Preparation, Optimization/Characterization and Ion-Exchange Behaviour of V(II) Formulations

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Abstract

The low oxidation state metal ion, V^{2+} being a strong reducing agent can be formulated/complexed with suitable chelating agents to obtain a significant dissolution (reductive) of iron oxides, commonly found on the primary system surfaces (iron base alloys) of water-cooled nuclear reactors. The relative strength of the complexes of V^{2+} (as formate) with different chelating agents, L such as picolinic acid, EDTA and citric acid is studied by measurements of redox potential and UV-Visible spectra. The decay kinetics of the reduction of water by V(II)-picolinate i.e. V^{2+} to V^{3+} conversion under deaerated condition was estimated using redox potential and decay was found to follow two stages of first order kinetics with a faster initial stage \( k_1 = 3.45 \times 10^{-3} \text{ min}^{-1} \) and a slower second stage \( k_2 = 3.84 \times 10^{-4} \text{ min}^{-1} \). The cation and anion exchange resin behaviour of the complexes/formulations in their different oxidation states with their derived species is reported and the V(III)-picolinate is shown to exist as an anionic species in formate medium. The use of V(II)-EDTA and V(II)-citrate for dissolution has an advantage as their oxidation to V(III) stage at concentrations > 7mM has not resulted in any precipitation/crystallization unlike in the case of V(II)-picolinate.

Introduction

The chemical decontamination of primary coolant circuit in water-cooled nuclear power reactors involves the dissolution of corrosion films (Ni, Cr-substituted as well as simple iron oxides) accumulated on the structural surfaces. The Cr-containing iron oxides are not easily amenable for dissolution in conventional organic acid based formulations like citric acid-EDTA-ascorbic acid (CEA) mixture. However, low oxidation state metal ions (LOMI) such as V^{2+} and Cr^{2+} in presence of suitable chelating agents are known to be very strong reducing agents (rapid kinetics) towards the dissolution of such oxide matrices. Normally V(II) based LOMI formulations involving V(II)-picolinate is employed for such purposes. Use of V(II) picolinate complex is limited to concentration levels below 7 mM. Above this concentration level, V(III) picolinate (which is generated either during reductive dissolution of corrosion films accumulated on structural surfaces or some times by air oxidation due to system air leaks) precipitates/crystallizes out. The use of EDTA and citric acid as complexing agents can overcome such solubility problems. The electrochemical method of preparing V(II) enables the generation of composition specific formulations, which is an important consideration towards base material compatibility aspects in real system applications. The relative stability of electrochemically prepared V(II)-picolinate, V(II)-EDTA and V(II)-citrate complexes/formulations as derived from the redox and UV-Visible spectra are reported in this paper. The behaviour of these complexes in their different oxidation states on the conventional ion-exchange resin is studied, and the derived species getting sorbed is reported. The detailed studies on the dissolution of Cr-substituted oxides in these formulations are published elsewhere.

Experimental Set Up

Electrochemical Assembly: A flat bottomed glass vessel of 500 mL capacity
was used for preparing $V^{2+}$ (as formate). Fig. 1 shows the electrode compartments and its power supply unit as well as arrangement for cathode/solution potential measurements. The cylindrical Pt gauze was made as anode, and Hg pool served as cathode. A sintered glass disc separated the anode and cathode compartments. A saturated calomel electrode (SCE) was used as reference electrode.

![Electrochemical assembly for the preparation, and online estimation of $V(II)$ formate](image)

**Table 1: The optimized parameters for the electrochemical generation of $V(II)$ formate**

<table>
<thead>
<tr>
<th>Catholyte, NaVO$_3$ pH 2.8</th>
<th>HCOOH</th>
<th>Current</th>
<th>Voltage</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mM</td>
<td>2.0 M</td>
<td>80 mA</td>
<td>40 V</td>
<td>60</td>
</tr>
<tr>
<td>11 mM</td>
<td>2.6 M</td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>22 mM</td>
<td>3.5 M</td>
<td></td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>44 mM</td>
<td>4.0 M</td>
<td></td>
<td></td>
<td>90</td>
</tr>
</tbody>
</table>

