been carried out to study their compatibility with different decontamination formulations, employing a computer controlled corrosion measurement system. Investigations on Zircaloy-2, Stainless Steel-304, Carbon Steel, Monel-400, Inconel-600 and Incoloy-800 were carried out in the following media: 1) EDTA (1.4mM) + Citric acid (1.4mM); 2) EDTA(1.4mM) + Oxalic acid (2.4mM) + Citric acid(1.4mM) ; 3) EDTA(1.4mM) + Ascorbic acid(10mM) + Citric acid(1.4mM); 4) Picolinic acid (10mM) + Ascorbic acid (10mM) at temperatures of 298, 313, 333 and 353 K (Table 1.1.3). Zircaloy-2 has shown the least corrosion rate in all the four media. The corrosion rate of carbon steel was higher than that of other materials in all the four media while for stainless steel and nickel alloys the corrosion rates fell in between those of zircaloy-2 and carbon steel. Increase in temperature increased the corrosion rate of carbon steel in all the media. In the case of SS-304, a positive temperature
<table>
<thead>
<tr>
<th>Medium</th>
<th>Temp. °C</th>
<th>Corrosion rate (microns/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zicaloy</td>
<td>SS-304</td>
</tr>
<tr>
<td>I</td>
<td>25</td>
<td>8.1E-5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.0E-4</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.7E-4</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>8.5E-5</td>
</tr>
<tr>
<td>II</td>
<td>25</td>
<td>4.3E-5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>4.1E-5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>7.2E-5</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>9.1E-5</td>
</tr>
<tr>
<td>III</td>
<td>25</td>
<td>4.0E-5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.1E-4</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>7.7E-5</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>6.4E-5</td>
</tr>
<tr>
<td>IV</td>
<td>25</td>
<td>2.1E-4</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.2E-4</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>6.5E-5</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>3.9E-5</td>
</tr>
</tbody>
</table>

Medium-I : EDTA(1.4mM) + Citric Acid(1.4mM)
Medium-II : EDTA(1.4mM) + Oxalic Acid(2.4mM) + Citric Acid(1.4mM)
Medium-III : EDTA(1.4mM) + Ascorbic Acid(10mM) + Citric Acid(1.4mM)
Medium-IV : Picolinic Acid(10mM) + Ascorbic Acid(10mM)

These data have been obtained by the Tafel plot plus Linear Polarisation techniques using a computer controlled corrosion monitoring system.
coefficient was observed in media 1, 2 and 4 whereas in medium 3 the corrosion rate was almost independent of temperature. Monel-400 showed a positive temperature coefficient in all the four media. The corrosion rate of inconel-600 did not show temperature dependence in media 1 and 3 but in media 2 and 4, it was temperature dependent. In the case of Incoloy-800 and Zircaloy-2, the corrosion rates were low and exhibited no significant temperature dependence.

1.1.4 Compositional characteristics of magnetite synthesised from aqueous solutions at temperatures upto 523 K
(G. Visalakshi, G. Venkateswaran, S.K. Kulshrestha* and P.N. Moorthy)

A comparative study has been made of the composition of magnetite prepared by different aqueous routes. Wet chemical analysis, powder XRD, T.G and Mossbauer studies were employed to characterise the ferro-ferrites obtained.

A defect spinel oxide was always obtained by alkalising Fe\textsuperscript{2+}/Fe\textsuperscript{3+} mixture. The composition of these oxides was found to be Fe\textsubscript{2.81±0.04}O\textsubscript{4} irrespective of dissolved O\textsubscript{2} concentration, initial Fe\textsuperscript{2+}/Fe\textsubscript{total} ratio (in the range 0.333-0.454) and duration of aging (2 to 150 hr) of the oxide in the mother liquor. A spinel oxide very close to stoichiometric magnetite was obtained by the digestion of Fe(OH)\textsubscript{2} gel in presence of KNO\textsubscript{3} as oxidant at 363 K in an inert atmosphere. The films deposited on the corroding CS specimens exposed to a pH 10.0 solution in presence and absence of chelants at 473 K revealed the presence of spinel type of compound with no significant presence of α-Fe\textsubscript{2}O\textsubscript{3} but the crud contained mainly α-Fe\textsubscript{2}O\textsubscript{3}. Direct autoclaving of Fe(OH)\textsubscript{2} at 523 K showed the formation of α-Fe\textsubscript{2}O\textsubscript{3} and magnetite in comparable amounts.

(* Chemistry Division)
1.1.5 Kinetics of metal oxide dissolution from the point of view of chemical decontamination
(M. Shailaja* and S.V. Narasimhan)

The interaction of high temperature water with the iron based construction materials in the PHT system of PHWRs produces ferrites with varying degrees of substitution of elements like nickel, chromium etc. Dilute chemical decontamination involves removal of these ferrites from pipe surfaces. In order to improve the efficiency of decontamination, a clear understanding of the oxide dissolution by the formulation is essential.

Studies have been carried out to investigate the role of individual components in a dilute chemical decontaminant mixture in determining the mechanistic pathway and to optimise the concentration (limited to 0.5g/dm$^3$), pH and temperature of dissolution. Initially, nickel ferrites with the general formula $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ (where $x = 0.66$, 0.47 and 0) have been studied.

The aspects studied include the effect of varying the concentration of ligands such as EDTA, HEDTA, DTPA, NTA and HIDA on the dissolution rates, temperature of dissolution, the effect of both inert and aerated conditions and the role of the reducing agent. The experiments were carried out by dispersing the oxides in the formulations which had been deaerated earlier at the predetermined temperature. The kinetics of dissolution were followed by analysing the iron and nickel content in the solution. The salient inferences from the study are:

(a) The extent of dissolution of magnetite and nickel ferrite in aminopolycarboxylic acids depends not only on the thermodynamic stability of the iron-chelate complexes but also on the extent of adsorption of the ligand onto the oxide and the reducing ability of the Fe(II)-chelate complex.
(b) The dissolution rate constants for both magnetite and nickel ferrite show a linear dependence on the concentration of EDTA in the concentration range 0.25 - 0.20 mM in the absence of oxygen. Under aerated conditions, however, the rate constant for nickel ferrite dissolution is independent of EDTA concentration. In other ligand solutions viz., HEDTA, DTPA, NTA, oxalic acid and HIDA, the dissolution of nickel ferrite shows Langmuirian dependence on the ligand concentration in the range 1-8 mM ($k_{\text{obs.}} = \frac{Rb[Y^{n-}]}{(1 + b[Y^{n-}])}$) in the absence of oxygen. Under aerated conditions also, the dissolution of nickel ferrite in oxalic acid followed a Langmuirian behaviour. Using the zeta potential data, ligand adsorption on the oxide surface was confirmed. The extent of adsorption of ligands on nickel ferrite was found to decrease in the order oxalic acid > ascorbic acid > EDTA > HEDTA.

(c) A maximum in the dissolution rate of both magnetite and nickel ferrite was observed at a pH of ≈ 2, for all the ligands studied in both oxygenated and deoxygenated solutions. However, the value of the rate constant was much lower in oxygen containing solutions than under inert conditions. The extent of dissolution of nickel ferrite in citric acid or in HCl alone was found to be insignificant.

(d) The activation energy for the dissolution of nickel ferrite in EDTA at pH 2.7 under inert conditions was found to be half that in air saturated solutions.

(e) The rate constants for the dissolution of the three oxides studied increased with increasing ferrous content of the oxides for all ligands. The dissolution of magnetite was faster than that of nickel ferrite in EDTA medium at all the pHs. The ferrous ligand complex seems to play a major role in controlling the dissolution kinetics of iron oxides.
(f) Addition of organic reducing agents such as oxalic acid, ascorbic acid and the corresponding ferrous-ligand complex (concentration one-half or one-fourth of the iron to be dissolved) to the ferrite-ligand system caused enhancement in the dissolution rates. The maximum enhancement was observed on addition of ferrous-ligand complex. Dissolution was faster in presence of oxalic acid than in presence of ascorbic acid, probably due to better complexing ability of the former.

(g) When magnetite was present as a uniform deposit on the carbon steel surface, reductive dissolution in a formulation consisting of EDTA, ascorbic acid and citric acid was found to be aided by the base metal iron getting oxidised to ferrous ions. External reductants did not contribute additionally to the rate.

(h) If carbon steel surfaces are non-uniformly coated with magnetite, then base metal attack was found to occur at the cost of oxide dissolution.

(i) Increased surface area/volume ratio suppressed both oxide dissolution rate and metal oxidation rate, provided acid and ligand content diminish with time. Increasing the pH suppressed base metal attack while oxide dissolution was not seriously affected upto pH 4.7. Even for a divalent ion like ferrous, purification half lives during the ferrous ion pick up on cation exchanger were longer than theoretically calculated ones due to competing back reaction and contact times. Purification half lives that are normally employed in PHWRs with existing hardware are inadequate to bring about rapid regeneration of EDTA to control the dissolution rates. These low rates are useful for metal uptake and not for reaction control through regeneration. However, as the concentrations were further lowered to minimise base metal attack, the rates of oxide dissolution also went down. Under such conditions, the regeneration rate will become
rate controlling. The present studies have shown that relatively rapid kinetics of dissolution exist even at low concentrations of chemicals. Concentration of ligands can be lowered further below 1g/l and in that region of concentration, control can be effected by the extent of ion exchange regeneration.

(* Ph.D. Student, University of Madras)

1.1.6 Ion exchange studies relating to the development of decontamination processes
(S. Velmurugan, V.S. Sathyaseelan, A.L. Rufus, S.V. Narasimhan and P.K. Mathur)

Dilute chemical decontamination process uses ion exchange resins for regenerating the formulation chemicals, removal of dissolved radioactive isotopes and metal ions from the coolant and for the removal of decontaminating chemicals and their decomposition products from the coolant at the end of the decontamination. A detailed study of the ion exchange behaviour of the formulation components, radioactive isotopes and metal ions was carried out on strong acid cation exchange resin and strong base anion exchange resin.

The following radionuclides viz., $^{144}$Ce, $^{141}$Ce, $^{65}$Zn, $^{95}$Nb, $^{103}$Ru and $^{106}$Ru as fission products and $^{125}$Sb, $^{58}$Co, $^{60}$Co as activated corrosion products are expected to be present in the spent decontaminant solution. The absorption behaviour of these isotopes from a solution containing EDTA showed that $H^+$ form of cation exchanger absorbed $^{141}$Ce, $^{144}$Ce, $^{144}$Pr, $^{154}$Eu, $^{58}$Co and $^{60}$Co and traces of $^{95}$Zr, $^{95}$Nb, $^{103}$Ru and $^{106}$Ru, while EDTA equilibrated anion exchanger absorbed $^{125}$Sb, $^{103}$Ru, $^{106}$Ru, $^{95}$Nb and $^{65}$Zn and -OH form of anion exchanger absorbed $^{103}$Ru, $^{125}$Sb and $^{60}$Co.
Similar observations were made with dilute chemical decontamination formulation containing oxalic acid, citric acid and EDTA confirming thereby that it is EDTA which largely determines the anion exchange behaviour of the various isotopes. This study revealed that cation exchanger alone cannot efficiently collect all the radioactive isotopes and formulation equilibrated anion exchange resin helps to augment its efficiency. This may be useful during reagent regeneration stage.

a) Absorption of EDTA and its analogues on H\(^+\) form of cation exchange resin

When EDTA was used in closed loop decontamination experiments involving reagent regeneration by ion exchange, it was observed that a significant fraction of EDTA was absorbed by the cation exchange resin through ion exchange mechanism and not by precipitation. Studies on the solubility of EDTA at 32°C in solutions of different pHs (0-3.0) showed that the solubility is minimum (125 mg/l) at a pH of 1.6. Absorption experiments carried out on cation exchanger at EDTA concentrations lower than the above minimum solubility (100 mg/l) showed that there is maximum absorption at pH 1.6 and the amount of EDTA absorbed is directly proportional to the EDTA concentration in solution for a given pH. Species distribution curve for EDTA showed that in the pH range 0-3, monoprotonated and diprotonated forms of EDTA are formed in the solution which exchange with the H\(^+\) ions from the cation exchanger. A mathematical model based on ion exchange equilibria was worked out to substantiate the experimental data. Equilibration studies carried out with NTA, EDTA and HEEDTA revealed that the selectivity coefficients for these chelants varied in the order HEEDTA > EDTA > NTA. Picolinic acid was also found to be absorbed to the extent of 0.42 moles per litre of cation exchange resin in column experiments.
b) **Pick up of dilute chemical decontamination formulation components by anion exchangers**

Decontamination formulation components viz., oxalic acid, EDTA and citric acid were found to be picked up by -OH form of anion exchange resin till its bed capacity was exhausted. Thereafter, selective absorption of one component took place at the expense of the other due to ion chromatographic displacement. The three organic acids viz., EDTA, citric acid and oxalic acid were not neutralised completely on absorption over the ion exchange resin. They existed partially in the protonated form.

Anion exchange capacities for EDTA, OA, CA, HEEDTA and ascorbic acid with strong base anion exchanger were determined to be 0.44, 0.73, 0.54, 0.46 and 0.79 moles per litre respectively. When Fe(III) EDTA solution along with other formulation components was passed through EDTA loaded anion exchanger, EDTA was found to be preferentially eluted out in exchange for Fe(III) EDTA.

c) **Effect of gamma radiation on the ion exchange removal of EAC formulation**

EDTA, Ascorbic acid, Citric acid (EAC) formulation of total concentration 1g/l and component ratio 4:3:3 by weight was irradiated to gamma doses of 1 and 5 Mrad and passed through a mixed bed (1:1 cation : anion) resin to remove the reagents. Total organics in the effluent was found to be less than 23 ppm. It was observed that when dissolved iron is present in the formulation during irradiation, the ion exchange removal was more effective (<7 ppm total residual organics).
1.1.7 Development of analytical procedures for estimation of various constituents of the decontaminant formulation
(V.S. Sathyaseelan, A.L. Rufus, S. Velmurugan, S.V. Narasimhan and P.K. Mathur)

Spectrophotometric, titrimetric and ion chromatographic procedures have been evolved to estimate the concentrations of the individual components of the EAC formulation containing iron:

(a) Estimation of iron: Iron could be estimated by forming a red coloured iron (II)-O-phenanthroline complex in the presence of hydroxylamine hydrochloride and acetate buffer of pH 5.0. The absorbance of the iron (II) phenanthroline complex thus formed was measured at 535 nm. But this complex formation reaction was found to be rather slow because of the presence of other complexing agents viz., EDTA, citric acid etc. Hence, an alternative method of using thioglycolic acid as complexant was evaluated. The iron-thioglycolate complex formed by the addition of thioglycolic acid to the ammoniated solution of the iron containing EAC formulation, was estimated spectrophotometrically. The complex formation reaction was found to be faster in this case.

A DC polarographic method (in acetate buffer) was also standardised to distinguish and to estimate the concentrations of ferrous and ferric complexes in the formulation.

(b) Estimation of total EDTA: The free EDTA in the solution was first complexed as Fe(III)EDTA by addition of FeSO$_4$ and aeration which also helped to oxidise any Fe(II)EDTA initially present. The labile complexes of iron with other ligands were then removed by passing the solution through a cation exchange resin in H$^+$ form. The Fe(III)EDTA in the effluent was determined spectrophotometrically at 310 nm to arrive at the concentration.
of total (i.e. free as well as complexed) EDTA in the solution.

(c) Estimation of ascorbic acid: Ascorbic acid reacts with iodine to form dehydroascorbic acid, and hence could be estimated iodimetrically using starch as indicator. It was established that there is no interference from any other components of the formulation including Fe$^{2+}$. However, presence of Fe$^{3+}$ leads to errors since Fe$^{3+}$ reacts with ascorbic acid.

(d) Estimation using ion chromatography: It was established that the EAC formulation components viz., EDTA, citric acid and ascorbic acid could be separated by ion chromatography on a special anion column with 1 mM H$_3$PO$_4$ as eluant and using conductivity detector. The retention time values of the component peaks matched with values for the individual components under identical conditions. However, as the formulation containing iron posed problems, pretreatment of the solution by passing through cation exchanger was found to be necessary.

1.1.8 Dissolution of magnetite in decontaminant formulations and the effect of gamma irradiation on their efficacy
(G.R. Dey, D.B. Naik, K. Kishore and P.N. Moorthy)

Magnetite was chosen as a model oxide to compare the dissolution efficiencies of a number of decontaminant formulations such as EDTA/OA/CA, EDTA/CA, EDTA/AA/CA, PA/OA, PA/AA etc. It was found that among the different formulations, EDTA(1.4 mM)/OA(2.4 mM)/CA(1.4 mM) and EDTA(1.4 mM)/AA(1.7 mM)/CA (1.4 mM) formulations were most effective in dissolving magnetite. The effect of pH on the dissolution was also studied and the optimum pH region was found to be 2.7-3.5 in the case of the EDTA/AA/CA formulation.
The effect of hydrogen peroxide (a radiolysis product in aqueous solutions) on the dissolution efficiency was studied and it was observed that below 0.1 mM concentration it did not have any effect on the dissolution rate. The replacement of EDTA by other amino polycarboxylic acids such DTPA, HEDTA, HIDA, NTA etc., led to comparable dissolution efficiency. These dilute chemical decontaminant formulations are expected to be exposed to high radiation fields during decontamination and undergo degradation. This can lead to a deterioration in their efficiency of dissolution of the oxide layer containing the radioactivity. A study of their radiation stability with respect to dissolution efficiency was therefore carried out. The three formulations viz. EDTA(1.4 mM)/ Oxalic acid(OA)(2.4 mM)/ Citric acid(CA)(1.4 mM), EDTA(1.4 mM)/ Ascorbic acid(AA)(1.7 mM)/ CA(1.4 mM) and Picolinic acid(PA)(10 mM)/ AA(10 mM) were irradiated to various gamma doses and dissolution of magnetite at 80°C was studied for various durations under an atmosphere of nitrogen. The plots of percent dissolution of magnetite vs time are shown in Fig. 1.1.8. It is observed that although dissolution rate was slower in PA/AA system as compared to EDTA/OA/CA or EDTA/AA/CA systems, the effect of irradiation on the efficiency of dissolution is negligible even after a dose of 1 Mrad in the former. This may be partly due to the high concentration of the reagents in this formulation and also due to the inherent radiation stability of PA, a heteroaromatic compound. Out of the other two systems, the dissolution efficiency of EDTA/AA/CA system was affected to a lesser extent than that of EDTA/OA/CA system. By carrying out dissolution experiments under simultaneous irradiation it was observed that the adverse effect of radiation on dissolution efficiency is less as compared to that in preirradiated solutions. In the case of EDTA/AA/CA system another problem was the appearance of a precipitate after a dose of about 3.5-4 Mrad. However, with dissolved iron present in the solution, there was no precipitate even after irradiation to a dose of 10 Mrad.
Fig. 1.1.8 Effect of gamma irradiation on the efficiency of magnetite dissolution of various decontamination formulations. (a) EDTA/OA/CA (b) EDTA/AA/CA (c) PA/AA. ▲ - unirradiated; ▼ - 0.1 Mrad; ◦ - 0.33 Mrad; ○ - 1 Mrad
1.1.9 Effect of corrosion inhibitors on the corrosion rate of carbon steel in EAC decontaminant formulation

The corrosion rate of carbon steel (CS) in EAC formulations at 80°C, although within the acceptable limit, is nevertheless appreciable. In order to see if it can be reduced by employing corrosion inhibitors, the corrosion rate of CS specimens was measured by dc electrochemical method in EAC solutions containing 1 mM of various corrosion inhibitors and the results are given in Table 1.1.9. It is seen that among the different compounds tried CI R-82 (commercial proprietary formulation) is the best corrosion inhibitor as it can bring down the corrosion rate of CS to as low as $3.5 \times 10^{-3} \, \mu m/hr$ even when it is present at a concentration of only 0.03% in the formulation.

1.1.10 Methodology of decontaminant formulation preparation
(V.S. Sathyaseelan, S. Rangarajan, M.P. Srinivasan and S.V. Narasimhan)

For the decontamination to be successful on the plant scale, the formulation should achieve the required concentration of chemicals in the system as quickly as possible. Initial experiments were carried out in a glass loop of 10 litre volume by addition of solid chemicals through specially devised vessels. DM water adjusted to pH 10 with LiOH and preheated to 50°C was used to dissolve EDTA first and then calculated quantities of ascorbic acid and citric acid were added simultaneously valving in the cation exchanger. Removal of Li and presaturation of the ion exchanger by EDTA occurred in less than 1 hour. Purification flow rate was maintained at 1 bed volume per hour.
Table 1.1.9

Effect of corrosion inhibitors on the corrosion rate of carbon-steel in EAC formulation

(EDTA 1.4 mM, AA 1.7 mM, CA 1.4 mM)

<table>
<thead>
<tr>
<th>Corrosion inhibitor*</th>
<th>Corrosion rate at 80°C (μm/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>1.206</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>0.209</td>
</tr>
<tr>
<td>Phenylthiourea</td>
<td>0.043</td>
</tr>
<tr>
<td>Thiosemicarbamide</td>
<td>0.122</td>
</tr>
<tr>
<td>2-Mercapto benzimidazole</td>
<td>0.043</td>
</tr>
<tr>
<td>Diethylthiourea</td>
<td>0.072</td>
</tr>
<tr>
<td>5-Amino tetrazole</td>
<td>0.157</td>
</tr>
<tr>
<td>3-Hexyne 1-ol</td>
<td>0.186</td>
</tr>
<tr>
<td>Cysteine</td>
<td>0.130</td>
</tr>
<tr>
<td>8-Hydroxy quinoline</td>
<td>0.288</td>
</tr>
<tr>
<td>Lumazine</td>
<td>0.072</td>
</tr>
<tr>
<td>Riboflavin (0.3 mM)</td>
<td>0.413</td>
</tr>
<tr>
<td>Folic acid (1 mM)</td>
<td>0.252</td>
</tr>
<tr>
<td>CI R-82 (1%)#</td>
<td>0.006</td>
</tr>
<tr>
<td>CI R-82 (0.3%)</td>
<td>0.005</td>
</tr>
<tr>
<td>CI R-82 (0.1%)</td>
<td>0.003</td>
</tr>
<tr>
<td>CI R-82 (0.03%)</td>
<td>0.003</td>
</tr>
<tr>
<td>CI R-82 (0.01%)</td>
<td>0.007</td>
</tr>
</tbody>
</table>

(* concentration 1 mM, except where otherwise stated)
(# proprietary formulation)
The same experiment was repeated in a stainless steel loop (provided by MAPS) of total volume 170 litres having a purification flow capability of 2-3 lpm with 5 litres of strong cation exchanger. The total time taken for EDTA dissolution was less than 30 minutes and for the completed formulation to reach the required concentration, it took a total of 60 minutes. Fig.1.1.10 shows the variation of different chemical parameters during the loop study.

1.2 Decontamination of BWRs

The deposits on the stainless steel surfaces in the primary coolant circuit of BWRs contain a large proportion of hematite (Fe₂O₃) which requires a strong reductant such as V²⁺ (vanadous) ion complexed as picolinate (LOMI reagent) to facilitate dissolution. This reagent is not commercially available and is also sensitive to oxygen and hence it has to be prepared in situ. The R & D programme was therefore directed towards preparation of the reagent and its use in dissolution (and hence decontamination) of deposits on the surface of coupons from TAPS-BWR clean up recirculation system.

1.2.1 Polarographic studies on VO₃⁻ ion
(G. Visalakshi, G. Venkateswaran and P.N. Moorthy)

To arrive at optimum conditions for the electrochemical preparation of V(II) from VO₂⁺, DC polarographic study of 2 mM sodium metavanadate was carried out in pH 4.2 solution containing formate buffer. The log \( i/(i_d-i) \) vs E plot indicated the presence of overlapping waves. The first wave limiting current was only a fraction of the total limiting current and was due to one electron reduction of \( V^{5+} \) to \( V^{4+} \) (irreversible) with \( E_1 = -0.122 \) V vs SCE and transfer coefficient, \( \alpha = 0.58 \). The second wave corresponded to a two electron reduction wave (\( V^{4+} \) to \( V^{2+} \)),
Fig 1.1.10 Variation of chemical parameters during preparation of decontaminant formulation
also irreversible with \( E^\circ = -1.36 \text{V vs SCE} \) and \( \alpha = 0.32 \). These values are in agreement with published data for \( \text{VO}_2^+ \) in other aqueous media and are very useful in fixing the optimum electrode potential for carrying out the bulk electrolysis of NaVO\(_3\) to get vanadous ions in solution.

As picolinic acid undergoes reduction at -1.17 V and -1.50 V vs SCE respectively at pH 5 and 9, it is not possible to prepare V(II)·picolinate solution directly from a solution containing a mixture of \( \text{VO}_2^+ \), formate buffer and picolinic acid by carrying out bulk electrolysis.

1.2.2 Electrochemical preparation of LOMI formulation
(G. Venkateswaran, A.S. Gokhale, and P.N. Moorthy)

An electrolytic cell of \( \approx 1 \) litre capacity with Hg cathode and Pt gauze anode was set up for the preparation of LOMI solution. A saturated calomel electrode in a lug-in probe was housed in the cell to monitor the potential of the cathode. The catholyte was sodium metavanadate with required amounts of formic acid while the anolyte was dilute solution of formic acid, the two being separated by a porous frit. Constant potential electrolysis was carried out at 1.5 V vs SCE with continuous \( \text{N}_2 \) bubbling. Distinct colour changes from deep yellow to sky blue to dark green and finally lavender were observed as the reduction progressed through \( \text{V}^{5+} \rightarrow \text{V}^{4+} \rightarrow \text{V}^{3+} \rightarrow \text{V}^{2+} \). An acidic KMnO\(_4\) titration method was developed to estimate quantitatively the \( \text{V}^{2+} \) generated. Near 100\% current efficiency was realised. Redox potential measurements with Pt electrode showed distinctive shifts as the reduction progressed. Starting with +450 mV in the case of NaVO\(_3\), the potential shifted to -600 mV when complete conversion to \( \text{V}^{2+} \) occurred. A weighed amount of picolinic acid was introduced at this stage to complex \( \text{V}^{2+} \) as \( \text{V}^{3+}(\text{pic})_3^- \) and the pH stabilised at \( \approx 4.3 \).
1.2.3 Vanadium estimation
(A.S. Gokhale and B.N. Wani)

The concentration of vanadium in its various oxidation states was estimated at different stages during preparation of vanadium(II) formate solution by electrolysis. Since the lower oxidation states of vanadium are stable only in an inert atmosphere, the estimation has to be carried out without exposing the samples to atmospheric oxygen. Two independent methods were employed. The distinctly different absorption maxima of solutions of the different oxidation states of vanadium were made use of in the spectrophotometric technique.

Since the standard method for obtaining V(II) is by reduction with Zn in H$_2$SO$_4$ medium, the estimations of V(II), V(III) and V(IV) were carried out in 10% H$_2$SO$_4$. The absorption maxima of V(II), V(III) and V(IV) were found to be at 556, 610 and 765 nm respectively in this medium. Beer-Lamberts law was found to be obeyed in solutions having total vanadium concentration in the 10-50 mM range.

As the spectra of V(II), V(III) and V(IV) overlap, this method could not be used to analyse a sample containing a mixture of two or three oxidation states of vanadium. Hence the molar extinction coefficients of the different species were determined at different wavelengths in the 400 to 800 nm range. The concentration of individual vanadium species in synthetic binary mixtures was computed from the measured absorbance and the determined extinction coefficients at a number of wavelengths and the computed values agreed well with the concentrations taken. Thus by this method vanadium could be estimated even when it is present as a mixture of different oxidation states.
A reverse permanganate titration procedure was also developed to estimate V(II), V(III) and V(IV). The sample was prepared and delivered through a burette to acidified and deoxygenated KMnO₄ solution in an inert atmosphere. The observed titre values corresponded to the quantity of electricity passed during electrolysis to obtain complete reduction from one oxidation state to the next lower one.

1.2.4 Decontamination studies on coupons from TAPS clean up recirculation system
(G. Venkateswaran, A.S. Gokhale, B. Yuvaraju, C.K. Vinaykumar and P.N. Moorthy)

For studies on the decontamination of test coupons, LOMI solution prepared as described in 1.2.2 was transferred under inert atmosphere to another half litre flask in which the coupon was suspended. The solution was kept agitated with magnetic stirrer and continuously heated to maintain temperature in the range 343-363K with N₂ gas purging to maintain oxygen free atmosphere. Initial experiments showed that the oxide coated test coupon surfaces removed from the high temperature (553 K) and high pressure (~ 70 Kg/cm²) portion of the clean up (C/U) system of TAPS are not attacked to any significant extent by the LOMI solution (~ 5 mM - 50 mM V²⁺) at 343-363K irrespective of the time of exposure. On the other hand if these surfaces are pre-treated by alkaline permanganate (AP: 0.3% KMnO₄ in 1.5% NaOH) at ~ 343 K for 4 hours, then the LOMI formulation was found to successfully descale the surface even when employed at low concentrations (~ 4 mM) and at temperatures of ~ 323 K. This pre-treatment step by AP has been found to bring appreciable amounts of chromium in solution from these surfaces. Thus the clean up system surfaces of TAPS BWRs seem to contain appreciable amounts of Cr³⁺ and in order to decontaminate these surfaces by the reductive LOMI formulation it is necessary to first oxidise Cr³⁺.
to CrO$_4^{2-}$. Among the different pre-treatments tried namely alkaline permanganate (0.3%(w/v) KMnO$_4$ in 1.5% NaOH, 3% KMnO$_4$ in 15% NaOH), permanganic acid (0.23% and 0.023% solutions of HMnO$_4$) and H$_2$O$_2$ (3%), 0.3% KMnO$_4$ in 1.5% NaOH at 343 K was found to be the best from the point of view of base metal compatibility as well as adequate Cr leaching from the oxide coatings.

Two cycles of AP-LOMI at ≈ 343K were found to give decontamination factors (DFs) of ≈ 10 and higher. The AP step was found to remove only insignificant radioactivity whereas the activity removal mainly took place in the subsequent LOMI step. Therefore the AP effluent does not pose waste disposal problems. Compared to citrate formulations with or without a reductant like ascorbic acid, LOMI was found to be more efficient.

The radioactive effluent from the LOMI step on passing through a cation exchanger followed by an anion exchanger column was found to contain only very low levels of radioactivity (≈ 10$^{-4}$ μCi/ml) and was also free from the LOMI chemicals.

1.3 Soluble chemical poisons for PHWRs

A reactor has to be maintained in critical state throughout its operation. Among factors affecting reactivity, build-up of fission products which act as poisons poses the maximum concern. Maintaining reactivity during prolonged shut down and initial start-up is achieved by adding a soluble chemical poison to the moderator. Subsequently the poison is removed gradually. In Indian PHWRs boron in the form of boric anhydride is being currently employed as the soluble chemical poison. However, recently interest is being centered on using gadolinium nitrate as an alternative soluble chemical poison.
1.3.1 Studies on gadolinium nitrate for possible use as chemical poison in NPRs (K. Kishore, G.R. Dey, V. Ramshesh, P.N. Moorthy and S.B. Srivastava)

a) Preparation, ion exchange behaviour and compatibility studies

Conditions were standardised for the preparation of Gd(NO)$_3$.6H$_2$O. TG analysis was used for confirming the number of water molecules. A 5000 ppm (with respect to Gd) solution of the compound stored under ambient conditions was found to be stable for periods exceeding one week. Suitably polished circular coupons of cupronickel 90/10 (moderator HX structural material in NAPP) were autoclaved in a 50 ppm gadolinium nitrate solution at 370 K for one week. It was observed that : (i) the solution pH did not change, (ii) specific conductivity decreased from 100 $\mu$S/cm to 45 $\mu$S/cm (iii) precipitation was observed in the solution, and (iv) most coupons showed weight loss and the total Cu leached into solution as estimated by spectrophotometric analysis of the solution was 0.5% which was in agreement with the weight loss of the coupons.

On the basis of both visual observation and nephelometric measurements it was found that gadolinium nitrate solution is not stable above pH 6.5 at $\approx$ 300 K. From alkalimetric titration the extent of hydrolysis of a 5000 ppm gadolinium (as nitrate) solution was estimated to be $\approx$ 10%. Ion exchange studies showed that Gd could be completely absorbed on a strong acid cation exchanger to its break-through capacity and then eluted with HCl.
b) **Estimation of radiolytic hydrogen release**

In order to assess the extent of enhancement of radiolytic D\(_2\) generation in the moderator system by addition of Gd(NO\(_3\))\(_3\), G(H\(_2\)) was determined in gamma-irradiated H\(_2\)O in the absence of any additive and in presence of 100 ppm Gd (as nitrate); the values were \(\approx 0.05\) and 0.45 respectively, the latter being equal to the primary molecular H\(_2\) yield. The same G - value was also obtained in the case of solution containing the same concentration of NO\(_3^-\) (as Na salt) as contributed by 100 ppm Gd (as nitrate). These results conclusively establish that Gd ion as such does not contribute to enhancement in the rate of hydrogen generation, the observed enhancement being due to interception of the recombination reactions by nitrate ions.

