



## **Technical Articles**

 Investigation of Ln(III) Coordination in a Combined Extractants System using Luminescence Spectroscopy

#### Young Officer's Forum

 Thermochemical properties over LiCI-KCI-UCI<sub>3</sub> ternary salt system: High Temperature Mass Spectrometric Study

#### Young Researcher's Forum

 Molten Salt Synthesis: A Versatile Route to Phase Pure PdCoO<sub>2</sub>

### **IGCAR Lecture Series**

- Advances in Welding Technologies for Applications in the Nuclear Industry
- An Overview of Radiation Damage Studies at MSG
- Comprehensive Monitoring of Hydrogen for Sodium Systems
- Emerging opportunities at the upcoming Atal Incubation Centre: AIC-IGCAR-FAST-Foundation
- Decision Support System ONERS for Nuclear Emergency Response
- Independent Verification & Validation: Concepts & Experiences from V&V of PFBR I&C Systems
- CENTRAL WORKSHOP DIVISION Fulfilling In-House Manufacturing Needs of IGCAR and Other DAE Units

### News and Events

- 32<sup>nd</sup> Prof. Brahm Prakash Memorial Materials Quiz (BPMMQ) programme
- BITS Practice School
- Graduation Function of the 18th Batch of Trainee Scientific Officers of BARC Training School at IGCAR

Awards, Honours and Recognitions

Bio-diversity @ DAE Campus, Kalpakkam









INDIRA GANDHI CENTRE FOR ATOMIC RESEARCH http://www.igcar.gov.in/lis/nl141/igc141.pdf

ю

h



Ъ

## Dear Reader

## Greetings

It is my pleasant privilege to forward the latest issue of IGC Newsletter (Volume 141, October 2024, Issue 3). I thank my team for their timely inputs, cooperation, and support in bringing out this issue.

The technical article of this issue "Investigation of Ln(III) Coordination in a Combined Extractants System using Luminescence Spectroscopy" is by Dr. Alok Rout and Colleagues from MCMFG, IGCAR.

Young Officer's Forum features an article on "Thermochemical properties over LiCI-KCI-UCI<sub>3</sub> ternary salt system: High Temperature Mass Spectrometric Study" by Dr. Venkata Trinadh Vinjavarapu from FCHD, MC&MFCG, IGCAR.

The article on "Molten Salt Synthesis: A Versatile Route to Phase Pure PdCoO<sub>2</sub>" by Ms. Lisa John, SRF from MCMFG, IGCAR is categorised as this issue's Young Researcher article.

The Lectures series articles on "Advances in Welding Technologies for Applications in the Nuclear Industry" by Dr. M. Vasudevan, MMG, "An Overview of Radiation Damage Studies at MSG" by Dr. Sandip Kumar Dhara, MSG, "Comprehensive Monitoring of Hydrogen for Sodium Systems" by Dr. Rajesh Ganesan and his colleagues of MC&MFCG, "Emerging opportunities at the upcoming Atal Incubation Centre: AIC-IGCAR-FAST-Foundation" by Dr. N. Subramanian, Incubation Centre, "Independent Verification & Validation: Concepts & Experiences from V&V of PFBR I&C Systems" by Ms. Saritha P. Menon & her colleagues of EIG, "CENTRAL WORKSHOP DIVISION - Fulfilling In-House Manufacturing Needs of IGCAR and Other DAE Units" by Shri Utpal Borah,& his colleagues of Central Workshop Division, ESG and "Decision Support System ONERS for Nuclear Emergency Response" by Dr. C. Venkata Srinivas, EAD, SQRMG are included in this Newsletter.

The Editorial Committee would like to thank all the contributors. We look forward to receiving constructive suggestions from readers towards improving the IGC Newsletter content.

We express our deepest gratitude to Director IGCAR for his keen interest and guidance.

With best wishes and regards, Shri J. Rajan Chairman, Editorial Committee, IGC Newsletter and Head, Scientific Information & Networking Division, IGCAR



## Dr. Alok Rout and Colleagues

Materials Chemistry and Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, Kalpakkam Tamil Nadu, India.



## Investigation of Ln(III) Coordination in a Combined Extractants System using Luminescence Spectroscopy

Post separation of U(VI) and Pu(IV) by PUREX (Plutonium Uranium Reduction EXtraction) process, the raffinate persisted is known as High Level Liquid Waste (HLLW) solution which contains minor actinides (MA), lanthanides and other fission products with the feed acidity of 3-4 M. To deal with this HLLW solution during the process of partitioning of trivalent lanthanides and actinides, the single-cycle methods for the separation of trivalent actinides are being regarded as the best suited alternative to the conventional twocycle process. In a single cycle process, a combination of neutral extractant with an acidic extractant is used for trivalent lanthanide/actinide (Ln(III)/An(III)) partitioning. The neutral extractant helps the extraction of both trivalent actinides (An(III)) and lanthanides (Ln(III)) and acidic extractant helps mutual separation during stripping of An(III) by using suitable aqueous complexing agents. A large number of extraction reports are available on the one cycle separation of Ln(III) and An(III) from the nitric acid using the combination of a neutral and acidic extractants. However, to support this solvent extraction results of the target metal ions, there are various spectroscopic techniques being employed which essentially pertain the basic insights into the metal ion coordination with the proposed ligands and their mode of complexation. Based on the functional moieties present in approaching extractants (neutral and acidic), the metal - ligand complex in the organic phase is formed which in turn decides the effectiveness of the extraction process. One such spectroscopic tool suited for the aforementioned application is the luminescence spectroscopy and is a potential tool for exploring the nature of the chemical environment of the target metalion. The local environment of Eu(III) (as the representative for Ln(III)/An(III)) in its complex form with the extracting moieties or in the aqueous phase can be probed from the absorption and luminescence spectra which basically gives the information about the fine structure and relative transition intensities. A luminescence spectrum (or emission spectrum) is recorded by fixing the excitation wavelength, while the emission wavelength is scanned. Generally, Eu(III) compounds exhibit intense photoluminescence, due to the  ${}^5D_{_0} \rightarrow {}^7F_{_J}$  transitions (J=0–6). Out of these transitions,  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  are the transitions identified as the magnetic dipole and electric



Figure 1: The structure of T2EHDGA and D2EHPA.



Figure 2: Emission spectra of Eu(III) in the organic phase as a function of nitric acid concentration. Aqueous phase: 0.5 M to 3 M nitric acid +  $10^{-3}$  M Eu(III); Organic phase: 0.1 M T2EHDGA/n-DD; Emission spectra recorded with the excitation at 394 nm.

dipole transitions respectively and these transitions exhibit intense peak and are considered in identifying the chemical status and coordination behavior of the metal species. The transition,  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  is highly sensitive to the ligand field and is known as a hypersensitive transition (occurs around 615 nm) and its intensity changes upon the formation of the metal-ligand complex. The primary reason for this is the loss of the symmetry of Eu(III) aqua complex. In contrast to this, the intensity of  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition appeared at 592 nm, remains unchanged and is independent of the ligand field effect. Therefore, it is feasible to find out the information about the strength of Eu(III) complexation by observing the area ratio (or intensity ratio) between the two transition peaks which is otherwise known as the asymmetry ratio or AR value  $(A_2/A_1 \text{ or } I_2/I_1; \text{ where}$ 2 stands for  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition and 1 stands for  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition). In the present report, the mode and degree of coordination of Eu(III) with two different classes of extractants in a synergic extraction process has been accessed by Luminescence spectroscopy. T2EHDGA (N,N,N',N'tetra-(2-ethylhexyl)diglycolamide), a molecular extractant and D2EHPA (Di-(2-ethylhexyl)phosphoric acid), an acidic extractant were dissolved in n-Dodecane (n-DD) diluent and used as the extracting phase to extract Eu(III) from feed nitric acid phase. The structures of T2EHDGA and

D2EHPA are given in Figure

### Eu(III) luminescence in T2EHDGA (or D2EHPA)/n-DD

The emission spectra of loaded Eu(III) in 0.1 M T2EHDGA/n-DD extracted from different nitric acid concentration (0.5 M to 3 M) is displayed in Figure 2. The intensity of electric dipole transition around 615 nm increases sharply with an increase in the feed acidity and is more intense as compared to the corresponding magnetic dipole transition around 592 nm. An increase in AR values (from 2 to 2.9) with feed

acid strength indicates the changes in the local symmetry of Eu(III) during the formation of Eu(III) – T2EHDGA complex in a neutral solvation pathway. The corresponding life time ( $\tau$ ) value ranges between 1.2 ms and 1.9 ms suggesting the formation of inner-sphere complex by expelling out all the water molecules from inner-sphere of central Eu(III).

In a similar manner, the emission lines of Eu(III) in D2EHPA/ n-DD is shown in Figure 3. Since D2EHPA is an acidic extractant, the concentration of nitric acid was varied from 0.01 M to 1 M and it was found that the emission spectra are more intense and the intensity gradually decreases with an increase in nitric acid concentration. The corresponding AR values and ' $\tau$ '

values for 0.1 M D2EHPA/n-DD range from 2.58 to 1.48 and 1.8 ms to 1.9 ms respectively against the aqueous phase acidity change from 001 M to 1 M. While comparing the results of both Figures, it is interesting to note that the splitting pattern of  $(^{5}D_{0} \rightarrow ^{7}F_{2})$ hypersensitive transition of Eu(III) emission T2EHDGA in phase is different from that in D2EHPA This phase. observation reflects the characteristics of both the extractants and their mode of coordination approach towards Eu(III).

#### Technical Article

# Eu(III) luminescence in the combined extractants system

As discussed above, T2EHDGA is a neutral extractant while D2EHPA is an acidic extractant and due to this the mode of coordination with Eu(III) was observed to be completely different. To see their synergic effect on Eu(III) complexation, Eu(III) was extracted from 3 M nitric acid medium using the mixture of 0.1M T2EHDGA and 0.25 M D2EHPA in n-DD medium (the concentration was chosen based on the solvent extraction report on single cycle method of Ln(III)/An(III) separation) and the excitation spectra of Eu(III) in the extracted phase were compared with that in T2EHDGA phase without D2EHPA. Figure 4 displays the excitation pattern of Eu(III) in 0.1 M T2EHDGA/n-DD and 0.1 M T2EHDGA + 0.25 M D2EHPA/n-DD recorded at 394 nm monitoring the emission wavelength of 592 nm. It is noticed that in the case of the binary solution (mixture of two extractants), the excitation patterns are noticeably intense in contrast to that of 0.1 M T2EHDGA/n-DD.

These findings infer that there exists a synergic operation of T2EHDGA and D2EHPA in the complexation process and hence the metal – solvate species (metal-ligand complex formation) formed during the complexation process is stabilized more in the binary mixture than the individual solution (0.1 M T2EHDGA/n-DD). With this prospect, the emission



Figure 3: Emission spectra of Eu(III) in the organic phase as a function of nitric acid concentration. Aqueous phase: 0.01 M to 1 M nitric acid +  $10^{-3}$ M Eu(III); Organic phase: 0.1 M D2EHPA/n-DD; Emission spectra recorded with the excitation at 394 nm.





solvent

to

acid

on

understand

The

0.01

D2EHPA/n-DD

M to 1 M

of

and the extraction was

carried out using 0.1

M T2EHDGA + 0.25 M

6). The results are very

much appealing given the

fact that at low nitric acid

concentrations (0.01 M

and 0.1 M), the peak due

to  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition is

splitted into three different

peaks (610 nm, 615 nm,

and 620 nm). The peak

at 610 nm is more intense

which agrees to the fact

the main driving force for

the extraction at low acidity

is due to D2EHPA. The

(Figure

the

T2EHDGA

D2EHPA.

concentration

nitric acid was varied

from

spectra of loaded Eu(III) in the binary solution phase was recorded by varying the concentration of D2EHPA in the solution of 0.1 M T2EHDGA/n-DD to envisage the precise effect of D2EHPA (Figure 5). The emission spectra suggest that there is an increase in the intensity of the electric dipole transition with an increase in the concentration of D2EHPA from 0 M to 0.3 M in 0.1 M T2EHDGA/ n-DD phase. This indicates the simultaneous coordination of D2EHPA and T2EHDGA with Eu(III) that essentially raises the abundance of more metal - solvate species in organic phase and hence enhances the transition intensity. Another significant observation from Figure



Figure 5: Emission spectra of Eu(III)as a function of the concentration of D2EHPA in 0.1 M T2EHDGA/ n-DD. Aqueous phase: 3 M nitric acid + 10<sup>-3</sup> M Eu(III); Organic phase: 0.1 M T2EHDGA + (0 M - 0.3 M) D2EHPA/ n-DD; Emission spectra recorded with the excitation at 394 nm.

