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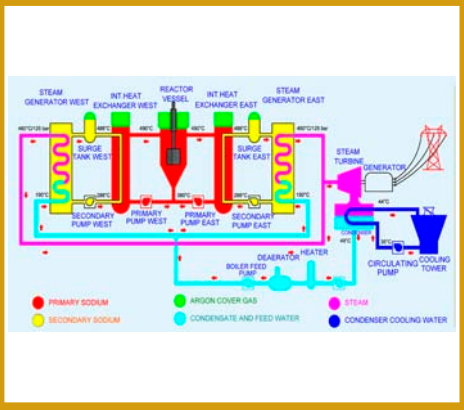
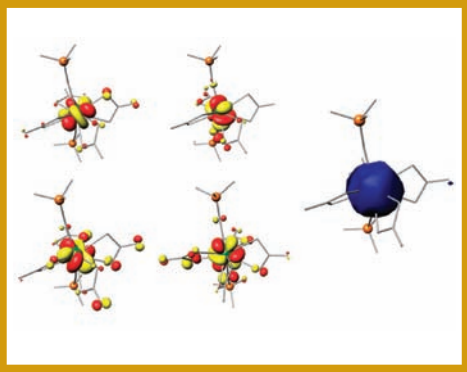
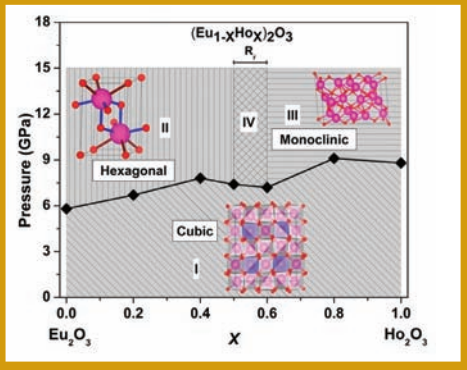
IGC Newsletter







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From the Editorial Committee

Dear Reader

It is our pleasant privilege to forward a copy of the latest issue of IGC Newsletter (Volume 118, October 2018 issue).

In the special technical article Ms. K. Vinolia and colleagues from Reactor Facilities Group have shared their experience on Online Sodium Purity Monitoring System for Fast Breeder Test Reactor.

In the first technical article Shri Ajay Rawat and colleagues from Health, Safety & Environment Group have discussed about the "Estimation of Critical Parameters for Pu-Nitrate Solution Applicable to Fast Reactor Fuel Cycle using Open Monte Carlo Code".

In the second technical article Dr. P. Selvaraj and colleagues from Fast Reactor Technology Group have discussed about the "Commissioning and Operation of Mobile Purification Loop".

This issue's Young Officer's Forum features an article by Dr. G. Gopakumar from Materials Chemistry & Metal Fuel Cycle Group discussing about the Computational Studies on Extraction of Actinide Metal Ions.

Shri K. A. Irshad has described about Phase Structure of Rare Earth Sesquioxides: Cation Size and Pressure Dependence in the Young Researcher's Forum.

We are happy to share with you the awards, honours and distinctions earned by our colleagues.

We look forward to your comments, continued guidance and support.

With best wishes and personal regards

Editorial Committee, IGC Newsletter

Online Sodium Purity Monitoring System for Fast Breeder Test Reactor

Fast Breeder Test Reactor (Figure 1) uses liquid sodium as coolant in primary and secondary circuits. Maintaining purity of nuclear grade sodium is very important to minimize corrosion of structural materials and also to avoid plugging of narrow flow passages in the reactor core and coolant circuits. The main impurities present in sodium are oxygen, hydrogen, calcium and carbon.

Purity is maintained by controlling the source of impurity ingress and also by online purification and monitoring system.

Sodium purification

Cold trapping is based on the property of decrease in solubility of impurities in sodium when temperature is lowered. The same principle is used for measurement of the plugging temperature which is an indication of measure of dissolved impurities in sodium. To measure the plugging temperature, a part of sodium is taken and passed through a small orifice of the plugging indicator as shown in Figure 2.

The liquid sodium flowing through the plugging indicator is cooled by air blown from a blower. The cooling rate is maintained by opening and closing of the damper valve and carried out either in fast or slow mode. While cooling, care should be taken to avoid solidification of the coolant. Above 150°C faster cooling rate is maintained and below 150°C slower cooling rate is followed. This ensures measurement of plugging temperature accurately.