(* Since retired. * in collaboration with K.A. Rao and K.K. Pushpa of Chemistry Division)

1.3.2 **Stability of Gd(NO\(_3\))\(_3\) solution under moderator system conditions**

(B. Yuvaraju, G. Venkateswaran and P.N. Moorthy)

A study on the compatibility of gadolinium nitrate with stainless steel and zircaloy-2 was carried out. A 25 ppm Gd\(^{3+}\) solution with initial pH of 6.5, held in separate, fresh stainless steel and zircaloy-2 containers at 353 and 300 K showed that there was a decrease in the concentration of Gd\(^{3+}\) in the first two days accompanied by a lowering of pH. When fresh Gd\(^{3+}\) solutions with initial pH adjusted to 5 were employed, the solutions did not show any decrease in Gd\(^{3+}\) concentration or pH at the end of the experiment. Further experiments carried out showed that the decrease in pH in the case of pH 6.5 solution was due to precipitation of Gd as hydroxide. It is concluded that the moderator pH should not exceed 5 if Gd(NO\(_3\))\(_3\) solution is to be directly injected into the moderator to control reactivity.
1.3.3 Aspects of boron chemistry
(V. Ramshesh, R. Shanker* and K.S. Venkateswarlu*)

Among several design changes introduced in NAPS as compared to earlier PHWRs, an important aspect concerns reactivity control. Instead of moderator dumping, lithium pentaborate decahydrate injected into a set of twelve empty zircaloy-2 tubes positioned inside the calandria serves as a secondary shut down system. Solubility of lithium pentaborate and its chemical and radiation stability are important considerations in this context. Besides, reactivity control (due to fission product build-up) during prolonged shutdown is maintained by addition of boric anhydride to the moderator. Hence the moderator purification circuit has to take care of two eventualities:

(a) Shutdown conditions: In this case, the usual impurities such as Cl\(^-\), NO\(^3\)\(^-\) etc. have to be removed from the moderator D\(_2\)O without removing boron.

(b) Start-up: Here, besides the above usual impurities, boron also has to be removed from the moderator D\(_2\)O.

At the specific request from NPC, investigations were carried out to obtain information regarding the above aspects which are classified and hence not available in the literature. The solubility of lithium pentaborate decahydrate was found to be adequate: 0.22 Kg/l at 10\(^\circ\)C and 0.37 Kg/l at 55\(^\circ\)C. Its solution exhibited radiation stability up to a gamma dose of 20 Mrad. Both the irradiated and unirradiated solutions were found to be chemically stable under prolonged storage (2 months). Corrosion studies showed that the solution is compatible with zircaloy-2.

For removal of boron and/or usual impurities (such as nitrate, chloride etc.) from the moderator, advantage was taken
of the fact that while a strong base anion exchanger removes all of them, a weak base exchanger does not remove boron. It was also observed that the pentaborate ion behaves similarly to boric anhydride as far as removal by ion exchanger is concerned. Based on the laboratory experiments, two sequential streams of ion exchangers were recommended for moderator purification.

In the first stream, the moderator is passed through a column consisting of a mixture of strong acid cation resin (10%) and weak base anion resin (90%), to remove all impurities except boron. In the second stream the moderator is passed through a column consisting of a mixture of strong base anion resin (90%) and small amount of strong acid cation resin (10%) to remove all impurities including boron.

Depending on the situation the purification can be terminated after passing the moderator through either of the streams. The presence of small amount of strong acid cation exchanger in each column will help to remove cationic impurities in either sequence. The second stream will be particularly important in the eventuality of the zircaloy-2 tubes developing pin holes and consequent leakage of secondary shut down chemical into the moderator circuit.

(* Since retired)

1.4 Mass transport behaviour of corrosion and fission product species in pressure tube and SG materials

Owing to its excellent resistance against corrosion in high-temperature water and steam environments, Incoloy-800 is increasingly being used as steam generator (SG) tube material in nuclear power reactors. Although detailed investigations on the corrosion behaviour of this alloy have been carried out, studies on the diffusion of various corrosion and erosion products that
could be picked up by the material from high temperature water are meagre. In addition, very little work has been carried out on the mass transport of the constituents in the alloy. A program was therefore initiated to study the rates of diffusion of various activated corrosion and erosion products as well as of the different constituent elements of this alloy. In the past, the diffusion of Ni, Co and Cu in Incoloy-800 had been studied. In continuation of this programme, investigations have now been carried out to study the migration of $^{51}$Cr and $^{59}$Fe in the bulk as well as along the grain boundaries of Incoloy-800. Similarly, knowledge of behaviour of corrosion products in the newly introduced clad material (Zr-2.5 wt% Nb) is also important.

1.4.1 Studies on the migration and segregation of activated corrosion and erosion products in steam generator tube materials (A.R. Paul, K.N.G. Kaimal and M.C. Naik)

Volume diffusion was studied in the temperature range 1020-1510 K in specimens in which the grains were grown to big sizes ($\approx 1.5$ mm). Radioactive metal ($^{51}$Cr/$^{59}$Fe) was deposited on the polished surface of the specimens by evaporation in high vacuum ($\approx 10^{-4}$ Pa). The specimens were then diffusion annealed at various temperatures and concentration profiles determined by serial sectioning technique.

The volume diffusion coefficients ($D$) were determined from the concentration profiles. The plots of $\log D$ vs $1/T$ for $^{51}$Cr and $^{59}$Fe are shown in Fig.1.4.1 (a) along with those for $^{60}$Co, $^{63}$Ni and $^{64}$Cu. The D values of $^{51}$Cr and $^{59}$Fe in Incoloy-800 were found to be similar to those for $^{60}$Co, $^{63}$Ni and $^{64}$Cu, as would be expected from considerations of similarity of sizes of these
Fig. 1.4.1(a) Temperature dependence of lattice and grain boundary diffusion of $^{51}\text{Cr}$ in Incoloy-800
tracer atoms. The temperature dependence of volume diffusion coefficient can be expressed by the following equations:

\[
D (\text{Cr/Incoloy-800}) = 3.24 \times 10^{-4} \exp\left(-\frac{287.38 (\text{kJ/mol})}{RT}\right) \text{m}^2/\text{s} \\
1060 < T/\text{K} < 1510
\]

\[
D (\text{Fe/Incoloy-800}) = 3.26 \times 10^{-5} \exp\left(-\frac{259.60 (\text{kJ/mol})}{RT}\right) \text{m}^2/\text{s} \\
1020 < T/\text{K} < 1500
\]

Frequency factor and activation energy values could be explained on the basis of vacancy mechanism of diffusion.

Grain boundary diffusion of $^{51}$Cr and $^{59}$Fe was studied in the temperature range 750-1170 K in small grained specimens (average grain dia $\approx$ 150 $\mu$m). Both Whipple and Suzuoka methods were used to analyse the concentration profiles and gave more or less similar values for diffusion coefficient ($D_{gb}$). The grainboundary diffusivities could be represented by:

\[
D_{gb} (\text{Cr/Incoloy-800}) = 5.80 \times 10^{-5} \exp\left(-\frac{184.16 (\text{kJ/mol})}{RT}\right) \text{m}^2/\text{s} \\
775 < T/\text{K} < 1170
\]

\[
D_{gb} (\text{Fe/Incoloy-800}) = 1.88 \times 10^{-5} \exp\left(-\frac{160.70 (\text{kJ/mol})}{RT}\right) \text{m}^2/\text{s} \\
750 < T/\text{K} < 1100
\]

$\log D_{gb}$ vs $1/T$ plots are shown in Fig.1.4.1 (a). It was observed that grain boundary diffusivities of $^{51}$Cr are considerably lower than those of the other tracers, viz. $^{59}$Fe,
$^{60}$Co, $^{63}$Ni and $^{64}$Cu. This could be due to the tendency of Cr atoms to form carbides (carbon is present as a major constituent of Incoloy-800).

Autoradiography technique was used to study the segregation behaviour of the tracer atoms in Incoloy-800. A typical autoradiograph taken at a depth of $\approx 4 \mu m$ showing $^{51}$Cr along the grainboundaries of Incoloy-800 is shown in Fig.1.4.1(b). In fine grained specimens the mass transport of these tracer atoms ($^{51}$Cr and $^{59}$Fe) in Incoloy-800 takes place mainly through the grainboundaries. The average penetration distance was calculated for 100 hr. heating at 570 K and found to be negligibly small.

1.4.2 Mass transport studies of iron in pressure tube material
(A.R. Paul, K.N.G. Kaimal and M.C. Naik)

Diffusion of $^{59}$Fe (an activated corrosion product) in Zr-2.5 wt% Nb alloy (pressure tube material) have been studied in the temperature range 750-1350 K. Concentration profiles have been determined both by serial sectioning and residual activity techniques. Autoradiographs were taken at different depths of penetration. Diffusivity values were calculated in both $\alpha$-(750-880 K) and $\beta$-phases (1050-1350 K). Diffusion coefficient values for Fe atoms in both the phases were found to be several orders of magnitude higher than the self diffusivity values.

1.4.3 Studies on the release of gaseous and volatile fission products from 'SIMFUEL'
(K.N.G. Kaimal, A.R. Paul and S.R. Dharwadkar)

With a view to understand the release behaviour of gaseous and volatile fission products from fuel and fertile materials, the release kinetics of $^{133}$Xe and $^{131}$I from pure as well as fission product doped ThO$_2$ and UO$_2$ at comparatively low burnups.
Fig. 1.4.1(b)  Autoradiograph showing $^{51}$Cr along the grain boundaries of Incoloy-800 at a depth of about 6.5 $\mu$m. The specimen was heated for 100 hr at 1105 K. ($\approx$80x)
(upto $\approx 100$ MWD/t) had been studied earlier. In continuation of this, a programme has been initiated to study the effect of high concentration of fission products (corresponding to that at high burnups) on the release behaviour of $^{133}$Xe from simulated UO$_2$ pellets ("SIMFUEL").

Pellets of UO$_2$ containing oxides of major fission products such as Zr, Mo, Sr, Ba, Y, La, Nd and Ce in appropriate quantities have been prepared by sintering at 1800 K in He atmosphere to $\approx 80\%$ T.D. The concentrations of these fission products were so selected as to simulate the composition of UO$_2$ irradiated to a high burnup of $\approx 40,000$ MWD/t. These pellets were then characterized for density, homogeneity, open and closed porosity and composition. The pellets were then irradiated to very low burnup ($\approx 0.02$ MWD/t).

Study of the initial burst and diffusion controlled thermal release from these pellets were carried out in the temperature range 1100-1500 K. The values of diffusion coefficient (D) and initial burst release were determined from the plots of fractional release ($f$) as a function of square root of time ($t$) following Booth's model.

The temperature dependence of diffusivity was found to follow Arrhenius behaviour in the temperature range studied (Fig.1.4.3). Frequency factor and activation energy for the migration of Xe in the "SIMFUEL" pellets were calculated to be $4.36 \times 10^{-11}$ m$^2$/s and 270.85 kJ/mol. These values are comparable to those observed for the diffusion of xenon in low dose irradiated UO$_2$ studied earlier (272 kJ/mol). This suggests that high dopant concentration in UO$_2$ has no effect on the release kinetics of $^{133}$Xe (i.e. changes in vacancy concentration due to fission products doping do not affect release kinetics). Low value of activation energy (compared to $\approx 375$ kJ/mol for self diffusion)
Fig. 1.4.3 Temperature dependence of diffusivity of $^{133}$Xe in SIMFUEL
suggests that the diffusion is through the intestitials or vacancy clusters. The initial burst release values were also similar to those in low dose irradiated undoped UO$_2$ pellets.

1.5 Water Chemistry Studies

The closed loop process cooling water system in Madras Atomic Power Station (MAPS) currently employs sodium dichromate (400 mg/l) to control corrosion of materials (Carbon steel, Monel 400, Cupronickel, SS 304 and Aluminium brass). Leakages, if any, from the system are collected and discharged into the sea (Bay of Bengal). As the state pollution control boards insist on the absence of chromate in the discharges it was necessary to develop alternate non chromate based treatments. Hence, work was initiated to develop a suitable corrosion inhibitor formulation to treat this system.

1.5.1 Comparative study of hydrazine and dichromate treatments (M.S. Eswaran and P.K. Mathur)

Laboratory experiments were carried out on aqueous corrosion of carbon steel and cupronickel 70:30 in demineralised water (DMW), DMW + 20 mg/l N$_2$H$_4$ and DMW + 400 mg/l Na$_2$Cr$_2$O$_7$. Studies carried out with carbon steel (ASTM-A-53) coupons in DM water at 55°C and at three different pH values, viz., 8.5, 9.0 and 9.5 showed that the corrosion rates after 5 days of exposure were 0.083, 0.073 and 0.07 μm/hr respectively. After 30 days exposure, corrosion rates for both carbon steel and cupronickel were in the order DMW > DMW+N$_2$H$_4$ > DMW+Na$_2$Cr$_2$O$_7$. For cupro nickel, the corrosion rates after 30 days exposure were much lower than for carbon steel under identical conditions. XRD and IR spectroscopic analyses of the deposited corrosion products showed the following major components (Table 1.5.1).
### Table 1.5.1
Corrosion product composition

<table>
<thead>
<tr>
<th>Medium*</th>
<th>Chemical composition of Deposit on carbon steel coupons</th>
<th>Chemical composition of Deposit on cupro-nickel coupons</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMW</td>
<td>FeOOH, β-FeOOH</td>
<td>(Cu,Ni)$_2$CO$_3$(OH)$_2$</td>
</tr>
<tr>
<td>DMW + 20 mg/l $N_2H_4$</td>
<td>β-FeOOH, Fe(NO$_2$)$_2$</td>
<td>NaNO$_2$, NaNO$_3$, NaNiO$_2$</td>
</tr>
<tr>
<td>DMW + 20 mg/l $Na_2Cr_2O_7$</td>
<td>β-FeOOH, δ-FeOOH</td>
<td>CuCrO$_4$</td>
</tr>
</tbody>
</table>

(*Exposure condition: 30 days at pH 9, T ≈ 55°C)

### 1.5.2 Studies on different corrosion inhibitor formulations
(S.B. Karweer, B.P. Pillai and R.K. Iyer)

Experiments were carried out by exposing coupons of carbon steel, aluminium brass and cupronickel in DM water containing various concentrations of corrosion inhibitors in a closed system (initial pH, 9.0 ± 0.1, duration, 25-35 days).

a) **Corrosion inhibition using nitrite-borate-benzotriazole**

Electrochemical anodic polarization studies were carried out to determine the optimum concentration of benzotriazole to be used along with nitrite and borate to minimise corrosion of
copper. The optimum value was found to be in the range of 3-4 ppm. Corrosion inhibition studies were carried out using synthetic mixtures with various concentrations of nitrite and borate. The final pH of solution was 9.2-9.8. When the concentration of nitrite was 1200 ppm, that of benzotriazole, 4 ppm and the concentration of borax varied from 500 to 1200 ppm, the corrosion rates observed with carbon steel, cupronickel and aluminium brass were 0.07-0.3, 0.15-3.0 and 0.15-1.0 µm/y respectively. These are well within the permissible limits viz. 75µm/y for carbon steel and 5 µm/y for copper based alloys.

b) Corrosion inhibition using hydrazine

The concentration of hydrazine was varied from 5-15 ppm. The hydrazine content was determined periodically and the desired quantity of hydrazine was injected into the system to maintain the concentration at the desired level. At the end of the exposure period of 30 days the pH was in the range 8.4-9.2. The corrosion rates of carbon steel, cupronickel and aluminium brass were 6-11, nil and 0.1-0.2 µm/y respectively which are much lower than the permissible limits.

The results indicate that both the above inhibitor systems are suitable for corrosion control. However, in view of considerable leakage at MAPS use of hydrazine at 10-15 ppm (pH 8.5-9.0) is recommended for corrosion control in the process cooling water system from cost consideration.
1.6 Work related to nuclear power stations

1.6.1 Hot conditioning evaluation of primary heat transport system surfaces of NAPP-2 and KAPP-1
(A.K. Sriraman)*

The carbon steel coupons and the crud samples obtained during the hot conditioning of NAPP-2 and KAPP-1 PHT system were examined by powder XRD. In both the cases, it was observed that on the surfaces of the carbon steel coupons removed during the first two days of hot conditioning, the peaks due to magnetite were less pronounced as compared to those due to the base metal. From the third day onwards the intensity of the peaks due to magnetite grew at the expense of peaks due to base metal. This is consistent with the conclusion of coverage of carbon steel surface by magnetite at the end of hot conditioning as observed independently by optical microscopy at the site. The X-ray diffraction analysis of crud samples from the PHT system showed that the crud collected during the pre-hotconditioning period contained $\text{Fe}_2\text{O}_3$ as well as magnetite, whereas samples collected at the end of hot conditioning were predominantly magnetite. The chemical analysis of the crud samples showed considerable increase in the iron level towards the end of hot conditioning, whereas the increase in chromium and nickel levels was marginal.

The estimated maximum thickness of magnetite coating on carbon steel surfaces at NAPP-2 was 0.75 microns (operating temperature $265^0\text{C}$) at the end of six days, while the corresponding value at KAPP-1 was 0.7 microns (operating temperature $250^0\text{C}$) at the end of seven days.

(*Work done as a part of Chemical Task Force for the two reactors, which consisted of members from RSMD, MetD., RED, ApCD, and Chemical laboratories of KAPP and NAPP).
PHWRs of CANDU design use large surface area (≈ 3000 m² for a 235 MWe reactor) of carbon steel alloy in the PHT system. Compatibility of this alloy with alkaline D₂O is ensured by effective passivation of the surfaces before the nuclear reactor is commissioned. During the light water commissioning stage, the PHT System is therefore subjected to hot conditioning wherein the surfaces of all the structural materials including carbon steel are contacted with high temperature (473 - 523 K), deoxygenated, LiOH treated (pH 10 at 298K) water, in order to obtain a protective magnetite coating on the surface of carbon steel. Improving the quality of magnetite film is important for minimising the corrosion and activity transport problems encountered in the PHT system during operation of the reactor. This can be done by modifying the nature of passivating medium.

Much of the work reported in the literature in this area is centered around the use of EDTA whose beneficial effect seems to be realised at high temperatures (≥ 523 K). However, during hot conditioning of Indian PHWRs, it is experienced that temperatures of around 473 K are more readily achievable than ≥ 523 K. Hence investigations have been carried out in a laboratory static autoclave to produce protective magnetite films on carbon steel surfaces at 473 K in pH 10 deoxygenated aqueous solutions in presence of ligands such as DTPA, NTA, HEDTA and EDTA etc. each at 350 ppm concentration. In addition, the influence of AVT chemicals such as hydrazine, cyclohexylamine and morpholine at 350 ppm levels on the quality of the passivating film has also been studied. The relative merits of the different passivating media have been evaluated from the data on base metal loss, soluble and insoluble iron concentration in the medium, scanning
electron microscopic studies of the topography of the oxide coating and electrochemical investigations on the protectivity of the oxide coating and by comparing with the results obtained under simple pH 10 LiOH treatment. These results have also been compared with the ones obtained in presence of (a) glucose which is known to accelerate the magnetite formation and (b) boric acid which at 350 ppm levels acts as a corrosion inhibitor. Salient findings are given below:

The efficiency of passivation treatment is greatly enhanced by hydrazine and boric acid while it is adversely affected by the presence of glucose. The AVT chemicals are found to act as effective corrosion inhibitors. Chelating agents such as DTPA, NTA, HEDTA and EDTA greatly increase the base metal loss but the oxide film formed is more protective than the one formed in presence of LiOH or EDTA although a lower base metal loss is observed in the former case. The morphology of the coating formed in presence of complexing agents is indicative of formation of highly developed crystallite faces on the outer surface of the oxide layer.

It is concluded that, at 473 K passivation is best done in presence of hydrazine or boric acid whereas passivation in presence of chelants such as EDTA, DTPA etc., generates high base metal loss and releases corrosion products into the system and hence passivation in presence of LiOH is to be preferred to that in presence of chelants.

(* Ph.D Student, University of Bombay)

1.6.3 Evaluation of coolant sea water for TAPP - 3 & 4
(A.K. Sriraman, A.S. Gokhale, B.N. Wani and B. Yuvaraju)

The appearance of sea weeds in the coolant sea water of TAPS-1 & 2 since 1988 raised the question as to whether any
characteristics of sea water had changed in the recent past which could explain the occurrence of sea weeds and consequently whether chlorination practices hitherto followed by TAPS-1&2 need to be modified for adoption to TAPP-3&4. A one year comprehensive study was therefore undertaken to analyse the chemical and biofouling characteristics of coolant sea water and to evaluate the current chlorination practices at TAPS-1&2.

The findings revealed that, amongst the micronutrients, the concentration of nitrate nitrogen had gone up to 8-30 μg atom/1 during 1990 against the earlier values of 1-9 μg atom/1 during 1972-1973. Although the source of additional nitrate nitrogen is not known, the enhanced level of nitrate nitrogen is believed to be a possible cause for the growth of seaweeds.

The chlorine demand of seawater for one hour contact time during 1990 ranged from 3.5-6.3 mg/l (average value 4.1 mg/l). This value which was arrived at on the basis of laboratory experiments was comparable with the chlorine demand (value 5 mg/l for 1 hour contact time) in the real system. It was further observed that the current targetted chlorination practice at TAPS-1&2 is effective against the microfouling and the total residual oxidants (TRO) at the outfall is nil. Hence it was concluded that the current chlorination practices of TAPS-1&2 are adequate and may also be followed at the proposed TAPP-3&4 with total residual oxidant values in the range 2-5 mg/l.

1.6.4 The zinc addition approach to radiation field reduction in nuclear power reactors
(V. Ramshesh and P.N. Moorthy)

In view of recent reports suggesting that addition of zinc to feed water leads to reduction in radiation fields, a detailed literature survey was carried out to obtain all relevant
information on the subject. The following conclusions could be drawn: (i) for BWRs operating on normal water chemistry, zinc addition (5 to 15 ppb) to reactor water leads to lower pipe dose rates, (ii) for BWRs operating on hydrogen water chemistry, zinc addition seems to be beneficial but data on long term trends are not available, (iii) in mock up loops employing PWR conditions, preliminary results indicate that zinc addition leads to lower corrosion rates and thinner oxide films, (iv) the passive method of zinc addition ( passing the final feed water through a bed of sintered zinc oxide pellets ) is superior to the active method ( introducing a suitable zinc source in the system ), (v) the amount of zinc required to bring about the desired reduction in activity levels depends on the iron content in feed water and (vi) since PHWRs operate with similar water chemistry as PWRs, zinc addition might also prove beneficial in the former case.

1.7 Other aspects

1.7.1 High temperature pH measurement
(S. Rangarajan, M.P. Srinivasan, S.V. Narasimhan, P.K. Mathur, B. Yuvaraju and G. Venkateswaran)

The general corrosion problem in the primary coolant circuit of nuclear power reactors has been overcome as a result of the ability to maintain pH of the primary coolant within a very narrow range. However, mass transport between the various surfaces of the primary coolant system is found to be sensitive to minor changes in pH. At present, no satisfactory method is available for monitoring and controlling the high temperature pH in reactors to achieve minimum mass redistribution. Theoretical computations have been carried out for calculating the high temperature pH of reactor coolants with known compositions of added pH maintaining agents like LiOH, H₃BO₃.
etc. These calculations make use of temperature effects of dissociation equilibria of boric acid, LiOH and water. Using the standard Newton-Raphson methodology employing correlations of $K_w$, $Q_B$ (of $H_3BO_3$), density and viscosity of the medium as a function of temperature, these computations have been carried out and compared with literature values. These computations are necessary for evaluating the high temperature pH ($pH_T$) data generated in the laboratory.

The effect of uncertainty in the value of $K_w$ in determining the $pH_T$ was studied. It was found that for an uncertainty of 10-20% in $K_w$, the variation in $pH_T$ was 0.05 - 0.1 units. Also, the influence of dimeric and trimeric hydroxylated species of boron on $pH_T$ calculations was found to be significant only at high concentrations of boron (10 mM). The influence of ionic strength on calculated $pH_T$ values was also studied and approximately an increase of 0.15 pH units was observed for a decadic increase in the ionic strength.

A high temperature pH measurement system consisting of the cell: Cu/Cu$_2$O/ZrO$_2$/Test solution/Cl$^-$ (10 mM) AgCl/Ag was set up. The pH probe was fabricated by filling the Yttria stabilised Zirconia tube with 1:1 mixture of copper powder and Cu$_2$O, and an internal Ag/AgCl electrode was constructed with teflon encasing and teflon compartments to hold the electrolyte solution. Experiments were carried out to test the stability of the electrodes and the response of the pH probe to various acid/base solutions. Mixtures of boric acid (10 mM) and LiOH (0.1 - 10 mM) were taken in the cell and the cell potentials were measured. These values were then converted to actual $pH_T$ values using a computer program. The stability of the electrodes was found to be very good and the maximum variation in the cell potential corresponded to a pH variation of 0.04 units. In many experiments the theoretically
calculated and experimentally measured $pH_T$ values differed only by ± 0.3 units. However, in some of the experiments the absolute cell potentials differed significantly from computed values and the $pH_T$ values calculated were higher by as much as +2 units. This behaviour was attributed to the dilution of the electrolyte solution in the reference electrode compartment. Efforts are being made to modify the reference electrode design or to use an external reference electrode with a liquid junction.

To carry out calibration of the high temperature pH probe, a flow cell has been designed with minimum resident liquid volume. The pH standard stored in a reservoir will be pumped by a pressure pump into the cell with suitable heating arrangement to control the liquid temperature at any desired value between 200-300°C under pressure. After passing through the cell, the standard will be cooled and returned to the reservoir. Fig 1.7.1 gives a schematic of the flow cell.

1.7.2 Copper speciation in MAPS moderator system
(A.G. Kumbhar and S.V. Narasimhan)

In the moderator system of MAPS significant quantity of dissolved copper was observed and since the specific conductivity of the water was low, it was decided to identify the nature of the copper species present. Copper speciation using differential pulse polarographic technique was carried out with three different treatments of the heavy water samples (acidified, ammoniated and as such). 70% copper was found in the $Cu(OH)_2$ form and 30% in ionic form. No metallic copper was observed.
Fig. 1.7.1 High temperature pH measurement facility

Legend:

- **H**: Heater
- **C**: Cooler
- **P**: Pump
- **WT**: Water tank
- **CE**: Cell for electrodes
- **R1**: Ref. electrode
- **R2**: Ref. electrode
- **W**: YSZ electrode
- **CL**: Counter electrode
- **D**: Depressuriser
1.7.3 Behaviour of iodine species in chemical environments relevant to nuclear applications
(A.S. Gokhale, G. Venkateswaran and P.N. Moorthy)

Iodine is one of the major fission products in the slow neutron fission of U-235. Due to the presence of tramp uranium in the reactor core and clad defects developed during reactor operation, it comes in contact and reacts with the coolant forming various iodine species such as $I_2^-$, $I^-$, $IO_3^-$, $IO_4^-$, colloidal iodines such as $AgI$ and $PdI_2$, and possibly some organic iodides ($CH_3I$). All these forms of iodine are in a state of equilibrium, their concentrations being determined by the chemical environments in which they exist. In a BWR the iodine speciates in a high purity aqueous medium at nearly neutral pH under slightly oxidizing conditions whereas in a PHWR or PWR it reacts with moderately alkaline medium in a reducing atmosphere. During reactor accident conditions, alkaline oxygen saturated water is used to keep the iodine in solution. In a fuel reprocessing plant the fuel is dissolved in oxygen saturated concentrated $HNO_3$ and iodine exists in strongly oxidising and acidic environment.

Work was initiated to study the speciation of iodine in the above mentioned environments by simulating conditions in the laboratory as well as by carrying out experiments on actual samples at the respective plant sites. A solvent extraction separation cum radioanalytical method was standardised for the estimation of iodine species under the above mentioned experimental conditions. Synthetic samples containing the iodine species were prepared by equilibration of 1 ppm of $I^-$ ions (labelled with I-131 tracer) with $H^+$ and $OH^-$ ions of the aqueous medium at various pHs ranging from 3.0 to 10.0 and analysed by the standardised procedure. The results are given in Table 1.7.3(1).
Table 1.7.3(1)

% Speciation of iodine as function of pH at room temperature

<table>
<thead>
<tr>
<th>Iodine species</th>
<th>3.0</th>
<th>5.0</th>
<th>6.5</th>
<th>7.5</th>
<th>9.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I^0$</td>
<td>2.3</td>
<td>1.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>$I^-$</td>
<td>97.4</td>
<td>97.7</td>
<td>98.2</td>
<td>97.4</td>
<td>97.4</td>
<td>96.6</td>
</tr>
<tr>
<td>$IO_3^-$</td>
<td>0.3</td>
<td>0.4</td>
<td>0.9</td>
<td>1.7</td>
<td>1.7</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 1.7.3(2)

% Speciation of iodine in BWR coolant

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$I^0$</th>
<th>$I^-$</th>
<th>$IO_3^-$ &amp; $IO_4^-$</th>
<th>Colloidal iodines</th>
<th>Organic iodines</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-131</td>
<td>1.4</td>
<td>56</td>
<td>41</td>
<td>1.6</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>I-132</td>
<td>1.3</td>
<td>57</td>
<td>41</td>
<td>0.8</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>I-133</td>
<td>0.7</td>
<td>56</td>
<td>42</td>
<td>1.2</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>I-134</td>
<td>1.8</td>
<td>53</td>
<td>43</td>
<td>1.8</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>I-135</td>
<td>0.9</td>
<td>57</td>
<td>41</td>
<td>0.8</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>
The reproducibility of the analysis was studied by allowing 1 ppm of labelled I\(^-\) to speciate at a constant pH of 6.5. The procedure was then applied to the actual reactor water samples at TAPS. The samples were collected at the inlet points of the purification system under stable operating conditions and analysed by the standardised method. The results are given in Table 1.7.3(2).

1.7.4 Chemical speciation of iodine in MAPS PHT system
(A.G. Kumbhar and S.V. Narsimhan)

The release of radioactive iodine to the environment under accident conditions may lead to ingestion by human beings. A knowledge of iodine species in PHT system coolant may be helpful in this context. Using a previously standardised solvent extraction method, iodine speciation was carried out on heavy water samples from MAPS PHT system taken during steady operation of the reactor. All the iodine was found to be in the I\(^-\) (iodide) form. No molecular or organic form of iodine was detected. This is expected since the PHT system is maintained at pH 10.5 and iodine will be present only as iodide under such alkaline condition in reducing environment.

1.7.5 Particle size and zeta potential measurements on metal oxides
(M.P. Srinivasan and S.V. Narasimhan)

Nickel ferrite and magnetite, with particle size in the range 1-5 \(\mu\)m, were synthesised under both inert atmosphere and in presence of oxygen. \(\text{Ni}_{0.15}\text{Fe}_{2.85}\text{O}_4\) showed zeta potential \((Z_p)\) value of -28.8 mV, and -37.0 mV in 10 mM \(\text{KNO}_3\) at pH 8.5 and 9.5 respectively while \(\text{Fe}_3\text{O}_4\) exhibited \(Z_p\) values of 11.3, 8.0, -35.0 and -42.0 mV in 1 mM \(\text{KNO}_3\) at pH 2, 4, 6, 8 respectively. Both
Fe₃O₄ and nickel ferrite showed negative Zₚ at pH > 8.

Particle size and Zₚ measured for Boehmite [AlO(OH)] suspensions (in 0.1 - 0.2 mM KMnO₄) at concentrations of 0.05-0.25 wt % at pHs 2-10 showed that size increased (80 - 400 nm) with increasing pH. The size increase is inferred to be due to coagulation. Particle size analysis of TiO₂ and ZrO₂ suspensions used in ultrafilters was carried out: no definite correlation was observed between particle size, the concentration of the oxides in the suspension and ionic strength.

1.7.6 Simulation loop (SIMLOOP) for decontamination studies
(Y.V. Harinath, V.K. Gupta, V.T. Apar, T.V.K. Mohan and S.V. Narsimhan)

In order to test the laboratory developed decontamination formulations under real system conditions, a dynamic simulation loop is being set up as part of the VIII plan project. Schematic layout drawing (Fig. 1.7.6) for this loop and engineering drawings for the different systems were completed. [see also Appendix IIA]

1.7.7 High temperature-high pressure loop
(T.V.K. Mohan, V.T. Apar, V.K. Gupta, Y.V. Harinath and P. Madasamy)

Work on the erection of this loop was continued. Model steam generator control logic was finalised, schematics of logic diagrams were prepared and the loop control logic was frozen. The first drafts of the design and safety manuals prepared by NPC were reviewed in detail and the design basis, operational feasibility, safety aspects and control logics were finalised prior to their review and approval by the Safety Evaluation Working Group (SEWG), IGCAR. The loop flow sheet and the Design
FIG 1.7.6 Schematic description of SIM LOOP

Legends:
- TS TEST SECTION
- CP CORROSION PROBE
- DO DISSOLVED OXYGEN
- CAB CHEMICAL ADDITION BOMB
- LPUMP METEERING PUMP
and Safety Report were further modified to incorporate the suggestions and comments of SEWG. On the basis of this modified Design and Safety Report including the revised flow sheet, AERB has since given clearance for operation of the loop.