**Electrolysis:** The electrolysis was carried out after charging required amounts of catholyte and anolyte. In cathode compartment a known amount of aqueous NaVO$_3$ in formic acid media ($pH \sim 2.8$) was placed, while in the anode compartment only formic acid of appropriate concentration was taken. Before starting the electrolysis the solutions (both anolyte and catholyte) were kept for deoxygenating ca.~30 min using high purity N$_2$ gas (scrubbed through V$_2^+$ trap generated by Zn-amalgum in HCl) and N$_2$ bubbling was continued throughout the electrolysis. The concentration of formic acid (anolyte), cell-current, cell-voltage and time required for completion of electrolysis (Table 1) to obtain $V^{2+}$ (as $V^{II}(HCOO)_2$) in the concentration range of 4 - 44 mM were optimized/standardized from the initial experiments. The optimization was done by number of initial trial experiments based on the stoichiometric amount of formate ions required as well as the reduction potentials reported in the literature$^7$ for the reduction of vanadium species.

**Estimation of $V(II)$-formate:** The electro-generation of $V^{2+}$ species was confirmed by online redox potential ($\sim -0.580$ V vs. SCE) measurements. During electrolysis, the solution was kept circulating from the vessel through a burette using a peristaltic pump. This arrangement helped in titrating the solution periodically against standard KMnO$_4$ solution to estimate the extent of $V^{2+}$ generation. The oxidation of $V^{2+}$ by permanganate can be represented as,

$$5V^{2+} + 3MnO_4^- + 24H^+ (10\% H_2SO_4) \rightarrow 5V^{5+} + 3Mn^{2+} + 12H_2O$$

The electrolysis proceeded with the accompanying colour changes viz. yellow, blue, green and purple for $V(V)$, $V(IV)$, $V(III)$ and $V(II)$ respectively during electrolysis.

**Estimation free formic acid:** The total formic acid content was estimated at the end of the electrolysis by passing the sample through the strong acid cation exchange resin. The eluate was titrated against standard NaOH solution using phenolphthalein indicator. The free formic acid was calculated from the total formic acid by subtracting two times the $V^{2+}$ concentration and the sodium concentration from the initial sodium metavenadate used for the preparation of $V^{II}$ (Table 2).
Table 2: Composition of V(II) formulations (in mM) containing stoichiometric amount of L for the dissolution of 20 at.% csh/csm

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>3.0±0.3</td>
<td>4.0±0.3</td>
<td>3.6±0.3</td>
<td>2.6±0.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>93</td>
<td>31</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td>11</td>
<td>114</td>
<td>38</td>
<td>38</td>
<td>39</td>
</tr>
<tr>
<td>22</td>
<td>147</td>
<td>49</td>
<td>49</td>
<td>43</td>
</tr>
</tbody>
</table>

*equivalent to 22 mM iron and ~5.5 mM Cr (from Fe_{1.6}Cr_{0.4}O_{3}/Fe_{2.4}Cr_{0.8}O_{4}) in 200 mL formulation (see ref 5).

Formulation/Complexation of V^{2+} species: After confirmation and estimation of V^{2+} species, the electrolysis was stopped and the Hg (cathode) was removed carefully (through the outlet provided with the flask). The V^{2+} formic acid thus generated was then made to complex with different chelating agents viz. picolinic acid (H$_3$Pic), EDTA (disodium salt, Na$_2$EDTA) and citric acid (C$_6$H$_8$O$_7$). The EDTA and citric acid were added directly in to the cell containing V(II) formate. However, the picolinic acid required to complex with V^{2+} was neutralized (in order to provide the ligand in readily complexable form) with NaOH separately in a deaerated aqueous medium before its addition. In all the cases, stoichiometrically excess (w.r.t V^{2+}) amounts of chelating agent, L viz. H$_3$Pic, Na$_2$EDTA and C$_6$H$_8$O$_7$ were added. Table 3 shows the composition of V(II) based formulations which have been employed in the dissolution studies of Cr-substituted iron oxides. The amount of chelating agent provided in each case is stoichiometrically equivalent to that required for complexation with V^{2+} species as well as Fe and Cr from the oxide ca. 20 metal atom% Cr-substituted hematite/magnetite (as a typical case).