The solidified impurities partially or fully block the sodium flow through the orifice. When the sodium flow through the orifice drops to about 80% of the unplugged orifice flow, temperature measured at the cold point of the plugging indicator is taken as plugging temperature. The plugging temperature measured at the time of decrease in sodium flow indicates the level of impurities present in the sodium based on its impurities saturation curve (Figure 3).

The process of accurate estimation of the impurities present in the sodium has been automated using a simple closed loop controller.

A PID Controller is a feedback control loop mechanism widely used in many industrial control systems. It calculates an error

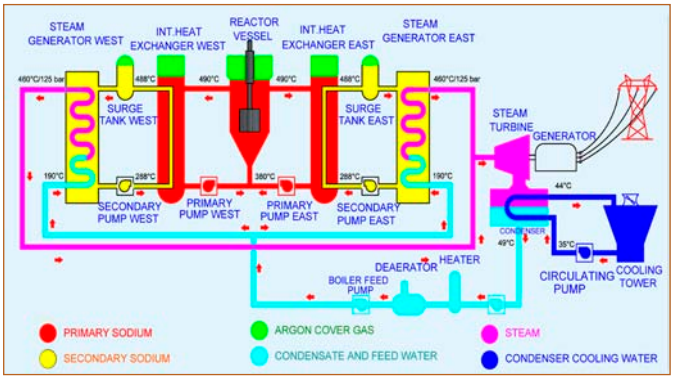

Figure 1:Schematic flow diagram of FBTR

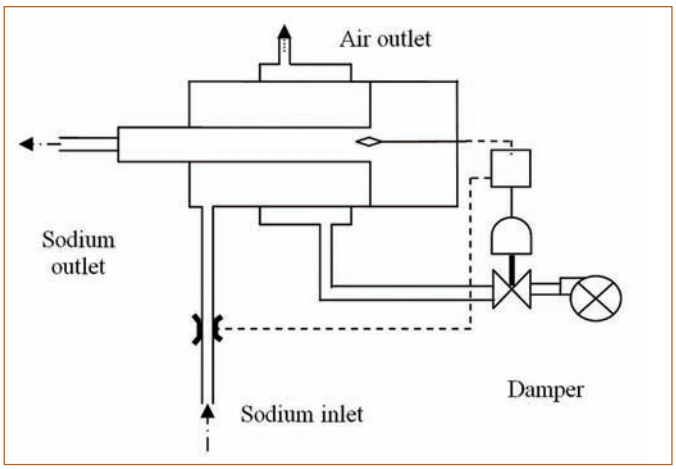

Figure 2: Plugging indicator schematic

signal by taking the difference between the outputs of a system i.e. measured process variable and desired process value or set point.

Comparative study of performance of proportional (P), proportional integral (PI) and proportional integral derivative (PID) controllers reveals that PI controller shall be used when large disturbances and noise are present during operation process and PID controller shall be used when dealing with higher order capacitive processes. Most loops adopt PI control because derivative action is used only when there is a sudden change in the process.

In the manual process, the operator has to watch the temperature and adjust the damper position i.e. cooling air flow rate accordingly. When the sodium temperature is high, operator has to switch on the blower and adjust the damper so that air will be blown to bring the temperature to the desired value. Once it reaches the desired value (20% flow reduction), the damper has to be closed and the blower shall be switched off.