Erection of surge tank and primary and secondary side circulating pumps was completed. Fabrication and fitting assistance was provided for erection of the operating platform and for laying the pipe from overhead tank to DM plant. Design and piping layout was provided for construction of the cooling water pump room. Cooling water pipe supports were designed, and fabricated. A schematic of the loop is given in Fig. 1.7.7. [see also Appendix IIB]

1.7.8 Biofouling test facility
(K.K. Satpathy, V.P. Venugopalan and K.V.K. Nair)

Coordination necessary for implementation of the VIII Plan Project "Biofouling Test Loop Facility" was provided with respect to project review and design inputs for the loop and its subsystems. A simplified schematic of the loop is given in Fig. 1.7.8.

An outline of the experimental programme envisaged has been prepared. Detailed design notes for the seawater as well as raw water loops have also been prepared. The civil design of the building to house the loop has been frozen and made ready for tendering. [See also Appendix IIC]
Fig 1.7.7 Schematic description of HTHP LOOP

Legend:

TK-1 SURGE TANK
TK-2 D.M. WATER STORAGE TANK
TK-3 AND TK-4 CHEMICAL ADDITION TANK
TK-5 CONDENSATE COLLECTION TANK
TK-6 EMERGENCY STORAGE TANK
P-5 & P-6 COOLING WATER PUMPS

P-1 AND P-3 CIRCULATING PUMPS
P-2 AND P-4 MAKE UP PUMPS
FR FILTERS
DIK ION EXCHANGERS

TS TEST SECTIONS
SG MODEL STEAM GENERATOR
HR HEATER
CD COOLER
Fig. 1.7.8 A schematic of the biofouling test loop facility
2. RADIATION CHEMISTRY

2.1 Radiolysis in nitrogen-water systems
(G.R. Dey, K. Kishore, P.N. Moorthy, V. Ramshesh and S.B. Srivastava*)

Air ingress into the moderator system of pressurized heavy water reactors is known to lead to the formation of nitric acid with consequent increase in conductivity of water and radiolytic hydrogen production and its accumulation in the cover gas to levels beyond technical control specifications necessitating shutdown of the reactor. Consequently radiolysis of \( \text{N}_2 \)-water and air-water systems has been studied to understand the mechanism of nitric acid formation in reactors. Concentrations of radiolysis products such as nitrate, nitrite, ammonia and hydrogen peroxide were determined in gamma irradiated nitrogen/air-water systems at room temperature and 60°C (moderator temperature) and the effect of dose, dose rate, ambient gas, gas to liquid volume ratio and \( \text{OH} \)-scavenger such as \( \text{N}_3^- \) (azide ion) on their yields has been studied.

The effect of total dose on the product yields is shown in Fig.2.1(a). It can be seen that the yields reach plateau values at about 50-60 Mrad dose. The yield of nitrate is about ten times higher than that of nitrite or ammonia. The yield of nitrate is lower in air-water system as compared to nitrogen-water system indicating that it is the radiolysis of nitrogen which is responsible for the formation of nitric acid and the role of oxygen is less important. The effect of gas to liquid volume ratio on the yields of the products is shown in Fig.2.1(b). The yield of nitrate increases linearly with increasing gas to liquid volume ratio emphasizing the role of vapour phase radiolysis in nitric acid formation. However, in presence of azide ions (known to be \( \text{OH} \) radical scavengers) the formation of nitrate was
Fig. 2.1(b) Effect of gas to liquid volume ratio on the radiolytic yields. \( \text{N}_2 \)-water system: • - \( \text{H}_2\text{O}_2 \); \( \Delta \) - \( \text{NO}_3^- \); Air-water system: o - \( \text{H}_2\text{O}_2 \); \( \triangle \) - \( \text{NO}_3^- \); \( \text{N}_2 \)-water system with \( \text{N}_3^- \): □ - \( \text{NH}_3 \); ■ - \( \text{NO}_2^- \)
suppressed indicating the participation of OH radicals (generated in the liquid phase by radiolysis) in the overall reaction mechanism. Nitrogen oxides formed as a result of vapour phase radiolysis can react with OH radicals formed in the liquid phase to produce nitrate and nitrite:

\[
\begin{align*}
NO_2 + OH & \rightarrow HNO_3 \\
NO + OH & \rightarrow HNO_2
\end{align*}
\]

At higher temperature \( (60^\circ C) \), the yield of nitrate was lower as compared to that obtained under room temperature irradiation. However, there was a corresponding increase in the yield of nitrite and ammonia. This indicates that at the higher temperature, reactions leading to the reduction of nitrate to nitrite and ammonia assume importance.

(* Since retired)

2.2 Radiation degradation of EDTA, ascorbic acid and citric acid


EDTA(1.4 mM), ascorbic acid(1.7 mM) and citric acid(1.4 mM) solutions were irradiated to various gamma doses individually and analysed for the parent compound by ion chromatography using Dionex Ion Chromatograph. The plots of concentration of the parent compound vs dose for the three compounds are given in Fig.2.2. It can be seen that EDTA and ascorbic acid are more sensitive to radiation than citric acid. The initial G-values for the decomposition of these compounds were determined to be 4.2, 4.4 and 2.2 for EDTA, ascorbic acid and citric acid respectively. In the case of EDTA and ascorbic acid the G-value should be \( \frac{1}{2}(G_H + G_{OH}) \) i.e., about 3.2 in acidic solutions but it appears that \( H_2O_2 \) reacts either with these compounds (e.g., with ascorbic
Fig. 2.2  Radiation degradation of the individual components of EDTA/AA/CA formulation
acid) or with the secondary radicals produced from these compounds to give a higher decomposition yield. In the case of citric acid, due to lower reactivity with $\text{H}$ and OH radicals, the yield is expected to be lower although the reaction mechanism would be the same as in the case of EDTA. The reaction scheme can be written as:

\[
\begin{align*}
\text{AH}_2 + \text{OH}(\text{H}) & \rightarrow \text{AH}^- + \text{H}_2\text{O}(\text{H}_2) \\
2\text{AH}^- & \rightarrow \text{AH}_2 + \text{A} \\
\text{RR'}\text{NCH}_2\text{COOH} + \text{OH}(\text{H}) & \rightarrow \text{RR'}\text{NCHCOOH} + \text{H}_2\text{O}(\text{H}_2) \\
2\text{RR'}\text{NCHCOOH} + \text{H}_2\text{O} & \rightarrow \text{RR'}\text{NCH}_2\text{COOH} + \text{RR'}\text{NH} + \text{CHOCOOH}
\end{align*}
\]

[\text{AH}_2: \text{ascorbic acid; A: dehydro ascorbic acid; RR'}\text{NCH}_2\text{COOH: EDTA; RR'}\text{NH: EDTr}i\text{A}]

Although EDTA is degraded and converted to products such as EDTrA and EDDA, the chelating properties of the latter are comparable to that of EDTA.

2.3 Pulse radiolysis studies

(G.R. Dey, D.B. Naik, K. Kishore and P.N. Moorthy)

Pulse radiolysis studies have been carried out on a number of compounds such as picolinic acid, benzidine, aromatic sulfoxides, phenylthiourea, diethylthiourea, thiosemicarbazide, diphenylcarbazide, 3-hexyn 1-ol, 2-mercapto benzimidazole, 5-amino tetrazole, benzotriazole and pyridinols. Rate constants for the reactions of these compounds with the primary species of water radiolysis viz. $\text{e}^-_{\text{aq}}$, $\text{H}$ and OH radicals are given in Table 2.3. The rate constants for the reaction of $\text{e}^-_{\text{aq}}$ were determined by following the decay of its absorbance at 720 nm whereas the reaction rate constants for the other species were determined from the build up kinetics of the product transients from these solutes. A summary of the other important findings from the different compounds are given below.
Corrosion Inhibitors

In decontamination formulations composed of a chelant, reductant and a buffering agent, a corrosion inhibitor is also added to minimise base metal attack. As these compounds also get exposed to radiation during decontamination, their radiation chemistry is also of interest.

2.3.1 Phenyl thiourea \([C_6H_5NHCSNH_2]\)

It shows high reactivity towards the primary species of water radiolysis. The electron reaction at pH 7 gave a transient species with absorption maximum at 345 nm. This species was found to be a strong reductant. The H-atom reaction led to the formation of cyclohexadienyl type of radicals in addition to H-addition at the C=S bond. OH reaction with phenyl thiourea also led to the formation of two types of species, formed by addition of OH to the benzene ring and by addition to the C=S bond followed by water elimination to give a 3-e electron bonded species between sulphur and nitrogen atoms. These two species had absorption maxima at 315 and 490 nm respectively. CO\(_2^-\) and isopropylketyl radicals could react with this compound only at pHs less than 0 to give species having absorption maximum at 410 nm which was similar to that obtained by OH radical reaction at pH -0 and could be due to the protonated form of the semioxidised species.

2.3.2 Diethyl thiourea \([C_2H_5NHCSNHC_2H_5]\)

Diethyl thiourea (DTU) was comparatively less reactive with e\(^-\)aq and OH radicals. The transient species formed by e\(^-\)aq reaction at pH 9 had absorption maximum at 300 nm indicating the formation of a C-centred radical as in the case of phenyl thiourea and also was a strong reductant. Br\(_2^-\) radicals reacted with DTU to give a transient having similar absorption spectrum as obtained by OH radical reaction at pH 9.
Table 2.3
Rate constants for the reactions of various solutes with the primary species of water radiolysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH</th>
<th>Rate constant $k_{aq}$ (x10^{-9} dm^3 mol^{-1} s^{-1})</th>
<th>$k_{H}$</th>
<th>$k_{OH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenyl sulphoxide</td>
<td>2</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dibenzyl sulphoxide</td>
<td>2</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Di 4-chloro phenyl sulphoxide</td>
<td>7</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Picolinic acid</td>
<td>3.9</td>
<td>17</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>0-2.4</td>
<td>-</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>5</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>Phenyl thiourea</td>
<td>~0</td>
<td>-</td>
<td>12</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>4.2</td>
<td>-</td>
<td>3.8</td>
</tr>
<tr>
<td>Thiosemicarbazide</td>
<td>~0</td>
<td>-</td>
<td>1.9</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-</td>
<td>0.96</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>1.1</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>Diethyl thiourea</td>
<td>~0</td>
<td>-</td>
<td>-</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.5</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>2-Mercapto benzimidazole</td>
<td>~0</td>
<td>-</td>
<td>5.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2.3</td>
<td>-</td>
<td>9.3</td>
</tr>
<tr>
<td>Diphenyl carbazide</td>
<td>2</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.26</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>Benzidine</td>
<td>2</td>
<td>-</td>
<td>1.3</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2.1</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>3-Hexyn 1-ol</td>
<td>9</td>
<td>0.06</td>
<td>-</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>-</td>
<td>-</td>
<td>4.7*</td>
</tr>
<tr>
<td>5-Amino tetrazole</td>
<td>0</td>
<td>-</td>
<td>0.37</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>&lt; 0.1</td>
<td>-</td>
<td>5.2</td>
</tr>
</tbody>
</table>

*O^−* reaction
2.3.3 **Thiosemicarbazide** \([\text{NH}_2\text{NHCSNH}_2]\)

Thiosemicarbazide (TSC) was found to be reactive with all the primary species of water radiolysis viz., \(\text{e}^-_{\text{aq}}\), \(\text{H}\) and \(\text{OH}\). The \(\text{e}^-_{\text{aq}}\) and \(\text{H-atom}\) essentially gave the same product species. The electron adduct appears to get neutralised by the addition of a proton. The \(\text{OH}\) radicals reacted with TSC to give a neutral transient species with absorption maximum at 500 nm, which appears to have a 3-electron bond between sulphur and nitrogen atoms. As in the case of phenyl thiourea, \(\text{H}, \text{CO}_2^-\) and isopropyl ketyl radicals reacted with TSC at \(\text{pH} < 0\) to give similar transient absorption with absorption maximum at \(\approx 400\) nm.

2.3.4 **Diphenylcarbazide** \([\text{C}_6\text{H}_5\text{NHCONHC}_6\text{H}_5]\)

In the case of diphenylcarbazide (DPC), \(\text{OH}\) radical reaction was much faster as compared to \(\text{e}^-_{\text{aq}}\) and \(\text{H-atom}\) reactions. The electron adduct at \(\text{pH} 7\) exhibited an absorption spectrum with maxima at 320, 360 and 480 nm whereas at \(\text{pH} 10\) only one peak was observed at 320 nm. The semi-reduced species had a \(\text{pK}_a\) value of 8. The \(\text{H-atom}\) reaction gave transient absorption in the uv region only. The \(\text{OH}\) reaction produced a transient with absorption maximum at 340 nm.

2.3.5 **2-Mercapto benzimidazole** \([\text{C}_6\text{H}_4\text{NHCSNH}]\)

Hydrated electrons reacted with this compound (MBZ) at \(\text{pH} 7\) to give initially an intermediate species with absorption maximum at 360 nm. This intermediate species decayed by first order kinetics (not dependent on the concentration of the solute) to give another transient with absorption maximum at 590 nm. This latter intermediate was found to be a neutral species. The reaction of \(\text{H-atom}\)s with MBZ also gave an initial transient absorbing in the uv region which later decayed to give another transient species with absorption maximum at 590 nm as in the case of electron reaction. \(\text{OH}\) radicals and other one electron oxidants also reacted with MBZ to give a neutral transient with
absorption spectrum similar to that obtained in the case of $e^{-}$aq and H-atom reaction. Thus in this case, all the primary radicals react to give a similar intermediate.

2.3.6 5-Amino tetrazole [NH$_2$C=N-N=N-NH]

This compound (ATZ) reacted only with OH radicals to give a transient with absorption maximum at 340 nm. Reaction with SO$_4^{2-}$ radicals at neutral pH also gave rise to a similar transient spectrum indicating that the two species are identical and must be the semioxidised species. The reaction with $e^{-}$aq and H-atoms was very slow and did not produce any light absorbing species.

2.3.7 Benzotriazole [C$_6$H$_4$N=NNH]

This compound (BZ) was found to react with $e^{-}$aq and OH radicals with rate constants of the order of 10$^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at pH 5.8. $e^{-}$aq reaction with the deprotonated form of BZ was slower by an order of magnitude. Semi-reduced form of BZ was found to be a good reductant. SO$_4^{2-}$ radicals brought about one electron oxidation of this compound to give a transient with a strong absorption band in the region of 550 nm. Both the semireduced and semioxidised forms of BZ have been postulated to be 3 electron bonded species.

2.3.8 Pyridinols [C$_5$H$_4$N(OH)]

Rate constants for the reaction of $e^{-}$aq, H and OH/O$^{-}$ with 2- and 4-pyridinols were determined at various pHs where they exist in different conjugate acid-base forms. pK$_a$ for the semireduced 2-pyridinol was determined to be 7.6 and it was found to be a strong reductant. OH adduct of 2-pyridinol was found to have a pK$_a$ at 3.6. 2-pyridinol was easily oxidised by one electron oxidants like N$_3^-$, Br$_2^-$ etc. at pH 13.3. Semireduced 4-pyridinol was also found to be a strong reductant and at the same time it
was found to undergo reversible reaction with the parent molecule with equilibrium constant of 97 dm$^3$ mol$^{-1}$ to give a dimer anion radical. OH adduct of 4-pyridinol was found to have the same pK$_a$ as the parent molecule.

2.3.9 3-Hexyn-1-ol [C$_2$H$_5$CCCH$_2$CH$_2$OH]

This corrosion inhibitor (3-HX) was found to be least sensitive to radiation as indicated by the reaction rate constants with e$^-_{aq}$, H and OH radicals. Reaction of both e$^-_{aq}$ and OH radicals with 3-HX produced reducing species: electron by addition to the triple bond and OH by abstraction of an H-atom from the $\alpha$-carbon atom. OH radicals also reacted by addition to the triple bond. H-atom reaction did not produce any light absorbing species, whereas the transients produced by e$^-_{aq}$ and OH radical reaction absorbed in the uv region with absorption maximum around 300 nm. HO$_2$, O$_2^-$ and O$^-$ radicals were found to react much faster with 3-HX as compared to e$^-_{aq}$, H and OH radicals.

Pharmaceuticals
(S. Sabharwal*, K. Kishore and P.N. Moorthy)

Radiation chemistry of tetracycline and sulpha drugs have been studied in the context of radiation sterilization of pharmaceuticals.

2.3.10 Tetracycline
[HOC$_6$H$_3$C$_4$(O)(OH)(CH$_3$)C$_4$H(OH)$_2$C$_4$OH(O)(N(CH$_3$)$_2$)(CONH$_2$)]

The reactions of tetracycline (TC) with reducing radicals has been studied using the pulse radiolysis technique. The rate constant for the reaction of e$^-_{aq}$ with this compound was determined to be 2.8x10$^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at pH 4. The semi-reduced species formed by the reaction of e$^-_{aq}$, CO$_2^-$, and isopropylketyl
radicals was found to have absorption maximum at 630 nm and was a good reductant. It showed two pK\textsubscript{a}s at 5.5 and 8.6. H-atoms reacted with TC largely by addition/abstraction reactions and only to a limited extent by electron transfer.

### 2.3.11 Sulpha drugs

Pulse radiolysis technique was used to study the reactions of sulphacetamide and sulphadiazine with e\textsuperscript{-aq}, H and OH radicals. The spectral, kinetic, redox and acid dissociation characteristics of the transients formed by these reactions were determined. The main findings are:

- **(a)** OH radicals react with these compounds primarily by addition reaction. In the case of sulphacetamide the OH-adduct decayed at pH 9.2 to give semioxidised species which could oxidise ascorbate. In the case of sulphadiazine semioxidised species could be produced only through the reaction of one electron oxidants.

- **(b)** The reactions of e\textsuperscript{-aq} and H-atoms were similar in both the cases. The electron adduct was found to be a good reductant. The H-atom reaction led to the formation of a semi-reduced species at neutral pH whereas at pH 2 it gave rise to two transients, an adduct and a semi-reduced species.

The kinetic and spectral data for the transients formed from these compounds are given in Table 2.3.11.

(* Isotope Division *)
Table 2.3.11
Kinetic and spectral data for sulpha drugs

<table>
<thead>
<tr>
<th>Species</th>
<th>pH</th>
<th>Sulphacetamide</th>
<th>Sulphadiazine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>abs. max. k (nm)</td>
<td>abs. max. k (nm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(x10^-9 dm^3 mol^-1 s^-1)</td>
<td>(x10^-9 dm^3 mol^-1 s^-1)</td>
</tr>
<tr>
<td>e^-aq</td>
<td>3.8</td>
<td>390</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>9.2</td>
<td>370</td>
<td>2.0</td>
</tr>
<tr>
<td>H</td>
<td>2.0</td>
<td>330</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>380</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>5.8</td>
<td>380</td>
<td>3.6</td>
</tr>
<tr>
<td>OH</td>
<td>3.8</td>
<td>420</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>9.2</td>
<td>400</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Other compounds
(G.R. Dey, D.B. Naik, K. Kishore and P.N. Moorthy)

2.3.12 Aromatic sulfoxides
The reaction of e^-aq with dibenzyl sulphoxide at neutral pH led to the breakage of C-S bond giving benzyl radicals. In the case of diphenyl sulphoxide and di-4-chloro phenyl sulphonyl sulphoxide, the e^-aq reaction did not lead to scission of the C-S bond and the electron adduct reacted with the parent compound to give a dimer anion radical. In the case of di-4-chloro phenyl sulfoxide, e^-aq reacted partly at the chlorine site to give chloride as a product. The reaction of H-atoms with these compounds at pH 2 takes place on the benzene ring to give cyclohexadienyl type of radicals.
2.3.13 **Picolinic acid** \([C_5H_4N(COOH)]\)

Picolinic acid (PA) is one of the chelating compounds used in decontamination formulations. Its radiation chemistry is of interest from the point of view of its radiation degradation during decontamination. The reaction of \(e^-_{aq}\) with PA in the pH range 4-9 gave a transient absorption with absorption maxima at 305 and 350 nm. The species exhibited a \(pK_a\) of 5.7 as compared to the parent \(pK_a\) of 5.4. This intermediate species was found to be a good reductant which could reduce many solutes such as methyl viologen, safranine-T and thionine. Its one-electron reduction potential was determined to be \(-1.33V\) vs NHE. The OH adduct showed absorption bands in the 345 nm region and two \(pK_a\)s at 2.1 and 5.2. \(H\)-atom reaction with PA gave a mixture of a reducing species and an \(H\)-adduct on the ring.

2.3.14 **Benzidine** \([NH_2C_6H_4C_6H_4NH_2]\)

Benzidine (BZN) is a carcinogenic compound. OH radicals react with this compound to give initially an adduct which later gives rise to a cation radical or its protonated form depending on the pH. The cation radical has absorption maxima at 455 and 780 nm. At higher pHs (\(> 11.8\)) the cation radical is converted into anilino radical with the elimination of a water molecule. \(O^-\) radicals also react with BZN to give a similar transient species. The anilino radical has absorption maxima at 380 and 620 nm. Similar transient species are formed by the reaction of one electron oxidants such as \(N_3^-\) and \(Br_2^-\) radicals. The cation radical oxidises ascorbate thus indicating that any damage due to BZN cation radicals can be eliminated by this compound. On reaction with \(e^-_{aq}\), BZN loses a molecule of ammonia and gives a transient with absorption maximum at 390 nm. \(H\)-atoms react with this compound to give a species having weak absorption in the uv region.
2.4 Studies on triplets of some biphenyl derivatives
(G.R. Dey, D.B. Naik, K. Kishore and P.N. Moorthy)

With the aim of understanding the effect of substitution on biphenyl ring on the triplet state properties, 4,4'-dimethyl biphenyl (DMBP), 4,4'-dimethoxy biphenyl (DMXBp) and 4,4'-diamino biphenyl (benzidine, BZN) were investigated in benzene solutions using pulse radiolysis technique. Their triplet-triplet absorption spectra were recorded in UV-visible region. Absorption maxima of the triplets of DMBP, DMXBP and BZN were found to be 380, 390 and 430 nm with extinction coefficients of 34075, 34700 and 30600 dm$^3$ mol$^{-1}$ cm$^{-1}$ respectively.

By using various triplet acceptors and donors the triplet energy levels of these compounds were determined to be 65±1.5, 65±1.5 and 61±1.5 kcal mol$^{-1}$ for DMBP, DMXBP and BZN respectively. Triplet life times of DMBP and DMXBP were determined to be 16.1 and 7.7 μs respectively whereas BZN triplet was found to undergo reaction with the parent molecule with a rate constant of 5.4x10$^8$ dm$^3$ mol$^{-1}$ s$^{-1}$, giving a transient species having absorption maxima at 380 and 620 nm. By comparison of this spectrum with the spectra of the neutral semioxidised BZN radical and the radical formed by the reaction of e$^{-}$aq with BZN, it has been concluded that the latter two species are the products in the reaction of BZN triplet with parent BZN molecule. Other interesting observation was that, although benzophenone triplet energy (68.5 kcal mol$^{-1}$) is higher than that of BZN (61 kcal mol$^{-1}$), instead of electron transfer occurring from benzophenone triplet to BZN, an exciplex between these two is formed. This species has absorption maximum at 380 nm and decays slowly by first order kinetics (k = 9.3x10$^3$ s$^{-1}$).
3. COMPLEX CHEMISTRY

3.1 Studies on aluminium chelates with some organic ligands

The chemistry of aluminium in aqueous medium is of environmental importance as it has a direct bearing on the mobility, bioavailability and ecological impact of this metal. There is growing evidence to suggest that the specific toxic effects of Al on terrestrial and aquatic organisms are related to its chemical identity. Hence studies on characterisation of aluminium complexes with various organic ligands were initiated.

3.1.1 Aminopolycarboxylic acids
(S.B. Karweer, B.P. Pillai and R.K. Iyer)

The reactions of Al(III) ion with a series of aminocarboxylic acids such as glycine(G), picolinic acid(PA), nitrilotriacetic acid(NTA), ethylenediamine tetraacetic acid(EDTA), 1,2 propylene diamine tetraaceticacid(PDTA) and triethylene tetramine hexacetic acid(TTHA) were studied by potentiometric and $^{27}$Al NMR techniques. The results indicate the existence of a nearly linear relationship between $^{27}$Al chemical shift of the normal chelate and denticity (n) of the ligand for values of n up to 6. The complex species in solution at different pH values were identified. Acid hydrolysis of the Al-PDTA complex results in the formation of $[\text{Al(H}_2\text{O)}\text{LH}]$ and $[\text{Al(H}_2\text{O)}_2\text{LH}_2]$ (L: PDTA) prior to dissociation, while base hydrolysis leading to the formation of aluminate takes place through the monohydroxo species. Although TTHA is a decadentate ligand, the maximum number of donor sites utilised in the formation of the 1:1 Al-TTHA complex is only five.
3.1.2 Malic acid

High field variable pH $^{27}\text{Al}$ NMR spectral studies of $\text{AlCl}_3$-malic acid system indicated the formation of as many as four complex species in the pH range 2-8. The binding of malate to aluminium takes place through the hydroxyl and carboxyl groups resulting in five and six membered chelate rings with deprotonation of the hydroxyl group. Malate functions either as bidentate or tridentate. The 1:1 Al-malate chelate was isolated and characterised by elemental analysis, potentiometric titration and infrared spectroscopy. The results indicate deprotonation of the hydroxyl group with the carboxylate group functioning as bidentate. A bridged polymeric structure has been proposed for the chelate.

(* Ph.D Student, University of Bombay)

3.1.3 Orthodihydroxy phenols and aromatic orthohydroxy carboxylic acids
(S.N. Mhatre*, S.B. Karweer, R.K. Iyer and P.N. Moorthy)

The complexation of $\text{Al}^{3+}$ ion with some phenolic ligands (catechol, tiron, salicylic acid and sulphosalicylic acid) was studied by $^{27}\text{Al}$ NMR spectroscopy. The complex species in solution at different pH values were identified by making use of both $^{27}\text{Al}$ NMR and potentiometric data. With tiron, aluminium forms 1:1, 1:2 and 1:3 chelates depending on the pH and ligand concentration. In addition, dimeric and polymeric dihydroxo chelates containing bridged hydroxyl groups are also formed at high pH (δ 36 ppm). Hydrolysis of 1:1 chelate leading to the formation of aluminate takes place through the formation of a tetrahedral dihydroxo 1:1 chelate (δ 53 ppm). In the case of
Al-catechol system, complex species and aluminate coexist in a 1:2 mixture at pH 12.5.

Unlike in the Al-tiron system, a tetrahedral 1:2 chelate (δ 58.5 ppm) is also formed during hydrolysis of 1:2 chelate with catechol. The maximum chemical shifts observed for octahedral chelates with salicylic acid and sulphosalicylic acid were 4.3 and 5.5 ppm respectively compared to 36 ppm for Al-tiron chelates. This could be attributed to the difference in size of the chelate ring formed as a result of complex formation. In the case of Al-tiron-salicylic acid system, $^{27}$Al NMR data indicate the formation of two mixed Al-tiron-salicylate chelates.

(* Ph.D Student, University of Bombay)

3.2 Characterization of aluminium complexes in tea extract
(S.N. Mhatre*, R.K. Iyer and P.N. Moorthy)

Tea plant is a typical Al accumulator. The Al contents in various samples of Indian Nilgiri and Assam black tea were in the range 600-750 ppm. Studies were carried out to identify the complex species of Al in aqueous tea extract.

The high field $^{27}$Al NMR spectrum of aqueous tea extract contained two narrow resonances at 9.85 and 16.15 ppm, the intensity of the former being much higher. The intensity of the resonance at 16.15 ppm increased considerably on concentration of the extract. Absence of any signal at 0 and 62.5 ppm indicated that tea infusion does not contain either free or hydrolysed aluminium ions.

A knowledge of the chemical shifts and linewidths of $^{27}$Al in its complexes with the ligands present in tea was necessary for the assignment of the two resonances. The major ligands present in tea are flavanols (catechin, epicatechin, gallocatechin etc.),
polyphenolic acids, theaflavin, caffeine and aminoacids. The $^{27}$Al NMR spectra of Al chelates with a number of model ligands (catechol, pyrogallol, catechin, kojic acid, protocatechuic acid and ascorbic acid) containing chelating moieties present in the constituents of tea showed broad resonances in the range 8-36 ppm.

From a comparison of the NMR spectra of tea infusions at different pH values with those of aluminium chelates with malic acid and oxalic acid (minor constituents in tea), the resonance at 16.15 ppm was assigned to the highly symmetric octahedral anionic chelate trisoxalato aluminium, $[\text{Al(C}_2\text{O}_4)_3]^{3-}$. This was confirmed by anion exchange separation of the chelate and its identification by $^{27}$Al NMR spectroscopy. The signal at 9.8 ppm could be due to a mixed ligand chelate containing oxalate. (* Ph.D. Student, University of Bombay)

3.3 Copper speciation studies

Under all volatile treatment (AVT), volatile amines are added in steam generator (SG) water to raise the pH and provide corrosion protection to the SG and condenser part of the steam water circuit of a power plant. Metal ions, generated by corrosion, can form complexes with these amines and thereby influence their transport behaviour. Localised electrical potential or reducing atmosphere existing in the SG can lead to reduction of these metal-amine complex species and deposition of metal on SG surface affecting heat transfer efficiency and possibly causing localised overheating, galvanic corrosion etc. Mode and ease of electroreduction of metal amine complex is species dependent. Electroreduction could be one of the deciding criteria for the choice of an AVT reagent.
Copper being a major constituent of SG alloying material, studies on its speciation with a number of amines likely to be used as AVT reagents have been initiated.

3.3.1 3-Methoxy Propylamine (MPA), 1-Dimethylamino 2-Propanol (DMPA), Dimethylamino Ethanol (DMAE) and Piperidine (PIP) (A.G. Kumbhar and S.V. Narasimhan)

Direct current (DC), differential pulse (DP) polarographic and differential pulse anodic stripping voltametric (DPASV) studies were carried out in amine-amine nitrate buffer media at ionic strength of 1 M (adjusted with KNO₃). Copper concentrations of 0.0475 mM for DCP and DPP, and 0.079 nM for DPASV were used. The important findings are:

(a) MPA forms complex \([\text{Cu(I)}(\text{MPA})_2]\) having stability constant (log K) value of 9.67. The complex undergoes one electron reversible reduction at the dropping mercury electrode (dme). Due to masking of \(\text{Cu(II)}\rightarrow\text{Cu(I)}\) reduction wave by the high current mercury oxidation wave, DC polarographic studies of \(\text{Cu(II)}\)-MPA could not be performed although formation of this species was inferred from uv-visible spectrophotometric and ESR data and it was concluded that \(\text{Cu(II)}\) undergoes stepwise two 1-electron reductions.

(b) DMPA and DMAE form the copper complexes \([\text{Cu(II)}(\text{OH})_2(\text{L})_2]\) with log K values of 18.7 and 20.12 respectively. They undergo direct two electron reduction on dme.

(c) Piperidine forms both \(\text{Cu(I)}\) and \(\text{Cu(II)}\) complexes. \(\text{Cu-PIP}\) complexes \([\text{Cu(I)}(\text{PIP})], [\text{Cu(I)}(\text{PIP})_2]\) and \([\text{Cu(II)}(\text{OH})(\text{PIP})_2]\) with log K values of 7.56, 9.24 and 16.67 respectively were identified using DPP and DPASV techniques. The secondary and tertiary amines cause electro reduction of \(\text{Cu(II)}\) directly to \(\text{Cu(0)}\).
The ligands that did not stabilise Cu(I) viz., DMPA and DMAE may inhibit the disproportionation route to the formation of metallic copper in either a reducing atmosphere or under localised electrical potential. Cu\(^{2+}\) ions will then be retained in solution as the complexes and can then be removed by blow down from the SG, thus providing minimal chance for deposition as Cu on metal heat transfer surfaces. Thus the amine which stabilise Cu\(^{2+}\) and will not bring about reduction through Cu\(^{+}\) may be preferred as an AVT reagent.