5 acquired is that the peak shape is entirely different from that noticed in Figure 2 and 3 which concludes the existence of synergic operation of both extractants in the complex formation with Eu(III).

#### Role of aqueous acidity phase on Eu(III) emission in combined system

Aqueous phase acid strength plays a crucial role in perturbing the extent of coordination

peak at 615 nm and 620 nm suggest the participation of T2EHDGA at low acidity, in the coordination process when it is with D2EHPA.

With an increase in nitric acid concentration, the peak height at 610 nm decreases and that of 615 nm and 620 nm increases and ultimately the peaks at 615 nm and 620 nm merges at 0.5 M nitric acid concentration to give an intense peak at 618 nm with a small soldier at 612 nm as noticed in Figure 5. The plausible reason for such peak shift could be due to the gradual involvement of T2EHDGA in the coordination process along with D2EHPA against an increase in nitric acid concentration. Further



Figure 6: Emission spectra of Eu(III)as a function of nitric acid concentration. Aqueous phase (0.01 M - 1 M) HNO, + 10<sup>-3</sup> M Eu(III); Organic phase: 0.1 M T2EHDGA + 0.25 M D2EHPA/ n-DD; Emission spectra recorded with the excitation at 394 nm.

increase in acid concentration up to 1 M results in a peak shape similar to that portrayed in Figure 5. These findings confirm that the effect of D2EHPA for complexation is more at low nitric acid and it decreases with an increase in the concentration of nitric acid and subsequently the effect of T2EHDGA dominates at higher acidity, thereby altering the shape of the hypersensitive transition. Overall, the present report offers an analysis method to reveal the mode of coordination and the extent of coordination of two different classes of ligands with Ln(III) and the type of complex formed during the extraction process.

Young Officer's Forum

Young Officer's \_\_\_\_Forum



Dr. Venkata Trinadh Vinjavarapu completed his Master's in Analytical Chemistry from Andhra University. He joined the Mass Spectrometric Studies Section, FCHD, MC&MFCG, IGCAR in 2014 after completing OCES-2013 in NFCC discipline from 57<sup>th</sup> batch of BARC Training School. He obtained a Doctoral degree in Chemistry from HBNI in 2022. Recipient of the Young Mass Spectrometrist Award 2019 from the Indian Society for Mass Spectrometry. He received 3 Best Poster awards and 1 Editor's Choice Best Paper Award. His field of research has been vaporisation thermodynamic studies using High-Temperature Mass Spectrometry.

## Thermochemical properties over LiCl-KCl-UCl<sub>3</sub> ternary salt system: High Temperature Mass Spectrometric Study

Vaporisation studies LiClover KCI-UCI, ternary salt system are of fundamental importance to the pyrometallurgical reprocessing of spent metallic nuclear fuel by employing molten salt electrorefining process. The mass spectrometric Knudsen effusion method is an important tool for study of equilibrium between condensed and gaseous species at high temperatures, investigation of the kinetics of heterogeneous reactions. High Temperature Mass Spectrometry (HTMS: Figure 1) is a hyphenated technique in which classical Knudsen effusion method coupled with sophisticated mass spectrometry facilitates a unique opportunity to ascertain the neutral vapour species and also to determine their partial pressures. The aim is to understand the vaporisation behaviour and properties of vapours at high temperature. The partial pressure measurements for individual species makes it possible to determine their thermodynamic properties as well as those of condensed the phases or of other gaseous species with which they are in equilibrium. This method has a wide dynamic range 10<sup>-6</sup> -10 Pa. The elements in the vapour phase may have valence markedly different from those in the condensed

phase and one of the problem in high temperature chemistry was to establish and characterise these through the identification of the species. Measurements of relative pressure and thus chemical activities can be readily made by this method and thermodynamic data are obtained for the condensed phases which may be difficult or tedious to obtain by the other methods.

LiCl(cr) (purity > 99%, M/s Fluka, Switzerland), analytical grade





KCI(cr) (purity > 99.8%, M/s Glaxo Laboratories, India) and uranium metal of nuclear grade (BARC, Mumbai, India) were used for the preparation of LiCI-KCI-UCI<sub>3</sub> with 4.46 wt.% UCI<sub>3</sub> (58.1 mol% LiCI -41.2 mol% KCI - 0.7 mol% UCI<sub>3</sub>). For each salt system (LiCI(cr), KCI(cr) and LiCI-KCI-UCI<sub>3</sub> with 4.46 wt.% UCI<sub>3</sub> (58.1 mol% LiCI - 41.2 mol% KCI - 0.7 mol% UCI<sub>3</sub>), about 200 mg of sample was taken in a zirconia Knudsen cell fitted with a zirconia lid. A typical vacuum of  $\sim$  3-4 x10<sup>-8</sup> Pa

#### Young Officer's Forum

maintained during the was vaporisation experiments. Samples were heated by bombarding with the electrons emitted from the two tungsten filaments surrounding the Knudsen cell assembly. The temperatures of sample were measured by a Type K (Chromel-Alumel) thermocouple which is in contact with outer tantalum cup. Hiden Analytical make Quadrupole Mass Spectrometer (Hiden HAL/3F RC 1001 PIC series, having mass range up to 1000 amu) was employed in the present study. The effusion flux was ionised by electrons of energy 13.2 eV (for LiCl and KCl vapour species over pure and ternary salt) and 28.2 eV (for UCl<sub>3</sub> vapour species over LiCI-KCI-UCI, system) at an emission current 100  $\mu$ A. The ions were mass filtered by using a quadrupole triple filter geometry and subsequent detection by a secondary electron multiplier operating in pulse ion counting mode (PIC). The pressure calibration constant (k') deduced from calibration experiments using pure silver was employed for converting the measured ion intensity data into partial pressure. k' was also derived using in-situ calibration from pressure dependent equilibrium constant.

<sup>7</sup>Li<sup>+</sup>, <sup>42</sup>LiCl<sup>+</sup> and <sup>49</sup>Li<sub>2</sub>Cl<sup>+</sup> were the major ionic species observed in the mass spectrum of equilibrium vapour

over pure LiCl(cr). <sup>39</sup>K<sup>+</sup>, <sup>74</sup>KCl<sup>+</sup> and <sup>113</sup>K<sub>2</sub>Cl<sup>+</sup> were the major ionic species observed over pure KCI(cr). 7Li+, <sup>42</sup>LiCl<sup>+</sup>, <sup>49</sup>Li<sub>2</sub>Cl<sup>+</sup>, <sup>39</sup>K<sup>+</sup>, <sup>74</sup>KCl<sup>+</sup>, <sup>113</sup>K<sub>2</sub>Cl<sup>+</sup>,  ${}^{273}\text{UCI}^+$ ,  ${}^{308}\text{UCI}_2^+$  and  ${}^{343}\text{UCI}_3^+$  were the major ionic species observed over LiCI-KCI-UCI, ternary salt system. No shutterable peaks were observed for trimeric, polymeric species over LiCI(cr), KCI(cr) and UCI<sub>3</sub> dimeric species over ternary salt. Ionisation efficiency curves for ions <sup>39</sup>K<sup>+</sup>, <sup>74</sup>KCl<sup>+</sup> and <sup>113</sup>K<sub>2</sub>Cl<sup>+</sup> were recorded over pure KCI(cr) as a function of electron appearance energies energy and were obtained from these plots by linear extrapolation method.

These plots are shown in Figure 2(ac). The appearance energies deduced for the ionic species over KCI(cr) are in good agreement with literature data. KCI<sup>+</sup> results from the simple ionisation of KCI(g) whereas K<sub>2</sub>CI<sup>+</sup> results from dissociative ionisation of  $K_2Cl_2(g)$ . Appearance energy of  $K^+$ obtained in the present study (10.5 eV) is greater than the first ionisation energy (4.3 eV) of K(g) indicating that K<sup>+</sup> is the fragment species and it originates from KCI(g) since the electron energy used (13.2 eV) is just below the fragmentation energy (13.3 eV) of dimer (Figure 2a). From massto-charge ratio (m/z) and appearance energies, the neutral species were deduced as KCI(g) and K<sub>2</sub>CI<sub>2</sub>(g) over pure KCl salt. The simplified ionisation pattern of alkali-halide vapours, by electron bombardment ionisation, which contains MX(g) and  $M_{2}X_{2}(g)$  can be written as  $M_{2}X_{2}(g)$ :  $M_{a}X^{+}$  and MX(g) :  $MX^{+}$  and  $M^{+}$ . In the case of pure LiCl(cr), based on the mass numbers of the major ionic species observed in the present study and appearance energies, LiCl(g) and Li<sub>2</sub>Cl<sub>2</sub>(g) were considered to be possible major vapour species. On the basis of neutral species over pure LiCl(cr) and KCl(cr), and from the mass numbers of ions, LiCl(g), Li<sub>2</sub>Cl<sub>2</sub>(g), KCl(g), K<sub>2</sub>Cl<sub>2</sub>(g) and UCl<sub>3</sub>(g) were considered to be possible major vapour species over LiCI-KCI-UCI, ternary salt. The ion intensities of 7Li<sup>+</sup>, <sup>42</sup>LiCl<sup>+</sup>, <sup>49</sup>Li<sub>2</sub>Cl<sup>+</sup>, <sup>39</sup>K<sup>+</sup>, <sup>74</sup>KCl<sup>+</sup>, <sup>113</sup>K<sub>2</sub>Cl<sup>+</sup>,  ${}^{273}\text{UCI}^+$ ,  ${}^{308}\text{UCI}_2^+$  and  ${}^{343}\text{UCI}_3^+$  were recorded as a function of temperature in the range of 715 - 913 K. Two runs were conducted for LiCl species over pure salt and ternary salt system. For KCl species, one run over pure salt and two runs over ternary salt were conducted. Pure silver was used for deducing pressure calibration constant.

The measured ion intensity of the species 'i' was converted to partial pressure using the following relation:

$$p_{i} = k'_{i} \cdot I_{i^{+}} \cdot T$$

$$k'_{i} = k_{i} / \{\sigma_{i} \cdot \gamma_{i^{+}} \cdot n_{i^{+}}\}$$

$$(1)$$

$$(2)$$

$$\mathbf{k}_{i}^{\prime} = \mathbf{k}_{j}^{\prime} \left\{ \frac{J}{\sigma_{i}} \right\} \left\{ \frac{J}{\gamma_{i^{+}}} \right\} \left\{ \frac{J}{n_{i^{+}}} \right\} \tag{3}$$

where j=Ag and i=LiCl, Li<sub>2</sub>Cl<sub>2</sub>, KCl, K<sub>2</sub>Cl<sub>2</sub> and UCl<sub>2</sub>.  $\vec{k}_{i}^{c}$ 



Figure 2: Ionisation efficiency curves of K<sup>+</sup>, KCI<sup>+</sup> and K<sub>2</sub>CI<sup>+</sup> recorded over KCI(cr)



Figure 3. Combined 2<sup>nd</sup> law plots of log(pi) vs 1/T for the all species recorded over LiCI(cr), KCI(cr) and LiCI-KCI-UCI<sub>3</sub> ternary salt using in-situ method.

pressure calibration constant; k is the instrument calibration constant; I<sup>+</sup> is the ion intensity of LiCl<sup>+</sup>, Li<sub>2</sub>Cl<sup>+</sup>, KCl<sup>+</sup>, K<sub>2</sub>Cl<sup>+</sup>, UCl<sub>3</sub><sup>+</sup>; T is the temperature in Kelvin;  $\sigma$  is the ionisation cross section;  $\gamma$  is the yield of secondary electron multiplier and n is the isotopic abundance.