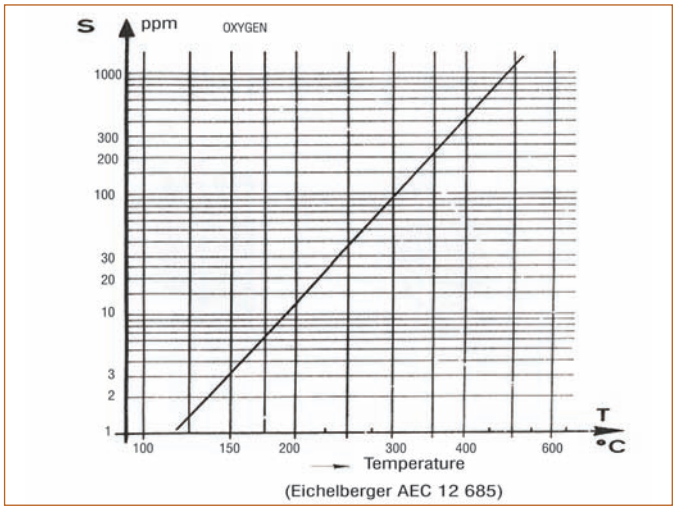

Figure 3: Solubility diagram

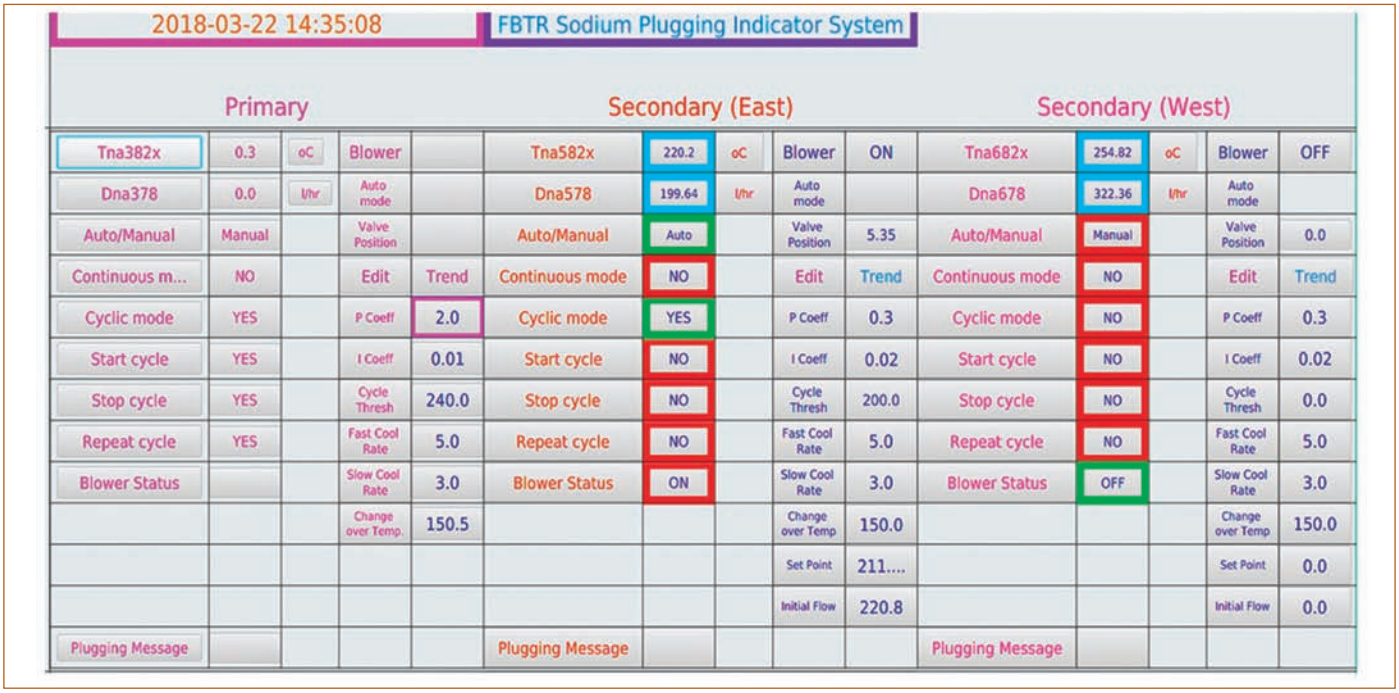

Figure 4: Front end GUI diagram

The process has been automated using stand alone dedicated PC based system with distributed data acquisition and control module and software based control algorithm.

Data acquisition and control system has been used for acquiring field input signals like temperature and flow. Relay output module is used for ON/OFF control of blower. The damper position is controlled by Analog Output (AO) module. Software based PI control algorithm is operated in the Industrial PC based system.

The system will control the cooling rate of sodium by opening and closing the damper in the air flow path. Faster cooling rate is to be maintained up to change over temperature and slower cooling rate below the change over temperature. When the sodium flow drops to about 80% of the normal flow, the temperature at which the flow drops is measured as Plugging Temperature. Then the damper is closed and the blower switched off. Due to this, the temperature will increase. Once the temperature reaches initial threshold value, plugging run is repeated i.e. blower is switched on and the damper opened for air flow. This is known as cyclic mode.

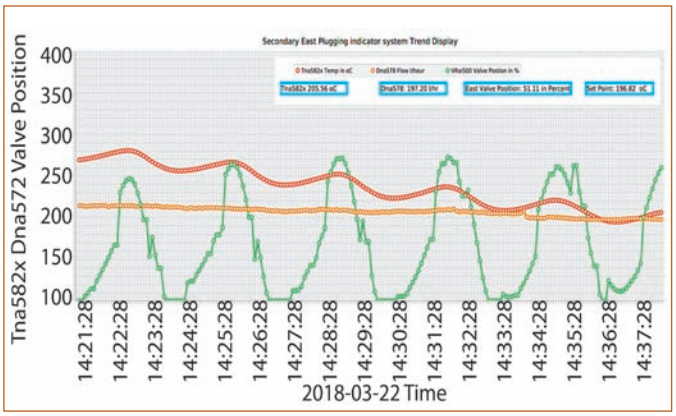

Figure 5: Online trend of controller parameters

Human Machine Interface (HMI) is executed through the front end Graphical User Interface (GUI) as shown in Figure 4.