Dissolution behaviour: Fig. 2 shows the typical dissolution profiles of Cr-substituted hematite/magnetite in V(II)-EDTA and CEA (citric acid-EDTA-ascorbic acid) formulations. The details of experiment, and the determination of dissolution rate coefficients using general kinetic equation applicable for polydispersed particles are reported. It is observed that the Cr substitution in hexagonal lattice (α-Fe$_2$O$_3$) has hindered the dissolution to a greater extent than that observed when Cr is substituted in cubic lattice (Fe$_3$O$_4$). Using CEA, the complete dissolution of simple iron oxides viz., α-Fe$_2$O$_3$ and upto 10% Cr-substituted magnetite can be obtained to the reductive mechanism of internally generated (during the course of dissolution) Fe(II)-EDTA. However, when Cr is substituted to the extent of >10 at%, there was no dissolution even on employing higher concentrations of CEA. As shown in Fig.2, vanadous formulation, V(II)-EDTA has resulted higher dissolution when compared to CEA, and there is a higher dissolution in the case of csm. This observation documents the advantage of employing vanadous formulations over conventional formulations like CEA in dissolving Cr-substituted iron oxides encountered on the structural surfaces of water-cooled nuclear reactors.
**Ion-exchange behaviour**: During this particular study, the L was added equivalent to the stoichiometric complexation of V(II) alone and no extra L (free L) was provided. The V(II)-L (formic acid, picolinic acid, EDTA and citric acid) were passed through strong acid cation and/or anion exchange resin (polystyrene based gel type resin). The resin bed was regenerated (by 5% H₂SO₄ or NaOH) freshly and deoxygenated by circulating deaerated water before passing the V(II)-L. For this purpose, a closed loop was setup from electrolytic cell and resin column with the help of peristaltic pump. Uniform flow rate, 5mL/min was maintained in each case. The oxidized forms of V(II)-L viz., V(III) (IV) (V)-L were obtained on controlled air oxidation of V(II)-L for which the conversions were monitored by redox potential measurements.

**Results and Discussions**

**Electrochemical Generation of V²⁺**: The vanadous ion, V²⁺ was prepared as V(II) formate by the electrochemical reduction over the surface of Hg, using deoxygenated aqueous solution containing required amounts of sodium metavanadate (NaVO₃) and formic acid at pH 2.8. The cell parameters such as current, voltage and duration of electrolysis are shown in Table 1. During electrolysis, the step-wise reduction of VO₂⁺ to V²⁺ can be represented by the following equations (V versus SHE).

\[
\text{NaVO}_3 \rightarrow \text{Na}^+ + \text{VO}_3^- \quad \text{on ionization}
\]

\[
\text{VO}_3^- + 2\text{H}^+ \rightarrow \text{VO}_2^+ + \text{H}_2\text{O} \quad \text{chemical process}
\]

\[
\text{VO}_2^+ + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{V}^2+ + \text{H}_2\text{O}, \quad E^0 = 1.00\text{V}
\]

... (1)

VO²⁺ directly goes to V²⁺ irreversibly as

\[
\text{VO}_2^+ + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{V}^2+ + \text{H}_2\text{O} \quad ... (2)
\]

Also, V²⁺ thus generated reduces VO²⁺ to V²⁺ easily and in the process gets oxidized to V³⁺ as

\[
\text{V}^2+ + \text{VO}_2^+ + 2\text{H}^+ \rightarrow \text{V}^3+ + \text{V}^2+ + \text{H}_2\text{O} \quad ... (3)
\]

Then V³⁺ from Eq. (3) was reduced to V²⁺ as

\[
\text{V}^2+ + \text{e}^- \rightarrow \text{V}^2+, \quad E^0 = -0.255\text{V}
\]

... (4)

Due to H⁺ consumption during electrolysis, the initial pH (2.8) of catholyte was increased slightly to pH 3.0 at the end of electrolysis. In anode compartment the decomposition of water resulted in the liberation of O₂ during electrolysis and in order to improve the conductivity of the solution, an appropriate amount of formic acid was placed. Whenever the formic acid was not sufficient (during the initial experiments), a black precipitate of vanadic oxide, which is the hydrolysis product of vanadium was noticed. Monitoring the solution potential on Pt electrode helped in following the reduction process during electrolysis. The yellowish orange VO₂⁺ turns to sky blue colour of VO²⁺ which before going to the purplish violet colour of V³⁺ goes through a dark blackish green stage showing the formation of V³⁺ also in the solution according to the Eq. (3). The variation of cathode potential and solution potential during the time of electrolysis in a typical case of 11 mM is shown in Fig. 3.