In-situ determination of the instrument calibration constant is possible if a gas phase equilibrium between monomer and dimer species exists over the sample. From the knowledge of equilibrium constant for the reaction: dimer  $(A_2(g)) = monomer (A(g))$  (4)

Knowing the data of equilibrium constant  $k_p = \frac{p_{A_1}^2}{p_{A_2}}$  ionisation cross section, isotopic abundance and multiplier gain and from the measured ion intensities of monomer and dimer, the instrument constant was deduced by following equation

$$k = \frac{(\sigma_{A}}{(\sigma_{A2}} \frac{\gamma_{A}}{\gamma_{A2}} \frac{n_{A})^{2}}{r_{A2}} \frac{I_{A2}}{I_{A}^{2}} \frac{1}{T} K_{p}$$
(5)

Figure 3 shows the combined 2<sup>nd</sup> law plot of log(pi/Pa) vs 1/T for all the species obtained over LiCl(cr), KCl(cr) and ternary salt using in-situ calibration method. Table 1 shows the p-T relations deduced for various species over LiCl(cr), KCl(cr) and  $\text{LiCl-KCl-UCl}_3$  ternary salt from in-situ method. From the partial pressures, the equilibrium constant as well as enthalpy changes for the following heterogeneous reaction equilibria were evaluated by 2<sup>nd</sup> law methods:

LiCl(cr) = LiCl(g)	(6)
$2\text{LiCl}(\text{cr}) = \text{Li}_{2}\text{Cl}_{2}(g)$	(7)

KCI(cr) = KCI(g)(8)

 $2KCI(cr) = K_{2}CI_{2}(g)$ (9)

$$\log K_{n} = A/T + B \tag{10}$$

where

 $K_p = \left[\frac{p(products)}{p(reactants)}\right]^{\nu}; \text{ } p^{\circ} = 10^5 \text{ Pa}; \text{ } \text{A} = \frac{-\Delta_{\text{r}}\text{H}^{\circ}_{\text{Tm}}}{2.303 \times \text{R}}; \text{ } \text{B} = \frac{\Delta_{\text{r}}\text{s}^{\circ}_{\text{Tm}}}{2.303 \times \text{R}}$ 

Enthalpy changes of the reactions were also evaluated by using 3<sup>rd</sup> law method.

$$\Delta_{\rm r} {\rm H}_{298.15}^{\circ} = -T \left[ R \ln K_p + \Delta \frac{(G_T - H_{298.15})}{T} \right]$$
  
where  $\Delta_{\rm r} \frac{(G_T^{\circ} - H_{298.15})}{T} = \Delta_{\rm r} \frac{(H_T^{\circ} - H_{298.15})}{T} - \Delta_{\rm r} {\rm S}_{\rm T}^{\circ}$ 

is the change of the Gibbs energy function and can be obtained from Gibbs energy functions of the constituents involved in the reaction.

Dissociation energy of dimeric or polymeric species is of fundamental importance and thermochemical and spectroscopy methods are usually employed to deduce these data. In the present study, the dissociation equilibria of the following gas phase reactions were evaluated by using 2<sup>nd</sup> and 3<sup>rd</sup> law methods from the partial pressures of monomer and dimer species deduced over pure LiCl(Cr), KCl(cr) and ternary salt:

$$Li_{2}Cl_{2}(g) = 2LiCl(g); K = \frac{p_{LiCl(g)}^{2}}{p_{Li_{2}Cl_{2}(g)}} (12)$$
$$K_{2}Cl_{2}(g) = 2KCl(g); K = \frac{p_{KCl(g)}^{2}}{p_{K_{2}Cl_{2}(g)}} (13)$$

The enthalpies of following pressureindependent reactions were also evaluated by using 3<sup>rd</sup> law method. The equilibrium constants for these reactions are given below:

$LiCl(cr) + LiCl(g) = Li_2Cl_2(g);$	К	=	$\frac{p_{Li_2Cl_2(g)}}{a_{LiCl(cr)} \times p_{LiCl(g)}}$	(14)
$KCl(cr) + KCl(g) = K_2Cl_2(g);$	K	=	$= \frac{p_{K_2Cl_2(g)}}{a_{KCl(cr)} \times p_{KCl(g)}}$	(15)

Vaporisation studies on LiCl-KCl-UCl<sub>3</sub> ternary salt were carried out by using KEMS for the first time in the temperature range of 715 – 913 K. LiCl(g) and Li<sub>2</sub>Cl<sub>2</sub>(g) were considered to be possible major vapour species over LiCl(cr). KCl(g) and K<sub>2</sub>Cl<sub>2</sub>(g) were the major vapour species ascertained over pure KCl(cr). On the basis of neutral species over pure LiCl(cr) and KCl(cr) and mass numbers of ions, LiCl(g), Li<sub>2</sub>Cl<sub>2</sub>(g), KCl(g), K<sub>2</sub>Cl<sub>2</sub>(g) and UCl<sub>3</sub>(g) were assumed to be possible major vapour

Table 1. p-T relations for vapour species over LiCl	(cr), KCI(cr) and LiCI-KCI-UCI3 ternary salt
deduced using in-sit	u calibration

	Species	Run Temp. Ra		nge (K) T <sub>m</sub>	log(p <sub>i</sub> /Pa) =		
Sample			Temp. Range (K)		A <sup>a</sup>	B <sup>a</sup>	p <sub>i</sub> /Pa at T <sub>m</sub> : 814 K
Pure Li- Cl(cr)		Run 1	726-764	745	10484±594	11.89±0.80	1.02×10 <sup>-01</sup>
	LiCI(g)	Run 2	726-769	748	10823±490	12.28±0.65	9.64×10 <sup>-02</sup>
		Combined	726-769	748	10387±749	11.73±1.00	9.32×10 <sup>-02</sup>
	Li <sub>2</sub> Cl <sub>2</sub> (g)	Run 1	726-764	745	11996±451	14.08±0.61	2.20×10 <sup>-01</sup>
		Run 2	726-769	748	12111±336	14.19±0.45	2.05×10 <sup>-01</sup>
		Combined	726-769	748	11857±351	13.87±0.47	2.01×10 <sup>-01</sup>
Pure KCl(cr)	KCI(g)	Run 1	779-851	815	11239±130	12.47±0.16	4.60×10 <sup>-02</sup>
	K <sub>2</sub> Cl <sub>2</sub> (g)	Run 1	779-851	815	13678±211	14.85±0.26	1.11×10 <sup>-02</sup>
LiCI-KCI- UCI <sub>3</sub>	LiCl(g)	Run 1	812-913	863	9471±281	10.23±0.32	3.93×10 <sup>-02</sup>
		Run 2	715-913	814	9946±77	10.84±0.10	4.18×10 <sup>-02</sup>
		combined	715-913	814	9891±83	10.78±0.10	4.25×10 <sup>-02</sup>
	Li <sub>2</sub> Cl <sub>2</sub> (g)	Run 1	812-913	863	9312±281	10.00±0.34	3.63×10 <sup>-02</sup>
		Run 2	715-913	814	9441±64	10.12±0.08	3.32×10 <sup>-02</sup>
		combined	715-913	814	9517±80	10.24±0.10	3.53×10 <sup>-02</sup>
	KCI(g)	Run 1	812-913	863	10027±430	10.99±0.49	4.70×10 <sup>-02</sup>
		Run 2	715-913	814	10713±141	11.81±0.17	4.46×10 <sup>-02</sup>
		combined	812-913	863	10493±92	11.53±0.11	4.36×10 <sup>-02</sup>
	K <sub>2</sub> Cl <sub>2</sub> (g)	Run 1	812-913	863	11144±524	11.31±0.60	4.16×10 <sup>-03</sup>
		Run 2	715-913	814	11712±182	12.01±0.22	4.19×10 <sup>-03</sup>
		combined	812-913	863	11481±171	11.71±0.20	4.03×10 <sup>-03</sup>

 $T_m$  = Mean experimental temperature; <sup>a</sup>Errors quoted are the standard deviation; <sup>b</sup>Recommended equation was obtained by least-squares-fitting of all the data points from all the runs.

species over LiCl-KCI-UCl<sub>3</sub> ternary salt. Temperature dependence measurements of intensities of ionic species over pure LiCl, pure KCl and LiCl-KCI-UCl<sub>3</sub> ternary salt system were carried out in the range 715 – 913 K. Partial pressure - temperature relations for vapour species were derived using (i) in-situ calibration from pressure dependent equilibrium as well as (ii) using pure silver as external calibration. Using p-T relations various condensed phasegas phase and gas phase reactions were evaluated by  $2^{nd}$  and  $3^{rd}$  law methods. The dissociation equilibria of following gas phase reactions: Li<sub>2</sub>Cl<sub>2</sub>(g) = 2LiCl(g) and K<sub>2</sub>Cl<sub>2</sub>(g) = 2KCI(g) were evaluated using the partial pressures of monomer and dimer over pure and ternary salts deduced from the present study. Knudsen effusion mass spectrometric studies on LiCl-KCI-UCl<sub>3</sub> ternary salt system were reported for the first time.

Young Researcher's Forum

Young Researcher's Forum



Ms. Lisa John, SRF is currently pursuing her PhD in Chemistry at Homi Bhabha National Institute, Indira Gandhi Centre for Atomic Research Campus, Kalpakkam, under the guidance of Dr. K. I. Gnanasekar in the Material Chemistry Division, MC&MFCG. She completed her MSc in Chemistry from National Institute of Technology, Tiruchirappalli. Her research focuses on the synthesis and characterisation of metallic delafossite oxides (ABO<sub>2</sub>), a class of materials that are not amenable to conventional chemical methods. She has successfully stabilised phase-pure metallic delafossites in bulk form through the molten salt route and as thin films with exceptional metallic resistivity using Pulsed Laser Deposition. She has published three papers in peer-reviewed international journals so far.

## Molten Salt Synthesis: A Versatile Route to Phase Pure PdCoO<sub>2</sub>

 $PdCoO_2$ , a metallic delafossite having resistivity lower than that of Pd, has edge-shared  $CoO_6$  layers linked by linearly coordinated Pd with charge carriers confined to the 2D Pd sublattice. Palladium, known for catalytic cracking of hydrogen, becomes part of the lattice of  $PdCoO_2$  with retention of its conductivity and is envisaged to be a potential hydrogen sensor material. It is demonstrated as a catalyst for purifying exhaust gases and for oxidation of gaseous compounds in the absence of  $O_2$ in solid electrolyte fuel cells, as electrodes for aluminium reduction cells and electrolysis of NaCI. Despite its discovery in 1971 by Shannon et al., only a handful of reports are available spanning over five decades

and the reason is traced to the challenges in synthesis. The only available method is the metathetic route, which involves heating a mixture of PdCl<sub>2</sub> and CoO at 700 °C in an evacuated sealed quartz tube. It yields impurities from which the pure phase is retrieved after acid treatment [Eq. 1]. Metathetic reaction proceeds via the formation of molten PdCl<sub>2</sub>



Figure 1. (a) PdCl<sub>2</sub>-CoCl<sub>2</sub> Phase diagram (adapted from ASM phase diagram database) (b)Le-Bail profile fit of PdCoO<sub>2</sub> (crystal structure of PdCoO<sub>2</sub> is seen in the inset).