The GUI has the following important features:

i. The instantaneous values of all the analog signals, status of digital input contacts, relay status and damper position is displayed and refreshed at every one second interval.

ii. The configurable parameters such as kp, ki, change over temperature etc. can be configured using a user name/ password security feature.

iii. The history of plugging temperature is stored with time & date for review.

The online trend of controller parameters is shown in Figure 5.

Using the aforesaid methodology the manual process of measuring the purity of sodium in terms of plugging temperature in primary and secondary circuits of FBTR has been automated. The online sodium purity monitoring system using PI control has been designed, developed & commissioned in FBTR. The blower and damper position control is now being carried out automatically. The performance of the system has been found to be satisfactory. The advantage of this system is that the data acquisition system (DAS) module can be used for distributed environment using ethernet interface.

K. Vinolia and colleagues
Reactor Facilities Group

Estimation of Critical Parameters for Pu-Nitrate Solution Applicable to Fast Reactor Fuel Cycle using Open Monte Carlo Code

Critical parameters of plutonium nitrate fissile solution is available in literature, but parameters pertaining to exact composition of fuel used in Fast Reactor Fuel Reprocessing is scarce. Estimation of critical dimensions for handling Pu nitrate solution specific to Fast Reactor Fuel programme has been studied extensively. The first step in this direction is to device a scheme for estimation of critical parameters for a spherical system to obtain minimum critical dimensions of Pu nitrate fissile solution system. The next step is to validate the same with the values reported elsewhere. After validation of the scheme, Minimum Critical Values (MCV) could be obtained for fuel composition used in the Fast Reactor Fuel Reprocessing.

In this regard this article discusses the methodology adopted for validating the scheme developed for evaluating the MCV for the Pu-nitrate, i.e., Pu(NO_3) solutions. MCV values are often used as a basis for the critical safety considerations during design and construction of fuel cycle facilities. All the criticality calculations are carried out with the OpenMC, a Monte Carlo transport particle simulation code designed for solving neutronic problems mainly the k-eigenvalue criticality, fission source and external fixed fission source using the continuous-energy cross sections ENDF/B-VII.1 retrieved from National Nuclear Data Center, BNL, USA.

The homogenous mixtures of Pu-nitrate solution, with various plutonium isotopic vectors in wt% are considered. The solution is assumed to be purely aqueous and without acidity [$H^+ = 0$] and is surrounded by 30 cm of water reflection. Most of the conventional Monte-Carlo codes solve the eigenvalue problem in fixed geometry, i.e., for a fixed dimensions and materials density, it evaluates the K_{eff}, neutron multiplication factor.

To perform the criticality searches in finding the MCV for critical systems, it is desirable that the Monte-Carlo codes iterate over the parameters until a desired target K_{eff} is achieved. For available criticality codes like MCNP and KENO, one has to manually sweep the parameters to arrive at the MCV, which is very tedious and also prone to manual errors. In this regard we have automated the process for the evaluation of MCV using OpenMC and Python scripts.

The steps involved are as follows:

1) Use of OpenMC for criticality searches in evaluating the MCV for a critical system

2) Validation and benchmarking of the scheme.

The Pu-nitrate solution density is one of the key parameter for criticality calculations. The composition of the homogenous aqueous Pu-nitrate solution was calculated using the density equation.

Based on the Pu-nitrate solution density, a computer code is written in Python programming language for evaluating number density of each isotopes present in the solution.

The minimum critical parameters are evaluated and validated for the critical systems, which includes, the spherical mass (Kg), the diameter (cm) and thickness (cm) for the axially infinite cylinder and the infinite slab and the minimum concentration limit (g/L) for the Pu-nitrate solution is evaluated for infinite system.

Computation of criticality parameters

Computation of K_{eff} is carried out using open source code, OpenMC. To model the complex three dimensional objects OpenMC uses the technique known as constructive solid geometry (CSG). OpenMC is written in FORTRAN 2008 standards. It uses Extensive Mark-up Language (XML) for all user input files. Similar to other Monte Carlo codes, OpenMC uses the neutron cross-section library in the ACE format. For present calculations OpenMC code is successfully linked to the ENDF/B- VII.1 cross-section dataset at 298 K.