![Fig. 3: Variation of cathode/solution potential with time during the electrogeneration of 11 mM V²⁺ (as formate) from aqueous sodium metavanadate in formic acid buffer (pH 2.8).](image-url)

The electrolytic generation of V(II)-picolinate and its application in the decontamination of BWR surfaces has been presented previously from our laboratory. During the same study, E_{1/2} was found to be -1.32V (vs. SCE) and the potential corresponding to the limiting diffusion current is -1.4 to -1.6V using DC polarogram. In the present case also a cell of ~40V yielded a cathode potential of ~-1.55V in the later stage of electrolysis. Also, the V²⁺ could be generated.
with the desired conditions in the concentration range of 4 to 44 mM. During the course of electrolysis, the cathode potential (Fig 2) was found to decrease in the first phase (lasting ~ 10 min), there was a slight increase and thereafter it decreased slowly reaching a plateau value of ~ -1.55V. The increase of cathode potential in the mid-way of electrolysis indicates the formation of V^{5+} during the process of reducing VO^{2+} by V^{2+} according to Eq. (2).

\[ V(II)-FA^{+} \rightarrow V(II)-Formate \]
\[ V(II)-Pi,alin \]
\[ E_V = V(II)-EDTA \]
\[ V(II)-Citrate \]

Fig. 4: Variation of solution potential for V(II)-L as a function of time in de-aerated followed by aerated condition at 353 ± 5 K.

On providing chelating agents, L viz. picolinic acid, EDTA and citric acid into the V(II) formate solution showed a negative shift in solution potential (Fig. 4). This is a clear indication of complex formation between V(II) and L. Relatively more potential shift was observed (Fig. 4, at t = 0) in case of EDTA and picolinic acid compared to citric acid, indicating their better complexing ability. This observation is in agreement with the UV-Visible spectra, which showed a blue shift as the ligand was changed successively from formic acid to citric acid to picolinic acid, and to EDTA (Fig. 5). The choice of L was based on the various dissolution studies reported in the literature.²

**Stability of V(II)-formulations**: Solution potential measurements using a Pt electrode against SCE were employed to assess the stability of V(II)-L (L = picolinic acid, EDTA or citric acid). Vanadous ion is very easily oxidized by exposing the solution to air (4V^{2+} + O_2 + 4H^+ \rightarrow 4V^{3+} + 2H_2O). The extent of oxidation was assessed when a typical concentration (ca. 11mM) of the formulation was kept stirred magnetically at 353 ± 5 K for about 6 h under deoxygenated condition using high purity nitrogen gas. Fig. 4 show the variation in the redox potential with time of V(II)-L under deaerated and aerated conditions. The initial negative shift \((t = 0)\) of redox potential upon adding different L to V(II)(as formate) under deaerated conditions was in the order: picolinate > EDTA > citrate > formate showing the chelating ability of the complexes as formate < citrate < -EDTA < picolinate. The V(II)-L (L = picolinate, EDTA and citrate) formulations upon storage under deaerated conditions (Fig. 4) showed a positive potential shift of ~ 25 mV in 6 h duration suggesting the reduction of water by the reaction \((V^{2+} - L + H^+ \rightarrow V^{3+} - L + \frac{1}{2} H_2)\) thereby contributing to the oxidation of V(II). Converting the potential values into
concentrations using the Nernst equation, the decay of \([V(II)]\) with time was computed. Fig. 6 shows the decay kinetics in a typical case of V(II)-picolinate when the solution was kept stirred under deaerated condition at 353±5 K. A two stage first order kinetics with a fast initial stage showing a rate constant \(k_1 = 3.45 \times 10^{-3} \text{ min}^{-1}\) and a slow second stage having a \(k_2 = 3.84 \times 10^{-4} \text{ min}^{-1}\) is observed. The lower rate constant in the second stage is probably due to V(III) build up in solution resisting the further decay of V(II). Since the potential shift observed in case of other two chelating agents is of same magnitude (< 30 mV) the rate constants for their decay are expected to be the same. However, when N\(_2\)-bubbling was stopped, all the formulations got oxidized V(III)-L in < 5 min. The further air oxidation leading to V(IV) state took ~ 15 min in case of EDTA and citrate. While picolinate and formate took ~ 90 min and 150 min respectively. This observation is of importance with respect to dissolution of oxides in these formulations as the V(III)-L (EDTA and citrate) can also serve as internally generated reducing agents for further dissolution unlike V(III)-picolinate whose oxidation appears to be kinetically hindered. In no case, V(V) state was reached even after a sufficient exposure to air ~ 6 h.