Figure 2: FESEM images of as-prepared PdCoO<sub>2</sub> (a) A single hexagonal flake and (b-c) lateral growth of PdCoO<sub>2</sub> planes

(mp = 678 °C) in which CoO powder (mp = 1900 °C) dissolves and reacts with the latter to yield PdCoO<sub>2</sub> and CoCl<sub>2</sub> (mp = 724 °C) as a byproduct [Fig. 1a].

$$PdCl_{2}(l) + 2CoO(s) \xrightarrow{700^{\circ}C} PdCoO_{2}(s) + CoCl_{2}(l) - eq(1)$$

The phase diagram of  $PdCl_2-CoCl_2$ is shown in Fig. 1a. As the reaction proceeds from A to B in Fig. 1a, concentration of  $PdCl_2$  decreases progressively with the formation of  $CoCl_2$  until the mole fraction of  $PdCl_2$ reaches ~15% (B), wherein  $CoCl_2$ starts precipitating along with the eutectic melt ( $PdCl_2:CoCl_2 \cong 74:26$ ) as the processing temperature falls below the liquidus line from B to C [Fig. 1a]. The volume of the molten medium shrinks, rendering the reaction incomplete and enforcing acid treatment to remove impurities. Instead of working with the composition whose melting point varies with the progress of the reaction, a molten salt mixture with a eutectic composition having a fixed melting point less than 700°C was preferred to attempt the formation of PdCoO<sub>2</sub> in pure phase. After surveying different mixtures, KCI-NaCl eutectic with a melting point of 650 °C offering the solubilities of  $1.58\,\times\,10^{\text{-5}}$  M and 9.81  $\times\,10^{\text{-3}}$  M for PdO and Co3O4 respectively was promising. Stoichiometric PdO and Co<sub>3</sub>O<sub>4</sub> were mixed with NaCl-KCl eutectic for different salt-to-precursor ratios (SPR) of 1, 2.5, 3, 4 & 6 and the mixture was heated to 800 °C at a rate of 3°C min<sup>-1</sup> in a tightly closed zirconia crucible for about 10-24 h. Sparkling black cake obtained was washed with hot double distilled water several times until the filtrate



Figure 3: TEM analysis of  $PdCoO_2$  powder (a) HRTEM image showing the lattice fringes (b) electron diffraction pattern with planes indexed.

was chloride-free.

$$3PdO(s) + Co_3O_4(s) \xrightarrow{800^{\circ}C} 3PdCoO_2(s) + \frac{1}{2}O_2(g) --- eq(2)$$

Phase pure PdCoO<sub>2</sub> is obtained for a reaction duration of 24 h at 800°C for the SPR of 3. XRD pattern of the PdCoO<sub>2</sub> specimen prepared under optimised conditions shows preferential texturing along (00I) direction as seen from Fig. 1b. Since authentic ICDD patterns are unavailable for PdCoO<sub>2</sub>, XRD data was processed using GSAS/ EXPGUI Rietveld program and the structureless Le-Bail full profile fit extraction model was used to get the lattice parameters. The XRD pattern was well fitted with the space group R3m (166) which yielded residual parameter values of Rp: 0.0490, Rwp: 0.0730 and  $\chi^2$ : 4.78. The calculated lattice parameters of PdCoO<sub>2</sub> are a= b= 2.84907(3) Å, c= 17.74623(4) Å with  $\alpha = \beta = 90.0^{\circ}$  and  $\gamma = 120.0^{\circ}$ .

FESEM images of the powder specimen reveal stacked hexagonal plate-like grains of ~300  $\mu$ m width and 3-4  $\mu$ m thickness [Fig. 2]. Fine grains of about 100-500 nm were also seen distributed on the large hexagons. HRTEM image shows that the lattice fringes correspond to (012) planes of PdCoO<sub>2</sub> [Fig. 3a]. The electron diffraction pattern shows non-continuous dotted rings with dots of different size distributions, revealing the polycrystalline nature. Energy dispersive X-ray (EDX) analysis reveals no traces of chloride ions despite being synthesised in a molten chloride medium.

The core-shell X-ray photoelectron spectrum of Co 2p (Fig. 4a) shows complex features at higher binding energy side. Intense peaks of 2p3/2 and  $2p_{1/2}$  were found at 779.7 eV and 794.6 eV respectively, which were accompanied by a less intense pair of peaks at 781.7 eV and 796.7 eV revealing cobalt in two different oxidation states. The peak at 779.7 eV with the characteristic satellite at 790.6 eV is assigned to Co3+, whereas the peak at 781.7 eV with a satellite at 783.5 eV is assigned to Co4+. The relative area under respective peaks of Co3+ and Co4+ shows that about 30% of cobalt ions are in a +4 oxidation state. On the other hand, Pd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks at 335.9 eV and 341.2 eV respectively confirm the Pd in monovalent state in PdCoO<sub>2</sub>. The reported binding energy values of Pd 3d<sub>5/2</sub> for elemental Pd and Pd2+ are 335.0 eV and 336.7 eV respectively, which are not found. No peak corresponding to CI 2p confirmed the product to be chloride-free.

Young Researcher's Forum





Magnetic susceptibility ( $\chi$ ) recorded at an applied field of 1000 Oe is fitted with Curie Weiss law,  $\chi = \chi_0 + \frac{c}{T-\theta}$  where  $\chi_0$  is the temperature-independent susceptibility, 0 is Weiss temperature and Curie constant,  $C = \frac{N_A \mu_{ef}^2}{3k_B}$  with  $\mu_{af}$  being the effective magnetic Pauli paramagnetic moment. nature of the conduction electrons confined within the Pd sub-lattice along with the diamagnetic nature and Van Vleck paramagnetism for low spin Co<sup>3+</sup> contribute to  $\chi_0$ . The  $\mu_{\rm ef}$  of 0.79  $\mu_{\rm B}$  calculated from C = 0.078 emuK • (mol-Oe)<sup>-1</sup> compares favourably with the literature. As low spin Co<sup>3+</sup> is non-magnetic,  $\mu_{ef}$ of 0.79  $\mu_{\rm\scriptscriptstyle B}$  implies a mixed valence state for cobalt and the XPS confirms the presence of Co4+ ions. Since the  $R\bar{3}m$  structure allows a single lattice site for cobalt wherein the octahedral crystal field enforces Co<sup>3+</sup> to be in a low spin state. This field should also enforce Co4+ occupying the same lattice position to be in low spin state and its single unpaired electron contributes to the low magnetic moment undergoing antiferromagnetic ordering at 30 K. The negative value of Weiss temperature (-142 K) further confirms the same. Cation-deficient PdCoO, or excess oxygen in interstitial sites can generate Co4+ ions. LA-ICPMS analysis of the specimen yields Pd:Co ratio of 1.111 (PdCo<sub>0.00</sub>O<sub>2</sub>) confirming cobalt deficiency (Fig. 5b).

The molten salt route evolved from the metathetic reaction yields phase pure PdCoO<sub>2</sub>. Le-Bail refinements

> and electron diffraction confirm studies rhombohedral PdCoO<sub>2</sub> [S.G.  $R\bar{3}m$ (166)] without any impurities. Acid treatment step and evacuated sealed crucibles are no longer required. The characterisations by XPS and magnetic studies confirm the presence of Co<sup>4+</sup>

> > low spin



Fig. 5: (a) Susceptibility vs temperature curve of  $PdCoO_2$ . The hysteresis curve observed at 300 K and 4 K are seen in the inset and (b) LA-ICPMS calibration plot of <sup>105</sup>Pd/<sup>59</sup>Co intensity ratio vs Pd/Co intensity ratio vs Pd/Co intensity ratio for standard samples (R<sup>2</sup>=0.998) fitted linearly with a slope of 0.4390  $\pm$  0.0055.

configuration.



Dr. M. Vasudevan Materials Development and Technology Group Metallurgy and Materials Group Indira Gandhi Centre for Atomic Research, Kalpakkam Tamil Nadu, India.



## Advances in Welding Technologies for Applications in the Nuclear Industry

There is growing worldwide interest in enhancing the power production by nuclear energy. Welding is the main fabrication method employed in the construction of nuclear power plants. The developments in advanced materials for structural components and their associated processing and welding technologies for nuclear power plant construction are receiving greater interest among researchers worldwide. The advancement in materials technologies are expected to bring down the overall cost of construction of nuclear power plants. At Indira Gandhi Centre for Atomic

Research, Kalpakkam, innovative welding technologies have been developed for carrying out welding of similar weld joints of austenitic stainless steel, ferritic-martensitic steel and dissimilar weld joint between austenitic stainless steel and ferriticmartensitic steel.

Shielded Metal Arc welding and Tungsten Inert gas welding are the two major processes have been used during the construction of Prototype Fast Breeder Reactor (PFBR). Though high quality weld deposits can be made by TIG welding, the main disadvantages of TIG welding lie in the limited thickness of material which can be welded in a single pass, poor tolerance to cast to cast variations in chemical composition and the low productivity. Weld penetration achievable in single pass TIG welding of stainless steel is limited to 3 mm when using argon as shielding gas. In addition, austenitic stainless steel exhibits variable weld joint penetration during TIG welding due to small differences in chemical composition between different heats of material. Poor productivity in TIG welding results from a combination of low welding speeds and in thicker



Figure 1: Photographs of the 11 mm thick 316LN SS weld joint made by A-TIG welding



Figure 2: Comparison of Creep behavior of 316LN SS, and Its TIG and A-TIG weld joints

material the high number of passes required to fill the joint. Over the years, several strategies have been adopted to improve penetration depth of the TIG welding process. The penetration capability of the arc in TIG welding can be significantly increased by application of a flux coating containing certain inorganic compounds on the joint surface prior to welding. The process is called Activated TIG (A-TIG) welding process. At IGCAR, A-TIG welding process has been developed and international patent obtained. A-TIG welding technology has already been transferred to Indian Industries.

A-TIG welding technology has been developed for welding up to 10-12 mm thick steel and stainless steel plates in single pass welding with a square butt joint configuration, without any filler material addition. A-TIG is more cost effective compared to TIG welding and the overall cost of fabricating the weldment can be reduced up to 50% if A-TIG welding is employed. The advantages of A-TIG welding are listed below.

#### Advantages of A-TIG welding

 Increases penetration depth; stainless steel up to 12 mm thick may be welded in a single pass, compared to 3 mm with standard TIG welding.

- · Eliminates the issue of cast-tocast variance in low sulphur (less 0.002%) stainless than steel, which would ordinarily generate a wide and shallow weld bead with traditional TIG.
- Reduced weld shrinkage and distortion.
- Bevel preparation is not required.
- requirement for • No welding consumable.
- · Removal of back gouging and grinding
- Improved productivity
- · High potential for reduced reject rates
- High level of repeatability
- Reduced number of weld procedure specifications

### A-TIG welding of Steels and **Stainless steels**

A-TIG welding process has been successfully developed for welding of steels, stainless steels and titanium. There was no degradation in the microstructure and mechanical properties of the A-TIG welded joints. A-TIG welding technology has been developed for enhancing the penetration performance for autogenous welding of type 304LN and 316LN stainless steels. The A-TIG welding produced a significant increase in penetration of 10-12 mm in single pass welding of the above stainless steels. 20 mm thick plate has been welded by double side welding procedure which is also a benchmark internationally. The significant improvement in penetration achieved using the A-TIG welding technology developed in the present work has been attributed to the constriction of the arc and as well as reversal of Marangoni flow in the molten weld pool. There was no significant difference found in the chemical composition between the base metal and A-TIG weld metals for both 304 LN SS & 316 LN stainless steels except for oxygen pick up of 400 ppm in the weld metal. The presence of 400 ppm of oxygen in the weld pool would influence the fluid flow by changing the temperature coefficient of surface tension to a positive value. This would cause the molten metal to flow inward and lead to an increased depth of penetration. This kind of fluid flow behaviour is often described as reversal of Marangoni flow. Figure 1 shows the photographs of the 11 m thick 316LN SS weld joint made by A-TIG welding process.