The MCV's are evaluated by varying the Pu concentration for a fixed geometrical dimension and search for the optimum critical parameter where K_{eff} is 1. Operations are repeated to get a curve of constant K_{eff} (=1) for different critical parameters as a function of concentrations. The MCV is where critical parameters are at minimum as a function of Pu concentrations, is shown in Figure 1. In Figure 1a it is observed that the minimum critical mass for Pu-nitrate solution is ~518 g for Pu vector of 100/0/0/0. Similarly critical diameter and slab thickness for Pu vector of 95/5/0/0 and 71/17/1/1 are shown in Figures 1b and 1c respectively. For carrying out these calculations repeatedly, a Python script was written to manipulate the geometry and materials composition and to interface it with the OpenMC. An iterative bisection technique is adopted for converging to the target K_{eff}, which in our case is 1.0. The bisection method begin with bracketing the target parameter within a critical parameter bound, which for a sphere is its radius, and for cylinder its diameter and for slab its thickness. The bisection process is repeated till K_{eff} is converged to the

Table 1: Minimum critical values for Pu-nitrate with [H^+=0] for spherical geometry			
Isotopic vector (wt%) $^{239}Pu/^{240}Pu/^{241}Pu/^{242}Pu$	Spherical Pu Mass (kg)		
	IRSN (20 cm of water as reflector)	ORNL (30 cm of water as reflector)	Present study (30 cm of water as reflector)
100/0/0/0	0.51	0.509	0.518
95/5/0/0	0.63	0.618	0.631
90/5/5/0#	0.60	0.572	0.605
80/10/10/0	0.71	0.683	0.700
71/17/11/1	0.92	0.902	0.926

Table 2: Minimum critical values for Pu-nitrate with [H^+=0] for an axially infinite cylinder			
Isotopic vector (wt%) $^{239}Pu/^{240}Pu/^{241}Pu/^{242}Pu$	Cylinder Diameter (cm)		
	IRSN (20 cm of water as reflector)	ORNL (30 cm of water as reflector)	Present study (30 cm of water as reflector)
100/0/0/0	15.66	15.63	15.49
95/5/0/0	17.94	17.88	17.85
90/5/5/0#	17.64	17.60	17.56
80/10/10/0	18.74	18.71	18.69
71/17/11/1	20.66	20.65	20.65

Table 3: Minimum critical values for Pu-nitrate with [H^+=0] for infinite slab			
Isotopic vector (wt%) $^{239}Pu/^{240}Pu/^{241}Pu/^{242}Pu$	Slab Thickness (cm)		
	IRSN (20 cm of water as reflector)	ORNL (30 cm of water as reflector)	Present study (30 cm of water as reflector)
100/0/0/0	5.84	5.68	5.58
95/5/0/0	7.24	7.15	7.09
90/5/5/0#	7.04	6.96	6.90
80/10/10/0	7.70	7.65	7.59
71/17/11/1	8.90	8.88	8.81

Table 4: Critical concentration of Pu in g/L for which K_{inf}= 1 with [H^+=0]			
Isotopic vector (wt%) $^{239}Pu/^{240}Pu/^{241}Pu/^{242}Pu$	Critical concentration limit (g Pu/L)		
	IRSN	ORNL	Present study
100/0/0/0	7.2	7.21	7.25
95/5/0/0	7.8	7.77	7.84
90/5/5/0#	7.64	7.60	7.66
80/10/10/0	8.07	8.05	8.11
71/17/11/1	9.2	9.15	9.22

[Note: # the decrease in value of critical parameter is due to the presence of ^{241}Pu which has higher thermal fission cross section (σ_f =1012 b) compared to ^{239}Pu (σ_f =745 b)]

desired target value within the required tolerance which is set as 5E-04. Figure 2 shows the flowchart diagram employed for the algorithm used for the optimization.

Tables 1, 2 & 3 present the MCV obtained using the methodology discussed above with different Pu isotopic vector composition for the sphere, axially infinite cylinder and infinite slab respectively. Apart from these values, the critical concentration limit of Pu in g/L is presented in Table 4 for which the infinite medium multiplication