In the case of V(II)-picolinate when the concentration was >7 mM, the air oxidation over a period of time > 5 h resulted in precipitation as brick-red crystals due to poor solubility of V(III)-picolinate. Although, its effect is insignificant on the dissolution of iron based oxides in a lab scale studies, it will be of serious concern during the large scale application such as reactor system decontamination as it can hinder the dissolution by forming a protective layer (of fine crystals) on the underlying oxide surface at the oxide-solution interface. Also, it may require lot of washings to bring the system to normalcy for operation. In this regard, however, the other two formulations, V(II)-EDTA and V(II)-citrate will be of advantageous when it is required to use higher concentration of formulations as they do not pose any such type of precipitation or crystallization ca, in the concentration range of 4 to 44 mM prepared in this study.

UV-Visible spectra: The UV-Visible spectra of pure V(II)-formate showed a \(\lambda_{\text{max}}\) at 570nm. When different chelating agents viz. citric acid, picolinic acid and EDTA were added, the maxima shifted to 550, 510 and 440 nm respectively (Fig. 5). The shift in \(\lambda_{\text{max}}\) towards blue region suggests the relative strength of complexes in the order as V(II)-formate < citrate < picolinate < EDTA. This is in corroboration with the inferences obtained from initial shift in redox potential measurements (Fig. 4). Fig. 5 shows the absorption maxima values for V(III)-L also since a small fraction (~10%) of V(II)-L got oxidized to V(III) state during spectral measurements. The \(\lambda_{\text{max}}\) values of vanadium species at different oxidation states are also shown in Table 3. The reported stability constants\(^7\), log \(K\) of V(II)-EDTA and V(II)-picolinate of 12.7 and 12.8 respectively lend support to the conclusion reached in this study from the spectral data are in agreement with the above
observations. Though, the stability constant value of V(II)-citrate is not available, and VO^{2+}-citrate is reported to have a log K of 8.8, from the present study it is expected that citric acid forms relatively weaker complex with V(II).

**Ion-exchange behaviour**

The decontamination is generally followed by the removal of all the chemical constituents of the decontaminating formulations. Passing the dissolved species (aqueous) through cation and/or anion exchange resin normally does this exercise. The VO^{2+} species after reducing the ferric oxides (corrosion products) can go to higher oxidation state of +3 and +4 and some times to even +5 due to the increase in dissolved oxygen content in the system. Hence, the ion exchange behaviour of these complexes of vanadium with citric acid, EDTA and picolinic acid becomes important when spent decontamination solution is treated by synthetic organic ion exchange resin as a part of waste solidification. Thus in this study, all these formulations at different oxidation states of vanadium (higher oxidation states were obtained by air oxidation of V^{2+} formulations) were passed through strong cation and strong anion exchange resin independently. It was found that the anion resin picked up all these species while the V^{2+}, V^{3+} and VO^{2+} excepting VO_{2}^{+}-citrate complexes were dissociating on the cation exchanger. The fact that, the V(III)-picolinate which is usually referred as V(pic)$_3^-$ (neutral complex), gets sorbed on the anion exchanger shows that it is existing as anionic complex in formate medium and may be represented as [V(pic)$_3$(HCOO)$_3$]. Existence of vanadium species in different oxidation states with different chelating agents and their sorption behaviour on the cation/ anion exchanger is shown in Table 4. Thus the ion exchange behaviour of V(II) formulations is highly encouraging for their application in nuclear reactors as a decontamination formulations.