The use of A-TIG welding has been found to overcome the variable weld penetration observed in 316LN stainless steel with less than 50 ppm of sulphur. There was no

Lecture Series



Figure 3: Creep rupture life plots (a) Similar 316LN SS weld joints made by advanced welding processes (b) Dissimilar EB weld joint between 316L SS and P91 steel

has been developed by employing

degradation in the microstructure and mechanical properties of the A-TIG welds compared to that of the welds produced by conventional TIG welding. Significant improvement in creep rupture life of stainless steel weld joints have been found (figure 2). Corrosion resistance is found better for A-TIG weld joint. Self pressing, a post welding treatment on the A-TIG welded joint was found to significantly reduce the residual stresses and improve the weld bead profile. The use of the A-TIG welding technology have been evaluated for wide variety of stainless steel alloys and found suitable for a wide range of applications. The A-TIG welding technology has been deployed for fabricating various stainless steel components used in Industrial applications. The process has been extensively used for making number of components with enhanced productivity and reduced cost in fabrication shops and engineering industries. Thus, the A-TIG welding process exhibit greater potential to perform welding on the complex and challenging jobs with significant reduction in the cost.

For fabricating dissimilar weld joints between 316L SS and Mod. 9Cr-1Mo steel, a novel Functionally graded joint between the two steels A-TIG welding procedure. Chemical analysis revealed gradual change in the composition of the major alloying elements and the joint exhibited 6 times better fatigue life during thermal cycling test compared to that of the tri-metallic joint used in PFBR. The following list gives the industrial applications of A-TIG welding already demonstrated in India. A-TIG welding has already been deployed for welding of demineralised water storage tanks made of 304 L SS, Sodium carrying pipes of 5 mm thick stainless steel used in FBRs, welding of sleeves to grid plate for FBRs, Welding of SS components in Pharmaceutical industries, Spiral 304 L SS pipe welding for application in LIGO India, Remote Repair Welding of FBR components, welding of 304 L SS tubes and pipes in reprocessing plants, welding of Stainless steel components in chemical and food industries. Other applications demonstrated worldwide include nuclear reactor components (pipes and tubes), car wheel rim, hydraulic cylinders and undercarriage legs in aerospace industry, Steel bottles for compressed air for cars, Pressure vessels and tube to tube sheets in heat exchangers, Stainless steel pipe welding for surface ships &

submarines, gas turbine components, power plant tubes and repair welding etc..

### A-TIG Welding of Titanium

A-TIG welding of titanium has attracted considerable interest in scientific and industrial community in recent years. Deep penetration, narrow weld, small HAZ, low heat input and lower residual stresses are some of the distinct advantages of the above process. A-TIG welding of titanium was successfully carried out in 6mm thick CP titanium plate in single pass welding using activating flux consisting of halides. Use of A-TIG welding for titanium considerably reduced the porosity and reduced the cost by half. Maximum achieved depth of penetration in titanium is 16 mm employing A-TIG welding in single pass welding procedure.

## Laser, Hybrid Laser and Electron Beam Welding

Laser, Hybrid Laser-TIG, Hybrid Laser-MIG and Electron beam welding technologies have been developed for welding 316LN SS. Hybrid Laser-MIG welding was found to enhance significantly the high temperature mechanical properties of similar 316LN SS weld joints. Electron beam welding of dissimilar weld joint between 316L stainless



Figure 4: Real time monitoring and Prediction of Depth of Penetration using CMOS camera and AI tool

steel and mod. 9Cr-1Mo steel has enhanced the creep rupture life 10 times compared to that SMA weld joint. Figure 3 shows the applied stress versus the rupture life for the hybrid laser-MIG similar and the EB welded dissimilar joints.

## Real Time Monitoring and Prediction of Depth of Penetration during A-TIG welding of 316LN Stainless steel using AI tool and the COMS camera

GTAW process is often chosen for welding pipes and pressure vessels due to high quality weld deposit. However, controlling the weld quality remains still a challenge because difficulties involved in predicting the depth of penetration during welding. The major challenge is that penetration needs to be determined from the bottom of the weld joint which is not observable directly. Innovative concepts are needed to obtain topside information that has adequate/fundamental relationship with the depth of penetration. Real time monitoring of the top side of the weld pool using appropriate sensors and AI based tool during GTAW is essential for estimating the real time evolution of depth of penetration.

Artificial Intelligence (AI) based tool has been developed for real time monitoring and prediction of depth of penetration during A-TIG welding of 3 to 10 mm thick 316LN SS plates. From the acquired real time images of weld pool using CMOS camera, semantic segmentation model employing Convolutional Neural Network (CNN) has been developed for generating weld pool segment images for 316LN SS welds. Then deep learning model using CNN with fully connected layers was developed to classify the state of penetration into four states namely lack of penetration, small penetration, large penetration and full penetration. The performance accuracy of the classification model was found to be more than 99.75 percent.

Then, weld pool dimensions were estimated from the segmented images and correlated with depth of penetration using back propagation neural network (BPNN). CNN image segmentation model, image processing for estimating weld pool dimensions and BPNN model were all combined to predict the depth of penetration in real time. Figure 4 shows the real time prediction of the evolution of depth of penetration during welding as a function of weld distance. The error on the predicted depth of penetration was determined to be 0.3 mm. The developed AI based welding technology would find applications during in-situ and remote welding applications of components.



Dr. Sandip Kumar Dhara Materials Science Group Indira Gandhi Centre for Atomic Research, Kalpakkam Tamil Nadu, India.



## An Overview of Radiation Damage Studies at MSG

Defects and damage studies in materials are an important core activity of Materials Science Group (MSG). 1.7 MV Tandetron accelerator is being effectively utilized to study the radiation effects in reactor materials using heavy ions, giving the defect production rate of up to five orders of magnitude higher than reactor irradiation conditions, providing a test bed for simulating the condition of both thermal and fast reactor. The irradiation damage studies in D9 (titanium-modified, 316 stainless steel) alloys have given crucial insight into the importance of Ti to C ratio on the void swelling behaviour, thus pointing that the Ti/C ratio of 6 % is suitable and taken up for PFBR core structural material after testing under neutron irradiation in FBTR. Oxide dispersion strengthened (ODS) steels are the candidate material for future fast and fission reactors due to their better radiation resistance. The Density Functional Theory (DFT) simulations along with Transmission Electron Microscopy (TEM) and Positron Annihilation Spectroscopy (PAS) have shown that in comparison to AI, Zr containing ODS steels give rise to finer distribution of particles along with high number densities and the onset of the defect production is also at higher dose of 150 dpa as compared to the corresponding dose of 100 dpa for AI containing ODS

steels. lonoluminiscence studies of the  $Y_{4}Zr_{3}O_{12}$ , which is identified to be the composition of nano-dispersoids in Zr containing ODS, show that the major defects are anionic defects, which also corroborates with the threshold displacement energies calculated using ab-initio Molecular dynamics (AIMD). The presence of nano-metric regions of expanded lattice parameter has been identified in 200 keV He ion implanted thoria, understood to be due to the He ordering at octahedral interstitial sites in ThO<sub>2</sub>. Nanocrystalline Ni, which is a coating material for molten salt reactor upon irradiation with 14 MeV Ni ions, shows that void-denuded zone at the surface is absent, and there is the presence of voids which are five times more than predicted by TRIM software. The interaction of O solute with defects and the effect of grain size in FeCr alloy is studied using ion-channelling, high-resolution Rutherford backscattering (HRBS) and DFT. RBS and Channeling are done to study recovery the irradiation-induced of defects in 3C-SiC. The defects produced by 200 keV Si ions were found to be annealed by irradiating 14 MeV Si ions. PAS has been used extensively to study vacancy defects, voids and their evolution with annealing temperature in Indian reduced activation ferritic martensitic

(INRAFM) steels for both fission and fusion reactor applications and high entropy alloys. Besides providing the comprehension of the experimental results, the computational activity at MSG plays a key role in understating defects energetics and calculation of binding energies in bcc Fe, bcc U and U<sub>s</sub>Si<sub>2</sub> using DFT. The random network structures of glass are modelled using AIMD and Monte Carlo methods for Iron Phosphate Glass (IPG) envisaged as powerful tools for the studies on the retention and stability of IPG after insertion of Cs and Pu for waste immobilization applications. The displacement cascades are studied in Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, Y<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> and Gd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> to understand the basic processes in defect production using MD simulations. MSG equipped with a dual ion beam facility (400 kV ion accelerator for He ions and 1.7 MV Tandetron accelerator for heavy metal ion irradiation) for simulating radiation nearly the damage conditions in the reactor and powerful characterization tools, including PAS (variable low energy DC beam and upcoming pulsed beam of positrons), HRBS/ Channeling, SEM, TEM and lonoluminiscence along with the computational modeling would contribute significantly in providing greater insights to devise strategies for defects studies in the materials of interest for current and future reactors.

Lecture Series

Lecture Series - 3



Dr. Rajesh Ganesan & his colleagues of MC&MFCG Indira Gandhi Centre for Atomic Research, Kalpakkam Tamil Nadu, India.

## Comprehensive Monitoring of Hydrogen for Sodium Systems

Development and deployment of sensors for nuclear facilities are one of the key activities of MC&MFCG. This article focuses on the challenges and accomplishments of comprehensive monitoring of hydrogen for sodium systems. The eventuality of steam leak into sodium needs to be detected at its incipient stage itself using reliable online sensors, which is a safety requirement. As hydrogen is one of the products of steamsodium reaction, online monitoring of hydrogen levels in liquid sodium as well as in argon cover gas helps in the identification of steam leaks into sodium. Hydrogen distribution between liquid sodium and argon cover gas is complex and it depends on sodium temperature, total inventory, residence time, etc. Hydrogen in sodium is detected by a conventional diffusion-based hydrogen meter. methodology, the As a diverse electrochemical hydrogen meter (ECHM) is designed, developed and employed for improved safety and reliability of the system. ECHM is a concentration cell used to measure hydrogen concentration in sodium at ppb levels. The development involves the identification of suitable electrolytes and reference electrodes appropriate for the measurement. The sensors with associated electronics are calibrated in the laboratory and

installed in FBTR, SOWART and SGTF. ECHMs were also tested in Phenix and Superfennec sodium facilities in CEA, France as part of the IGCAR-CEA collaboration of fast reactor safety. Among the ten numbers of ECHMs for PFBR, five numbers are installed in SGB-1 and installation in five more locations in SGB-2 will be scheduled shortly.

During the low power operation or reactor shutdown conditions, the temperature of liquid sodium will be low and under this condition, a major amount of hydrogen would escape to the argon cover gas which can be detected using hydrogen in argon detector (HAD). HAD comprises a nickel coil assembly, argon gas module and a Wheatstone bridge with a thermal conductivity detector (TCD). The difference in the thermal conductivity of hydrogen in argon and pure argon is used as a detection method. The detection range is 30 to 3000 ppm of hydrogen in argon. In order to detect hydrogen concentrations below 30 ppm, a semi-conducting metal oxide (SMO) based sensor was developed, which can be connected to the outlet of TCD. The working principle is the measurement of change in surface conductivity of the metal oxide during the interaction with hydrogen, which is directly related to its concentration. Both HAD and SMO sensors with associated electronics are calibrated in the laboratory and also in the plant. The laboratory-calibrated HADs are positioned in FBTR, SOWART and SGTF; SMO sensors are installed at the TCD outlet in SOWART, SGTF and FBTR. Four HADs are installed and calibrated in PFBR.

Hydrogen sensors for percentage level detection are needed to measure hydrogen levels during the sodium removal process from large components and also during secondary cold trap regeneration. In the sodium removal process, steam or water vapour reacts with adhering wetted sodium over steel surfaces and releases hydrogen. In the cold trap regeneration process, sodium hydride precipitation in the cold trap module is decomposed to release hydrogen by the thermo-vacuum process. In both these processes, hydrogen has to be monitored and maintained at less than the lower explosion level of 4% and mitigated further. A polymer electrolyte-based hydrogen sensor (PEMHS) operating in amperometric mode with the cell configuration of H<sub>a</sub>/Pt//Nafion//Pt/O<sub>a</sub>, was developed for the purpose. The sensor cell uses proton-conducting polymer membrane, Nafion 212 as electrolyte and Pt supported on carbon as electrodes. The sample

#### Lecture Series

gas containing hydrogen is passed over the sensing electrode while exposing the counter electrode to flowing ambient air. A diffusion barrier is placed over the sensing electrode that limits the supply of hydrogen flux. The limiting current is measured as a signal which is linearly proportional to hydrogen concentration in the range of 0-4%. The PEMHSs were calibrated, tested in the laboratory and used in the field applications successfully for sodium removal of leak SG of FBTR, dummy PFBR subassembly, failed fuel-subassembly location module (FFLM), under sodium ultrasonic sensors (USUSS), etc. The performance of PEMHSs is not only useful for the safe removal of sodium but also used for quantification. PEMHSs were also used for the regeneration of model secondary cold trap (MSCT) for PFBR and quantification of regeneration efficiency, in collaboration with FRTG. The technical support of colleagues of FRTG, RFG, QAD and BHAVINI is acknowldeged. The support of colleagues of CEA, France is also acknowledged.