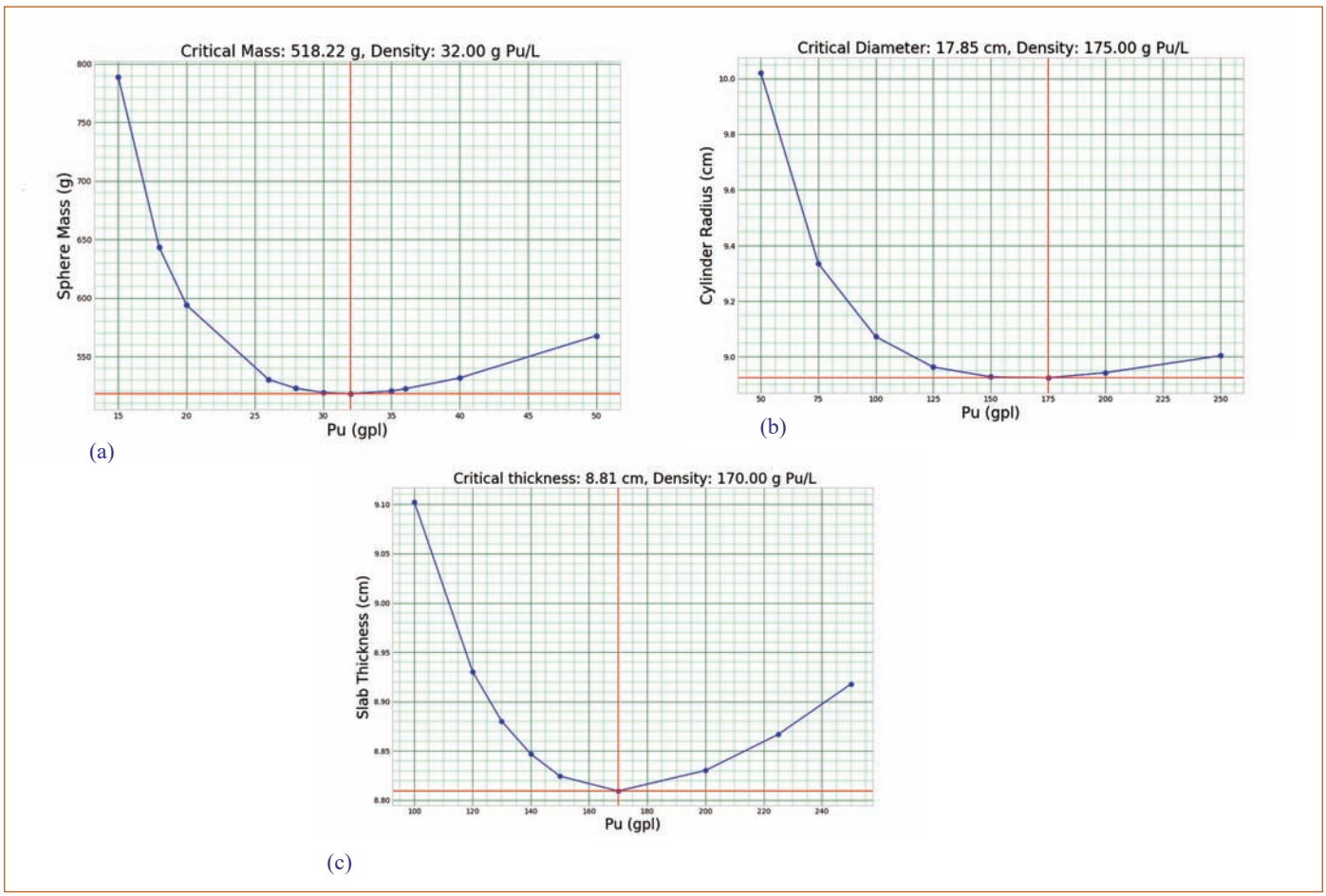

Figure 1:The critical parameter as a function of Pu concentrations in g/L for different $^{239}Pu/^{240}Pu/^{241}Pu/^{242}Pu$ in wt% (a) critical mass for 100/0/0/0 (b) cylindrical diameter for 95/5/0/0 and (c) slab thickness for 71/17/1/1