3.3.2 2-Amino. 2-methyl propanol (AMP), diethylamino ethanol (DEAE) and methyl pyrrolidine (MPy) 
(S. Rangarajan and S.V. Narasimhan)

Polarographic data on the speciation of copper in the presence of AMP, DEAE and MPy were processed using the standard programs CONSEL and POLAG, suitably modified to include the mixed hydroxy complexes. The program CONSEL uses the modified least squares linear regression to fit the data applying appropriate statistical tests. It gives the estimates of the stability constant values of possible complex species without requiring any initial guess. They were then subjected to non-linear optimisation procedure using the POLAG program for the simultaneous presence of different assumed complexes. Various equilibrium models consisting of the species having the general formula \(M_m(OH)_kL_n\) were tested and only those that converged were made use of. The following conclusions were drawn:

(a) Cu-AMP system is similar to the Cu-NH\(_3\) system. Either a direct (single step) two electron reduction or a stepwise (two steps) one electron reduction behaviour was observed depending upon a threshold concentration of amine at a given pH. From the current and potential parameters of cyclic voltammograms, the stabilisation of Cu(I) in some of the
solutions was confirmed and based on this, a two step reduction mechanism was proposed. The copper (II) species Cu L₂(OH)₂, Cu L₂(OH) and Cu L(OH)₂ have the stability constant (log K) values of 21.6, 16.9 and 18.6 respectively, while the log K values for Cu(I) species Cu L₂ and Cu (OH)₂ are 10.5 and 17.7 respectively.

(b) In the Cu-DEAE system a direct 2- electron reduction behaviour was observed. Copper (I) was not stabilised in the amine concentration range of 1 - 500 mM and pH range 8.5 - 11. The log K values of Cu L₂(OH), Cu L₂(OH)₂, Cu L(OH)₃ and Cu L₂(OH)₃ were found to be 14.8, 20.4, 22.8 and 24.2 respectively.

(c) In the Cu-MPy system only a single step 2-electron reduction behaviour was observed at amine concentrations below 10, 50 and 100 mM at pH 9, 9.5 and 10 respectively. However, it approached two 1-electron reduction behaviour when the ligand concentration at the respective pHs exceeded the above limits.

3.3.3 ESR and UV-Visible spectroscopic studies of Cu-amine complexes
(A.G. Kumbhar and S.V. Narasimhan)

The complexes formed by copper with the AVT amines were investigated by uv-visible and ESR spectroscopic techniques to establish a correlation between electrochemical reduction behaviour and ESR and uv-visible spectroscopic characteristics. The studies were carried out with the amines: 2-methyl 2-amino propanol (AMP), 2-diethyl amino ethanol (DEAE), morpholine (MOR), ammonia and cyclohexylamine (CHA). The electrochemical study showed that the primary amines and some secondary amines containing OH group stabilise Cu(I) state and hence stepwise electroreduction occurs in these cases. The uv-visible absorption maxima in the cases of these amines (abs. max: 600 -
620 nm) show formation of weak Cu(II) complex while ESR coupling constant values lie in the range of 70 - 80 G.

A few secondary and tertiary amines form Cu(II) complexes, which undergo direct two electron reduction at the dme. The observed uv-visible absorption maxima (abs. max: 520 - 570 nM) show strong Cu(II) complex formation. ESR coupling constants observed lie in the range 80 - 85 G. Four line ESR spectra observed in the case of all the copper complexes rules out formation of polynuclear complexes. Thus it appears that the covalency of metal - ligand bond as reflected by the ESR hyperfine coupling constant is possibly an important factor in directing the electroreduction of Cu(II) in presence of complex forming amines either through a single 2-electron route or a two step 1-electron pathway.
The use of metal hydrogen fluorides of the general formula $\text{MHF}_2$ (where $M = \text{NH}_4, \text{Li, Na, K, Rb}$) to fluorinate a large number of inorganic compounds such as vanadates, binary oxides, high $T_c$ oxides, metals and alloys has been demonstrated in these studies. Most of these reactions take place on grinding together the two reactants at room temperature in the solid state. The reactions proceed in a reasonably short time and the products are crystalline. In a few cases, the reactions proceed at either the phase transition temperature or the melting point of the metal hydrogen fluoride. The reaction path as well as the thermal degradation route of the products formed were established using XRD, TG and DTA techniques.

A very interesting outcome of this work is the observation that even grinding together the two reactants is not required to bring about the reaction at room temperature. By merely keeping in contact the two reactant solids at room temperature, the reaction commences by the formation of a crystalline product layer at the interface of the two solids. In a majority of reactant pairs the reaction progresses by the unidirectional transport of the fluorinating agent across the product layer onto the side of the other reactant. A pellet-inside-pellet reaction configuration was devised to study the reaction kinetics in these systems. The reactions were found to obey the simple Tammann law.

In addition to the above mentioned solid state reactions, a number of compounds which are likely to be formed in an operating nuclear reactor due to the fuel-fission product-clad interactions, were prepared and characterized. These compounds were prepared for use in experiments to obtain basic thermodynamic information on such compounds (see 5.5).
4.1 Fluorination of oxides of iron by ammonium hydrogen fluoride
(S.V. Adhyapak*, B.N. Wani and U.R.K. Rao)

The use of ammonium hydrogen fluoride (AHF) as a reagent to fluorinate oxides of iron viz., $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$ and $\Gamma$-Fe$_2$O$_3$ in the solid state at or slightly above the room temperature has been studied.

The reactants were mixed in the following proportions:

- $\alpha$-Fe$_2$O$_3$ + 6NH$_4$HF$_2$ ------ [I]
- Fe$_3$O$_4$ + 9NH$_4$HF$_2$ ------ [II]
- $\Gamma$-Fe$_2$O$_3$ + 6NH$_4$HF$_2$ ------ [III]

The mixtures were ground for half an hour and stored in a desiccator over P$_2$O$_5$. The progress of reaction was monitored by powder XRD technique. In the case of $\alpha$-Fe$_2$O$_3$, the reaction did not go to completion even after 3 days. When the mixture was heated at around 353 K for a few minutes, its XRD pattern matched with that of the known compound, (NH$_4$)$_3$FeF$_6$.nH$_2$O, with no reactants left over. In the case of Fe$_3$O$_4$, the reaction was found to go to completion after three hours at room temperature, giving (NH$_4$)$_3$FeF$_6$.nH$_2$O as the product. The reaction between $\Gamma$-Fe$_2$O$_3$ and AHF at room temperature was complete in a few minutes. All the three oxides were found to give the same final product. This was confirmed by DSC and Mössbauer spectral studies. The Mössbauer spectra of all the products were identical, exhibiting a singlet with an isomer shift of 0.4 mm/sec with respect to $^{57}$Fe in Fe metal, attributable to the symmetric hexafluoro anion of iron, FeF$_6^{3-}$.

The initial mixtures were subjected to simultaneous TG/DTA and XRD. Based on the results of these, the following mode of thermal decomposition has been proposed:
\[(\text{NH}_4)_3\text{FeF}_6 \cdot \text{H}_2\text{O} \rightarrow 3\text{NH}_4\text{F} + \text{FeF}_3 \cdot \text{H}_2\text{O}\]
\[\text{FeF}_3 + 1.5 \text{H}_2\text{O} \rightarrow \text{FeO}_{1.5} + 3\text{HF}\]

The chemical analysis of the products obtained from the mixtures [I], [II] and [III] was performed by standard permanganate titrimetric method for determining the amounts of Fe\(^{2+}\) and Fe\(^{3+}\). It was found that the iron is present entirely as Fe\(^{3+}\). This is surprising, since Fe\(_3\)O\(_4\) contains both Fe\(^{2+}\) and Fe\(^{3+}\) and the product of reaction should have contained in addition to \((\text{NH}_4)_3\text{FeF}_6\), Fe\(^{2+}\) in some form, which was not the case. Thus it appears that during the course of reaction of Fe\(_3\)O\(_4\) with AHF in air at room temperature, the Fe\(^{2+}\) gets oxidised to Fe\(^{3+}\).

(* Ph.D Student, University of Bombay)

4.2 Solid state reactions between metal bifluorides and vanadates

(S.J. Patwe, B.N. Wani and U.R.K. Rao)

Alkali metal bifluorides react with alkali metal vanadates at room temperature in the solid state. The alkali metal vanadates used were synthesised in the solid state by the high temperature reaction between V\(_2\)O\(_5\) and alkali metal carbonate. The general equation for the reactions carried out between vanadates and bifluorides can be written as:

\[\text{MVO}_3 + 2\text{M'}\text{HF}_2 \rightarrow \text{MM'}_2\text{VO}_2\text{F}_4 \cdot \text{H}_2\text{O}\]

where M and M' are combination of Na, K and \(\text{NH}_4^+\).

The reactants corresponding to the above stoichiometry were thoroughly ground in a polythene bag for about 20-30 minutes. The progress of the reaction was monitored by powder XRD. The absence of the diffraction lines due to the reactants was taken as the
indication for the completion of the reaction. It was observed that it takes two to three days for the completion of the reaction at room temperature. In all, sixteen oxyfluoro compounds with the above general formula were synthesized. They were characterized by the powder XRD technique and also indexed for the respective crystal systems by using standard computer programs. Their course of thermal degradation was established by using simultaneous TG/DTA technique. The intermediates formed during the course of degradation were synthesized separately by the solid state reaction route for confirming the decomposition path.

To study the nature of the solid state reaction and reactivity of different bifluorides towards a given vanadate or a given bifluoride towards different vanadates the pellet-inside-pellet (PIP) configuration technique (Fig. 4.2) was adopted in which an inner smaller bifluoride pellet was embedded in a larger outer pellet of vanadate. It was found that during the course of the reaction, the bifluoride (HF$_2^-$) ion along with its cation M$^{+}$ moves towards vanadate as was confirmed by SEM technique. In PIP experiment, once the product layer is formed at the interface the diffusing species has to first pass through this product layer and then react with the vanadate. Hence diffusion through product layer becomes the rate determining step. To study the rate of the reaction in PIP configuration the rate of growth of the thickness of the product layer was measured as a function of time. It was found that this rate is initially high and then decreases with time and becomes constant after about 27 to 30 hrs. The rate of the reaction is the least when the cation in both the reactants i.e., bifluoride and vanadate is the same. For instance, for the reaction between KH$_2$F as one of the reactants and different vanadates as the other, the initial reaction is the fastest (750±125 Å'/sec) in the case of NH$_4$VO$_3$ whereas it is too slow to be measured with the KH$_2$F-KVO$_3$ pair. The order of
**Fig. 4.2** The pellet-inside-pellet (PIP) configuration technique in which an inner smaller bifluoride pellet is embedded in a larger outer oxide pellet.
reactivity of potassium bifluoride towards different vanadates was found to be, $\text{NH}_4\text{VO}_3 > \text{NaVO}_3 >> \text{KVO}_3$. The order of reactivity for other bifluorides towards vanadates were similarly established.

4.3 **Interfacial reaction between ammonium bifluoride and binary oxides at room temperature**

(B.N. Wani and U.R.K. Rao)

Many fluoro/oxyfluoro compounds were prepared at room temperature as reported in 4.7 by grinding together a mixture in which $\text{NH}_4\text{HF}_2$ forms one component and a binary oxide the other. This solid state reaction was further studied using the pellet-inside-pellet (PIP) technique. The oxides chosen are $\text{V}_2\text{O}_3$, $\text{V}_2\text{O}_5$, $\text{ThO}_2$, $\text{UO}_2$, $\text{U}_3\text{O}_8$, $\text{La}_2\text{O}_3$, $\text{CeO}_2$, $\text{Nd}_2\text{O}_3$, $\text{Y}_2\text{O}_3$ etc.

In all the cases the bifluoride was found to diffuse into the oxide pellet. Once the product layer is formed at the interface, in all cases except $\text{U}_3\text{O}_8$, no further growth of product ring was observed at the interface even after a month. Thus the product layer seems to be impervious to bifluoride. This may be due to the structure of the product formed at the interface which plays a vital role in PIP experiments. The products formed at the interface were identified using XRD method, and it was observed that although no stoichiometry is implied in these experiments one gets a single phase crystalline compound at the interface.

In the case of $\text{U}_3\text{O}_8/\text{NH}_4\text{HF}_2$ pair, the product layer as it forms, peels off from the interface. The kinetics of the reaction was studied by monitoring the thickness of the coloured ring of the product with time. The thickness increased linearly with time, with a constant rate of $\approx 200 \, \text{Å/sec}$. Due to its higher constant rate of product formation and incompatibility of the cell volumes of the product and the reactants, the outer pellet
broke off within twelve hours. These two aspects of the reactivity of ammonium bifluoride towards oxides, viz., (i) the constant rate of reaction and (ii) resistance of the product layer to the transport of bifluoride, are in contrast with observations in the case of reaction between bifluorides and vanadates in PIP configuration. While grinding, all the oxides react at the same rate with bifluoride, as in this case, a fresh reaction surface is provided continuously between the reactants which is not the case in a PIP experiment.

4.4 Solid state reaction at room temperature between α-naphthol and 1,4 naphthoquinone
(B.N. Wani, S.V. Adhyapak* and U.R.K. Rao)

Solid state reactions normally occur at high temperatures. On the contrary reactions involving bifluorides reported in 4.1 - 4.3 occur at room temperatures. In order to rule out the possibility of such reactions involving the moisture sensitive bifluorides being catalysed by water, two organic compounds viz., α-naphthol (AN) and 1,4 naphthoquinone (NQ) were selected which are not hygroscopic and which are known to react to form a coloured 1:1 charge transfer complex (CTC).

The kinetics of the solid state reaction across the interface between NQ and AN was studied at room temperature using PIP configuration. NQ was found to diffuse into AN at room temperature. According to Tammann, the kinetics of a diffusion controlled reaction can be expressed as:

\[ L^2 = kt \]

where \( L \) is the thickness of the product formed at time \( t \) and \( k \) is rate constant. The kinetics of the reaction observed at room temperature in the case of this pair are consistent with those
reported at higher temperature. The activation energy for the diffusion is \( \approx 28 \text{ kJ mole}^{-1} \).

The occurrence of these low temperature solid state reactions can be rationalised on the basis of Tammann temperature, \( T_m(=0.52xT_{mp} \text{ in K}) \). Above this temperature, large number of defects are created in the solid facilitating diffusion of ions and molecules. The bifluorides and NQ have \( T_m < 25^\circ\text{C} \) and hence solid state reactions at room temperatures involving diffusion of one of the reactants can be expected to be facile.

(* Ph.D Student, University of Bombay)

4.5 Reaction between \( \text{NH}_4\text{HF}_2 \) and metallic Al, Ni and Cr


In order to study the reaction between ammonium hydrogen fluoride (AHF) and Al metal, an Al metal sheet was heated with excess of AHF. After about 1.5 hours, a white powder was obtained as product. Powder XRD pattern of the product showed the presence of \((\text{NH}_4)_3\text{AlF}_6\) and \(\text{NH}_4\text{AlF}_4\). The \((\text{NH}_4)_3\text{AlF}_6\) might have got partly decomposed to \(\text{NH}_4\text{AlF}_4\) due to over heating. In order to avoid this some Al turnings were heated with AHF melt in a platinum boat at around 413 K. After 8 hours of heat treatment all the Al turnings were converted to a white powder which was identified as \((\text{NH}_4)_3\text{AlF}_6\) by powder XRD. The course of thermal decomposition of this product in flowing \(\text{N}_2\) atmosphere was studied by simultaneous TG/DTA upto 1173 K and XRD showed the residue to be \(\text{AlF}_3\). The room temperature reaction between Al metal and AHF took about four days to show the formation of \((\text{NH}_4)_3\text{AlF}_6\) layer on the Al sheet. Similar studies were explored with Ni and Cr metals also. In the case of Cr, \((\text{NH}_4)_3\text{CrF}_6\) was obtained after heat treatment with \(\text{NH}_4\text{HF}_2\) melt, whereas Ni was found to be unreactive.
4.6 **Superconducting materials: preparation, characterization and thermal studies**  

A low temperature reaction scheme was developed for the quantitative fluorination of 90 K oxide superconductor, YBa$_2$Cu$_3$O$_{6.5+\delta}$ (123), using NH$_4$HF$_2$ as fluorinating agent. The amount of fluorine incorporated was controlled by varying the relative amounts of NH$_4$HF$_2$ and the 123 oxide in the mechanical mixtures. The upper limit of fluorine incorporation in this oxide was also studied and the composition of the maximum fluorinated product was established by TG and chemical analysis as YBa$_2$Cu$_3$O$_3$F$_7$. This product was found to have the same superconducting transition temperature as the parent oxide, but was thermally more stable than the latter. Thermal decomposition of YBa$_2$Cu$_3$O$_3$F$_7$ was studied both in air as well as in vacuum. Its weight loss data in flowing air was consistent with the following scheme:

\[
\text{YBa}_2\text{Cu}_3\text{O}_3\text{F}_7 + \frac{3}{2}\text{H}_2\text{O} \rightarrow 0.5\text{Y}_2\text{O}_3 + 3\text{CuO} + 2\text{BaF}_2 + 3\text{HF}
\]

YBa$_2$Cu$_3$O$_3$F$_7$ on heating at 1073 K in an evacuated sealed quartz tube gave CuO and some unidentified compound. If all the Cu is lost as CuO then the remaining product should be YBa$_2$F$_7$, which has not been reported in the literature. An attempt was made to prepare this compound by heating YF$_3$ and BaF$_2$ in 1:2 ratio in an evacuated sealed quartz tube at 1173 K for about 5 hours. Powder XRD pattern of the product exactly matched with that of the unidentified product. Hence the following course of decomposition in vacuum was proposed for YBa$_2$Cu$_3$O$_3$F$_7$:

\[
\text{YBa}_2\text{Cu}_3\text{O}_3\text{F}_7 \rightarrow 3\text{CuO} + \text{YBa}_2\text{F}_7
\]
4.7 Preparation of other rare earth analogues of YBa$_2$F$_7$

Having prepared the new compound YBa$_2$F$_7$, preparation of its other rare earth analogues was attempted. The compounds that were prepared contained La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb in place of Y. In order to prepare these 127 type compounds, first the trifluoride of each rare earth was prepared by heating the corresponding oxide with excess NH$_4$HF$_2$ at 723 K till complete conversion of the oxide. A mechanical mixture of each trifluoride and BaF$_2$ in 1:2 ratio was prepared, pelletised, wrapped in a platinum foil and heated at 1173 K for about 5 hours in a sealed evacuated quartz tube. Powder XRD pattern of all the products showed the absence of BaF$_2$ or the rare earth trifluoride, and hence formation of 127 phase was inferred. XRD pattern of compounds with Y upto Nd showed the presence of 10 singlets which were fitted to a cubic unit cell whereas that of compounds of rare earths beyond Nd showed the splitting of all the 10 singlets. These were fitted to an orthorhombic unit cell. This shows that there is an orthorhombic distortion in this series of compounds with Y beyond Nd. The magnetic behaviour of compounds with Y = Nd, Gd, Pr and Sm were studied from room temperature down to 5 K using a SQUID magnetometer. The compounds with Nd, Gd and Pr were found to be paramagnetic with a Curie-Wiess behaviour whereas SmBa$_2$F$_7$ showed a non Curie-Wiess behaviour. In fact Sm compounds are known to show a non Curie-Wiess behaviour due to mixing of the ground state with the first excited J=7/2 level. The magnetic moment on the rare earth ion and $\theta_p$ for each compound were also computed.

(* TIFR)
4.8 **Oxygen loading and its effect on \( T_c \) and other properties of fluorinated 123 oxide**

Two fluorine atoms were incorporated into the lattice of tetragonal 123 oxide by the low temperature solid state reaction route using \( \text{NH}_4\text{HF}_2 \) and the product was pelletised. It was heated at 673 K for 30 hours in a sealed quartz tube in presence of oxygen. The product was found to be superconducting (by EPR) with a \( T_c \) of 45 K whereas the parent tetragonal oxide gives only a weak EPR signal at 30 K. The fluorine substituted product shows the presence of a Cu triplet (\( S=1 \)) signal in its EPR spectrum which is rather unusual in 123 oxide and related compounds because of antiferromagnetic coupling of Cu in these oxides. One of the possible explanations is the breaking of some of the antiferromagnetic pairing during the heat treatment. In order to look into the origin of this signal in the product, detailed EPR experiments on CuO and on tetragonal 123 oxide subjected to various heat treatments are in progress.

(* Radiochemistry Division)

4.9 **Preparation of electron superconductor \( \text{Nd}_2\text{CuO}_4-x\text{F}_x \)**

In order to prepare F-containing \( \text{Nd}_2\text{CuO}_4 \), an electron superconductor, both high temperature ceramic route and low temperature reaction route were attempted. A mechanical mixture of \( \text{Nd}_2\text{O}_3 \), \( \text{NdOF} \) and CuO in 0.9:0.2:1.0 ratio was heated in air at 1163 K for 14 hours. Powder XRD pattern showed the formation of 214 phase.

This compound is known to become superconductor only after controlled reduction. Among the various methods tried for
reducing the 214 phase, heating at 1163 K for 10 hours in a dynamic vacuum gave a product superconducting with $T_c$ of $\approx 25$ K, but this could not be repeated. In the low temperature reaction scheme a mixture of $\text{Nd}_2\text{CuO}_4$ and $\text{NH}_4\text{HF}_2$ in the ratio 1:0.3 was heated to 583 K in air and cooled back to room temperature. The low temperature reaction product was heated at 1163 K for 6 hours in a dynamic vacuum of the order of $2 \times 10^{-6}$ torr. The AC susceptibility of the product was measured down to 12 K. The product was found to be superconducting with $T_c = 25$ K. Although, the superconducting fraction was small, the preparation could be reproduced.

(* TIFR)

4.10 Preparation and characterization of $\text{ZrMo}_2\text{O}_8$ and $\text{HfMo}_2\text{O}_8$
(M.S. Samant*, P.N. Namboodiri, A.B. Phadnis and S.R. Dharwadkar)

A procedure for the synthesis of pure $\text{ZrMo}_2\text{O}_8$ phase was standardized based on the results of TG, DTA, X-ray diffraction and chemical analysis. Effect of heating rate, sample size and time of isothermal heating of the reaction mixture on the purity of the final product was investigated systematically and a general procedure was evolved for the synthesis of molybdates free of reactants in the final product. Using similar procedure, pure $\text{HfMo}_2\text{O}_8$ was also prepared.

(* Ph.D Student, University of Bombay)

4.11 Preparation and characterization of cesium uranates
(S.R. Bharadwaj, A.B. Phadnis and S.R. Dharwadkar)

Cesium uranates viz., $\text{Cs}_2\text{U}_2\text{O}_7$, $\text{Cs}_4\text{U}_5\text{O}_{17}$, $\text{Cs}_2\text{U}_4\text{O}_{12}$ and $\text{Cs}_2\text{U}_4\text{O}_{13}$ were prepared, and were characterized by X-ray diffraction. Their thermal stability in air and flowing oxygen was investigated using thermogravimetry. In static air, $\text{Cs}_2\text{U}_2\text{O}_7$
was found to convert successively to $\text{Cs}_4\text{U}_5\text{O}_{17}$ (at 1173 K) and $\text{Cs}_2\text{U}_4\text{O}_{12}$ (at 1323 K). These compounds could be isolated and characterized as pure phases. The sequence of reactions undergone by $\text{Cs}_2\text{U}_2\text{O}_7$ on heating provided an elegant method for the preparation of $\text{Cs}_4\text{U}_5\text{O}_{17}$ and other higher uranates starting from the diuranate.

4.12 Solid state synthesis of cesium molybdates
(A.B. Phadnis, P.N. Namboodiri, M.S. Samant* and S.R. Dharwadkar)

The solid state reaction between $\text{Cs}_2\text{CO}_3$ and $\text{MoO}_3$ was followed by employing thermogravimetry and differential thermal analysis. Though $\text{Cs}_2\text{CO}_3$ decomposed after melting above 1073 K, the reaction between 1:1 and 1:2 mixtures of $\text{Cs}_2\text{CO}_3$ and $\text{MoO}_3$ commenced at temperatures as low as 523 K resulting in the liberation of carbon dioxide and the formation of $\text{Cs}_2\text{MoO}_4$ and $\text{Cs}_2\text{Mo}_2\text{O}_7$ respectively. The formation of these compounds could be confirmed from the mass changes in the reaction and the melting points observed in DTA. Attempts are being made to isolate these compounds for identification by X-ray powder diffraction technique.

(* Ph.D Student, University of Bombay)

4.13 Reaction of boric acid with cesium iodide
(A.B. Phadnis, P.N. Namboodiri, M.S. Samant* and S.R. Dharwadkar)

The chemical reaction between boric acid and cesium iodide in 1:1 ratio was followed employing the TG, DTA and XRD techniques. Preliminary observations indicated that there is no liberation of HI in the early stages of the reaction. The boric acid in the mixture was found to be first dehydrated to HBO$_2$ which subsequently lost the remaining water to yield B$_2$O$_3$ which
then reacted with cesium iodide to liberate iodine. The exact nature of the reaction is not yet clear. The solid phase obtained at the end of the reaction was only partially crystalline. (* Ph.D Student, University of Bombay)
5. STRUCTURE, THERMODYNAMICS AND THERMOCHEMISTRY

5.1 X-ray crystal structure determination of platinum complexes

Single crystal X-ray structural analysis of a few platinum complexes have been carried out and the results are summarized below.

5.1.1 \([\text{PtMe}(\eta^2-\text{Ph}_2\text{Ppy})(\text{Ph}_2\text{Ppy})][\text{BPh}_4]\)

(V.S. Jakkal, V.K. Jain* and R. Bohra **)

This compound \((C_{59}H_{51}N_2P_2Bt)\) belongs to the triclinic system with space group P1-bar and has two molecules in the unit cell. The unit cell parameters are \(a = 10.006(6), b = 14.240(8), c = 18.368(6)\ Å, \alpha = 80.93(4), \beta = 74.60(3)\) and \(\gamma = 89.23(5)\). The crystal structure consists of discrete molecular units of \([\text{PtMe}(\eta^2-\text{Ph}_2\text{Ppy})(\text{Ph}_2\text{Ppy})]^+\) and \([\text{BPh}_4]^-.\) The platinum atom has square planar geometry with Pt atom in the centre, with one methyl carbon atom, one pyridyl nitrogen and two phosphorous atoms from the phosphine group taking part in the coordination. \([\text{BPh}_4]\) has the usual tetrahedral geometry. The final R-factor is 7.96%.

(* Chemistry Division, ** Dept. of Chemistry, Univ. of Rajasthan)

5.1.2 \([\text{PtMe}_3(\text{SSPPPh})_2]\)

(V.S. Jakkal, S. Chaudhury*, V.K. Jain** and K. Venkatasubramanian***)

This compound \((C_{30}H_{36}P_2S_4Pt_2)\) belongs to the monoclinic system with space group \(P2_1/n\) and has four molecules in the unit cell. The unit cell parameters are \(a = 10.045(1), b = 20.027(2),\) \(c = 16.691(2)\ Å\) and \(\beta = 92.19(1)\). Both the Pt atoms show distorted octahedral geometry and are coordinated through
the three methyl carbon atoms and the three sulphur atoms, so that the dithiophosphorous moiety is attached to platinum atoms giving rise to a triconnective bridge. The four-membered $Pt_2S_2$ ring is planar. The structure was refined to an accuracy of 4.0% R-factor.

(* Fuel Chemistry Division, **Chemistry Division, ***Central Salt and Marine Chemicals Research Laboratory, Bhavnagar)

5.1.3 $[PtMe_3(py)SSPPh_2]$

(V.S. Jakkal, S. Chaudhury*, V.K. Jain** and K. Venkatasubramanian***)

This compound ($C_{20}H_{24}NPS_2Pt$) belongs to the monoclinic system with space group $P2_1/c$. The unit cell parameters are $a = 15.055(1)$, $b = 9.844(1)$ and $c = 15.770(2)\text{Å}$ with the monoclinic angle $\beta = 114.58(1)^\circ$. There are four molecules in the unit cell. The structure of this compound consists of discrete monomeric molecules with approximately octahedral geometry around the platinum atom. The three methyl carbon atoms, the pyridyl nitrogen atom and two sulphur atoms take part in the coordination around the central platinum atom. The four-membered $PtSSP$ ring is distinctly nonplanar. The structure was refined to an R-factor of 3.7%.

(* FCD, **CD, ***CSMCRL, Bhavnagar)

5.2 Setting up of the Cambridge Crystallographic Database

(V.S. Jakkal and K.K. Kannan*)

The copy of the above database, compiled by the University of Cambridge on magnetic tapes was obtained from the University of Madras. This database consists of the crystal structure data of organic and organometallic compounds excluding proteins. The EBCDIC coded information on these tapes were converted into ASCII code and retrieved into the disk space of NORSK DATA (ND).
computer system. In addition to the data, the tapes contained
the FORTRAN computer programs ADAPT, QUESTA, QUESTB, QUESTC and
GEOMSTAT to work with the database. These programs were modified
extensively so as to make them suitable for ND computer. A brief
description of these programs is given below:

(a) The program ADAPT is used for converting the formatted
database files into one searchable binary file, ASER. Several
attempts were made to form one binary file, but it was found that
in the ND environment, it would be more appropriate to prepare
smaller files instead of one large binary file. Hence the program
ADAPT was modified to prepare 11 ASER files, each approximately
10000 pages of ND disk space.

(b) The programs QUESTA and QUESTB can be used for the batch
mode operation of the database. When QUESTC is also added to them
after some modifications, an interactive mode of operation of the
database could be achieved. These three programs were suitably
modified, so that they could be used for accessing the 11 ASER
binary files of the database and the complete search program is
called QUEST.

(c) The program GEOMSTAT is useful for geometrical and
statistical calculations pertaining to the data accessed from the
above database.

The complete ASER data now consist of 93262 searchable
entries consisting of subfiles: FBIB (bibliographic), FCONN
(connectivity) and FDAT (coordinate data) in an integrated
fashion. The output of the QUEST program will consist of one or
all of these subfiles. A few FORTRAN programs such as INTERP,
SEARCH etc., were written to view the database output in a simple
and easily understandable manner.

(* Solid State Physics Division)
5.3 Cambridge Crystallographic Database searches
(V.S. Jakkal, K.K. Kannan*, M. Ramanadham*, Vinaykumar* and S. Chakravarty*)

Some of the database searches carried out are as follows:
(a) In order to get the list of the structures worked out at BARC, search for 22 names of authors contributing to the Cambridge database was made. In all 87 hits were obtained for this search. The molecular plots for all these entries were drawn.

(b) A bibliographic search for all compounds containing the amino acid 'PROLINE' was made and this gave 417 hits.

(c) For the bibliographic search strings 'CYCLOHEXANE', 'CYCLOHEPTANE' and 'CYCLOBUTANE' 61, 8 and 15 hits were obtained respectively.

(d) A bibliographic search for amino acid derivatives of Hg, Cd or Zn gave 86 hits, out of which 16 were for Hg compounds.

(e) A connectivity search for the compounds containing two fused benzene rings was made resulting in 509 hits. 16 of these compounds had the text string 'NAPHTHA' in their bibliographic field.

(f) Two connectivity searches were made for chromophore model building. One was for searching a six membered ring having five carbon atoms and one oxygen atom, which yielded 844 hits of which 22 compounds were useful for model building. The second connectivity search was made for cyclic carbonates, which showed 481 possibilities. Only five from these were useful for model building.

(* Solid State Physics Division)
5.4 Analysis of hydrogen bonding in compounds containing carboxyl and amino acid groups
(V.S. Jakkal and M. Ramanadham *)

In order to analyse the systematics of hydrogen bonding geometry, the hydrogen atom positions must be known with a very high degree of precision. Only the structure determinations carried out using neutron diffraction can provide this precision. A search of the compounds, the structures of which have been worked out by neutron diffraction was therefore carried out in the Cambridge Crystallographic Database. A total of 770 such entries were retrieved. The program GEOMSTAT was then used to analyse these structures for the occurrence of -COOH, -COO\(^-\) and -NH\(_2\) groups, to yield 95, 85 and 241 possible compounds containing these groups respectively.


The scatter plots of the hydrogen bonding donor atoms surrounding -COO\(^-\) and -COOH were drawn. The -COO\(^-\) group showed a concentration of donors in the direction of lone pairs on the oxygen atoms projected onto the carboxyl plane. The scatter plots, in which the view direction is along the C1-C2 bond showed that a majority of donors are outside the carbonyl plane. The scatter plots of the hydrogen bond donor atoms surrounding the -COOH showed that the distribution of hydrogen bonds involving carbonyl oxygen atoms is similar to the case of -COO\(^-\) group.
mentioned above. The hydroxyl oxygen of -COOH, however, acts as a hydrogen bond donor and hence the concentration of acceptors is seen in the OH direction. For 127 compounds containing -COOH groups the hydrogen bond in the donor group is in a cis configuration, compared to only 24 in the trans form. (* Solid State Physics Division)

5.5 Thermodynamic properties and thermochemical behaviour of nuclear materials

Knowledge of thermodynamic properties of fission products and their chemical interactions with the fuel and the clad are very important in predicting the long term integrity of the nuclear fuel under irradiation. Changes in various properties of the fuel following the formation of these compounds, such as volume, thermal conductivity etc., influence the fuel performance to a great extent. The fission product-fuel-clad interactions are important in every stage of the fuel cycle, viz., (i) during the normal operation of the reactor, (ii) during the reprocessing of the fuel, (iii) for the disposal of the nuclear waste in the ceramic form and (iv) to predict the release behaviour of the various volatile fission product species during a severe accident. These considerations have added new dimensions to nuclear fuel chemistry and have further enhanced the need for acquisition and evaluation of thermodynamic data on a wide variety of compounds involving fission products and the fuel.