Dr. N. Subramanian Incubation Centre, IGCAR Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu, India.

(With contributions from Dr. Anita Toppo, IC-IGCAR)

## Emerging opportunities at the upcoming Atal Incubation Centre: AIC-IGCAR-FAST-Foundation

primary mission of IGCAR The to conduct a broad-based is multidisciplinary R&D programme focussed on establishment of Fast Breeder Reactors and associated unique fuel cycle facilities. The mission includes the development and applications of novel/improved materials, techniques, equipment and systems for FBRs and pursues basic research to achieve breakthroughs in Fast Reactor technology. A number of spin-off techniques and products have been developed during the above pursuit. Nearly 60 patent applications have been filed, several have been granted both within India and abroad. Few more patents have been applied for at this point of time. A large pool of experienced technical experts and mentors over a wide spectrum of R&D exists at IGCAR and in the various DAE Units on campus. State-of-the-art facilities for performing world-class R&D in science and engineering have been set-up in IGCAR over the last several decades. The technologies developed have very good potential applications in industries and so far eleven technology transfers have been done to different start-ups/industries for commercial utilization through DAE's established technology transfer route. A total of 16 IGCAR technologies are listed in IGCAR's Incubation Centre website as available for incubation, out of which nine are mature for technology transfer and/or valueadditions through incubation. Seven technologies of technology readiness level ('TRL') lower than six have been listed for collaborative incubation. Incubation agreements have been signed with start-ups for three of these and the incubations are currently in progress.

As part of the Atomic Energy Reforms announced by Honourable Finance Minister in May'2020, DAE had announced establishing incubation centres in BARC, IGCAR, RRCAT and IPR on 30 October 2020 with an aim to participate and support Government of India's Atmanirbhar Bharat programme. A document defining policy and guidelines for incubation centres was released by DAE vide ID note ref. 23015/2021/ Gen/R&D-I/2212 dated 16 February 2021. As per DAE's requirement, the four DAE incubation centres would be transformed into Atal Incubation Centres of Atal Innovation Mission (AIM, Niti Aayog) to align with the Nation's mission.

Based on the in-principle approval of AIM-NITI Aayog for IGCAR to set up an AIC and considering the need of complying to AIM-NITI Aayog norms as communicated by AIM to DAE, IGCAR is required to setup the Atal Incubation Centre as a Special Purpose Vehicle (SPV), under section 8 of the Companies Act, 2013 with a ready-to-occupy incubation space of at least 10,000 sq.ft. area. This is aimed at fostering rapid translation of technologies from the lab to start-ups and subsequent commercialization by the start-ups, which are aligned with DAE's objectives and creating leverage from the ecosystem established under and in congruence with the philosophy of AIM's AIC framework of the Government of India. Competent authority of DAE has accorded approval to IGCAR for setting up of this SPV, or section 8 company, in June'2024 with the name "AIC-IGCAR-FAST Foundation". Here, "FAST" signifies that all IGCAR technologies are spin-offs from our R&D pursuits in 'FAST REACTOR TECHNOLOGY'. Further "FAST" also signifies that the AIC will enable FAST ('rapid') translation of technologies from the IGCAR laboratories to the start-ups/MSMEs/Industries. This SPV will provide necessary leverage to AIC-FAST to promote, and accelerate translation of the developed knowhow into marketable products/ processes or products required for DAE projects by joining hand with startups and industries through incubation and technology development agreements, respectively. AIC-FAST will provide preference in support to innovators/entrepreneurs startups/ that have applications and/or impact in the core sectors of the economy (including but not limited agriculture, healthcare, to clean

energy and sustainable technologies, manufacturing, education, housing, transportation, cyber security, IoT, Robotics and AI, water and sanitation) and in the domain of IGCAR expertise (including but not limited to advanced sensors for nuclear installations, process industry, chemical industries, environmental monitoring, security electronics, instrumentation and controls, materials and metallurgical processes etc.).

The proposed SPV will be under the auspices of IGCAR and located in DAE Township, Anupuram with an area of at least 10,000 sq.ft. as required by AIM (Niti Aayog). World-class incubation facilities such as a Rapid Prototyping Space, Maker/FabSpace, Co-working office space etc. and incubation related services will be offered at the AIC-FAST premises. IGCAR will be responsible for the governance and overall operational activities based on DAE's policy and guidelines on incubation centres. It will also follow the guidelines of AIM in this regard. The operations of AIC-FAST as SPV will be governed by a Board of Directors (BoD) that will be formed by Director, IGCAR. The composition of the BoD will be in compliance with AIM-Niti Aayog's guidelines for SPVs. The BoD will endeavour for a smooth, seamless, professional, transparent, and accountable functioning of AIC-FAST as a section 8 company.

AIC-FAST is expected to offer plenty of opportunities for IGCAR scientists and technologists. They can, for instance, play the role of technology mentors at AIC-FAST to mentor the start-ups incubating with us on the technologies with which the mentors are associated with. This can lead to fruitful development of niche technologies under a collaborative incubation mode with the private sector (start-ups/MSMEs) in areas of interest to the department and our Nation in general. Such collaborations are expected to lead to accelerated technology development rapid commercialisation and prospects. The incubatee startups are most likely to contribute towards manpower requirements technology development, for procuring crucial raw materials, tools etc. that may be needed and also provide complementary expertise in most cases. IGCAR mentors can also gain valuable experience by empathising with the needs of the start-up sector. Over and above these opportunities, possibilities of incentivizing technology mentors are also emerging.

AIC-FAST will also provide opportunities for HBNI faculty and students of IGCAR to translate the technologies they may be developing as part of their academic R&D into commercialisable entities through the incubation route. HBNI Students will be encouraged to incubate with AIC-FAST and emerge as start-ups through the recently formed HBNI's Institution Innovation Council (as per AICTE, Ministry of Education's requirements). As per the HBNI's IPR policy, students can also seek technology transfer of patented IGCAR technologies, incubate with the AIC and emerge as entrepreneurs. Opportunities for students to associate with external start-ups involved in incubating IGCAR's technologies may also emerge.

In summary, plenty of exciting opportunities for IGCAR's scientists, technologists and HBNI students are expected to emerge at the upcoming AIC-IGCAR-FAST Foundation leading to win-win kind of opportunities for all involved. Lecture Series



Dr. C. Venkata Srinivas & his colleagues of SQRMG Indira Gandhi Centre for Atomic Research, Kalpakkam Tamil Nadu, India.



## Decision Support System ONERS for Nuclear Emergency Response

Emergency preparedness is an integral part of the activities of Department of Atomic Energy. In the unlikely event of accidental releases from nuclear facilities the emergency response actions require prompt estimation of radiological dose to the surrounding population. Under the DAE initiative in 2005, IGCAR in collaboration with NRSC-ISRO and NCMRWF, N.Delhi has developed 'Online Nuclear Emergency Response System (ONERS)' for guidance on protective actions towards mitigating radiological risk to the public during nuclear emergencies at NPP Sites. ONERS is a Web enabled GIS based decision support system (DSS) designed with generic architecture as a client-server application and developed in opensource tools (flex, GD, Proj, GDAL, PHP, CGI-BIN Map Server, JDK, JRE) in Linux environment. System uses generic shape files for GIS data, MySQL for database with SQL, CGI-BIN Map Server for Web GIS-Server and PHP Map scripts as GIS language. Main components are i) Sensor network consisting Meteorological Towers and Autonomous Gamma Dose Loggers (AGDL), ii) Meteorological and Dispersion Models iii) Spatial & Non-spatial database iv) GIS based visualization and analysis tools.

ONERS can project radionuclide concentration, deposition and radiation dose in the public domain upto 3-days using accident source term, dispersion model simulations using numerical weather forecast data upto 3-days. The basic version was developed and made operational during 2007-2012 and upgraded to ONERS2.0 during 2016-2018 in common frame work to all NPP sites with geographical, Remote Sensing and infrastructure database for each site. ONERS at Kalpakkam site is connected with 28 Autonomous Gamma dose loggers (AGDLs) and two 50-m meteorological masts. AGDL measures environmental gamma dose using GM detectors. It is solar powered detector with battery backup and transmits data from remote location using wireless communication. AGDLs are installed in a two-ring manner approximately at 1.5 km and 0.75 km radii from MAPS and PFBR reactor stacks and covering different wind direction sectors. On the sea side the AGDLs are installed on the Jetties of MAPS and BHAVINI and a Met-Ocean data buoy approximately at 0.75 km radius. Recently an Online Isotope Monitor and Noble Gas Monitor are installed in the northern sector to measure the radionuclide composition in

air during an accident scenario for detection and improved source term information. The system autosenses accident using real-time AGDL dose rate observations.

The weather predictions for dispersion forecasting are performed using the non-hydrostatic mesoscale weather model WRF at 3 km resolution with initial and boundary condition data taken online from global forecast system (GFS) of NCMRWF, Noida and local data assimilation using **3D-Variational** Data Assimilation (3D-VAR) scheme. WRF is operationally run on the HPC at IGCAR. The radioactivity dispersion and deposition are simulated using FLEXPART Lagrangian Particle Dispersion model considering radioactivity decay, dry and wet deposition phenomena. Dispersion calculations are performed upto 2 hours in short-range using onsite real-time meteorological tower data and upto 72 hours using WRF forecasts. ONERS has a number of provisions for source term input i) inverse model estimated release data ii) potential source terms for postulated accidents and iii) user defined etc.. The release rate can be either uniform or time-dependent. The system back calculates release rate in case of accident using an

inversion model ASTER using AGDL data. The counter measure evaluation tool of ONERS identifies areas requiring protective actions like distribution of iodine tablets, sheltering, food and water control, evacuation, decontamination etc., based on projected doses through different pathways by aggregating dose from each grid-point in the villages. System also identifies safe along zones with infrastructure information such as rallying posts, sheltering places, hospitals, transport routes in the domain.

The WRF meteorological model is evaluated by conducting flow field modelling exercise under BRNS RRE involving different national institutes and universities and also by testing for large number of cyclones, heavy rainfall events and micro-mesoscale phenomena with physics sensitivity and data assimilation experiments. The dispersion model is validated by conducting field SF6 Tracer and Sodium aerosol dispersion experiments and source term model is validated with Ar41 release data from MAPS. AERB reviewed the DSS in June 2016 and recommended for implementation at various NPP sites. ONERS has been used in site and off-site emergency exercises at Kalpakkam site as well as for various other NPP sites. The system along with all models was installed at NREMC-AERB, Mumbai and NPCIL Head Quarters in 2018-2022.

Under the ministrv initiative 'Application of Space Technology in DAE', a C-Band Dual Polarized Doppler Weather Radar and a 204 MHz Mid-Tropospheric Wind Profiler are installed and commissioned at IGCAR. The data from these facilities will be used in numerical weather forecasting system with data assimilation for improved predictions. Based on the framework of ONERS a Chemical Emergency Response System (CERS) has been developed industrial sites in collaboration with Factories and Boilers, Govt of Kerala, and NRSC-ISRO, and the first version was installed at CHEMREC, Kochin for ammonia storage facilities in Ernakulam district, Kerala. Presently CERS is being further upgraded for other toxic gases like Chlorine, H2S etc and the upgraded version will be implemented for the Heavy Water Plant sites of Manuguru and Hazira Kota. It is proposed that ONERS will be further upgraded by incorporating i) Kalman-Filter in source term model, ii) aquatic dispersion models for radiological impact assessment for marine biota, iii) site-specific Tsunami model for alert during extreme wave events iv) fine grid short-range models along with building information, uban-canopy effects for accurately radiation assessing impacts in limited site zones like SMRs and v) Back trajectory modeling based on detectors data for source location identification etc.

for chemical accidental releases at



Ms. Saritha P. Menon & her colleagues of EIG Indira Gandhi Centre for Atomic Research, Kalpakkam Tamil Nadu, India.