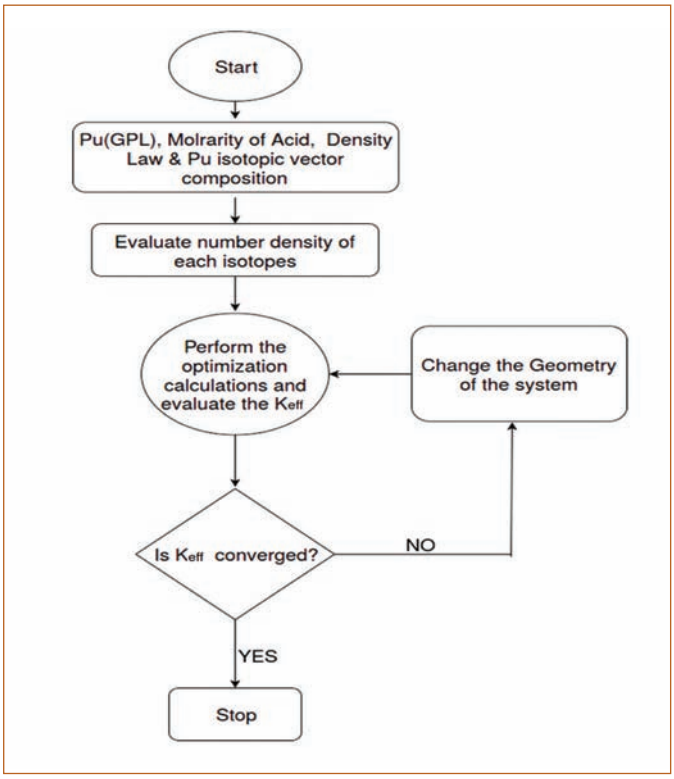

Figure 2: Flow diagram showing algorithm used for criticality search using bisection method

K_{inf} is unity. These values are compared with the similar studies performed at IRSN and ORNL, and the calculated critical parameters are in close agreement with the reported values.

In this article, a concept of K_{eff} search using OpenMC is demonstrated. To achieve this, Python code was written to manipulate the geometry and materials composition and interfacing these with the OpenMC for K_{eff} calculations. To perform the criticality searches in finding the MCV for critical system, it is desirable that the Monte-Carlo codes iterate over the parameters until a desired target K_{eff} is achieved. More than 100 individual cases have been run in the present study to arrive at the MCV values. Because of the automation in the process for MCV determination it eliminates the time associated with executing individual cases.

It is seen from the results that the calculated MCV are in close agreement with the reported values available in the open literature. The variation which is observed is due to the difference in density equations used to predict the density of Pu-Nitrate solution.

Ajay Rawat and colleagues
Health, Safety & Environment Group

Commissioning and Operation of Mobile Purification Loop

Flooding circuit of Fast Breeder Test Reactor consists of two sodium tanks containing total sodium inventory of 64 m^3. This sodium in flooding circuit will be flooded on the core during any sodium leak incident in reactor vessel and subsequent reduction in sodium level causing loss of coolant from core. The sodium flooded on the core will remove heat from the core which avoids core melt down accident. This circuit is called emergency core cooling system. The sodium tanks were erected and filled with sodium during the year 1985. After filling, the impurity level in sodium could not be measured since no purification circuit was available in the flooding circuit. As per Atomic Energy Regulatory Board (AERB) recommendation, a separate sodium purification system is to be installed for purifying this sodium. So it was decided to utilise a Mobile Purification Loop available at Fast Reactor Technology Group (FRTG). This loop was designed, constructed and operated at FRTG (then Reactor Engineering Laboratory) to purify the sodium required for different experiments by cold trapping method. After commissioning the loop, initially it was utilised to purify the sodium inventory required for FBTR. This loop can be connected to any sodium tank/vessel for purifying the sodium in the tank/vessel.

This loop was used for purification of sodium required for FBTR Control Rod Drive Mechanism test facility and FBTR Flowmeter Calibration test facility. Figure 1 shows the photograph of Mobile Purification Loop for FBTR flowmeter calibration. At present, it has been proposed to bring back this loop into operation at FRTG and ensure its performance before installing and operating in FBTR.

Description of mobile purification loop

This loop consists of Cold Trap, Plugging Indicator, Sodium Sampler, Vent Pots, Electromagnetic Pump, Permanent Magnet flowmeter, coarse filter and interconnecting pipe lines with valves. The material of construction of loop is AISI 316. Electrical and instrumentation panels are installed for preheating, pump control, monitoring loop parameters and leak detection. Figure 2 gives the photograph of Mobile Purification Loop.

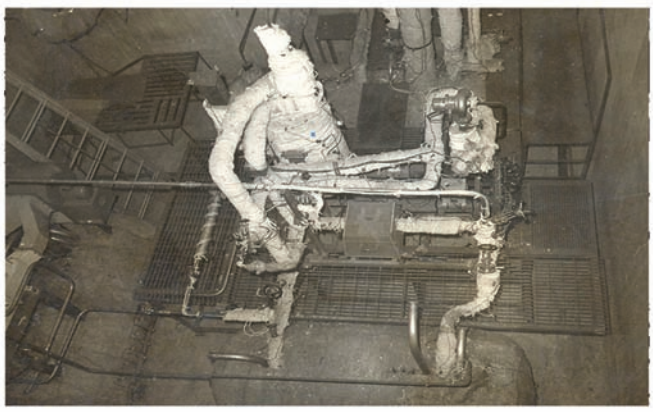

Figure 1: Mobile purification loop for FBTR flowmeter calibration (Year 1982)

Figure 2: Mobile purification loop (Year 2018)

Maximum operating temperature of loop is 550 °C. EM pump can develop a maximum pressure of 1.4 kg/cm^2 and a flow of 2 m^3/h. Sodium in loop can be circulated in two modes of operation.