5.5.1 Standard free energy of formation of ZrMo$_2$O$_8$ and HfMo$_2$O$_8$

As a prerequisite for the determination of standard free energy of formation of ZrMo$_2$O$_8$ and HfMo$_2$O$_8$ by the transpiration
technique, vapour pressure of molybdenum trioxide was measured in the temperature range 947-1048 K. The transpiration apparatus used for this purpose was built around the specially designed and fabricated microthermogravimetric system. The vapour pressure of molybdenum bearing species could be expressed as:

\[
\log(p, (\text{MoO}_3, s)/\text{Pa}) = -(18466.0 \pm 204.9)/T + (20.259 \pm 0.206)
\]

The enthalpy of sublimation of MoO$_3$ calculated using the above equation is 353.5 ± 7.4 kJ/mol and compares well with the best assessed literature value of 357.75 ± 7.4 kJ/mol.

The vapour pressure of ZrMo$_2$O$_8$ was measured in the temperature range 1029 to 1142 K employing the above mentioned technique. The standard free energy of formation of ZrMo$_2$O$_8$ derived from the vapour pressure measurements could be expressed as a function of temperature by the relation:

\[
\Delta G'_f<\text{ZrMo}_2\text{O}_8> \text{ (kJ/mol)} = -(2525.51 \pm 4.88) + (0.6115 \pm 0.0045)T
\]

The standard free energy of formation of ZrMo$_2$O$_8$ obtained in this work compares very well with the free energy of formation reported by Pankajavalli and Sreedharan from measurements using the solid electrolyte galvanic cell technique (J. Nucl. Mater., 172, 151, 1990). The standard free energy of formation of HfMo$_2$O$_8$ was also determined by the same technique in the temperature range 1023 to 1185 K and could be expressed as a function of temperature by the relation:

\[
\Delta G'_f<\text{HfMo}_2\text{O}_8> \text{ (kJ/mol)} = -(2498.0 \pm 4.06) + (0.6039 \pm 0.0037)T
\]

The values of \(\Delta G'_f\) of HfMo$_2$O$_8$ from this work were about 50-60 kJ more positive than the values reported from galvanic cell measurements. Attempts were made to explain the discrepancy by
considering the solid solubility of HfO$_2$ and ZrO$_2$, the nonstoichiometry in MoO$_2$ etc. But none of these factors could explain the differences in free energy values. Fig.5.5.1 shows the standard free energy of formation of ZrMo$_2$O$_8$ and HfMo$_2$O$_8$ as a function of temperature as measured by the two different techniques, viz., vapour pressure measurement and solid electrolyte galvanic cell.

(* Ph.D Student, University of Bombay)

5.5.2 Thermodynamic data for pure palladium
(G. Chattopadhyay)

Thermodynamic data for pure palladium are very essential for understanding the behaviour of palladium alloys. At present there is a dichotomy that for solid and liquid Pd, the SGTE (Scientific Group Thermodata Europe, a consortium of data bases from several European laboratories) data are used in the computer calculations of phase diagrams, whereas in thermodynamic measurements, Hultgren's data are generally made use of. To resolve this, $T_{\text{fusion}}$, $\Delta H_{\text{fusion}}$, $\Delta S_{\text{fusion}}$ and $S_{298}$ for palladium, were updated from SGTE. Recent reviews of low temperature heat capacity data agree with the earlier accepted values. High temperature heat capacities and thermodynamic functions of solid palladium and liquid palladium given by SGTE differ from those of Hultgren et al.

Experimental data on vaporization of palladium has been reviewed. In all 21 citations were available in the literature. It was felt necessary to recalculate the enthalpy of vaporization with the SGTE set of data. A preliminary calculation shows that an accuracy of ±20% in the vapour pressure measurement cannot yield the enthalpy of vaporization to better than ±2.5 kJ accuracy.
Fig. 5.5.1 The standard free energy of formation of ZrMo$_2$O$_8$ and HfMo$_2$O$_8$ as a function of temperature
5.5.3 Chemical state of palladium in the nuclear fuel cycle and the binary phase diagrams of palladium
(G. Chattopadhyay, S.R. Bharadwaj, S.N. Tripathi, A.B. Phadnis, P.N. Namboodiri and S.R. Dharwadkar)

A database containing the latest information on the chemical state of palladium in the nuclear fuel cycle and binary phase diagrams of palladium bearing systems was compiled. This forms an important part of thermodynamics of palladium bearing systems. The current status of the database is shown in Fig. 5.5.3 which can be summarized as follows: (i) out of the 86 possible binary systems, phase diagrams have not been compiled for 21 systems and (ii) for important fission products such as Cs, Sr, La and Pr no phase diagram is available.

5.5.4 Critical evaluation of the binary phase diagrams of platinum group metals
(S.N. Tripathi, S.R. Bharadwaj and S.R. Dharwadkar)

As contributory editors for the critical evaluation of the binary phase diagrams of platinum group metals by the American Society of Metals (ASM), critical evaluation of Nb-Pt and Pd-Ru systems were completed. The evaluation of thermodynamic parameters for the systems Hf-Pd, Ir-Pt, Ir-Rh, Pd-Rh and Pd-Ir done earlier was updated taking into account additional information available.

5.5.5 Thermodynamic investigations on Pd-Pt alloys
(S.R. Bharadwaj, A.S. Kerkar, S.N. Tripathi, S.R. Dharwadkar and R. Kameswaran*)

Vapour pressure measurements were carried out on Pd-Pt alloys of 10-90 atom % Pt composition in the temperature range 1600-1900 K, using the Knudsen effusion forward collection technique.
<table>
<thead>
<tr>
<th>Ac</th>
<th>Ag</th>
<th>Al</th>
<th>As</th>
<th>Au</th>
<th>B</th>
<th>Ba</th>
<th>Be</th>
<th>Bi</th>
<th>Br</th>
<th>C</th>
<th>Ca</th>
<th>Cd</th>
<th>Ce</th>
<th>Cl</th>
<th>Co</th>
<th>Cr</th>
<th>Cs</th>
<th>Cu</th>
<th>Dy</th>
<th>Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Fe</td>
<td>Ga</td>
<td>Gd</td>
<td>Ge</td>
<td>H</td>
<td>He</td>
<td>Hf</td>
<td>Hg</td>
<td>Ho</td>
<td>I</td>
<td>In</td>
<td>Ir</td>
<td>K</td>
<td>I</td>
<td>Li</td>
<td>Lu</td>
<td>Mg</td>
<td>Mn</td>
<td>Mo</td>
<td>C</td>
</tr>
<tr>
<td>N</td>
<td>Na</td>
<td>Nb</td>
<td>Nd</td>
<td>Ni</td>
<td>O</td>
<td>Os</td>
<td>P</td>
<td>Pb</td>
<td>Pd</td>
<td>Pr</td>
<td>Pm</td>
<td>Po</td>
<td>Pt</td>
<td>Rh</td>
<td>Ru</td>
<td>S</td>
<td>Tm</td>
<td>U</td>
<td>V</td>
<td>W</td>
</tr>
<tr>
<td>Sb</td>
<td>Sc</td>
<td>Se</td>
<td>Si</td>
<td>Sm</td>
<td>Sn</td>
<td>Sr</td>
<td>Ta</td>
<td>Tb</td>
<td>Tc</td>
<td>Te</td>
<td>Ti</td>
<td>Tl</td>
<td>Tm</td>
<td>U</td>
<td>V</td>
<td>W</td>
<td>Y</td>
<td>Yb</td>
<td>Zn</td>
<td>Zr</td>
</tr>
</tbody>
</table>

- Assessed: Published in ASM Compilation
- Assessed: Published in Periodicals
- Updated; * Evaluated in our Division
- C Phase Diagram found in Compilations such as Hansen, Elliott, Shunk etc.

**FIG. 5.5.3** Current status of thermodynamic databases: A sample survey for binary phase diagrams of palladium

107
The activities for all these compositions were evaluated from the measured vapour pressures over the alloys. The other thermodynamic quantities such as $\Delta G_{\text{pd}}$, $\Delta G_{\text{pt}}$ and $\Delta G$ of the alloys were calculated from these data.

Computation of thermodynamic properties from the experimental data on Pd-Pt alloys and that of the other investigators has been carried out. Comparison of the activities shows a parallel trend of variation. In both the cases $\Delta G^\text{ex}$ at 1800 K is negative implying that the solid solution at that temperature is relatively more stable than an ideal one.

$\Delta G$ was plotted as a function of composition at various temperatures. These plots reflect a tendency for miscibility gap at lower temperatures.

(* Analytical Chemistry Division)

5.5.6 Correlation between thermodynamic properties and atomic orbital overlaps in noble metal alloys
(S.N. Tripathi)

A critical examination of the thermodynamic properties, in particular the enthalpy of formation $\Delta H_f$, of the binaries among the fcc metals e.g., Cu, Ag, Au, Pd, Pt, Rh and Ir has been made. A quantitative correlation could be obtained between the positive enthalpy effect upon alloy formation and the extension / contraction of d-orbitals and their overlap on the neighbouring atoms. Since most of these metals have more or less identical atomic sizes, the strain energy due to size mismatch is assumed to be insignificant. Based on the correlation obtained using these criteria, a positive deviation in activity vs composition is predicted for the Pd-Ir and Pt-Rh systems. This tendency is partly reflected in the miscibility gap experimentally observed in the Pd-Ir system.

108
5.5.7 Thermodynamic database for Te bearing species in Me-Te and Me-Te-O systems
(G. Chattopadhyay and J.M. Juneja*)

Work on a thermodynamic database for tellurium bearing systems of relevance to nuclear technology was completed. The database contains phase diagrams for the following systems: Pd-Te, Rh-Te, Pu-Te, Sm-Te, Cs-Te and Zr-Te binaries and Mo-Te-O, Zr-Te-O, Ag-Te-O, U-Te-O, Cs-Te-O and Ba-Te-O ternaries. It also contains thermodynamic data for crystalline Te, $\text{Fe}_{0.53}\text{Te}_{0.47}$, $\text{Mo}_{0.43}\text{Te}_{0.57}$, $\text{Ni}_{0.6}\text{Te}_{0.4}$, $\text{Cr}_{0.43}\text{Te}_{0.57}$, $\text{Ag}_2\text{Te}$, $\text{Cs}_2\text{Te}$, $\text{BaTe}$, $\text{SmTe}$, $\text{CeTe}$, $\text{SnTe}$, $\text{ZrTe}_2$ and $\text{RuTe}_2$, liquid Te and for the following vapour species: Te, $\text{Te}_2$, $\text{TeO}_2$, $\text{TeO}$, $\text{TeO(OH)}_2$, $\text{TeI}_4$, $\text{TeI}$, $\text{TeOI}_2$, $\text{SnTe}$, $\text{Cs}_2\text{Te}$, $\text{CsTe}$, $\text{Cs}_2\text{TeO}_3$, $\text{Cs}_2\text{Te}_2$, $\text{SnTe}_2$ and $\text{Sn}_2\text{Te}_2$.

In this work the thermodynamic data for elemental tellurium was re-evaluated superseding most of the hitherto accepted compilations. The relative importance of fission products and clad components in their ability to bind Te is highlighted in Fig.5.5.7 which shows that Zr, Pd and Ag bind Te most strongly in that order. This figure also delineates the domains of applicability of various techniques for high temperature thermodynamic studies of M-Te systems.

(* Metallurgy Division)

5.5.8 The chromium-tellurium system
(G. Chattopadhyay)

Among the transition metal - tellurium systems, the Cr-Te system is one of the most relevant in nuclear technology from the point of view of clad-fission product interactions. The phase diagram of this system as also the thermodynamic data have been critically evaluated. For the proper interpretation of the
Fig. 5.5.7 Dissociation pressure of tellurium over metal tellurides as a function of reciprocal temperature and the domains of applicability of various experimental techniques.
available data, it is necessary to hypothesise that Cr₃Te₄ might undergo an order-disorder transition to the completely disordered NiAs structure before melting congruently. This work pointed out the need for knowledge about the systems, Cr-Te-O, Cr-Te-C, Cr-Si-O and Cr-Si-Te-O.

5.5.9 Thermodynamic calculations using the SOLGAS MIX-PV program
(S.R. Bharadwaj, G. Chattopadhyay and S.R. Dharwadkar)

Partial pressures of ruthenium bearing species such as RuO₃(g), RuO₄(g), RuOH(g) and RuO₂H₂(g) in equilibrium with Ru metal and RuO₂(s) were calculated using SOLGAS MIX-PV computer program. The calculations were performed in the temperature range 1000 to 1500 K and in one atmosphere of air or argon containing PH₂O = 20 Torr. These calculations are necessary to find out the feasibility of using the transpiration technique for determining the thermodynamic properties of RuOH(g) and RuO₂H₂(g).

SOLGAS MIX-PV computer program was also used to calculate the partial pressures of various vapour species in the system TeO₂-H₂O-N₂-O₂ to validate the vapour pressure data and to find the limit of applicability of the transpiration technique for this system.

5.6 Thermochemical investigations

Thermal studies in the multi-component oxide systems of technological importance were initiated. The studies include the determination of high temperature thermal stability, phase transitions and thermal expansion characteristics of compounds formed in these systems.
5.6.1 Thermogravimetric and dilatometric studies on pure and doped ceramic superconducting materials

(A.C. Momin, E.B. Mirza* and M.D. Mathews)

The pure and doped superconducting compounds viz., YBa$_2$Cu$_3$O$_x$, LaBa$_2$Cu$_3$O$_x$, Bi$_2$CaSr$_2$Cu$_2$O$_x$, LaBa$_{2-y}$M$_y$O$_x$ (M = Ni, Li; y=0.1) and Ln$_{2-x}$M$_x$CuO$_4$ (Ln=La, Nd; M=Sr, Ce; x=0,0.15) were prepared by the standard ceramic techniques from the respective component oxides in the required molar proportions. The materials were characterized by X-ray powder diffractometry (XRD). Their thermal studies were carried out using microthermogravimetry (μTG) and dilatometry in the temperature range 298-1125 K in air. The values of the percentage weight loss calculated from the μTG data and the coefficients of average linear thermal expansion ($\alpha_1$) obtained from the dilatometric data are summarized in Table 5.6.1. The μTG and dilatometric results suggest that the compounds which showed negligible weight loss on heating have low $\alpha_1$ values. The $\alpha_1$ values for the doped compounds were found to be lower than those of the pure compounds and amongst all the pure and doped compounds, the $\alpha_1$ values as well as the percentage weight loss (attributed to oxygen loss) both were found to be the highest for the pure compound YBa$_2$Cu$_3$O$_x$ (Table 5.6.1). The results are interpreted in terms of oxygen mobility, bond strength and void space.

(* Since retired)
Table 5.6.1
Thermogravimetric and dilatometric data for some ceramic superconducting materials

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coefficient of linear thermal expansion $\alpha_1 \times 10^6 \text{ K}^{-1}$ (298-1125 K)</th>
<th>Oxygen loss % (298-1125 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBa$_2$Cu$_3$O$_x$</td>
<td>17.4</td>
<td>1.05</td>
</tr>
<tr>
<td>LaBa$_2$Cu$_3$O$_x$</td>
<td>15.5</td>
<td>0.93</td>
</tr>
<tr>
<td>LaBa$<em>2$Cu$</em>{2.9}$Li$_{0.1}$O$_x$</td>
<td>12.7</td>
<td>0.83</td>
</tr>
<tr>
<td>LaBa$<em>2$Cu$</em>{2.9}$Ni$_{0.1}$O$_x$</td>
<td>12.8</td>
<td>0.75</td>
</tr>
<tr>
<td>BiCaSrCu$_2$O$_x$</td>
<td>10.6</td>
<td>0.10</td>
</tr>
<tr>
<td>Bi$_2$CaSr$_2$Cu$_2$O$_x$</td>
<td>10.5</td>
<td>0.05</td>
</tr>
<tr>
<td>La$_2$CuO$_4$</td>
<td>10.0</td>
<td>0.00</td>
</tr>
<tr>
<td>La$<em>{1.85}$Sr$</em>{0.15}$CuO$_4$</td>
<td>9.8</td>
<td>0.00</td>
</tr>
<tr>
<td>Nd$_2$CuO$_4$</td>
<td>11.1</td>
<td>0.00</td>
</tr>
<tr>
<td>Nd$<em>{1.85}$Ce$</em>{0.15}$CuO$_4$</td>
<td>10.6</td>
<td>0.00</td>
</tr>
</tbody>
</table>

5.6.2 High temperature X-ray powder diffractometric studies on Bi$_2$CaSr$_2$Cu$_2$O$_x$
(A.C. Momin and M.D. Mathews)

High temperature XRD studies on this compound were carried out in the temperature range 298-1073 K in air. The X-ray powder diffractograms recorded at different temperatures from ambient to 1073 K did not indicate any phase transition. Temperature variation of the lattice parameters revealed that both $b$ and $c$ axes of an orthorhombic unit cell of this compound elongate with temperature while the $a$ axis is found to contract gradually with increasing temperature. The unit cell volume determined from the
cell parameters shows an overall increase with temperature. The values of the coefficients of average linear thermal expansion \( \alpha_1 \) obtained along all the three axes \( a, b \) and \( c \) show that \( \alpha_b \) and \( \alpha_c \) are almost the same and are much larger than \( \alpha_a \) indicating that the interatomic bonding along \( b \) and \( c \) axes is much weaker than along \( a \) axis.

5.6.3 Thermal studies on \( \text{Li}_2\text{O}.5\text{B}_2\text{O}_3.10\text{H}_2\text{O} \)

(A.C. Momin, E.B. Mirza* and M.D. Mathews)

The compound \( \text{Li}_2\text{O}.5\text{B}_2\text{O}_3.10\text{H}_2\text{O} \) was characterized by room temperature X-ray powder diffractometry (XRD) and its thermal studies were carried out from ambient to 873 K in air using microthermogravimetry (\( \mu TG \)), differential scanning calorimetry (DSC) and dilatometry. The \( \mu TG \) analysis revealed that the loss of water takes place in three steps. DSC data are in agreement with \( \mu TG \) data. Three endothermic peaks were observed for the corresponding steps. The dilatometric analysis showed an anomalous expansion behaviour. The anomalous expansion is attributed to the simultaneous processes of dehydration and densification.

(* Since retired)

5.6.4 Studies in the pseudo-binary system \( \text{Li}_2\text{O}-\text{B}_2\text{O}_3 \)

(M.D. Mathews, A.C. Momin and P.N. Moorthy)

Lithium borate compounds viz., \( \text{Li}_2\text{B}_8\text{O}_{13}, \text{Li}B_3\text{O}_5, \text{Li}_3\text{B}_7\text{O}_{12}, \text{Li}_2\text{B}_4\text{O}_7, \text{Li}B_2\text{O}_2, \text{Li}_6\text{B}_4\text{O}_9, \alpha-\text{Li}_4\text{B}_2\text{O}_5, \beta-\text{Li}_4\text{B}_2\text{O}_5 \) and \( \text{Li}_3\text{BO}_3 \) were prepared from the starting materials of pure lithium carbonate and boric acid using three different methods: (i) solid state reactions, (ii) slow cooling of the melts and (iii) heat treatment of the quenched melts. Solubility, density and lattice parameters of these compounds were determined at room temperature using saturated solution method, pyknometry and XRD respectively.
Analysis of the data revealed that the solubility of lithium borates decreased with an increase in Li/B ratio (or decrease in B₂O₃ content) up to 0.43 which corresponds to the compound Li₃B₇O₁₂ (30 mole % Li₂O, 70 mole % B₂O₃).

Beyond this composition, the solubility of the compounds increased with increase in Li/B ratio. Thus among all lithium borate compounds, the solubility is found to be maximum (-9 %) for the Li₃BO₃ (75 mole % Li₂O, 25 mole % B₂O₃) and that of Li₃B₇O₁₂ (30 mole % Li₂O, 70 mole % B₂O₃) is found to be minimum (-1 %). The density values of all the lithium borates are found to be in the range 2.0-2.5 kg/l. The values are found to be almost in agreement with the theoretical X-ray densities obtained from the lattice parameter data.
6. BIOFOULING, BIOCORROSION AND CHEMISTRY OF COOLING WATER SYSTEMS

The main thrust of activities related to biofouling and biocorrosion in power plant cooling systems. Besides, studies on chemical features of natural waters (both marine and freshwater) used for power plant cooling purposes were also carried out. An important component of the programme was to delineate the processes underlying the phenomenon of biofilm formation, especially during the early stages, to understand the interrelationship between biofouling, biocorrosion and water chemistry and to study the effectiveness of fouling control measures such as chlorination and heat treatment.

6.1 Macrofouling control
(S. Rajagopal*, N. Sasikumar*, V.P. Venugopalan, K.V.K. Nair, K.K. Satpathy, T.S. Rao** and P.K. Mathur)

Studies were carried out to assess the efficacy of the continuous low dose chlorination practice, presently being employed at MAPS, vis-a-vis the earlier intermittent chlorination and also to determine the usefulness of heat treatment as an alternative fouling control measure.

Size-frequency analysis of the mussel samples collected from the travelling water screens at the cooling water intake of MAPS showed that there is a gradual increase in the size of the mussels removed from the tunnel since start of low dose chlorination, indicating that removal of older mussels took longer time as compared to younger ones. Large quantity of small mussels were observed during periods which corresponded with the peak breeding periods in coastal waters. This showed that continuous low dose chlorination is helpful in 'flushing out' juvenile mussels without killing them. Laboratory studies
indicated that chlorine reduced the foot activity as well as byssus thread production in mussels. Thus it appears that continuous low dose chlorination is suitable for the control of mussels in seawater intake systems of power stations.

Studies using heat treatment of mussels and barnacles revealed that 100% kill of these organisms could be achieved by raising the incoming water temperature to 43°C for 30 min. Heat treatment therefore could be considered as an alternative fouling control measure in Indian coastal power plants.

A chemical formulation was developed for the dissolution of calcareous barnacle debris from the inside surface of the fouled high density poly ethylene (HDPE) lines at MAPS.

( * Ph.D Student, University of Madras; ** IGCAR staff member working at WSCL, ApCD)

6.2 Macrofouling ecology
(V.P. Venugopalan and K.V.K. Nair)

Experimental work was carried out to probe the community ecology of the fauna inhabiting the MAPS intake tunnel by characterising the water that goes into the tunnel at the intake end and that comes out of it at the forebay end. The study was restricted to three major physiological features of the suspension feeder community viz., respiration rate, particle filtration rate and suspended matter production rate.

The results of these investigations showed that all the three physiological functions increased with an increase in volume transport of seawater, indicating a stimulatory role of water flow over the physiology of the community. A statistically significant correlation was obtained between volume transport and oxygen consumption. Production of particulate matter by the
mussel community was found to be quite high; it was surmised that this was probably responsible for the heavy siltation observed in pump chambers in the forebay at MAPS.

This work brought out the importance of physical circulation processes on the growth of marine fouling organisms. As a result of the flow-induced increase in metabolism, mussels growing inside the intake tunnel were found to have significantly higher growth rates as compared to those growing in the adjacent coastal waters.

6.3 Chlorination of cooling water
(K.K. Satpathy, T.S. Rao*, C.A. Sargunam** and K.V.K. Nair)

Various aspects of chlorination of both freshwater and seawater have been studied during the last three years with a view to: (a) optimise chlorine doses in cooling water, (b) minimise impact on the environment, (c) understand chlorine decay and (d) control micro and macrofouling in cooling circuits.

Data collected on chlorine demand of seawater used for MAPS condenser cooling revealed relatively high values (3 ppm) during monsoon period as compared to the rest of the year (1.5 ppm). On comparison of the demand data with other similar water bodies it was found that Kalpakkam waters could be described as high demand water. Chlorine decay in coastal waters showed two distinct phases, one being rapid (about 50% decay in 15 min.) and the other extremely slow (decay continues even after 50 hr.). The latter followed approximately second order reaction kinetics for both high as well as low initial chlorine doses. The rate of reaction was relatively fast as compared to the other sea areas. Similarly, the initial demand for this coastal waters also appeared to be higher than for other sea areas. Chlorine demand
of the MAPS open reservoir water was higher than that of the seawater. Experiments were also carried out to study the decay pattern at various temperatures. Studies on the role of bromine on chlorine dissipation showed that hypobromite production was completed in about one minute after chlorination.

The efficacy of chlorine to remove slime was studied in a laboratory model cooling tower. A biofilm thickness of about 50 - 60 µm was observed after 48 hr. of immersion of coupons. A marginal reduction in biofilm thickness and 100 fold decrease in bacterial population was observed after the chlorination (5 ppm). Although diatoms were completely removed, fungi were observed in significant quantity (5×10^5 cfu/ml), indicating qualitative changes in species composition after chlorination.

Effect of chlorination (100-200 ppb) on photosynthesis and respiration were also investigated in the laboratory using Dunaliella. Gross and net primary productivity showed a marginal reduction on exposure to chlorine; there was no effect on respiration.

(* IGCAR staff member working at WSCL, ApCD ; ** Materials Science Laboratory, IGCAR)

6.4 Biofilm characterisation
(V.P. Venugopalan, T.S. Rao* and K.V.K. Nair)

An experimental programme has been initiated to delineate the physicochemical, biological and microbiological processes that take place during the initial periods of biofilm formation in Kalpakkam coastal waters. The results of this study showed bacteria (mostly gram negative rods) to be the major organism to colonise the surfaces submerged in seawater. The major diatom species observed on the test coupons were Nitzschia, Navicula, Amphora, Cyclotella and Asterionella. The combustible organic
matter on the film increased from 10% on the first day to 31% on the fifth day. Proteins and carbohydrates were found to be the major biochemical constituents of the film (1.01 and 2.20 μg/cm², respectively, after 5 days).

Bacteria isolated from the biofilm were further studied to find out their influence on the settlement of three species of fouling diatoms. The settlement response of the diatoms to the presence of bacteria was found to be rather variable. Some of the strains caused significant increase in the settlement of diatoms whereas some others a significant decrease. Further implications of these effects are being studied.

(* IGCAR staff member working at WSCL, ApCD)

6.5 Biocorrosion in FBTR service water system
(T.S. Rao* M.S. Eswaran, V.P. Venugopalan, K.V.K. Nair and P.K. Mathur)

FBTR service water system, which operates on an open recirculating mode, has been experiencing various problems such as fouling-induced flow blockage of pipes, valves and strainers, pipe punctures and unacceptably high general corrosion rates. A comprehensive investigation involving both field and laboratory studies was initiated to tackle these problems.

Laboratory studies using biofilm reactors showed that corrosion rates were high in a non-sterile system as compared to a sterile system, indicating that corrosion process was probably microbially influenced. This was further substantiated by SEM observations of the test coupons. Results of the microbiological analysis of the water showed high prevalence of sulphate reducing bacteria, iron oxidising bacteria and slime producing bacteria. Chemical analysis of the fouling debris showed organics in excess of 20% which was also an indication of microbially influenced
The existing fouling and corrosion control practices in FBTR were also tested in the laboratory for their efficacy. Chlorination experiments using a model cooling tower, designed and built in the laboratory, showed that the bacterial population which regenerates after a bout of slug chlorination was qualitatively different from the original population. A study of the decay pattern of chlorine in the FBTR service water system showed that chlorination, if done once a day, was grossly inadequate to control the bacteria. Twice a day chlorination was more effective to control the microbial load as the chlorine residuals were present in the water for sufficiently long periods of time. It was also found that polyphosphates added to the recirculating water as a corrosion inhibitor were getting converted into orthophosphates within a short period of time and that the latter was aiding bacterial proliferation by serving as a micronutrient. It was established that a 10 μmol/l increase in the orthophosphate levels led to a 10-fold increase in bacterial population within a period of one week. (* IGCAR staff member working at WSCL, ApCD)

6.6 Exopolymer production and bacterial adhesion
(T.S. Rao#, R. Kesavamoorthy*, C. Babu Rao** and K.V.K. Nair)

Experiments using an image analysis system were carried out on *Pseudomonas* sp. (a common heat exchanger fouling bacterium) to study ordering, orientation and distribution of bacterial cells in biofilms that develop on glass surfaces. The results showed that bacteria migrate to and attach on the surface in a single layer orienting themselves in specific directions. The average interbacterial separation perpendicular to its length was found to be about 1 μm. In the distribution of orientation, a distinct
peak was observed around 90°, when measured with respect to an arbitrary reference axis.

Two exopolymer producing bacteria (isolated from fresh and sea water) were tested for polymer production when grown in different culture media under different incubation conditions. Temperature-time variables were optimised for maximum yield. Analyses of the crude extracts showed that proteins and carbohydrates amounted to 60% of the weight. IR spectra revealed the presence of functional groups such as -CH, -OH, C-O- and -C=O. Metal binding by the exopolymers was studied at different pHs (4.0, 6.0 and 7.3) using ion selective electrodes. Complexation was observed with copper ions at pH 4.0 and 6.0, but not at 7.3.

(* IGCAR staff member working at WSCL, ApCD; ** Materials Science Laboratory, IGCAR; ** DPEND, IGCAR)

6.7 Diatom fouling in the coastal waters of Kalpakkam
(C.A. Sargunam* and K.V.K. Nair)

General features of the primary film formation by diatoms in Kalpakkam coastal waters were studied using perspex coupons. Variations in the type and extent of fouling were also correlated with changes in the hydrographic features of the study area. Diatom species isolated from the biofilm were used in laboratory experiments to study the effects of various factors like nutritional status, nature of substratum, temperature and salinity on the rate of fouling.

The results of the above study showed that 27 genera including diatoms, green algae, blue-green algae, dinoflagellates, silicoflagellates and tintinnids were involved in primary film formation in the coastal waters. Numerical density of the diatoms varied from $3.9 \times 10^4$ to $1.6 \times 10^5$ cells/cm$^2$
after a period of 7 hours immersion. Among the various types of coupons tested, cupronickel was found to be colonised by *Navicula sp.* whereas the copper tolerant *Amphora* were more evident on copper. Diatom cell number and biomass were low on copper and aluminium brass; maximum cell number and biomass were observed on cupronickel. Owing to very rapid exfoliation, fouling was minimal on mild steel. As for the effect of temperature, maximum biofilm thickness was observed at 33°C. The density decreased at higher temperatures and for longer exposure durations. Among the various salinities tested in the range 20-40 ppt, the most favourable salinity for biofilm development was found to be 35 ppt.

(* Materials Science Laboratory, IGCAR)

6.8 Studies related to RAPS and FBTR

6.8.1 RAPS cooling water

The condenser tube leakages in RAPS Unit II have resulted in continued deterioration of boiler water chemistry, often requiring continuous blow down and consequent energy losses. In this context a study was initiated to find out the cause of condenser tube failures. Water samples collected from intake and outfall of RAPS were analysed for various chemical and biological parameters. The results of various analyses carried out during plant shutdown have shown an increase in pH (8.3 to 8.9), dissolved oxygen (3.9 to 6.9 ppm), chlorine demand (1.0 to 1.5 ppm), nitrite (10 to 16 µg/l) and ammonia (13 to 47 µg/l) from intake to outfall. However, an opposite trend was observed with conductivity (233 to 212), nitrate (955 to 260 µg/l) and TDS. The increase in nitrite and ammonia and decrease in nitrate from intake to outfall can be attributed to the action of nitrate reducing bacteria ($10^4$ cfu/ml), which play important role in the nitrogen cycle. Total viable bacteria, sulphate reducing bacteria...
and chlorophyll content were found to be high ($10^6$ cfu/ml, 160 cfu/ml and 9.9 µg/l respectively). Studies were also carried out subsequently when the reactors were in operation. There was no noticeable change in the trends observed in the various parameters analysed. These suggest that the cooling water undergoes a significant change in the cooling circuit. Presence of ammonia, although in low levels, could be responsible for failure of condenser tubes (admiralty brass is known to suffer stress corrosion cracking in presence of ammonia). Moreover ammonia produced by the bacteria beneath slime may increase its localised action. The high pH of the cooling water points to the need to look for a biocide other than chlorine for biofouling control in the condenser cooling system.

6.8.2 FBTR service water

Different bacterial species available in the FBTR Service Water System were isolated and are being maintained as viable cultures by regular subculturing. The strains include sulphate reducing bacteria (SRB), iron oxidising bacteria and slime forming bacteria. Microbial load of the cooling water is regularly monitored at fortnightly intervals and the results used for modulating the biocide application schedule. In addition, a number of commercial biocides were tested in the laboratory for assessing their relative efficacy to control bacteria. The results were communicated to the FBTR authorities for selection of the most suitable biocide.