**Table 3: Absorption maxima, $\lambda_{max}$ (in nm) of the vanadous formulations at different oxidation states**

<table>
<thead>
<tr>
<th>Chelating agent</th>
<th>Vanadium species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V(II)</td>
</tr>
<tr>
<td>Formic acid</td>
<td>570</td>
</tr>
<tr>
<td>Picolinic acid</td>
<td>510</td>
</tr>
<tr>
<td>EDTA</td>
<td>440</td>
</tr>
<tr>
<td>Citric acid</td>
<td>550</td>
</tr>
</tbody>
</table>

**Table 4: Ion-exchange (IX) behaviour of vanadous based formulations and their oxidized forms on polystyrene based strong acid cation and anion exchange resin**

<table>
<thead>
<tr>
<th>o.s</th>
<th>Metal ion species</th>
<th>Likely metal ion species in the complexed form with different chelating agents</th>
<th>IX behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Picolinic acid</td>
<td>EDTA</td>
</tr>
<tr>
<td>+2</td>
<td>$V^{2+}$</td>
<td>$[V^{2+}$(pic)$_3$]^{-}$</td>
<td>$[V^{2+}$-EDTA]$^2$-$^{-}$</td>
</tr>
<tr>
<td>+3</td>
<td>$V^{3+}$</td>
<td>$[V^{3+}$(pic)$_2$(HCOO)$_2$]^{-}$</td>
<td>$[V^{3+}$-EDTA]$^{-}$</td>
</tr>
<tr>
<td>+4</td>
<td>$VO^{2+}$</td>
<td>$[VO^{2+}$(pic)$_3$]^{-}$</td>
<td>$[VO^{2+}$-EDTA]$^2$-$^{-}$</td>
</tr>
<tr>
<td>+5</td>
<td>$VO_{2}^{+}$</td>
<td>$[VO_{2}^{+}$(pic)$_3$]$^{2^{-}}$</td>
<td>$[VO_{2}^{+}$-EDTA]$^{3^{-}}$</td>
</tr>
</tbody>
</table>

Here (√) and (x) symbol indicates the removal and non-removal by resin respectively.

o.s : oxidation state
Conclusions

The relative complexing ability of chelating agents with \( V^{2+} \) (as formate) under deoxygenated condition follows the order can be shown as \( V(II)\)-formate < \( V(II)\)-citrate < \( V(II)\)-picolinate \( \equiv \) \( V(II)\)-EDTA. Their stability in aqueous medium under deoxygenated condition followed two-stage decay kinetics. The ion exchange behaviour of the vanadium complexes viz. \( V(II)\)-picolinate, \( V(II)\)-EDTA and \( V(II)\)-citrate and their oxidized species shows that they can be picked up both on anion and cation exchange resin column. The existence of \( V(III)\)-picolinate as an anionic species is shown by this study.

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References


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About the authors ...

Dr J. Manjanna, (M. Sc., Ph.D. - Industrial/ Applied Chemistry, Kuvempu University) was a Jr/ Sr. Research Fellow in Applied Chemistry Division, BARC, under BRNS/DAE Research project (Oct, 1997 to Sept, 2000), which formed part of his Ph.D. work. Currently (from Jan, 2002), he is a Dr. K. S. Krishnan's Research Associate in the same Division. He is a recipient of the "Young Scientist award" (2000) from the Indian Council of Chemists. His research activities are related to water chemistry of nuclear reactor systems. He is involved in the preparation, characterization and dissolution kinetics of corrosion products (oxides, powders/ scales) in reductive/complexing formulations. Presently, he has some 10 journal publications to his credit.

Dr G. Venkateswaran, (M. Sc Madras University, Ph.D. Physical chemistry, University of Mumbai) is currently heading the Reactor System Studies Section of Applied Chemistry Division. He joined BARC after graduating in Chemistry from 14th batch of Training School. He has over 30 years of research experience in the field of water chemistry in nuclear reactor systems. His research interests include studies on the chemical decontamination of nuclear reactors, oxide dissolution, metal-ion passivation of reactor system structural surfaces, fuel performance evaluation and ion-exchange behaviour of suspended and dissolved species, etc. Recently (2000) he led the team in successfully carrying out the decontamination of clean-up system of TAPS and now he is preparing for full system decontamination of the same unit. He has over 110 publications to his credit, which include journals, conference/symposia papers, and BARC reports.