## Independent Verification & Validation: Concepts & Experiences from V&V of PFBR I&C Systems

# Basic IV&V Concepts and Regulatory Requirements

The basic requirements for the design of safety critical Instrumentation and Control (I&C) systems for nuclear power plants have been detailed - 20 - IGCAR Newsletter October 2024 out in AERB Safety Guide AERB/ NPP-PHWR/SG/D-10 and those for safety related I&C systems in AERB/ NPP-PHWR/SG/D-20. Computer based systems are programmable and provide a number of advantages over non-programmable systems. However the features that give advantages also add complexity to software. Unlike in hardwired-based systems, faults in software, which does not wear-out, always result from

#### Lecture Series

Lecture Series



Figure 1. System Development Life Cycle

improper requirements, design or implementation. When I&C systems perform functions important to safety, these systems must be demonstrated to be safe and reliable with appropriate degree of confidence as outlined in the AERB Safety Guide AERB/NPP-PHWR/SG/D-25.

As per SG/D-25, computer based are not amenable to systems quantitative assessment of reliability, due to software component of these systems. Therefore integrity should be assured by developing system / software using systematic, technically appropriate, carefully controlled, fully documented and reviewable engineering process, which is suitably interfaced with V&V activities.

IV&V stands for Independent Verification & Validation. Verification focuses on the process followed while developing the system, i.e., whether the system is being built correctly. Every verification step produces a report of the analysis



Figure 2. Typical TMR Architecture (for Primary Sodium Pump Speed Measurement System)

performed and the conclusions reached. Validation checks the built system against the requirements, i.e., whether the correct system has been built. Validation produces the System Validation Report which reports the results of validation of each requirement for correct implementation in the built system. The V&V team must be independent from the design & development team.

## Safety Classification and V&V Requirement

I&C systems are classified, based on safety considerations, into four classes IA, IB, IC and NINS as per AERB safety guide AERB/NPP-PHWR/SG/D-1. V&V is mandatory for Class IA, IB & IC systems having programmable components in the form of software or programmable logic. The verification performed must be commensurate with the safety class of the system.

### System Development Life Cycle

The development life cycle of I&C systems consists of the entire stretch from defining the requirements through development to the installation and commissioning of the system (Fig. 1). Documents get generated at every step of the process, e.g., System Requirements Specification, System Architectural Design, System Validation Procedure, System Validation Report, etc.

#### **PFBR I&C Architecture**

In PFBR, I&C systems are classified

into 4 safety classes: Safety Class -1 (SC-Safety 1), Class-2 (SC-2), Safety Class-3 (SC-3) and Non Nuclear Safety (NNS), which mapped are to appropriate classes in the AERB Safety guide D-1. Only systems the



Figure 3. Typical Architecture for SC2 Systems: Dual RTCs with Switch Over Logic System

under IV&V purview are considered in this discussion.

PFBR has 8 SC-1 systems with programmable components including systems performing parameter monitoring & initiation of safety action (implemented with Triple Modular Redundant (TMR) Architecture (Fig. 2)) as well as Safety Logic Systems that control the Safety Actuation Systems. Of these, RTC-based Core Temperature Monitoring System is a software based system, and the others are hardware-based systems with programmable logic.

In addition, there are around 60 nos. of Safety Class-2 & Safety Class-3 Systems which are mostly computerbased systems that use standardized in-house developed hardware and software modules for development. These control nodes, located at the Local Control Centres (LCCs), interface with the field sensors and actuators and perform required processing. Most of these systems are connected to the plant network, or the Distributed Digital Control System (DDCS) using TCP/IP connections.

The Process computer of DDCS sends periodic soft inputs to control nodes (those which require soft inputs). The soft inputs are derived from the periodic inputs the Process Computer receives from source control nodes. In case source data is not available, default values are sent in place of the unavailable signals to meet failsafe criteria. For control nodes which support remote configuration of parameters, configuration change can be performed from Dedicated Display Station (DS). For nodes supporting soft commands, commands can be issued from Dedicated DS or CR-DSs. All communication between control nodes and computers of DDCS happens over two independent LANs of the network.

SC2 systems use a fault-tolerant VME bus based architecture (Fig. 3) with dual redundant Real Time Computers (RTCs) with relay-based Switch Over Logic System. Single board computers called Remote Terminal Units (RTUs) are used for data acquisition from a variety of sensors such as leak detectors, thermocouples, etc.

### Approach followed for IV&V of PFBR Systems

The IV&V procedure for PFBR I&C Systems details out the following:

-List of documents for Custom Built Systems as well as Pre-Developed systems of each of the 3 safety classes

-Definition of each V&V stage in terms of inputs, tasks to be performed and outputs

-Checklists for review of each artifact

-Formats for IV&V requisitions, Action Taken Reports and IV&V reports

-Traceability between AERB-SG-D-25 and the IV&V procedure

An online V&V work flow management interface has been developed to facilitate the IV&V process.

The IV&V committee is internally subdivided into multiple subcommittees, each having one lead member and 3-4 contributing members. System allocation to the subcommittees is done ensuring independence in review.

### **Major V&V Activities**

The major activities that are carried out as part of the IV&V process are:

- Document Verification
- Code Verification
- System Validation
- IV&V Audit & Audit Responses

### **Document Verification**

This process involves the review of the document by the IV&V sub-committee

for correctness, completeness. consistency, traceability to the previous stage and compliance with standards / guidelines. In case of no observations / anomalies, the artifact baselined and forms the basis is of the next stage in the life cycle. In case of any observations / anomalies, a report is issued to the developer listing the IV&V observations. The revised document along with Action Taken Report (ATR) is submitted by the developer. These steps are iterated till document is baselined.

### **Code Verification**

During this process, a combination of manual code walkthrough and review of tool-generated code analysis reports is employed to check the code for correct implementation of requirements, compliance to programming guidelines, traceability with design documentation, known bugs, as well as proper error & exception handling.

### **System Validation**

The validation process is carried out at various stages: at the lab, at factory, as well as on the installed system at site.

Lab validation is performed on sample hardware setup at the lab and helps to weed out errors before final validation at site. Negative test cases that are difficult / not possible to test at site are executed in the lab. Cases that cannot be tested using input simulation (such as card failures, memory corruption, etc.) are also tested using instrumented code in the lab.

Factory validation test is done at factory before shipping the system to site.

During site validation, testing is performed as per the baselined System Validation Procedure on the installed hardware at site. System build checks are performed and functional testing is done in integration with actual sensors, network, other computer-based systems and DDCS components. Mismatches in assumed signal conventions, units,

- 22 - IGCAR Newsletter October 2024

signal mappings, etc. are typical errors that get uncovered during site validation.

### **Audit-Related Activities**

All baselined documents and IV&V artifacts are submitted to the IV&V Audit Committee. All documents, ATRs and V&V reports are audited and an audit report is issued with audit observations on all audited systems. Response for all audit observations is prepared and submitted to the audit committee.

#### **Quantum of Work**

A total of more than 750 documents are to be baselined and submitted along with their IV&V artifacts for audit for completion of the IV&V process for PFBR I&C systems. Of these, over 600 documents have been already submitted. Submissions are being made phase-wise, based on the systems required for the current commissioning phase of the plant. However, in case of any change in requirement, even baselined documents will undergo revision and the V&V process will have to be repeated. Therefore, V&V is an ongoing, continuous work and requires strong commitment from the members as well as the designers and developers for successful conduct.

### Summary

The V&V process helps to establish a robust development model for producing high quality systems for safety applications. Some of the ways in which V&V contributes to system improvement are as follows:

- Ensuring quality of the system through emphasis on a systematic development and review process
- Generation of complete system documentation
- Weeding out errors at various stages
- Quality Improvement by introduction of features for boosting system robustness
- Generation of feedback for new designs, especially w.r.t. to failsafe design, diagnostics & testability.

Lecture Series



Shri Utpal Borah & his colleagues of Central Workshop Division, ESG, Indira Gandhi Centre for Atomic Research, Kalpakkam Tamil Nadu, India.



## CENTRAL WORKSHOP DIVISION - Fulfilling In-House Manufacturing Needs of IGCAR and Other DAE Units

Nestled within the Indira Gandhi Centre for Atomic Research (IGCAR) in Kalpakkam, the Central Workshop has emerged as a vital manufacturing hub, playing a crucial role in advancing atomic research and technology. The Mandate of CWD is to manufacture high quality products in accordance with applicable codes and specifications for FBTR, PFBR, KAMINI, Reprocessing, Post Irradiation Examination, R&D projects, Infrastructure Development, Operation Maintenance and requirements and also, for other DAE units. Recognizing the pressing need for dedicated in-house manufacturing facilities to support the burgeoning demands of nuclear research, Central Workshop was established in 1974 under the leadership of Shri B. S. lyengar and has continually evolved to meet these challenges. Over the years, facilities have been continually upgraded, notably introducing CNC machining during the VIII Five Year Plan. In 2004, the Central Workshop Division (CWD) was formally established under the Engineering Services Group (ESG), marking a significant milestone in its operational evolution. CWD manufactures as well as repairs/refurbishes nuclear components/assemblies quality with stringent tolerances and high

precision, which are otherwise commercially unviable and time consuming, through more than 400 work orders on average annually.

# Machining Excellence and Innovation

The Machine Shop Section (MSS) of CWD plays crucial role through machining as well as assembly of sub mm to reasonably large dimension parts and components with very high precision, surface finish and accuracy. The machine shop is equipped with a comprehensive range of advanced conventional and CNC machine tools to create complex and precise parts of wide range of materials. Facilities include various turning, boring, milling, drilling, taping, slotting, shaping, planning machines and machining centers. To enhance surface grinders, cylindrical grinders, tool and cutter grinders and honing machine. EDM wire cut, die-sinking and drilling machines aid in precision machining of intricate shapes, even in very hard materials.

The conventional turning capacities are up to 350 mm diameter x 5000 mm length and 1650 mm diameter x 3000 mm length while the CNC lathes, used for more precise applications as well as mass production, have capacity up to 450 mm diameter x 1200 mm length with position accuracy of  $\pm 0.005$  mm per 100 mm. Conventional milling can be done up to 400 x 200 x 200 mm while CNC milling capacity is up to 1800 x 800 x 800 mm x 2000 kg weight. Maximum capacities of EDM wire cut and die sinking are 800 mm x 500 mm x 450 mm x 1100 kg weight and 1800 mm x 1000 mm x 450 mm x 2000 kg weight.

# Fabrication, Welding, Hardfacing and Heat Treatment

Fabrication Section (FS), CWD with advanced welding, hardfacing, fabrication. and heat treatment facilities offers a wide range of capabilities fabricate very small as well as large components and assemblies. Welding techniques include GTAW, SMAW, and PTAW. Automated external hardfacing can be performed on flat surfaces up to 200 x 300 mm and circular surfaces with diameters ranging from 50 to 1000 mm. Automated GTAW accommodates linear lengths up to 2500 mm and circular diameters between 500 to 2500 mm. Shearing up to 3000 mm wide is available for both carbon steel (14 mm thick) and stainless steel (9 mm thick). Available cutting machines include plasma cutting (up to 60 mm thick, 2500 mm x 6000 mm), abrasive water jet

cutting (up to 200 mm thick, 3000 mm x 6000 mm) and double band saw cutting for diameters up to 500 mm. Plate bending machines can handle thicknesses up to 25 mm with a minimum bend radius of 200 mm, while pipe bending supports up to 100 NB and 150 NB with and without mandrel respectively. Heat treatment facilities are available for dimensions up to 2000 x 2000 x 1000 mm with maximum weight of 1000 kg, and temperatures up to 1050°C.