(* IGCAR staff member working at WSCL, ApCD)
7. NOVEL AREAS

7.1 Dental implants for BARC Hospital
(S.B. Karweer and R.K. Iyer)

At the suggestion from Dental Unit of BARC Hospital, a multidisciplinary research project was initiated to develop dental implants of titanium coated with hydroxylapatite. The process involves preparation of hydroxylapatite powder and its deposition on titanium substrate by plasma spray. The quality of the hydroxylapatite and deposition conditions should be such that a very adherent film (-50 microns thickness) of hydroxylapatite should be formed on the titanium substrate. During plasma spray, decomposition of hydroxylapatite to α and β tricalcium phosphate should be negligible. In this project, the preparation of hydroxylapatite powder is being carried out by the Applied Chemistry Division.

Hydroxylapatite powder was prepared by the following methods:

(a) Reaction of Ca(OH)$_2$ suspended in water with H$_3$PO$_4$ in the mole ratio 5:3; the final pH of the mixture was 6. The product was aged, filtered and dried at 80°C. The Ca/P ratio in a 50 g batch of the product was 1.59. The product prepared from this powder was superior to imported material with respect to particle size and flow characteristics. Two more samples were prepared by this method in 25 and 100 g batches with Ca/P ratios of 1.58 and 1.52 respectively.

(b) Reaction of Ca(OH)$_2$ suspended in water with H$_3$PO$_4$ (mole ratio 5:3) at 40°C (final pH 5.8), refluxing the mixture for 30 minutes, ageing followed by filtration and drying at 80°C. Ca/P ratio in the product was 1.54.
(c) Preparation was carried out as in method (a). However, addition of $H_3PO_4$ was stopped at a stage such that the final pH was 7. Ca/P ratio in the product was 1.57.

(d) Preparation was carried out as in method (a) except that the pH was maintained at 7 by addition of sodium hydroxide solution. Ca/P ratio in the product was 1.69 which is the desired value. Suitability of samples prepared by methods (c) and (d) is being tested.

7.2 Remote sealing of holes in mild steel pipes
(S.B. Karweer, B.P. Pillai and R.K. Iyer)

The problem encountered in the use of a mixture of polysilicate and zinc dust for plugging pin holes in biological shield cooling (BSC) coils in MAPS and RAPS is the retention of 5 to 10% of the material in the tube resulting in occasional choking of the coil. Hence work was taken up to develop a better method suitable for sealing holes upto 3 mm diameter using a mixture of bentonite clay, epoxy resin and hardener available indigenously. The qualities of different brands of bentonite clay varied in their settling and swelling characteristics when suspended in water. An intimate mixture of bentonite clay, epoxy resin, hardener and water was coated on mild steel plate. After 24 hours the coating was examined for adherence and stability in presence of water. The proportion of bentonite clay, epoxy resin and water was varied to optimise the composition suitable for plugging.

Studies on plugging of holes in mild steel tubes were carried out using bentonite clay, epoxy resin, hardener and water in the proportion 1:6:6:7 by weight. An intimate mixture of the constituents was filled in mild steel pipe (i.d. 25 mm, wall thickness 3 mm) with 1.5 and $\approx$ 3 mm circular holes backed by
asbestos cloth and pressurised if necessary. After half an hour the mixture was drained out and 24 hours later, the tube was dipped in water. The procedure was repeated till the leakage from the tube was very low. At this stage only bentonite clay was used. The results indicated that 1.5 mm circular holes were plugged in 2 to 3 cycles while 3 mm circular holes could be plugged in 6 cycles. Subsequent experiments were carried out under conditions existing in the BSC coils in MAPS. Satisfactory plugging of the holes in the coil could be achieved. However, the total volume of the mixture retained in the coil was about 17% of the volume of the coil which is not desirable. The retained material could not be removed by forcing water through the coil. If chokeup occurs in the coil it cannot be removed by chemical treatment and hence this method cannot be used for plugging of BSC coils. Attempts are being made to reduce the extent of retention of mixture in the coil.

7.3 Studies in "cold fusion"

In order to obtain evidence for the occurrence of 'cold fusion' phenomena in terms of measurement of fusion products such as neutron and tritium, a quartz electrolytic flow cell comprising of a palladium ring cathode and platinum mesh anodes arranged in a concentric geometry around the cathode so as to charge the cathode from both the sides, and with provision for external variation of temperature of the electrolyte was fabricated. The anodes were loosely sandwiched between pairs of nafion membrane so as to prevent oxygen evolved at the anode from diffusing to the cathode surface. 99.86% (w/w) D₂O containing 100 mM LiOD was used as the electrolyte. A saturated calomel electrode with a lug-in capillary was used as a reference
electrode to monitor the potential of the cathode.

The cell was housed inside the well of a neutron detector assembly (twelve four $^3$He detectors arranged in a circular geometry with paraffin surrounding the detectors for thermalisation of neutrons). Accumulation of tritium in the electrolyte was monitored by periodically withdrawing samples of electrolyte and measuring tritium using a liquid scintillation assembly. The cell was run for 32 days at a current density of $\approx 60 \text{ mA/cm}^2$. After the electrolysis run, the cathode was degassed at 680 K and the evolved gases were recombined over CuO also at 680 K. The water formed was counted for tritium.

Fig. 7.3 shows the observed burst neutron emission which lasted for $\approx 40$ hr. during the cell operational period of $\approx 32$ days. The maximum burst signal (at 14th hour from the commencement of the emission) corresponded to $1.42 \times 10^5$ counts with a signal to background ratio of $\approx 2000$. The total number of neutrons emitted in these bursts worked out to $1.8 \times 10^8$ in this period of 40 hr. which corresponded to a pseudo average emission rate of $1.3 \times 10^3$ n/s. The tritium activity increased by $\approx 200$ Bq amounting to about $10^{11}$ extra tritium atoms accumulating in the electrolyte. Thus the observed ratio of fusion events occurring via the tritium channel to the events occurring via the neutron channel was $10^3$. During the experimental run, whenever the polarisation voltage was switched off, the cathode potential attained a value of $-1.0$ V vs SCE indicating that at 100 mM alkali concentration, Pd behaved as a $\text{H}_2$ electrode. During the burst emission period, the neutron count rate peaks were found to coincide with the shifting of potentials to more positive values from $-1$ V vs SCE indicating that a depletion of $\text{H}_2$ on the electrode surface at the time of burst emission events.

(* Since retired, ** RSSD)
Fig. 7.3 The observed burst neutron emission which lasted for \( \approx 40 \) hr during the cell operational period of \( \approx 32 \) days
8. INSTRUMENTATION AND SOFTWARE DEVELOPMENT

8.1 Knudsen cell mass spectrometric system.
(A.S. Kerkar, S.R. Bharadwaj and S.R. Dharwadkar)

The EXTREL quadrupole mass spectrometer was interfaced with Knudsen cell assembly (earlier fabricated and commissioned in the Division) and tested for the masses of residual gases, Kr, Xe, and the organic fragments of PTA up to mass number 500. Bellow mounting for the quadrupole part of the mass spectrometric unit required for positioning the ion source in the line of sight of the molecular beam effusing from the Knudsen cell was fabricated. Attempts were made to calibrate the equipment by measuring the vapour pressure of silver and gold at high temperatures. The intensities of ion currents of these elements in the present configuration were found to be too low for accurate measurements of their vapour pressures up to their melting points, and hence certain modifications in the present system are being incorporated to enhance the sensitivity. Also the solid angle defined by the Knudsen cell orifice with the inlet of the ion source was modified in order to suppress background noise. A photograph of the Knudsen cell mass spectrometric system is given in Fig. 8.1.

8.2 Thermogravimetric assembly for transpiration experiments
(S.R. Dharwadkar, A.S. Kerkar and M.S. Samant*)

A novel automatic recording microthermogravimetric system for the measurement of vapour pressures at high temperatures by the transpiration method was designed and fabricated. This set up can be used for measurement of vapour pressures in the range $10^{-3}$ to $10^{-6}$ atm. up to 1425 K and is the first of its kind in which the mass loss due to vaporization is monitored continuously during the transpiration experiment. This system helps in considerable
Fig. 8.1 Photograph of the Knudsen Cell-Mass Spectrometric assembly
saving of time involved in the experiment and in minimization of the errors associated with the mass measurements in the conventional transpiration method currently in use. The performance of the system was checked by measuring the vapour pressure of anhydrous cadmium chloride in flowing dry argon in the temperature range 713 to 833 K. The vapour pressure of cadmium chloride in this range could be expressed as:

\[ \ln(p/Pa) = \frac{-20109.10\pm262.32}{T} + 29.46\pm0.34 \]

The enthalpy of sublimation of CdCl\(_2\) derived from this equation at the mean temperature of investigation was found to be 167.17\(\pm\)2.2 kJ/mol and agrees very well with the literature value of 166.52\(\pm\)4.74 kJ/mol. A schematic diagram of the assembly is shown in Fig. 8.2.

(* Ph.D Student, University of Bombay)

8.3 Heat capacity measurements of solids by differential scanning calorimeter (DSC)

(P.N. Namboodiri, A.B. Phadnis and S.R. Dharwadkar)

The ULVAC DSC instrument was checked for its suitability for determination of heat capacity of solids. Preliminary runs with benzoic acid, tin and indium gave heat capacity data which were in agreement within \(\pm5\)% with the values obtained by conventional calorimetric methods reported in the literature. To cover a wider temperature range for heat capacity measurements, the DSC instrument was calibrated for different temperatures employing melting points of Ga, Sn, In and cyclohexane. Heat capacity measurements on benzoic acid showed that the \(C_p\) values depend appreciably on a number of experimental parameters such as heating rate, size and crimping of the sample and reference etc. Experimental conditions which yielded values close to the conventional calorimetric values were optimized.
Fig. 8.2 Schematic diagram of the microthermogravimetric system used for transpiration studies.
8.4 Computer controlled differential thermal analysis (DTA) assembly*
(A.S. Kerkar and S.R. Dharwadkar)

A differential thermal analysis assembly was fabricated with several improved features. The unit was interfaced with a personal computer and the collection of data in the digital form was tested. The furnace of the system was also programmed through the computer.

A gas purification train comprising of BASF catalyst and molecular sieve columns was introduced in the inlet side of the DTA system. In addition, after passing through the inlet gas purification train, zirconium metal chips were located in the reaction zone to ensure the inertness of the argon gas flowing into the system. The melting points of tin, antimony, silver and copper were recorded under these conditions. The absence of eutectic peak due to \( \text{Cu}_2\text{O} + \text{Cu} \) prior to the melting of copper indicated that the oxygen potential in the system was much below that coexisting over \( \text{Cu}_2\text{O} + \text{Cu} \) system around the melting point of copper.

(* in collaboration with Computer Division)

8.5 Fabrication of sample assembly for differential scanning calorimeter
(A.S. Kerkar)

An assembly for containing the sample and reference materials in the differential scanning calorimeter (DSC) was machined from a stainless steel plate. This was placed above the two miniature matched resistance heaters. The assembly was insulated from the heaters by mica sheet. Two thermocouples were provided between the stainless steel sample assembly and the insulating mica sheet
to monitor the differential emf and the mean temperature in the system. The assembly was tested on the existing ULVAC DSC unit for its performance. The sensitivity of the differential signal was found to be much lower than that in the original instrument. Certain modifications are being introduced in the design to improve the sensitivity.

8.6 **Software for retrieval of powder XRD data from JCPDS database**
(V.S. Jakkal)

In order to access the CDROM database of the Joint Committee on Powder Diffraction Standards (JCPDS), a number of BASIC language programs were developed for use on the personal computer: LASTCARD - for determining the card image lines on the database; GENER - for generating a subfile of the entries from the CDROM PDF-2 database and STRING - for searching a string of text information from the selected search regions of the database.

The following FORTRAN programs were developed for use on ND computer: VIEWX - for retrieving the data when the JCPDS PDF card number is known; FORMULX - for generating a list of compounds containing the given elements in their formulae and MATCHX - for identifying an unknown compound on the basis of comparison of its strongest 10 lines with those of the standard compound. PC versions of these FORTRAN programs have also been made.

8.7 **Expert system for secondary side water chemistry monitoring in Pressurized Heavy Water Reactors**
(S. Rangarajan, M.N.K. Rehman and S.V. Narasimhan)

A modular PC based expert system for monitoring and controlling secondary side water chemistry in pressurized heavy
water reactors has been developed. The different modules determine the job priorities within each of them and regulate further activities. They also pass on/exchange information before arriving at any diagnostic conclusion and forecasting. The individual modules are: DATA HANDLER - for controlling all the data handling functions like input, list, edit/delete, store/retrieve, create/select files and graphical display of data parameters as a function of time; DATA INTERPRETER - for comparing the experimental data with the theoretically calculated values and predicting the presence of impurity ingress in the system and CHEMISTRY EXPERT - for containing the knowledge base about the various secondary sub-systems. All the water chemistry specifications are translated in the form of IF... THEN... rules and are stored. Initially, the expert creates a data base containing the experimental facts. Then inferences are drawn by the forward chain reasoning to identify the diagnostic parameters by consulting the knowledge base and applying the appropriate rules. The ACTION EXPERT module collects all the diagnostic parameters and suggests suitable remedial actions/counter measures to the operator.

8.8 A BASIC program for processing electrochemical data
(M.N.K. Rehman, S. Rangarajan and S.V. Narasimhan)

A software has been developed to transfer cyclic voltammetric data acquired by Nicolet digital oscilloscope and Keithley electrometer to IBM-PC using IEEE-488 interface. A program in BASIC language has been written to process these data to evaluate the electrochemical parameters such as peak potentials and peak currents, and also to give a hard copy output of the cyclic voltammogram or display it on the PC-monitor. This software has been found to be very useful in elucidating mechanisms of reactions at electrode surfaces.
8.9 Computerization of indents placed with Directorate of Purchase and Stores
(V. Ramshesh and B. Yuvaraju)

To streamline the indents placed with Directorate of Purchase and Stores as well as for quick retrieval of information, a computer program using dBASE III Plus has been developed. The program is able to retrieve information in different formats. Two menu driven user programs were also written. One is an executable program used for searching/ budgeting operations while the other is non-executable one used for editing/ appending records. It is possible to search or extract information for budgeting through either a single option or a combination of several options.
9. HUMAN RESOURCE DEVELOPMENT

9.1 Training School

Staff members of the Division continued to take active part in teaching various courses for the trainees of the 33rd, 34th and 35th batches of the BARC Training School. Some members participated in selection of the candidates. A brief summary of these activities is given below.

1. Lectures and Tutorials

<table>
<thead>
<tr>
<th>Course</th>
<th>Teachers</th>
<th>Lectures/Tutorials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Thermodynamics</td>
<td>S.R. Dharwadkar</td>
<td>5 lectures</td>
</tr>
<tr>
<td></td>
<td>S.R. Bharadwaj</td>
<td>35 lectures</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 tutorials</td>
</tr>
<tr>
<td>Reactor Chemistry</td>
<td>G. Venkateswaran</td>
<td>53 lectures</td>
</tr>
<tr>
<td></td>
<td>B. Yuvaraju</td>
<td>9 tutorials</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 tutorials</td>
</tr>
<tr>
<td>Radiation and Photochemistry</td>
<td>D.B. Naik</td>
<td>10 tutorials</td>
</tr>
<tr>
<td>Material Science</td>
<td>A.K. Tyagi</td>
<td>5 tutorials</td>
</tr>
</tbody>
</table>

2. Project Work

Practicals in 'Material Science' course and special experimental project work were conducted for the trainees under the guidance of S.R. Dharwadkar and G. Venkateswaran.

138
3. **Selection Committee**

U.R.K. Rao and S.R. Dharwadkar acted as Chairpersons in the BARC Training School Selection Committees. S.R. Bharadwaj and D.B. Naik were members of the Written Test Committee.

9.2 **Other Training Programmes**

<table>
<thead>
<tr>
<th>Course/ Programme</th>
<th>Lecturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Nuclear Reactor Chemistry for 3rd Batch of NPC Trainees (8 lectures)</td>
<td>G. Venkateswaran</td>
</tr>
<tr>
<td>2. Water Chemistry for the chemists of Ground Water Board, Rajasthan (1 lecture)</td>
<td>A.K. Sriraman</td>
</tr>
<tr>
<td>3. Demonstration experiments on heat capacity measurements by DSC for two</td>
<td>S.R. Dharwadkar</td>
</tr>
<tr>
<td>visiting Russian Scientists</td>
<td></td>
</tr>
<tr>
<td>4. Training Programme organised by Library and Information Services on JCPDS</td>
<td>V.S. Jakkal</td>
</tr>
<tr>
<td>Powder Diffractometer Database (6 lectures and demonstration)</td>
<td></td>
</tr>
<tr>
<td>5. Part of course for the Participants of &quot;Introductory Course on Neutrons as</td>
<td>V.S. Jakkal</td>
</tr>
<tr>
<td>probes of condensed matters&quot; on JCPDS Powder Diffractometer Database (1 lecture</td>
<td></td>
</tr>
<tr>
<td>and demonstration)</td>
<td></td>
</tr>
</tbody>
</table>
6. M.Sc. Course, University of Bombay
   (24 lectures on XRD techniques)

V.S. Jakkal

7. Part of Workshop for the participants of
   National Workshop on Radiochemistry,
   Applications of Radioisotopes and Allied
   Topics Mangalore University
   (4 practicals in Photochemistry and
   Radiation Chemistry)

D.B. Naik

8. A three day training programme
   of lectures and practicals spread over
   four sessions for shift chemists
   of TAPS

G. Venkateswaran

B. Yuvaraju

K. Kishore

A.S. Gokhale

9.3 Training undergone by staff members

1. In-plant Training at RED

V.T. Apar

Y.V. Harinath

V.K. Gupta

P. Madasamy

C. Soloman

A. Kumaresan

2. Home Guard Training

A.S. Kerkar

3. Training programme on "Training for Trainers" organised by DAE in
   coordination with Institute of
   Secretariat Training & Management,
   New Delhi at Bombay

G. Venkateswaran
4. Winter School on "Radiation Research: Principles, Applications and Recent Trends", University of Poona, Pune

9.4 Deputations

1. 1991 JAIF International Conference on "Water Chemistry in Nuclear Power Plants", Fukui City, Japan and Department of Nuclear Engineering, University of Tokyo, Japan, April 22-28, 1991
   (P.K. Mathur* and P.N. Moorthy)
   [* Also chaired one technical session]

2. IAEA/CRP meeting on WACOLIN, Vienna, Austria, May 6-9, 1991
   (P.K. Mathur)

3. (a) IAEA Training Course on "Decontamination of Research Reactors and Small Nuclear Facilities", Saclay, France
   June 18 - July 5, 1991

   (b) Visit to KWU, FRG (July 6-11, 1991) for discussions regarding current trends in the fields of decontamination, primary and secondary side water chemistry in power reactors and related topics
   (S.V. Narasimhan)

4. Indo-FRG bilateral collaboration program at KWU, Erlangen
   November 1990 - March 1992
   (S. Velmurugan)
### 9.5 Seminars

<table>
<thead>
<tr>
<th>Speaker</th>
<th>Title</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. P.K. Mathur</td>
<td>General water chemistry problems pertaining to nuclear and thermal power stations</td>
<td>18-01-90</td>
</tr>
<tr>
<td>2. R.K. Iyer</td>
<td>Industrial cooling water treatment</td>
<td>19-01-90</td>
</tr>
<tr>
<td>3. K.V.K. Nair</td>
<td>Cooling water investigations in Kalpakkam</td>
<td>19-01-90</td>
</tr>
<tr>
<td>4. S.V. Narasimhan</td>
<td>Primary and secondary system water chemistry investigations</td>
<td>19-01-90</td>
</tr>
<tr>
<td>6. G. Venkateswaran</td>
<td>Different aspects of metal water interactions</td>
<td>19-01-90</td>
</tr>
<tr>
<td>7. R.K. Iyer</td>
<td>Studies on speciation of Al complexes by $^{27}$Al NMR spectroscopy</td>
<td>19-01-90</td>
</tr>
<tr>
<td>8. P.K. Mathur</td>
<td>Controlling radiation fields in NPRs: Investigations on decontamination and chemical cleaning</td>
<td>19-01-90</td>
</tr>
<tr>
<td>9. Kamal Kishore</td>
<td>Pulse radiolysis studies</td>
<td>19-01-90</td>
</tr>
<tr>
<td>No.</td>
<td>Author(s)</td>
<td>Title</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>10</td>
<td>R. Shanker</td>
<td>Ion-exchange studies: purification of water</td>
</tr>
<tr>
<td>11</td>
<td>V. Ramshesh</td>
<td>Other aspects of water chemistry</td>
</tr>
<tr>
<td>12</td>
<td>G. Venkateswaran</td>
<td>Some studies in cold fusion</td>
</tr>
<tr>
<td>13</td>
<td>P.S. Malhan</td>
<td>A status report on laboratory instrumentation</td>
</tr>
<tr>
<td>14</td>
<td>V.S. Jakkal</td>
<td>X-ray diffraction and crystal structure determinations</td>
</tr>
<tr>
<td>15</td>
<td>A.K. Tyagi</td>
<td>Fluorination of oxides</td>
</tr>
<tr>
<td>16</td>
<td>S.R. Dharwadkar</td>
<td>High temperature and solid state chemistry</td>
</tr>
<tr>
<td>17</td>
<td>M.C. Naik</td>
<td>Release of gaseous and volatile fission products from fuel materials</td>
</tr>
<tr>
<td>18</td>
<td>G. Chattopadhyay</td>
<td>Phase diagram and thermodynamic studies</td>
</tr>
<tr>
<td>19</td>
<td>S. Rangarajan</td>
<td>Measurement of pH at elevated temperatures: An analysis</td>
</tr>
<tr>
<td>20</td>
<td>A.K. Sriraman</td>
<td>Studies on chlorination of coolant sea water as relevant to industrial cooling</td>
</tr>
<tr>
<td>21</td>
<td>G. Visalakshi</td>
<td>Speciation of metals in pure water systems</td>
</tr>
</tbody>
</table>

143
22. K.K. Satpathy  
Studies on chlorination of cooling water and related aspects  
17-05-90

23. A.K. Tyagi  
Fluorination of oxide superconductors  
19-05-90

24. P.N. Moorthy  
VIIth Plan Project: Augmentation of water chemistry research for nuclear power programme  
26-06-90

25. K.V.K. Nair*  
Biofouling and marine corrosion  
04-08-90

26. B.N. Wani  
A study of oxyfluorides  
17-08-90

27. A.G. Kumbhar (at WSCL)  
Compatibility of AVT and condensate polishing unit  
27-09-90

28. A.F. Mairova (USSR Acad.Sci.)  
Thermodynamic investigations on high Tc superconductors  
15-11-90

29. S.V. Adhyapak$  
Fluorination of oxides of iron by AHF  
14-12-90

30. S.N. Mhatre$  
Studies on aluminium complexes  
14-12-90

31. S.R. Dharwadkar  
Thermal techniques in materials research (I)  
04-04-91

32. S.R. Dharwadkar  
Thermal techniques in materials research (II)  
05-04-91

33. A.B. Phadnis  
Kinetics in thermal analysis  
03-05-91

34. V.S. Jakkal  
X-ray powder diffractometry  
26-07-91
<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Topic</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.</td>
<td>P.N. Namboodiri</td>
<td>Applications of DSC</td>
<td>22-08-91</td>
</tr>
<tr>
<td>36.</td>
<td>M.D. Mathews</td>
<td>Dilatometric and high temperature X-ray diffractometric studies</td>
<td>29-09-91</td>
</tr>
<tr>
<td>37.</td>
<td>P.N. Moorthy</td>
<td>Introduction to the use of PC's</td>
<td>15-11-91</td>
</tr>
<tr>
<td>38.</td>
<td>V. Ramsheesh</td>
<td>Applications of personal computers in management</td>
<td>15-11-91</td>
</tr>
<tr>
<td>39.</td>
<td>B. Yuvaraju</td>
<td>Data base III plus and the Fontasi software</td>
<td>15-11-91</td>
</tr>
<tr>
<td>40.</td>
<td>S.V. Narasimhan</td>
<td>Chemical decontamination of PHT system of PHWRs</td>
<td>19-11-91</td>
</tr>
<tr>
<td>41.</td>
<td>V.S. Jakkal</td>
<td>Automatic powder diffraction software</td>
<td>11-12-91</td>
</tr>
<tr>
<td>42.</td>
<td>S.R. Bharadwaj</td>
<td>SOLGASMIX-PV - A computer program for chemical equilibrium calculations</td>
<td>11-12-91</td>
</tr>
<tr>
<td>43.</td>
<td>P.N. Moorthy</td>
<td>Chemical decontamination of the PHT system</td>
<td>17-12-91</td>
</tr>
<tr>
<td>44.</td>
<td>U.R.K. Rao</td>
<td>Solid state studies on oxyflouro anionic compounds</td>
<td>11-12-91</td>
</tr>
<tr>
<td>45.</td>
<td>U.R.K. Rao</td>
<td>R &amp; D Programme of Structural &amp; Inorganic Chemistry Section</td>
<td>20-02-92</td>
</tr>
<tr>
<td>46.</td>
<td>G. Venkateswaran</td>
<td>The concept of training</td>
<td>26-03-92</td>
</tr>
</tbody>
</table>

145
47. G.R. Dey  Resume of the Winter School on Radiation Research, Univ. of Poona 26-03-92

48. S. Velmurugan  Recent developments in chemical decontamination 02-04-92

49. G. Venkateswaran  Passivation of carbon steel in presence of various additives 23-04-92

50. B. Yuvaraju  Corrosion aspects of decontamination 21-05-92

51. Kamal Kishore  Radiation chemical aspects of decontamination 23-07-92

52. S.R. Dharwadkar*  Thermodynamic investigations relevant to nuclear technology 27-07-92

53. S.R. Bharadwaj  Thermodynamics of Pd alloys 20-08-92

54. G. Chattopadhyay  Current trends in research in phase diagrams and thermochemistry 24-09-92

55. S.N. Tripathi  Thermodynamics of alloys 24-10-92

56. B.N. Wani  Solid state reaction at an interface at room temperature 26-11-92

57. S. Rangarajan  Expert system on water chemistry for nuclear power plants 14-12-92

(* Group Board Seminar; + Trombay Colloquium; @ Solid State Physics Divisional Seminar; # TSC Presentation; Others — Divisional Seminars; $ Ph.D. Student)
10. CONSULTANCY AND REPORTS

The expertise available in the Division in the areas of water chemistry related to the primary and secondary side of nuclear power reactors and the cooling water aspects of these and other industrial plants is often sought by other DAE units. One of the principal agencies through which this is channelised is the Committee on Steam and Water Chemistry (COSWAC)- constituted by DAE of which the Chairman (P.N. Moorthy) and Member -Secretary (P.K. Mathur) are from the Applied Chemistry Division. Besides, the Division is also represented in the Chemist's Committee of HWP (R.K. Iyer), Progress Review committee for 500 MW(e) NPR (V. Ramshesh), BARC-NPC Collaboration Committee (P.N. Moorthy), Implementation Group for Decontamination (P.N. Moorthy and S.V. Narasimhan), Senior Level Task Force for Decontamination (P.N. Moorthy), FBTR Task Forces on Service water and Steam-Water systems (P.K. Mathur and S.V. Narasimhan), and BIS committees related to water and environment (P.K. Mathur).

10.1 Work through COSWAC

One of the important activities has been coordination of the hot conditioning of the PHT system of NAPP-II and KAPP-I. Besides, regular meetings of the Committee were convened where problems concerning chemistry of water/steam systems of Power Stations/ Reactors/ Heavy Water Plants/Projects were discussed. Minutes of the meetings were communicated and necessary follow-up actions were taken. Some of the major recommendations/reviews made are:

(a) Finalisation of the chemical control technical specifications for PHWRs, and issuing of a COSWAC document.
(b) Review of NPC proposals for dilute chemical decontamination of PHT systems of RAPS and MAPS.

(c) Review of continued off-normal boiler water chemistry at RAPS-2.

(d) Thorough review of RAPS water chemistry and review and recommendations pertaining to (i) eddy current testing of leaky condenser tubes and their replacement, (ii) condenser cooling water chlorination,(iii) augmentation of boiler blow down and (iv) provision of on-line monitors.

(e) Temporary and marginal relaxations in the chemical control technical specifications for NAPS-1 boiler water chemistry in order to enable the station to operate the plant without frequent shutdowns and to enable easy identification of leaky condenser tubes during an interim period provided for implementing augmentation of DMW plant capacity and boiler blow down.

(f) Review of problems pertaining to clariflocculator system, active process water system, condenser cooling water system and steam generator water chemistry at NAPS with special reference to considerable mismatch between steam generator water blow down and feed water make-up capacity, based on the DM water availability.

(g) Recommendations pertaining to the calandria vault water chemistry at NAPS-1 to reduce rate of leaching of zinc from the zinc metallised CS liner of the vault.

(h) Recommendations pertaining to specifications for cooling water treatment at NAPS-1 and monitoring and evaluation of recommended treatments.
(i) Recommendations for specifications and comparative assessment of the condenser cooling water treatment offers for NAPS.

(j) Review of reports on the corrosion coupon evaluation of hot conditioning of the PHT systems of WAPS-2 and KAPP-1.

(k) Problems concerning water chemistry of different systems at KAPP-1 with special reference to Active Process Water and Suppression Pool System Water Chemistry.

(l) Currently followed chemical treatment for the service water/condenser cooling water system of FBTR for effective control of scaling, corrosion and biofouling.

(m) Recommendations concerning the proper mode of operation of the existing condensate polishing unit at FBTR.

(n) Biofouling problems in the recirculating cooling water system of the Heavy Water Plant, Tuticorin.

(o) Salient water chemistry aspects, design features of the cooling water system and operational history of a few typical heat exchangers at Heavy Water Plant, Tuticorin.

(p) Recommendations concerning the use of gadolinium nitrate hexahydrate as a soluble poison in the Indian PHWRs.

(q) Review of alternate methodologies for cooling water treatment to control scaling and biofouling -viability of ozone treatment.

(r) Review and recommendations pertaining to water chemistry control in the spent fuel storage bays of future 500 MW(e) NPRs. (P.K. Mathur and P.N. Moorthy)
10.2 Work directly for the Operating Power Stations

10.2.1 Tarapur Atomic Power Station

The recurring problem of appearance of sea weeds and fibrous growth in the condenser cooling water system at TAPS for the last four years, particularly during the months of November and December was reviewed.

(K.V.K. Nair)

10.2.2 Rajasthan Atomic Power Station

(a) For evolving a suitable methodology for decontamination of PHT system of RAPS-2 discussions were held with RAPS personnel on the operational history of the station, nature of deposits on PHT system surfaces and the radionuclides incorporated therein.

(P.K. Mathur)

(b) Discussions were held regarding problems related to the condenser tube leaks at RAPS-2, RAPS lake water characteristics and biofouling in the cooling circuits of HWP Kota in order to recommend appropriate methodology for cooling water treatment.

(K.V.K. Nair)

10.2.3 Narora Atomic Power Station

(a) Discussions were held regarding methodology for activity transport studies in the PHT system and the location of detectors for this purpose.

(P.K. Mathur and P.N. Moorthy)
(b) An interim report on the evaluation of hot conditioning of PHT system of NAPS-2 and a report on the recommendations regarding chemistry control of PHT system during post-hot conditioning period for NAPS-2 were prepared (jointly with the evaluation team members) and submitted to the station authorities.

(P.K. Mathur)

(c) Discussed with NAPS station chemists and tendered advice on: (i) recirculating cooling water system problems, particularly reduction in heat transfer efficiency due to heavy deposition of scales on condenser tube inside surfaces, (ii) development work carried out by Chemical Control Laboratory, NAPS regarding testing and optimization of a few chemical cleaning formulations for solubilizing/removal of the above mentioned scale deposits, (iii) recommendations on the use of a blend of alum and polyelectrolyte for raw water clariflocculation and (iv) suitable cooling water treatment for control of corrosion, scaling and biofouling. Suitable formulations were selected after evaluation of treatment programmes offered by different suppliers.

(R.K. Iyer)

10.2.4 Kakrapar Atomic Power Station

Chemistry of various water systems already commissioned/under process of commissioning prior to hot conditioning of KAPP-1 PHT system and associated problems pertaining to the plant were discussed with station authorities and appropriate recommendations made.