# Commitment to Quality: Inspection and Maintenance

The Maintenance and Inspection Section (MIS) at CWD carries out two activities: Inspection and Maintenance, both critical to maintaining product quality and equipment functionality. The Inspection activities ensure stringent quality assurance bv conducting detailed dimensional and geometric tolerance inspections perpendicularity. like parallelism. concentricity, symmetricity, flatness, and straightness, alongside tensile and bend tests, and Liquid Penetrant Examination (LPE) on machined, fabricated, heat treated and assembled jobs, as well as attending to various on-site inspection calls. The Section is equipped with advanced instruments such as Coordinate Measuring Machines with Laser Scanning for 3D Inspections, Vision Measuring Machines, Surface roughness cum Contour Measuring Machine. Profile Projectors, Ultrasonic Thickness Gauges, Video Borescopes, XRF Analysers, Bend Testing Apparatus, 100 Ton Universal Testing Machine and a host of other necessary equipment.

The Maintenance activities of MIS focuses on minimizing downtime and maximizing availability of more than 160 machine tools and equipment at CWD through scheduled preventive maintenance as well as breakdown maintenance as and when required. Refurbishment and upgrades of aging machines, load testing EOT cranes, erection of new machines, relocation of machines, and dismantling of old obsolete/ unserviceable machines are also undertaken by MIS. The inhouse Maintenance activities ensure zero reliance on Annual Maintenance Contracts (AMC) with OEMs or other vendors by providing turnkey standardized maintenance with minimum capital and recurring costs. Some of the major maintenance activities include complete refurbishment, upgradation and life extension of Cooper make Plano Milling Machine and Vertical Turret Lathe, both of which are more than 40 years old, relocation of plasma cutting machine apart from erection and commissioning of the newly procured machines.

## Planning: Efficient Work Flow Management and Future Directions

Planning Section (PS), CWD centrally receives all the work requests (online for IGCAR and offline for other DAE units), issues the work orders and controls the entire workflow and delivery. Introduction of computerized work management system in CWD in the year 2004, finally leading to the current CWD user interface module in the http://atoms, streamlined work requests, production planning and control. With aim of further enhancing overall efficiency and productivity, shortening of delivery times through centralized control of entire workflow and creating possible intellectual properties through better process documentation, Central workshop Integrated Manufacturing (CIM) system is being deployed through http://atoms2 in phased manner.

## Major Contributions and Achievements

PS, MSS, FS and MIS together uphold CWD's commitment towards precision, accuracy, productivity and operational excellence, ensuring high standards of quality and safety. Engineers, Supervisors and Technicians collaborate to develop detailed process plans and schedules, optimize resource allocation/usage and execute as per workflow to deliver

#### Lecture Series

the jobs in minimum possible time.

A host of manufacturing, repair and refurbishing activities are routinely undertaken at CWD on priority for PFBR commissioning. Recent noteworthy works include ~3.7 m long Outer Tube - 2 of Transfer Arm (TA) Guide Tube, spherical profile on Colmonoy-5 hard-faced TA Shielding Sleeves, facing, taper and pocket machining of ~1900 kg ISI plug, Anti-Convection Barrier plugs, Annular Linear Induction Pump (ALIP) duct assemblies, repair of the Intermediate Heat Exchangers (IHX) among others. The 14.5m long TA Guide Tube was refurbished with precision, achieving an overall straightness of 1.2mm against the required 3mm.731 Dummy and 384 Actual Sub-Assemblies (SA) of PFBR were modified by CWD in PFBR RCB and IFSB, RFG respectively despite facing challenges such as working in confined spaces and non-availability of standard tools. Necessarv radius gauges for QA of PFBR SAs were also manufactured and inspected in-house. CWD Technicians carried out in-situ ID buffing and inspection of PFBR Grid Plate Sleeves at hardfaced locations 470 mm deep from top surface in very confined workspace.

CWD makes significant contributions for the Reprocessing and Pyro Processing activities. Continuous Dissolvers, Connector Beds, NO Generator, Sampling Ports, Vent Ports etc. are a few major components manufactured for Reprocessing. The 500m3 Containment Box with 17 lighting and 31 viewing windows for Pyro Processing Metallic Fuel R&D Facility was manufactured and installed by CWD, showcasing capability to handle large, intricate works with stringent tolerances.

CWD contributes immensely to **FBTR** successful operation of by routinely manufacturing and refurbishing various parts and systems. Apart from others, 7 sets modified sub-headers of water with Alloy 800 orifices for Steam

#### Lecture Series

Generator, which was essential for FBTR reaching its design capacity 40MWt, were manufactured. of Tungsten Carbide (WC) pellets are being regularly manufactured, which are used as lower axial shield for FBTR Grid Plate life extension. Various test specimens of enriched Boron Carbide are also machined with very fine surface finish and tight geometric tolerances.

For the R&D projects, CWD routinely manufactures various test specimens, experimental facilities, large test vessels, tools and fixtures, calibration blocks etc. CWD refurbished more than 40 HPGe detectors till date resulting in significant savings.

As part of in-house R&D at CWD, innovative Wire Arc Additive Manufacturing process using existing Automated GTAW machine was demonstrated by building a Near Net Shape diffuser cone of PFBR ALIP dimensions. An impressive ~84% material saving compared to traditional machining methods was achieved. CWD regularly undertakes work requests from other DAE units. Some of the major works completed are feeder pipes for MAPS and RAPS PHT systems, turbine blade in-situ weld for MAPS, reclamation of 5th stage LP turbine tenons of NAPS, hard-facing of stem and disc of safety relieve valve for KKNP, fabrication of beam chamber & cryostat vacuum plumbing line for VECC Kolkata, 16port PVC valve for WSCD etc.

CWD introduced Quality Circle (QC) in 1999 and has been maintaining in structured manner. Currently, there are five QC teams in CWD, namely STAR, SKY, WAVES, HIKARU, and MICRON. These teams, active for over 15 years, have won numerous awards in state and national level competitions. In 2024, STAR, SKY and WAVES QC won the IGCAR QCAM awards.

Shri Adimoolam became the first welder to qualify under the stringent FBTR standards, surpassing ASME codes, showcasing the high level of expertise within CWD. In 2018, Shri S. Thiyagu won 3rd Prize in GTAW and Excellence Award in Finished Product Welding at the international ARC Cup competition in China. In the year 2024, Shri M. Krishnamoorthy, Head, FS was invited to deliver a key-note lecture at the International Congress of the International Institute of Welding (IIW), further underscoring CWD's contributions in the field.

### Summary

CWD, IGCAR stands as a testament skills. innovation, precision, to dedication, and excellence in the field of manufacturing for atomic research. CWD is proud to contribute by combining advanced technology with skilled craftsmanship to produce critical components for success of the projects that require the highest levels of engineering excellence. As it moves forward, CWD remains committed to modernize and augment its capacities and capabilities for continued contributions to the mission of IGCAR as well as other DAE units towards advancement and expansion of nuclear science and technology.



## 32<sup>nd</sup> Prof. Brahm Prakash Memorial Materials Quiz (BPMMQ) programme September 20 - 21, 2024

The 32nd Prof. Brahm Prakash Memorial Materials Quiz (BPMMQ) programme was conducted during September 20 - 21, 2024 at Kalpakkam. The national event is conducted with the objective of promoting awareness about the significant role of materials in various nation-building efforts, particularly the peaceful applications of atomic energy among high school students. The national event was attended by 120 participants from across the country. On 20th Sept, the



Left: Dr Divakar handing over a memento to Dr Balamuralikrishnan, Dir DMRL after the Prof. Brahm Prakash memorial lecture; Right: Distribution of prizes to winning student

students visited the Fast Reactor Test Reactor (FBTR) and the MAPS facility as part of the programme called Metal Camp. Besides quiz, the BPMMQ comprised of elocution contest and memorial lecture. Dr. R. Balamuralikrishnan, Outstanding Scientist and Director, Defence Metallurgical Research Laboratory (DMRL), Hyderabad, graced the occasion as the chief guest and delivered the 32nd Prof. Brahma Prakash Memorial Lecture titled "Science, Engineering and Technology: An Exploration from a Materials Perspective''. Dr. Balamuralikrishnan also visited the Fast Breeder Test Reactor (FBTR), Radio Metallurgical Laboratory and other advanced material characterization facilities of IGCAR and interacted with scientists and engineers on the current and future R&D trends in the area of materials development.

Reported by: Dr. V. Karthik Head, HMTD &PIED, MMG



## **BITS Practice School**

May 28 - July 23, 2024

Forty two students from BITS Pilani, Hyderabad and Goa campuses underwent Summer Practice School at our Centre during May 28 to July 23, 2024. This programme is aimed at exposing the students to industrial and research environments, how the organizations work, follow and maintain work ethics, study the core subjects and their applications in the organization, participate in the assignments given to them in the form of projects. The students were



Students from BITS Practice School with Shri C. G. Karhadkar, Director, IGCAR and colleagues of the Centre during valedictory function

from various disciplines like Chemical Engineering, Electrical & Electronics Engineering, Electronics & Instrumentation Engineering, Mechanical Engineering, Chemistry and Physics. Dr. Amalin Prince A, Professor, Department of Electrical and Electronics Engineering, Goa Campus was the programme coordinator. Students carried out challenging projects in various Groups of the Centre according to their discipline. During the period of their stay, they visited FBTR. As a part of the curriculum, quiz, project work presentations, group discussions, report writing and viva were done. The valedictory function was held on July 22, 2024 with Shri C. G. Karhadkar, Director, IGCAR delivering the valedictory address and distributing the certificates to the students.

Reported by: K. Saipriya Safety, Quality & Resource Management Group



July 26, 2024

The 18<sup>th</sup> batch of Twenty Trainee Scientific Officers from the BARC Training School at IGCAR have successfully completed their training and were graduated in a special ceremony that took place on July 26, 2024. Prof. A. K. Tyagi, FRSC, FNASc, FASc, FNAE, FNA, FTWAS Dean, Homi Bhabha National Institute, Mumbai, JC Bose National Fellow, Honorary Professor, JNCASR, Bengaluru & Former Director, Chemistry Group & Bio-Sciences Group, BARC was the Chief Guest. Dr. Vidya Sundararajan, Associate Director, Safety, Quality & Resources Management Group welcomed



Students from BITS Practice School with Shri C. G. Karhadkar, Director, IGCAR and colleagues of the Centre during valedictory function

the gathering. Shri C. G. Karhadkar, Distinguished Scientist and Director, IGCAR & GSO delivered the presidential address. Prof. A. K. Tyagi gave away the prestigious 'Homi Bhabha Prizes' comprising of a medallion and certificates to the toppers from each discipline and the course completion certificates to all the graduates passing out. The Chief guest also released the souvenir featuring the training school programme during the academic year and addressed the gathering. A few of the Trainee Scientific Officers passing out shared their experience, gave feedback on the academic programme and their stay at the hostel.

Reported by: K. Saipriya Safety, Quality & Resource Management Group





Editorial Committee Members:

Shri J. Rajan, Shri P. Vijaya Gopal, Dr. R. Mythili, Dr. N. R. Sanjay Kumar Dr. C. V. S. Brahmananda Rao, Shri M. Thangamani, Shri G. Venkat Kishore, Ms. Sujatha P. N, Shri M. Rajendra Kumar, Shri S. Kishore, Shri Biswanath Sen, Dr. N. Desigan, & Shri K. Varathan

## Bio-diversity @ DAE Campus, Kalpakkam



White-breasted Waterhens are medium sized birds with long legs for wading and short rounded wings. Their body is laterally compressed, enabling them to run through reeds and undergrowth. It has a white face, fore-neck and breast and grey upperparts. Lemon green long bill with red base. It is less shy and often feeds in the open areas and on dry land.

Published by Safety, Quality & Resource Management Group, IGCAR, Kalpakkam-603102