(P.K. Mathur)
10.3 **Senior Level Task Force for MAPS Decontamination**

Contributed to discussion pertaining to detailed design of the engineering interface for MAPS decontamination based on the feasibility report prepared by the Implementation Committee. (P.N. Moorthy and S.V. Narasimhan)

10.4 **NPC-BARC Collaboration Committee**

Contributed to discussions and recommendations pertaining to (i) decontamination; (ii) decommissioning, (iii) remote sealing of holes on embedded pipe lines in the biological shields and (iv) catalytic $\text{H}_2-\text{O}_2$ recombination in the vault. (P.N. Moorthy)

10.5 **500 MW(e) PHWRs**

Participated in quarterly meetings to review the status reports of activities on PHT system being undertaken by the Division for NPC. The status on the following tasks were discussed: (i) study of activity transport and deposition mechanism in PHT system to assess the extent of radiation field build-up around various equipments, (ii) water chemistry in PHT systems for improving the general corrosion resistance of system materials and (iii) chemical decontamination. The design basis report on secondary side chemistry control received from NPC was scrutinised and comments were communicated. (V. Ramshesh, P.K. Mathur and P.N. Moorthy)

10.6 **FBTR / IGCAR**

**10.6.1 Condenser cooling and service water system of FBTR**

The present commercial treatment of cooling and service water
was reviewed. Data generated by WSCL on: (a) bacterial assay of system water samples and (b) evaluation of various biocides for microfouling control in these water systems were presented and discussed in the context of efficiency of chlorination and microbiocide application.

(P.K. Mathur, T.S. Rao*, V.P. Venugopalan, K.V.K. Nair)
(* IGCAR staff member working at WSCL, ApCD)

10.6.2 FBTR Task Force on service water system

Contributed to review and recommendations on possible long term modifications in the design and operating procedures for achieving trouble free operation of the cooling and service water system of FBTR.

(P.K. Mathur)

10.6.3 Steam-water system of FBTR

Participated in reviewing the chemistry of the steam-water system of FBTR. Results on total hardness and total dissolved solids in deaerator water samples, increase in suspended solids due to hydrazine addition and settling, characterisation and removability of suspended solids were discussed. Necessity for urgent commissioning of the deaerator for effective control of dissolved O₂ in the system was pointed out. An alternative method of raising the system water pH to 10.5 using NaOH/KOH and conducting hot conditioning of a part of the system at 200°C for 7-8 days was suggested to obviate the problem of increased suspended solids, specifically due to iron, and choking of strainers in the system.

(P.K. Mathur and S.V. Narasimhan)
10.6.4 **Chilled water system of IGCAR**

At the suggestion from IGCAR-CWMF Safety Committee, Chilled Water Plant of IGCAR and the related pumping system inlet and outlet pipes were visually examined jointly with the personnel from Central Water Chilling Plant and Metallurgy Division, IGCAR. Despite the continuous large flow of water through the system pipes, there have been no major pipe leaks ascribable to corrosion during the last 12 years, though there had been no chemical treatment of the system water. Periodic examination of the buried pipe lines wherever feasible, and provision for their improved cathodic protection were recommended for ensuring trouble free continuous performance.

(P.K. Mathur)

10.7 **Consultancy to Heavy Water Plants**

10.7.1 **HWP Manuguru**

Cooling water treatment formulations were selected after evaluation of treatment programmes offered by different suppliers. During implementation of the programme, dissolved iron and biofouling were observed in the cooling water due to pH excursion and power shutdown. Maintenance of pH in the range 7-7.5 was recommended to control sulphate reducing bacteria. Subsequently the treatment stabilised and the performance of the system was satisfactory. Chlorination was suggested as a temporary measure to treat the cooling water in captive power plant since system design needed modification for comprehensive treatment.
10.7.2 HWP Kota

A few modifications in cooling water treatment programme were suggested to overcome corrosion and scaling problems. Stoppage of continuous bleed out was recommended to make the treatment effective, economical and to prevent environmental pollution. Water treatment carried out by a commercial firm on trial basis was not found to be satisfactory due to severe biofouling. Once a shift chlorination with FRC 0.3-0.5 ppm for 1 to 2 hours was suggested in addition to use of non-oxidising biocides for achieving biofouling control.

The chloride level in the cooling water increased to 170 -200 ppm which could probably be due to continuous chlorination by maintaining FRC at 0.5 ppm. In the case of continuous chlorination, maintenance of FRC at 0.1 -0.2 ppm was recommended to keep the chloride level below 80 ppm for prevention of stress corrosion cracking of stainless steel. With this, the chloride level was found to stabilise at 20 -30 ppm.

10.7.3 HWP Thal

To overcome the frequent problem of pH excursion of the cooling water, use of a biocide based on methylene bis-thiocyanate was recommended.

10.7.4 General

A proposal was put up to the committee of chief chemists of HWP for setting up a test facility for evaluation/development of cooling water treatment formulations. Details of the facility and specifications of the components were finalised and the proposal was submitted to HWB for approval. (R.K. Iyer)
10.8 Work in relation to Bureau of Indian Standards (BIS)

Served as Convener of the Water for Industrial and General Use Sub-Committee and a member of the Environmental Protection Sectional and Water Sectional Committees of BIS. Four documents on the methods of sampling and tests for cadmium, copper, lead and zinc in water and waste water, prepared and submitted to BIS were reviewed and approved for publication as Indian Standards. A draft document on methods of sampling and tests for steam purity was discussed. Three existing Indian Standards viz., (i) Guide for condensate polishing (power plant), (ii) Quality tolerances for water in textile industry and (iii) Water for general laboratory use and a draft document on Guidelines for methods of sampling and analysis of water formed deposits were examined for modifications. A draft British Standard, "Specification for the performance of corrosion and scale inhibitors for use in domestic hot water central heating systems" and an ISO document, "Guidance on sampling of water and steam in boiler plants" were critically reviewed. Participated in finalisation of the following Indian Standards, published recently by BIS: (i) Demineralization plant guidelines, (ii) Drinking water specification (first revision), (iii) Guide for defluoridation of water for drinking purposes (chemical treatment method).

(P.K. Mathur)
(# in collaboration with S. Rangarajan, WSCL)

10.9 Work in relation to International Atomic Energy Agency (IAEA)

The Division has been participating in the IAEA Co-ordinated Research Programme (CRP) on Investigations on Water Chemistry Control and Coolant Interaction with Fuel and Primary Circuit Materials in Water Cooled Power Reactors (WACOLIN), presently retitled as Coolant Technology of Water Cooled Reactors.
Contributed to discussions and review pertaining to the following four volumes forming part of IAEA - TECDOC series: (i) Chemistry of Primary Coolant in Water Cooled Reactors, (ii) Corrosion in the Primary Coolant Systems of Water Cooled Reactors, (iii) Activity Transport Mechanisms in Water Cooled Reactors and (iv) Decontamination of Water Cooled Reactors.
(P.K. Mathur, S.V. Narasimhan, G. Venkateswaran and K.S. Venkateswara*)
(* Since retired)

10.10 Work in relation to International Association for Properties of Water and Steam (IAPWS)

Served as a member of the Working Group - 'Power Cycle Chemistry' of IAPWS. Four Certified Research Needs drafts, viz., (i) Solubility of Spinels; Free energy of formation of spinels as a function of temperature and composition of nickel and cobalt containing ferrites and of associated ions, (ii) Evaluation of binary nucleation models, (iii) Interaction between anions and transition metal oxides and (iv) Occurrence and consequences of natural organic matter in steam condensate cycles were reviewed.
(P.K. Mathur and S.V. Narasimhan)

10.11 Work in relation to Board of Research in Nuclear Sciences (BRNS)

Served as a member of the Radiation and Environmental Studies Committee of BRNS and evaluated 19 research project proposals and also evaluated one project proposal for the Engineering Sciences Committee.
(P.K. Mathur)
10.12 Quarterly and Annual Reports

Coordinated editing and preparing the Quarterly Reports and portions of DAE Annual Reports/ BARC Annual Reports pertaining to the Division. Besides, coordinated in bringing out DAE Annual Report 1991-1992 and BARC Annual Report 1991 by being a member of the Editorial Committee. The reports for Divisions under Chemistry Group and Radiochemistry & Isotope Group were compiled. (V. Ramshesh)

10.13 Official Language Implementation Committee

Officiated as Member-Secretary, Official Language Implementation Committee, BARC and helped in implementing the two language formula. Regular quarterly meetings were held and minutes prepared for the same. The annual budgets were prepared and various Hindi programmes such as Elocution competition, seminars, workshops etc. were organised.
(V. Ramshesh in collaboration with Asstt.Director, OL)
11. SERVICE ANALYSES

11.1 Performance evaluation of Condensate Polishing Unit of Korba Super Thermal Power Station (KSTPS)

More than hundred samples from the three different streams of the condensate polishing unit of KSTPS in their two cycles of commissioning were analysed for sodium, chloride, silica, iron and copper at trace level, and pH and conductivity measurements were also made on these samples. The following conclusions were drawn from this study and communicated to KSTPS authorities:

(a) Ultimately realised NH$_3$ break through capacity of 170,000 m$^3$ was higher than the design capacity 90,000 m$^3$ per bed. This was attributed to the low influent ammonia concentration. It was also corroborated by the observed low influent pH values.

(b) Most of the time, chloride and sodium removal by CPU was found to be satisfactory and the concentrations of these ions in the effluent were within the technical specification limits (2 ppb) in H/OH cycle of operation.

(c) Effluent iron and copper concentrations were always below the technical specification upper limit (2 and 5 ppb respectively).

(d) On an average, 50-70 % silica removal was observed across the CPU. Effluent silica values were marginally higher than technical specification limits (2 ppb). The silica removal efficiency was found to deteriorate in ammonia cycle.

(e) Significant variations in effluent sodium, chloride, silica and iron concentrations were observed at the time of wide
variations in flow rate (100-600 m³/hr). This variation in concentration was attributed to the disturbance of bed equilibrium under nonsteady flow conditions.

(f) In ammonia cycle all parameters in the effluent showed increasing trend. This may be due to the breakthrough effect. (A.G. Kumbhar, T.V. Padmakumari and S.V. Narasimhan)

11.2 Analytical support to FBTR

During the commissioning of the CPU and steam water system of FBTR, trace analysis of system water for sodium, chloride, silica, iron and copper, and pH and conductivity measurements were carried out using ISE, spectrophotometry, ETAAS and ion chromatographic techniques to confirm the data obtained by the chemical control laboratory of FBTR. During initial stage of commissioning of steam water system all the above parameters were found to be higher than technical specifications expected to be achieved during the single phase operation. (A.G. Kumbhar and S.V. Narasimhan)

11.3 Sample Analyses

A total of 1328 samples were analysed by various techniques viz., TGA, DTA, DSC, XRD, HTXRD and water analysis (Table 11.3). These services were rendered to various units of BARC/DAE and also outside institutions.

11.4 Other Services

(a) Recommissioning XRD generator for NPD P.S. Malhan

(b) Servicing Model 174 polarographic analyser M.N.K. Rehman
(c) Data retrieval from Cambridge Crystallographic database V.S. Jakkal

(d) Repair of ULVAC Differential Scanning Calorimeter A.S. Kerkar and N. Manoj
Table 12.3

**Sample analyses**

<table>
<thead>
<tr>
<th>Technique</th>
<th>No. of Samples</th>
<th>Analysed by</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD</td>
<td>969</td>
<td>K.V. Muralidharan</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B.R. Ambekar</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V.S. Jakkal, S.J. Patwe</td>
</tr>
<tr>
<td></td>
<td></td>
<td>and A.C. Momin</td>
</tr>
<tr>
<td>HTXRD</td>
<td>2</td>
<td>M.D. Mathews</td>
</tr>
<tr>
<td>TGA</td>
<td>243</td>
<td>E.B. Mirza*, A.B. Phadnis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>and P.N. Namboodiri</td>
</tr>
<tr>
<td>DTA</td>
<td>55</td>
<td>A.B. Phadnis and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P.N. Namboodiri</td>
</tr>
<tr>
<td>DSC</td>
<td>20</td>
<td>P.N. Namboodiri</td>
</tr>
<tr>
<td>Water analysis</td>
<td>23</td>
<td>M.S. Eswaran,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.S. Gokhale, B.N. Wani</td>
</tr>
<tr>
<td></td>
<td></td>
<td>and A.G. Kumbhar</td>
</tr>
<tr>
<td>Particle size</td>
<td>8</td>
<td>M.P. Srinivasan</td>
</tr>
<tr>
<td>distribution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bacterial analysis</td>
<td>8</td>
<td>T.S. Rao#</td>
</tr>
</tbody>
</table>

(* Since retired; # IGCAR staff member working at WSCL, ApCD)
12. PUBLICATIONS

   A. Journal Papers

1990

1. P.V. Ananthapadmanabhan, N. Venkataramani, V.K. Rohatgi, A.C. Momin and K.S. Venkateswarlu
   'Structure and ionic conductivity of solid solutions in the system \(0.9(\text{ZrO}_2)_{1-x} - (\text{CeO}_2)_x - 0.1(\text{Y}_2\text{O}_3)\)'

2. S.R. Bharadwaj and S.N. Tripathi
   'The Pd-Pt system'
   J. Alloy Phase Diag., 6, 118 (1990)

   'Vaporization of pure palladium'

4. M.S. Chandrasekharaih and S.R. Bharadwaj
   'The Pd-Ta system'
   J. Alloy Phase Diag., 6, 103 (1990)

5. M.B. Daud, G. Venkateswaran and K.S. Venkateswaralu
   'Electrochemical corrosion characteristics of Ni-resistant type II alloy in sea water containing ferrous sulphate'
   British Corrosion J., 25, 303 (1990)

   'Differential thermal analysis and Knudsen effusion mass spectrometry in the determination of phase equilibrium diagrams in nickel based superalloys'
7. Hari Mohan and P.N. Moorthy  
'OH radical reactions with poly-iodo methanes: A pulse radiolysis study'

8. Hari Mohan and P.N. Moorthy  
'Oxidation reactions of thiodiglycollic acid: A pulse radiolysis study'

9. Hari Mohan and P.N. Moorthy  
'Oxidation reactions of thiazine and safranine dyes with halogenated peroxy radicals in aqueous solutions: A pulse radiolysis study'

10. Hari Mohan and P.N. Moorthy  
Pulse radiolysis investigation on the reactions of primary radiolytic species with atropine'
J. Radioanal. Nucl. Chem. Articles, 141, 327 (1990)

11. V.K. Jain, V.S. Jakkal and Rakesh Bohra  
Methylplatinum complexes containing 2-(diphenylphosphine) pyridine(Ph$_2$Ppy). Crystal and molecular structure of [PtMe(η^2-Ph$_2$Ppy)(Ph$_2$Ppy)][bPh$_4$]'

Effect of irradiation and dopant concentration on the migration of Xe in UO$_2$'
Metals, Materials and Processes, 1, 293 (1990)
'Studies on complex species of aluminium with amino carboxylic acid by $^{27}$Al NMR spectroscopy'

14. M. Kumar, M.H. Rao and P.N. Moorthy
'Transient species involved in radiation polymerization of aqueous divinyl sulphone'

15. M. Kumar, M.H. Rao and P.N. Moorthy
'Free radical species from methyl - vinyl ketone in aqueous solutions: A pulse radiolysis study'

'Polarographic reduction behaviour of copper in the presence of 1-amino 3-methoxy propane and 2-dimethyl amino ethanol'

17. A.G. Kumbhar and S.V. Narsimhan
'Polarographic speciation of copper(II) in the presence of 1-dimethylaminopropan-2-ol'

18. J. Mahadevan, S.N. Guha, K. Kishore and P.N. Moorthy
'One electron oxidation of toluidine blue. A pulse radiolysis study'

'Non radiative energy transfer from 7 - Amino coumarin dyes to thiazine dyes in methanolic solutions'
20. D.B. Naik and P.N. Moorthy
'Reactions of pyridin-3-ol with pulse radiolytically generated reducing species'

'Mass transport of cobalt and nickel in Incoloy-800'

22. S.V. Narasimhan, S. Rangarajan and M.N.K. Rehman
'Basic Programme for transfer of electrochemical data from a digital oscilloscope to a personal computer'
Analyt. Instrumentation, 19, 141 (1990)

'A study of the triplet state of 7-amino coumarin laser dye by the nanosecond pulse radiolysis technique'

24. V. Ramesh
'In the World of Basic-V' to 'In the World of Basic-XV'
Science Reporter, 27(1), 42 (1990); 27(2), 42 (1990); 27(3), 44 (1990); 27(4), 58 (1990); 27(5), 58 (1990); 27(6), 42 (1990); 27(7), 41 (1990); 27(8), 50 (1990); 27(9), 40 (1990); 27(10), 50 (1990); 27(12), 44 (1990)

25. N. Sasikumar, K.V.K. Nair and J. Azariah
'Influence of biofouling on oyster settlement in the vicinity of a power station in India'
Indian J. Fisheries, 27, 45 (1990)
26. N. Sasikumar, K.V.K. Nair and J. Azariah
'Colonization of marine foulants at a power plant site'

27. K.K. Satpathy and K.V.K. Nair
'Impact of power plant discharge on the physico-chemical characteristics of Kalpakkam coastal waters'
Mahasagar, 22, 117 (1990)

'Burst neutron emission and tritium generation from a palladium cathode electrolytically loaded with deuterium'
Fusion Technol., 18, 60 (1990)

29. K.S. Venkateswarlu, G. Venkateswaran and P.S. Joshi
'Chemical problems in the waste stripper tower of a heavy water plant'

30. V.P. Venugopalan and K.V.K. Nair
'Effects of a biofouling community on cooling water characteristics of a coastal power plant'
Indian J. Marine Sci., 19, 294 (1990)

'Attempts to prepare vanadium based oxide super conductor'
1991

1. P.V. Ananthapadmanabhan, K.P. Sreekumar, K.V. Muralidharan and N. Venkataramani
'Plasma-sprayed composite coatings for high temperature applications'

'The palladium-platinum phase diagram'

3. S.R. Dharwadkar, V. Venugopal, K. Hilpert and D. Kobertz
'Phase transitions in manganese for temperature calibration of differential thermal analysis'

'Synthesis and characterisation of chelates of Al, Ga and In with propylenediaminetetraacetic acid'

5. Kamal Kishore and Klaus-Dieter Asmus
'Nature of 2α/1α* three-electron-bonded chlorine adducts to sulfoxides'

6. K. Kishore, P.N. Moorthy and S.N. Guha
Pulse radiolysis study of one-electron oxidation of riboflavin'
7. K. Kishore and P.N. Moorthy
   'Nature of transient species in the one electron oxidation of diethyl dithiocarbanate as studied by pulse radiolysis'

8. M.D. Mathews, E.B. Mirza and A.C. Momin
   'High temperature X-ray diffractometric studies of CaZrO$_3$, SrZrO$_3$ and BaZrO$_3$'

9. A.C. Momin, E.B. Mirza and M.D. Mathews
   'Bulk thermal expansion studies of BiCaSrCu$_2$O$_x$ and Bi$_2$CaSr$_2$Cu$_2$O$_x$'

10. A.C. Momin, E.B. Mirza and M.D. Mathews
    'Thermogravimetric and dilatometric studies of LaBa$_2$Cu$_{3-y}$M$_y$O$_x$ (M = Ni, Li; y = 0, 0.1)'

11. A.C. Momin, E.B. Mirza and M.D. Mathews
    'High temperature X-ray diffractometric studies of LaCrO$_3$'

12. A.C. Momin, E.B. Mirza and M.D. Mathews
    'High temperature X-ray diffractometric studies on the lattice thermal expansion behaviour of UO$_2$, ThO$_2$ and (U$_{0.2}$Th$_{0.8}$)O$_2$ doped with fission product oxides'

13. D.B. Naik and P.N. Moorthy
    'Pulse radiolysis studies on the reactions of 3-pyridinol with oxidizing radicals'
14. D.B. Naik and P.N. Moorthy
'Redox reactions of 2-Hydroxy pyridine. A pulse radiolysis study'

15. K.V.K. Nair and (late) P. Murugan
'Biofouling by Perna Viridis in a deep submarine tunnel system at Kalpakkam'

'Mass transport of iron in Incoloy-800'

'Atomic migration of copper in superalloy Incoloy-800'

'Triplet - triplet and singlet - singlet energy transfer studies between t-stilbene and 7-amino coumarin laser dyes'

19. S. Rajagopal, N. Sasikumar, J. Azariah and K.V.K. Nair
'Some observations on biofouling in the cooling water conduits of a coastal power station'
Biofouling, 2, 311 (1991)

20. S. Rajagopal, V.P. Venugopalan, K.V.K. Nair and J. Azariah
'Biofouling and its control in a tropical coastal power station: A case study'
Biofouling, 2, 325 (1991)
21. V. Ramshesh
   "In the world of Basic-XVI"
   Science Reporter, 28(1), 36 (1991)

   "Thermoluminescence of Dy$^{3+}$ and Gd$^{3+}$ in different
crystallographic modifications of sodium sulphate"

23. N. Sasikumar, K.V.K. Nair and J. Azariah
   "Some observations on barnacle growth and corrosion of
   materials in seawater"
   Corrosion Prevention & Control, 145 (1991)

24. M. Shailja and S.V. Narsimhan
   "Dissolution kinetics of nickel ferrite in amino poly
   carboxylic acids"

25. B.K. Sharma, R. Subramanian and P.K. Mathur
   "Effect of complexing reagents on the ionization constant
   of boric acid and its relation to isotopic exchange
   separation factor"

26. B.K. Sharma, R. Subramanian and P.K. Mathur
   "Separation of boron isotopes by ion exchange chromatography"

27. S.N. Tripathi, S.R. Bharadwaj and M.S. Chandrasekharaih
   "The Ir-Pd (iridium-palladium) system"
   J. Phase Equilibria, 12, 603 (1991)
28. S.N. Tripathi, S.R. Bharadwaj and M.S. Chandrasekharaih
'The Ir-Rh (iridium-rhodium) system'
J. Phase Equilibria, 12, 606 (1991)

29. S. Velumurugan, V.S. Sathyaseelan, T.V. Padmakumari,
S.V. Narasimhan and P.K. Mathur
'Behaviour of ion exchange resins and corrosion inhibitors
in dilute chemical decontamination'

30. S. Velumurugan, S.V. Narasimhan, P.K. Mathur and
K.S. Venkateswarlu
'Evaluation of a dilute chemical decontaminant for
pressurised heavy water reactors'

'Mode of thermal decomposition of \((\text{NH}_4)_3\text{NbOF}_6 \cdot 1.5\text{H}_2\text{O}\)'

32. B.N. Wani and U.R.K. Rao
'Fluorination of vanadium oxides'

33. B.N. Wani and U.R.K. Rao
'Novel solid state reactions'

34. J.V. Yenagi, M.R. Gorbal, M.I. Savadatti and D.B. Naik
'A new laser dye'
1992

(i) Published

   'Synthesis of REBa$_2$VO$_6$ type of compounds (RE = rare earth)

   'Reactions of ammonium hydrogen fluoride with oxides of iron
   in solid state'

3. S. Choudhuri, Vimal K. Jain, V.S. Jakkal and
   K. Venkatsubramanian
   'Synthesis and characterization of trimethylplatinuH(IV)
   complexes with diphenylldithiophosphenic acid. Crystal and
   molecular stuctures of [PtMe$_3$(SSPPh$_2$)$_2$] and
   [PtMe$_3$(py)(SSPPh$_2$)]

   'Determination of solidus, solvus and liquidus temperatures
   for $\Gamma'$-hardened nickel base alloys'
   Z. Metallkunde., 82, 744 (1992)

   'Reaction of e$_{aq}^-$, H and OH with picolinic acid as studied by
   pulse radiolysis'
   J. Radioanal. Nucl. Chem. Articles, 163, 391 (1992)
6. S.N. Guha, J.P. Mittal and P.N. Moorthy
'Pulse radiolysis study of redox reactions of safranine-T in aqueous solutions: one-electron reduction'

7. P.S. Joshi, G. Venkateswaran and K.S. Venkateswarlu
'Chelant enhanced passivation of carbon steel in deoxygenated alkaline aqueous solutions'

8. P.S. Joshi, G. Venkateswaran and K.S. Venkateswarlu
'Passivation behaviour of carbon steel alloys in the presence of EDTA, Ni(II)EDTA and LiOH at 473 K'
Corrosion (NACE), 48, 501 (1992)

'Studies of the triplet state of biphenyl derivatives by nanosecond pulse radiolysis'

10. D.B. Naik
'Solar purification of water'
ISRAPS Bulletin, 3(2), 12 (1992)

'Preparation of YBa$_2$F$_7$ and its other rare earth analogues'

'The Fleischmann-Pons phenomenon - A different perspective'
'Thermodynamic investigation on the vaporization of molybdenum trioxide'

14. N. Sasikumar, K.V.K. Nair and Jayapaul Azariah
'Response of barnacles to chlorine and heat treatment: An experimental study for power plant biofouling control'
Biofouling, 6, 69 (1992)

15. M. Shafiq Ahmed, G. Durairaj, K. Suresh and K.V.K Nair
'Effect of power plant heated effluent on distribution of sedentary fauna and flora'
Indian J. Marine Sci. 21, 186 (1992)

16. K.P. Sreekumar, P.V. Ananthapadmanabhan, K.V. Muralidharan and N. Venkataramani
'Effect of thermal treatment on phase composition and thermal shock resistance of plasma sprayed calcia stabilized zirconia-alumina comoposite coatings'
J. Alloys and Compounds, 185, 169 (1992)

'Ecology of interstitial meiofauna at Kalpakkam coast, east coast of India'
Indian J. Marine Sci. 21, 217 (1992)

'On fluorine incorporation into YBa_2Cu_3O_6.5+x'
19. G. Venkateswaran
'Recent practices in reactor system water chemistry'
IANCAS Bull. 8(2), 2 (1992)

20. V. Venugopal, S.R. Dharwadkar, K. Hilpert and D. Kobertz
'The role of in situ reactive metal getter in the
determination of phase equilibrium diagram in metallic
system'

'Fast solid state reaction between bifluorides and vanadates
at ambient temperature'

(ii) Accepted

'Kinetic and spectral characteristics of transients formed in
the pulse radiolysis of phenylthiourea in aqueous solution'

2. S.R. Dharwadkar, A.S. Kerkar and M.S. Samant
'A microthermogravimetric system for the measurement of
vapour pressure by transpiration method'
Thermochim. Acta

3. M.S. Eswaran, K.V.K. Nair and P.K. Mathur
'Some observations on mild steel corrosion in fresh water'
Corrosion Prevention and Control

4. Shambhu N. Guha, Pervage N. Moorthy and Jai P. Mittal
'Redox reactions of Neutral Red. A pulse radiolysis study'
5. Pranav S. Joshi, G. Venkateswaran and K.S. Venkateswarlu
'Passivation of carbon steel alloy in deoxygenated alkaline pH medium effect of various additives'
Corrosion Science

6. P.S. Joshi, G. Venkateswaran, K.S. Venkateswarlu
and K. Annaji Rao
'Stimulated decomposition of Fe(OH)$_2$ in the presence of AVT chemicals and metallic surfaces - relevance to low temperature feed water line corrosion'
Corrosion(NACE)

'Studies on speciation of aluminium complexes with malic acid by high field $^{27}$Al NMR spectroscopy'
Indian J. Chem.

8. K. Kishore, G.R. Dey and P.N. Moorthy
'Pulse radiolysis studies of some aromatic sulphoxides in aqueous solution'

'Characterization of aluminium complexes in tea extract Part I: $^{27}$Al NMR studies'
Magnetic Resonance in Chem.

10. D.B. Naik and P.N. Moorthy
'Pulse radiolysis of 4-pyridinol: evidence for dimer anion formation'
'Synthesis and thermal stability of ammonium/potassium vanadium oxyfluoro compounds'
J. Thermal Analysis

12. T.S. Rao, M.S. Eswaran, V.P. Venugopalan, K.V.K. Nair and P.K. Mathur
'Fouling and corrosion in an open recirculating cooling system'
Biofouling

'Standard free energy of formation of ZrMo_2O_8 by the transpiration method'
J. Nucl. Mater.

14. N. Sasikumar, J. Azariah and K.V.K. Nair
'Changes in the composition of a tropical marine fouling community at a power plant discharge'
Biofouling

15. N. Sasikumar, K.V.K. Nair and J. Azariah
'Sublethal response of barnacles to chlorine: An experimental study for power plant biofouling control'
Marine Behaviour and Physiol.

16. N. Sasikumar, K.V.K. Nair and J. Azariah
'Sublethal response of barnacles to temperature: An experimental study for power plant biofouling control'
J. Thermal Biol.
17. M. Shailaja and S.V. Narasimhan
'Mechanism of oxide scale removal during dilute chemical decontamination of carbon steel surfaces'

18. B.K. Sharma, R. Subramanian and P.K. Mathur
'Conductimetric studies of boric acid in presence of some complexing reagents and separation of isotopes of boron by ion exchange chromatography'
Indian J. Chem.

'On magnetic behaviour of REBa$_2$F$_7$' (RE = Pr, Nd, Sm and Gd)
J. Magnetism and Magnetic Mater.

20. G. Visalakshi, S.V. Narasimhan and K.S. Venkateswarlu
'Investigation of nickel(II) reduction in aqueous morpholine medium by DC polarography'

'Compositional characteristics of magnetite synthesised from aqueous solutions at temperatures upto 523 K'

22. B.N. Wani and U.R.K. Rao
'Interfacial reaction between ammonium bifluoride and binary oxides at room temperature'
(iii) Communicated

1. G. Chattopadhyay
   'The chromium-tellurium system'
   J. Phase Equilibria

2. G. Chattopadhyay
   'A thermodynamic database for tellurium-bearing system relevant to nuclear technology'
   J. Nucl. Mater.

   'Pulse radiolysis of benzidine in aqueous solutions'

   'Electrochemical studies of copper complexes with 1- amino-3 methoxypropane and 2 - dimethylaminoethanol'
   Electrochim. Acta

5. A.G. Kumbhar, S.V. Narasimhan and P.K. Mathur
   'Trace level copper speciation with 1-amino 3-methoxy 2-propane and 2-dimethyl amino ethanol by pseudo polarographic method'
   Talanta

   'Studies on speciation of Copper (I) and Copper (II) complexes of 2 - amino - 2 methylpropan - 1 - ol (AMP) by DC and differential pulse polarography'

180
7. A.C. Sahayam, S. Gangadharan and A.K. Tyagi
"Chemical modification of tin in Graphite Furnace Atomic Absorption Spectroscopy"
Spectro Chim Acta B

"Thermoanalytical investigation on the solid state synthesis of pure zirconium molybdate (ZrMo2O8)"
Chem. and Phys. of Mater.

"On the optimization of experimental conditions for the solid state synthesis of pure molybdates - A case study of zirconium molybdate (ZrMo2O8)"
J. Mater. Sci.

"Some observations on the water quality characteristics of coastal sea water and a sub-seabed tunnel"
Mahasagar

"On the material transport during solid state reaction at room temperature"

"Spatial and temporal distribution and abundance of Emerita asiatica in the vicinity of a coastal power station"
Hydrobiologia
'On preparation and characterisation of REBa$_2$F$_7$ type compounds'

B. Conference Proceedings/ Symposia

1990

'Reactivity of ammonium hydrogen fluoride with oxides of iron'
Annual Convention of Chemists, Bodhgaya, Dec. 1990

2. S.R. Bharadwaj and K.S. Venkateswarlu
'Thermodynamic stability of noble metals'
Research Scholars Meet, Indian Chemical Society, Bombay, March 1990

3. S. Chakraborty, M.H. Rao and P.N. Moorthy
'Reradiation induced polymerisation of methacrylamide in non solvents'

4. S.N. Guha and P.N. Moorthy
'One electron oxidation of Safranine - T in aqueous solutions studied by pulse radiolysis'
ibid, Paper RC - 13

5. S.B. Karweer, B.P. Pillai and R.K. Iyer
'Characterization of complex species of aluminium with tartaric acid by $^{27}$Al NMR spectroscopy'
Annual Convention of Chemists, Bodhgaya, Dec. 1990
6. K. Kishore and P.N. Moorthy
'Reactions of OH radicals with diethyl dithiocarbamate as studied by pulse radiolysis'

7. K. Kishore and P.N. Moorthy
'Formation of 3 - electron bonded intermolecular and intramolecular S - centered species in the pulse radiolysis of diethyl dithiocarbamate and disulfiram'

8. M. Kumar, M.H. Rao and P.N. Moorthy
'Pulse radiolysis studies of aqueous solutions of dimethyl acrylic acid'

9. J. Mahadevan, S.N. Guha and P.N. Moorthy
One electron oxidation of Neutral Red: A pulse radiolysis study'
ibid, Paper RC - 15

10. S.N. Mhatre and R.K. Iyer
'Studies on complexes of aluminium present in tea'
Annual Convention of Chemists, Bodhgaya, Dec. 1990

11. H. Mohan and P.N. Moorthy
'Pulse radiolysis investigations on the reactions of \( e^{-}_{aq} \), H and OH with atropine sulphate solutions'
12. D.B. Naik and P.N. Moorthy
'Reactions of oxidising radicals with 2-pyridinol in alkaline aqueous solutions: A Pulse radiolysis study'
ibid, Paper RC - 5

13. D.B. Naik and P.N. Moorthy
'Reactions of reducing and oxidising species of water radiolysis with hydroxy pyridines'

14. K.V.K. Nair
'Marine fouling and allied problems in the condenser cooling system of MAPS'

15. K.V.K. Nair
'Primary productivity and photosynthetic pigments in the Edaiyar-Sadras estuarine systems at Kalpakkam '

16. K.V.K. Nair
'Marine fouling and its prevention-recent advances'

17. K.V.K. Nair and K.K. Satpathy
'VeIarity of heavy metal studies in Indian coastal waters and the mussel watch concept'
'Electrochemical investigations in water chemistry research'
One-day Electrochemical Awareness Meeting, SAEST, Kalpakkam, July, 1990

19. M.S. Panajkar, H. Mohan and P.N. Moorthy
'Pulse radiolysis studies of terephthalonitrile in aqueous solution'
Proc. DAE Symp. Radiochemistry and Radiation chemistry
Nagpur University, Feb. 1990, Paper RC - 18

'Triplet characteristics of coumarin 1 (C-1) studied by nano second pulse radiolysis'
ibid, Paper RC - 14

'Energy transfer studies of coumarin dyes using electron pulse radiolysis'
pp. 105-116

22. K.K. Satpathy
'Biofouling control measures in power plant cooling systems - A brief overview'
23. B.K. Sharma, R. Subramanian and P.K. Mathur
'Effect of ionisation constant of boric acid on the separation factor for separation of boron isotopes by the ion-exchange chromatography'

24. B.K. Sharma, R. Subramanian and P.K. Mathur
'The role of electrochemistry in the process of separation of boron isotopes by ion exchange chromatography'
One-day Electrochemical Awareness Meeting, SAEST, Kalpakkam, July, 1990, pp 21-23

25. A.K. Sriraman
'Behaviour of chlorine in lake water'

26. A.K. Sriraman
'Some aspects of sea water chlorination as relevant to coastal waters of India'

27. V.G. Thomas, S.B. Srivastava and P.N. Moorthy
'Pulse radiolysis studies of aqueous solutions of iodides'

'On the fluorination of oxide superconductors'
Research Scholars Meet, Indian Chemical Society, Bombay, March, 1990
'On $YF_{2}Cu_{3}O_{3}F_{7}$'

'Difficulties in preparing F-containing $Nd_{2}CuO_{4}$ superconductor'
ibid, 33C, 170 (1990)

31. K.S. Venkateswarlu, S.V. Narsimhan and G. Venkateswaran
'Initiation of $^{232}Th_{90}$ - $^{233}U_{92}$ cycle in the Indian Nuclear Energy Programmes'

1991

1. G. Chattopadhyay
'Interconnection between phase diagrams and solid electrolyte galvanic cells'
National Symp. Solid State Chemistry and Allied Sciences, University of Nagpur, Jan. 1991

2. G.R. Dey, K. Kishore, S.B. Srivastava and P.N. Moorthy
'Radiolysis of aqueous azide solutions'

'Radiolysis of $N_{2}$ - water systems: Relevance to pressurized water reactors'
4. S.R. Dharwadkar
'Thermogravimetric technique in the thermodynamic investigations of gas-solid reactions'
National Symp. Solid State Chemistry and Allied Sciences, University of Nagpur, Jan. 1991

5. S.R. Dharwadkar
'Differential thermal analysis (DTA) in the determination of equilibrium phase diagrams'
ibid

6. A.C. Momin, E.B. Mirza and M.D. Mathews
'Thermal studies on Li$_2$O.5B$_2$O$_3$.10H$_2$O'
ibid

7. A.C. Momin, E.B. Mirza and M.D. Mathews
'Bulk thermal expansion studies of La$_{2-y}$M$_{y}$CuO$_{4+x}$
(M=K,Sr; y=0,0.15)'

8. A.C. Momin and M.D. Mathews
'XRD and TMA studies on Ln$_{2-x}$M$_x$CuO$_4$
(Ln = La,Nd; M = K,Sr,Ce; x = 0, 0.075, 0.15 )'

9. D.B. Naik and P.N. Moorthy
'Dimer anion formation in the pulse radiolysis of 4-pyridinol in aqueous solutions'
10. D.B. Naik and P.N. Moorthy
   "Pulse radiolysis studies of hydroxypyridines"

   "Mass transport of iron in Zr-2.5% Nb alloy"

12. P.N. Namboodiri, S.R. Dharwadkar and M.S. Samant
   "Some problems in the determination of heat capacity of solids by Differential Scanning Calorimetry (DSC)"
   Proc. 8th National Symp. on Thermal Analysis,

13. S.V. Narasimhan, A.G. Kumbhar and S. Rangarajan
   "Additional criteria for selection of AVT reagents, metal speciation and CPU compatibility"

   "Impact of a coastal nuclear power plant: The Kalpakkam experience"
   Coastal Zone Management, Edited by R.Natarajan, S.N.Dwivedi and S.Ramachandran, Ocean Data Centre, Anna University, Madras, 1991, pp 294-302

   "Role of thermal analysis in flourination of oxide superconductors"
16. S. Sabharwal, K. Kishore and P.N. Moorthy
'A pulse radiolysis study of one electron oxidation of sulphacetamide'
DAE Intl. Symp. Radiochem. and Radiation Chemistry

17. M.S. Samant, S.R. Bharadwaj and S.R. Dharwadkar
'Vapour pressure measurement of molybdenum trioxide using a novel thermogravimetric system'
Proc. 8th National Symp. Thermal Analysis,

18. M.S. Samant, S.R. Dharwadkar, P.N. Namboodiri and A.B. Phadnis
'Role of thermal techniques in the solid state synthesis of pure molybdates: A case study of zirconium molybdate(ZrMo$_2$O$_8$)'
ibid, Paper No. I.5, pp. 20-28

'On thermal decomposition of YBa$_2$Cu$_3$O$_7$F$_7$ in the absence of air'
ibid, Paper No.VII.3, pp. 521-524

20. S. Velmurugan, V.S. Sathyaseelan, S.V. Narasimhan and P.K. Mathur
'Optimisation of parameters of DCD for PHWRs'
'Ion exchange characteristics of decontamination formulations as suited to nuclear reactors'

'Assessment and experience of design changes in the moderator circuit on D₂ levels in the cover gas of PHWR'

'Influence of AVT chemicals and metallic surfaces on the decomposition of ferrous hydroxide'
ibid, pp 695-700

24. V.P. Venugopalan, S. Rajagopal, N. Sasikumar and K.V.K. Nair
'Marine biology of a subseabed tunnel on the east coast of India'
In : Oceanography of the Indian Ocean (ed. B.N. Desai)

'Reaction between antimony oxides and bifluoride'
Proc. 8th National Symp. Thermal Analysis,

'Fast solid state reaction at room temperature'
1992

   'Role of structure in reactivity of KH$_2$F'
   11th Conf. Indian Council of Chemists, Muzaffarpur, Dec. 1992

   'Kinetic and spectral characteristics of transients formed in
   the pulse radiolysis of phenylthiourea in aqueous solutions'
   DAE Symp. Radiation and Photochemistry, BARC, Trombay
   Bombay, Jan. 1992, paper R - 15

   'Efficacy and radiation stability of some decontaminant
   formulations'
   Bournemouth, Oct. 1992, Paper 5P

4. A.S. Gokhale and G. Venkateswaran
   'Solvent extraction cum radioanalytical method for iodine
   separation. A Revisit'
   Proc. DAE Symp. Nuclear and Radiochemistry,
   Andhra University, Visakhapatnam, Dec. 1992, pp 415-417

5. Pranav S. Joshi and G. Venkateswaran
   'Role of EDTA, Ni(II) EDTA and LiOH in the passivation
   behaviour of carbon steel alloy at 473 K'
   National Conference on corrosion of metals and Alloys in
Corrosion control in a closed recirculating cooling water system
29th Annual Convention of Chemists, Rewa, Dec. 1992

7. K. Kishore, G.R. Dey and P.N. Moorthy
Pulse radiolysis of some aromatic sulfoxides in aqueous solutions

27Al NMR studies of aluminium chelates with orthodihydroxyphenols and aromatic o-hydroxycarboxylic acids
29th Annual Convention of Chemists, Rewa, Dec. 1992

9. P.N. Moorthy and P.K. Mathur
Water chemistry related to nuclear power reactors

Studies of triplet state of benzidine by pulse radiolysis

11. K.V.K. Nair
Biofouling and biocorrosion in industrial cooling systems
12. K.V.K. Nair
'Heat as an alternate fouling control technique in Indian coastal power plants'
Indo-US meeting on Recent Developments in the Control of Biodeterioration, Bangalore, July 1992

13. S.V. Narasimhan
'Chemical decontamination of nuclear reactors with special reference to corrosion aspects'

'High temperature and high pressure electrochemical measurements in aqueous systems - The present status'
National Workshop on Chemical Sensors, Kalpakkam, Nov. 1992

15. S.V. Narasimhan, S. Rangarajan, M.N.K. Rahman and R. Jalan
'Expert system for secondary side water chemistry control in pressurised heavy water reactors'

'Reactivity between solids at room temperature'

17. A.R. Paul and K.N.G. Kaimal
'Atomic migration of chromium in superalloy Incoloy-800'
ibid. p. 57
18. S. Rangarajan, S.V. Narasimhan and P.K. Mathur
'Spectro and photoelectrochemistry - blend of optical and electrochemical techniques'

19. T.S. Rao, M.S. Eswaran, V.P. Venugopalan, K.V.K. Nair and P.K. Mathur
'Some observations on fouling and corrosion in an open recirculating system at Kalpakkam'
Eurotherm seminar No.23 on Fouling Mechanisms : Practical and Theoretical Aspects, Grenoble, France, Apr. 1992

'Material transport across interface in solid state reaction at room temperature'

21. S. Sabharwal and K. Kishore
'Pulse radiolysis study of tetracycline reactions with radiolytically generated reducing species'

'The standard free energy of formation of HfMo$_2$O$_8$'
11th Conf. Indian Council of Chemists, Muzaffarpur, Dec. 1992

23. K.K. Satpathy, V.P. Venugopalan, K.V.K. Nair and P.K. Mathur
'Environmental and operational problems and their assessment at power plant sites - Kalpakkam experience'

195
"Chlorine demand and chemical control of biofouling in power plant cooling systems"
Indo-US meeting on Recent Developments in the Control of Biodeterioration, Bangalore, July 1992

25. B.K. Sharma, R. Subramanian and P.K. Mahur
"Use of electrochemical sensors in the process of separation of boron isotopes by ion exchange chromatography"
National Workshop on Chemical Sensors, Kalpakkam, Nov. 1992

"Micronutrient characteristics of coolant sea water at Tarapur Atomic Power Station"
29th Annual Convention of Chemists, Rewa, Dec. 1992

"On preparation and magnetic behaviour of REBa$_2$F$_y$ type compounds"

28. A.K. Tyagi
"A review on anionic sustitution in YBa$_2$Cu$_3$O$_{6.5}$"
11th Conf. Indian Council of Chemists, Muzaffarpur, Dec. 1992

29. G. Venkateswaran
"Boiler and cooling water treatments"
30. G. Venkateswaran and P.S. Joshi  
'Influence of chelants, AVT chemicals and other additives on the passivation behaviour of carbon steel in deoxygenated aqueous solutions at 473 K'  

31. V.P. Venugopalan, K.V.K. Nair and P.K. Mathur  
'Biofouling and associated corrosion problems in coastal nuclear power stations in India'  

32. V.P. Venugopalan, T.S. Rao, C.A. Sargunam and K.V.K. Nair  
'Some observations on the biological and biochemical aspects of biofilm development in Kalpakkam Coastal waters'  
Indo-US meeting on Recent Developments in the Control of Biodeterioration, Bangalore, July 1992

33. B.N. Wani and U.R.K. Rao  
'Mechanism of solid state reaction of bifluorides with vanadates'  

34. B.N. Wani, S.V. Adhyapak and U.R.K. Rao  
'Interfacial solid state reaction between organic-organic and organic-inorganic compound pair'  
ibid., 35C, 258 (1992)
C. Reports

1990

   'Palladium - metal binary phase diagrams'
   BARC - I - 1013 (1990)

2. G.R. Dey, K. Kishore, P.N. Moorthy, V. Ramshesh, S.B. Srivastava and V.G. Thomas
   'Water radiolysis at high temperatures and high pressures'
   BARC - 1533 (1990)

1991

1. R.K. Iyer
   'Production of CaSO₄:Dy Phosphor for dosimetric applications'
   in BARC - 1546 (1991) [ ed. A.S. Pradhan ]

2. P.N. Moorthy
   'Role of water chemistry in radiation field control in nuclear power plants'
   BARC/1991/I/008

3. P.N. Moorthy and S.V. Narasimhan
   'Chemical decontamination of the PHT system of MAPS Final feasibility report' Aug. 1991

4. V. Ramshesh, P.N. Moorthy and K. Kishore
   'Possible use of gadolinium as soluble poison in Indian PHWRS (A status report)'
   BARC/1991/I/012

198
1992

1. V. Ramshesh and P.N. Moorthy
   'The zinc addition approach to radiation field reduction in nuclear power reactors'
   BARC/1992/I/003

   'An investigation for identification of factors governing F & P phenomenon'
   BARC/1992/E/027

D. Invited Talks

1990

1. V.S. Jakkal
   'PC-PDF powder diffraction database on CD-ROM'
   IPA seminar-cum-workshop on Data base Applications in Physical Sciences, BARC, Bombay, Oct. 1990

1991

1. G. Chattopadhyay
   'Interconnection between phase diagrams and solid electrolyte galvanic cells'
2. S.R. Dharwadkar
'Thermal techniques in the study of high temperature phase equilibria'
Regional Research Laboratory, Bhubaneswar, Feb. 1991

3. S.R. Dharwadkar
'The state of art of thermal analysis'
Workshop on Thermal Analysis held at Regional Research Laboratory, Bhubaneswar, Dec. 1991

4. S.R. Dharwadkar
'Applications of thermal techniques in the study of solid state reactions, phase transformations and defect chemistry'
Lecture for Post Graduate Teachers, University of Bombay, Dec. 1991

5. R.K. Iyer
'Production of CaSO₄:Dy phosphor for dosimetric applications'
Workshop on Development of Scintillation and Luminescent Detectors, ISRP, Bombay, Mar. 1991

6. R.K. Iyer
'Role of ozone in cooling water treatment: Recent trends in water treatment with special reference to heavy water plants'
8th Meeting of Chief Chemists of HWPs, Oct., 1991

7. V.S. Jakkal
'Powder diffraction database PC-PDF'
Workshop on Retrieval of information from INIS and powder diffraction database PC-PDF, May, 1991
'Readiation Sources and Dosimetry'
Workshop on Radiation Damage in MOS Devices, IIT, Bombay, Aug. 1991

9. K.V.K. Nair
'Studies on algae and its relevance to a nuclear power programme'
Refresher Course on "Essentials of Taxonomy and Biology of Algae, Fungi and Higher Plants", Centre for Advanced Studies in Botany, University of Madras, Nov. 1991

10. G. Venkateswaran
'Reactor water chemistry'
3rd Appreciation Course on Nuclear Science and Technology
BARC, Bombay, Dec. 1991

1992

1. Kamal Kishore
'Readiation Dosimetry'
Winter School on "Radiation Research: Principles, Applications and Recent Trends"
University of Poona, Pune, Jan. 1992

2. P.K. Mathur
'Chemistry of corrosion and activation products in water'
DAE Symp. Nuclear and Radiochemistry,
Andhra University, Visakhapatnam, Dec. 1992
3. P.N. Moorthy
   (i) Nuclear energy, radiations and radiation chemistry
   (ii) Fast reaction studies
   (iii) Applications of radiations
   Guest lectures delivered at Mangalore University, Mangalgangotri, Feb. 1992

5. D.B. Naik and P.N. Moorthy
   'Use of particle accelerators in chemistry'
   Seminar on 'Microtron and its Applications' Mangalore University, Mangalgangotri, Oct. 1992

6. D.B. Naik
   'Radiation chemistry of water and aqueous solutions'
   National Workshop on 'Radiochemistry, Applications of Radioisotopes and Allied Topics'
   Mangalore University, Mangalgangotri, Nov. 1992

7. S.V. Narasimhan
   'Metal speciation in natural waters'
   Lecture delivered at University of Madras as part of Refresher Course for University Teachers, Feb. 1992

8. G. Venkateswaran
   'Reactor water chemistry'
   4th Appreciation Course on Nuclear Science and Technology, BARC, Bombay, Dec. 1992

9. A.K. Tyagi
   'Superconductivity: Unravelling of the mystery'
   Nehru Science Centre, Bombay, Aug. 1992
E. Theses

1990

1. A.K. Sriraman
   'Physico chemical aspects of sea water chlorination as relevant to industrial cooling'
   (Guide: K.S. Venkateswarlu)

1991

1. S.R. Bharadwaj
   'Thermal stability of noble-metal alloys and compounds'
   Ph.D. Thesis, University of Bombay
   (Guide: K.S. Venkateswarlu)

2. D.B. Naik
   'Radiation and photochemical studies on some organic compounds'
   Ph.D. Thesis, University of Bombay
   (Guide: P.N. Moorthy)

3. A.K. Tyagi
   'Fluorination and its effect on $T_C$ and other properties of oxide superconductors and related compounds'
   Ph.D. Thesis, University of Bombay
   (Guide: U.R.K. Rao)
1992

1. P.S. Joshi

'Physicochemical studies on corrosion-deposition problems in water cooled nuclear reactors and heavy water plants'
Ph.D. Thesis, University of Bombay
(Guide: K.S. Venkateswarlu)

2. S. Rajgopal

'Biofouling problems in the condenser cooling circuit of a coastal power station with special reference to green mussel *Perna viridis(L)*'
Ph.D. Thesis, University of Madras
(Guide: K.V.K. Nair)

3. N. Sasikumar

'Ecology and control of biofouling in a coastal power station with special reference to *Megabalanus tintinabulam*
Ph.D. Thesis, University of Madras
(Guide: K.V.K. Nair)

F. Articles in Books

1990

1. P.N. Moorthy

'An overview of some basic and applied radiation chemical studies at Trombay'
2. P.N. Moorthy
'Fast reaction techniques for radiation damage studies at the molecular level'

1992

1. D.B. Naik, K.I. Priyadarsini and T. Mukherjee

2. P.K. Mathur and S.V. Narasimhan
'Chemistry of primary coolant in water cooled nuclear reactors'

3. P.K. Mathur and S.V. Narasimhan
'Good water chemistry practices for PHWRs'
ibid. pp 90-93

4. K.S. Venkateswarlu and P.K. Mathur
'Preconditioning of primary heat transport systems of PHWRs: Indian experience'
ibid. pp 94-95
5. K.S. Venkateswarlu, P.K. Mathur, S.V. Narasimhan and G. Venkateswaran
'Material characteristics of primary heat transport systems-
material integrity during operation of PHWRs'
IAEA-TECDOC-667 on Coolant Technology of Water cooled Nuclear
Reactors Vol. 2: Corrosion in the Primary coolant systems of
water cooled Reactors, 1992, pp 49-50

6. K.S. Venkateswarlu, P.K. Mathur, S.V. Narashiman and
G. Venkateswaran
'Fuel cladding integrity in PHWRs'
ibid. pp 51-52

7. K.S. Venkateswarlu, P.K. Mathur, S.V. Narasimhan and
G. Venkateswaran
'Good practices of man-rem reduction in PHWRs'
IAEA-TECDOC-667 on Coolant Technology of Water cooled Nuclear
Reactors Vol. 3: Activity transport mechanisms in water
cooled Reactors, 1992, pp 89-91

G. Books/ Symp. Proceedings

1. K.V.K.Nair and V.P.Venugopalan (eds.)
Proc.Specialists' meeting on Marine Biodeterioration with
reference to Power Plants Cooling Systems,
IGCAR, Kalpakkam. 1990

2. S.R. Dharwadkar, A.C. Momin, S.R. Bharadwaj, K.B. Kanungo,
H.S. Ray (eds.)
Proc. Eighth National Symposium on Thermal Analysis
Bhubaneswar, 1991
Objectives and Thrust Areas*

Objectives

R&D programmes on chemistry aspects related to Nuclear Power Stations and Heavy Water Plants; consultancy for DAE units and outside agencies on water chemistry problems.

Thrust areas

1. On-line decontamination of nuclear facilities: synthesis, characterisation and dissolution studies on simple and mixed oxides of transition metals, base metal corrosion and its inhibition, ion exchange regeneration of formulation components and radiation effects. A dynamic mock-up loop is being set up to optimise the parameters for adapting the process for actual plant decontamination (VIII Plan Scheme). Periodic decontamination of PHT system of PHWRs is essential to reduce radiation fields.

2. Metal water interaction with emphasis on materials used in the PHT system, steam generator and condenser. A high temperature-high pressure loop for carrying out these studies is in an advanced stage of commissioning. Material selection for future NPRs:

3. Chemistry of soluble poisons: Studies on boron and gadolinium compounds from the point of view of suitability under various operational conditions in the moderator system of reactors. Search for alternate and better liquid poisons to replace lithium pentaborate currently used in NAPS-1.

*of Applied Chemistry Division, reproduced from the Document "Thrust Areas of Research and Development, Bhabha Atomic Research Centre, 1991 [BARC 1991/I/019]

Other major activities

Basic Research

1. Solid State reactions and high temperature thermodynamics: Synthesis and characterisation of high tech ceramics including superconductors; low temperature fluorination of oxides; alloy phase diagrams.

2. Primary coolant water chemistry: Developing experimental techniques for pH and other electrochemical measurements and aqueous corrosion studies at high temperature and high pressures. Understanding activated corrosion product generation transport and build up in the primary coolant circuits of PHWRs.

3. Speciation studies in metal-amine systems, ion exchange behaviour of aminium ions and selectivity with respect to inorganic ions. Performance of condensate polishing plants.

4. High temperature aqueous radiation chemistry: Steady state and transient studies with respect to moderator and coolant systems. Enhanced deuterium build up in the moderator cover gas due to air ingress.
Consultancy/Services

1. Advice to nuclear and thermal power stations, heavy water plants and other organisations regarding water chemistry problems (directly and through COSWAC).
PLAN PROJECTS

With the objective of augmenting the Division's capability to tackle various problems related to the primary, secondary and tertiary water circuits of nuclear power reactors in the context of expansion of nuclear power generation in the country during coming years, the Division has formulated an integrated VIII plan project proposal titled "Augmentation of Water Chemistry Research for Nuclear Energy Programme". This involves a total outlay of Rs 225 lakhs with FE component of 80 lakhs, and has since been sanctioned.

The project is divided into five principal segments:
1. High temperature - high pressure coolant water chemistry - Basic and Applied studies.
2. Development and testing of chemical formulations for decontamination of the primary heat transport system of PHWRs.
4. marine biofouling and biocorrosion.
5. High temperature and high pressure radiation chemistry.

Besides procuring a number of sophisticated analytical equipments for surface as well as bulk solution characterization (ESCA, HPLC, Ion Chromatograph etc.), the project has envisaged the setting up of a number of loop facilities, such as dynamic decontamination loop and biofouling test loop and a condensate polishing test set up. Also a high temperature - high pressure loop (continuation of earlier plan project) is in an advanced stage of construction.
A. Dynamic Decontamination Loop

Objectives

Development of dilute chemical decontamination technology necessitates an exhaustive qualification programme. The formulations developed on the basis of laboratory experiments need to be functionally demonstrated in a dynamic loop so that their application to real system will not lead to any surprises. In addition, key operational parameters also require to be optimised. In order to achieve this a model test loop is being set up.

Description

The facility consists of four mobile rigs. The first rig consists of deoxygenator columns, chemical make up and injection facility and sampling station and on-line analytical probes. The second rig is the most important one housing the surge tank, recirculating pump, heater, test sample holder for odd sized specimens, corrosion coupon holder, electrochemical monitoring facility and solid chemical injection facility. The third rig consists of only a sample piping of required material and surface area and coated with representative oxide by exposure to high temperature conditioned water in the HTHP loop. The fourth rig consists of the ion-exchange purification facility. A cooler, filter and liquid chemical addition facility are also included. Two different sized IX columns are provided along with flow variation capability. The facility can operate in the temperature range ambient to 120°C.

Proposed experimental work

It is proposed to test the efficacy of dissolution of oxide
coatings on CS initially formed at temperatures of 250-280°C in the HTHP loop. Different formulations, initially optimised in laboratory experiments will be tried out. Corrosion rates on different structural materials of the PHT system will be measured under dynamic conditions simulating the PHT system using both weight loss method and electrochemical techniques. Hydrogen generation during interaction of the formulation with system surfaces will be measured and the impact of corrosion inhibitors will be evaluated. Dynamic changes in the formulation component concentration will be monitored and the methodology of make up, if any, will be standardised.

Current progress

Detailed engineering design has been completed and procurement action has been initiated.

B. High Temperature High Pressure Loop (HTHP Loop)

Objectives

The overall objectives of the studies to be carried out in the HTHP loop are to improve the water chemistry specifications on both the primary and secondary circuits of nuclear reactors as necessitated by the reduced plant radiation levels and the ALARA criteria. It is also necessary to provide a firm basis for the chemistry specifications based on the R & D data generated during the last decade and arrive at action level parameters namely duration of exposure and concentration level of impurities suited to the PHWR water circuits. Oxide deposits on pipe surfaces for testing of decontamination formulations are also to be generated under PHT system operating conditions.
Description

The HTHP loop consists of five water circuits. The pressuriser circuit contains a make up pump and a surge tank with heater. The primary circuit consists of main circulating pump, heater, test sections and steam generator. It will be operated at a nominal temperature of 286°C and pressure of 90 kg/cm². The secondary circuit contains a steam generator, condenser, condensate collection tank, make up pump and chemical addition facility. It will operate at a temperature of 249°C and a pressure of 38.7kg/cm². The steaming rate will be 420 kg/hr. The primary purification circuit consists of coolers, filters, ion exchange columns and chemical addition facility. The cooling water circuit is used to condense the steam and consists of circulating pumps and cooling pond.

Current status and proposed commissioning

All major equipments like surge tank, heater, main circulating pumps, test sections, steam generator, condenser, condensate collection tank, filters, ion exchange columns, regenerative and non regenerative coolers, metering pumps and cooling water circulating pumps have been installed. Major part of piping work in the entire loop and a portion of instrumentation work are completed. After completion of the remaining instrumentation and piping work, the entire loop will be hydrotested and air leak test will be done to check for any leakage. Following this, commissioning will be carried out by Aug. '93.

Proposed experimental work

i) Effect of varying primary side water chemistry regimes on general material compatibility, nature of oxides formed and mass
distribution will be investigated by using metallographically prepared specimens installed in dynamic autoclaves.

ii) Generation of particulates in the presence of different levels of impurities will be studied by measuring particle size distribution and zeta potential at room temperature.

iii) Optimisation of parameters such as temperature, pH, complexing ligand concentration, concentration of amines and concentration of boric acid for hot conditioning of steels so that subsequent mass release will be minimum. The oxide coated pipes will be used for characterisation of oxides and also for testing decontaminant formulations in the dynamic decontamination loop.

iv) Thermal stability of different AVT chemicals, the nature of their decomposition products, the growth of impurity concentration and its impact on the various chemical equilibria existing in steam generator will be investigated.

v) High temperature corrosion potential of steam generator tubes and quality of blow down water under different levels of impurity ingress will be measured.

vi) Effect of flow restriction on steam generator tube corrosion, denting of steam generator tubes, specific attack at tube bends and tube to tube sheet joints will be investigated under off normal water chemistry conditions.

C. Biofouling Test Facility

Objectives

The project has as its objective a detailed study of all the
relevant aspects of biofouling (macrofouling as well as slime formation) and associated corrosion phenomena occurring in power plant systems. The study is expected to help combat more efficiently the problem being experienced at MAPS and also improve the design and operational procedures for seawater system in PFBR.

Description

The test facility consists of a series of seawater subsystems fed from a common intake. These are: (a) a model cooling water intake tunnel simulating the MAPS intake tunnel, (b) a heat treatment tunnel, (c) a toxicity experiment facility, (d) an aquarium section, (e) a test coupon module section for corrosion studies and (f) a condenser test section. Moreover, it will also have a raw water section with a model cooling tower to address problems related to recirculating systems. When completed, this facility will be the only one of its kind in the country.

Current status

The design part of the test facility and the building to house it is completed. MAPS authorities have agreed to provide the space required to locate the facility as well as meet the electrical power requirements. The construction of the building is expected to start shortly.

Proposed experimental work

A detailed outline of the experiments to be carried out has been prepared in consultation with power plant engineers. It is envisaged that all the relevant aspects of biofouling and fouling-induced corrosion will be studied with emphasis on the
basic features involved so as to identify critical areas amenable to interference. The experiments have been carefully drawn up to provide answers in respect of:

(a) biofouling build-up under varying conditions of substratum characteristics and flow regimes.

(b) response of fouling community to physical (heat treatment) and chemical (various biocides) control measures.

(c) physiological response of non-target organisms to effluents.

(d) dynamics of slime formation and initiation and progression of microbiologically influenced corrosion in test condenser tubes.

(e) water quality deterioration, scaling, corrosion and their control in recirculating systems.
STAFF CHART (As on 31-12-1992)
Dr P.N. Moorthy (Head of the Division)

**Reactor Systems Studies Section**
Section Head: Dr P.N. Moorthy
- Dr P.N. Moorthy (G)
- Dr G. Venkateswaran (SF)
- Dr D.B. Naik (SE)
- Shri A.S. Gokhale (SD)
- Shri C.K. Vinay Kumar (C)
- Shri G.R. Dey (SC)
- Dr (Smt) G. Visalakshi (SFI)
- Dr B.Yuvaraju (SC)
- Or K.Kishore (T/E)
- Dr V.Raishesh (SC)
- Dr S.B. Sriustm (SC)
- Or J.It. Iyer (SC)
- Dr N. Moorthy (SF)
- Shri B.P. Pillai (SE)
- Shri S.B. Karveer (SD)

**Structural & Inorg. Chem. Section**
Section Head: Dr U.R.K. Rao
- Dr U.R.K. Rao (SG)
- Dr L.U. Joshi (SF)
- Dr A.K. Sriramam (SE)
- Dr A.K. Tyagi (SD)
- Dr (Smt) B.N. Wani (C)
- Sat S.J. Patwe (SA/C)
- Shri B.R. Ambekar (T/G)
- Shri P.S. Naithan (SF)
- Shri M. Mathews (SC)
- Shri V.S. Jakkal (SF)
- Shri K.V. Muralidhara (ISE)

**Water & Steam Chemistry Laboratory**
Section Head: Dr P.K. Nathur
- Dr P.K. Nathur (SG)
- Shri S. Venurupan (SD)
- Shri M.S. Eswaran (SC)
- Shri V.S. Satyaseelan (SA/C)
- Shri P. Madasamy (SA/B)
- Shri T.V. Padmakumar (SA/B)
- Shri A. Kuresan (T/D)
- Shri C. Solomon (T/B)
- Dr K.K.K. Nair (SF)
- Shri K.K. Satpathy (SD)
- Dr V.P. Venugopalan (SD)
- Shri T.S. Rao (SA/C)
- Dr S.V. Harasstrim (SF)
- Shri S. Rangarajan (SD)
- Shri M.P. Srinisvanan (SD)
- Shri V.K. Mohan (SC)
- Shri A.L. Rufus (SC)
- Shri A.C. Kumbhar (SA/B)
- Shri V.T. Apar (SA/B)
- Shri V.K. Gupta (SA/B)
- Shri Y.V. Harinath (SA/B)
- Shri M.K. Rehman (SA/B)

**High Temperature & Solid State Chemistry Section**
Section Head: Dr S.R. Dharvadkar
- Dr S.R. Dharvadkar (SG)
- Dr G. Chattopadhyay (SF)
- Dr A.R. Paul (SF)
- Dr S.N. Tripathi (SF)
- Dr (Smt) S.R. Bhardvaj (SE)
- Dr P.N. Nanboodiri (SE)
- Dr K.N.G. Kaimal (SD)
- Dr A.B. Phadnis (SD)
- Shri A.S. Kerker (SA/D)

<table>
<thead>
<tr>
<th>SCIENTIFIC STAFF</th>
<th>TECHNICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>S01 (G)</td>
<td>1</td>
</tr>
<tr>
<td>S01(SG)</td>
<td>4</td>
</tr>
<tr>
<td>S01(SF)</td>
<td>13</td>
</tr>
<tr>
<td>S01(SE)</td>
<td>6</td>
</tr>
<tr>
<td>S01(SD)</td>
<td>10</td>
</tr>
<tr>
<td>S01 (C)</td>
<td>4</td>
</tr>
<tr>
<td>S01(SC)</td>
<td>5</td>
</tr>
<tr>
<td>S01(SB)</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>44</strong></td>
</tr>
</tbody>
</table>

**Administrative & Auxiliary**
- Shri P.V. Potdar
- Shri R. Gopinath
- Sat. Sodha Ranganathan
- K.P. B.V. Vastav
- Shri R. Veerasingan
- Shri E. Sundararajan
- Shri K. Ramachandran
- Sat. S. Venkatesh

**Summary**
- Total Staff Strength: 67