Re-qualification of loop

During shut down period, the loop was preserved under argon atmosphere in Engineering Hall-I. The component and piping were kept covered with polythene sheets. Before initiating the commissioning activities, it was decided to re-qualify the loop by carrying out required quality control checks. So the surfaces of the components and piping were cleaned with acetone. Then Liquid Penetrant Examination of the entire surface was carried out and the result was found to be satisfactory. Ultrasonic Examination, Ultrasonic thickness measurement and in-situ metallographic examination were carried out at earmarked locations and the examination results were satisfactory. The loop was shifted to Engineering Hall-III and erected in a steel structure in low bay.

Commissioning of loop

The loop was connected to a tank containing 600 litres of sodium. Argon line from vapour trap was also connected to a cover gas header. Then fixing of surface heaters, thermocouples, leak detectors and thermal insulation on pipe lines and components

Figure 3: Electrical and instrumentation panels of mobile purification loop

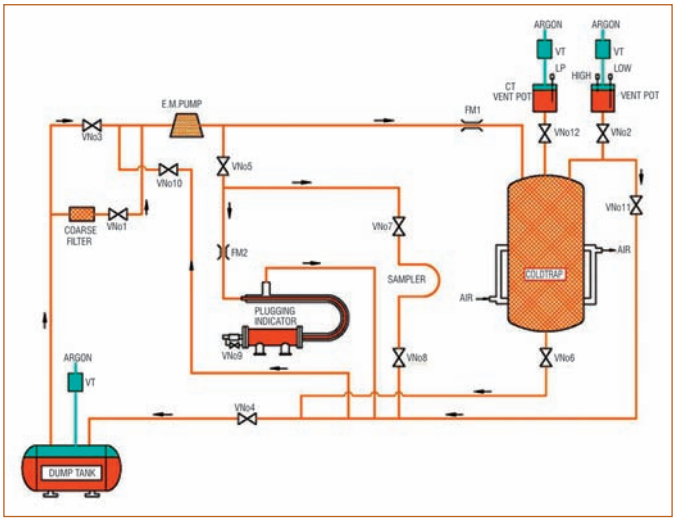

Figure 4: Flow sheet mobile purification loop

were completed. Electrical and instrumentation panels were made ready, installed and commissioned. Healthiness of EM pump, flow meters, level sensors and leak detectors were checked. Functioning of blowers of cold trap and plugging indicator were also checked. Pressure Hold Test of the loop and components were carried out at 1 kg/cm^2 for 24 hours at room temperature. No pressure drop was observed and the loop was cleared for further commissioning activity. Pre-commissioning checks of the loop, like checking of heaters, thermocouples, leak detectors, level probes, pressure gauges and control logics, etc., were completed. Then preheating of the loop was initiated. At a loop temperature of 250 °C, argon gas communication between loop and sodium tank was checked through different paths. Gas communication was found to be satisfactory through all paths.

Sodium filling into the loop was carried out by differential pressure method. After filling the loop, sodium flow through the main path could not be established even at a high temperature of 350 °C. Since the loop was relatively old it was suspected that the cold trap could have got saturated with impurities during the earlier sodium purification campaigns. Hence the cold trap was replaced with an available new cold trap of similar oxide trapping capacity. Once again the loop was filled with sodium; nevertheless sodium flow could not be established in the main path. It was doubted that there might be solid sodium oxide plug in the EM Pump duct and flow meters. So the pump was replaced with a similar type of EM pump of same capacity. Then the permanent magnet flowmeters located in the inlet lines of cold trap and plugging indicator were also replaced with new 20 NB size flowmeters.

The loop was preheated to 250 °C and it was filled with sodium. This time sodium flow was achieved in all the flow paths.

The Electromagnetic pump was operated at different voltages and the performance was found to be satisfactory. Figure 3 gives the photograph of electrical and instrumentation panels showing the parameters during operation of loop. Figure 4 gives the flow sheet of Mobile Purification Loop.

Purification of sodium in dump tank

The loop and dump tank sodium was circulated at 250 °C. Rated sodium flows were maintained at various flow paths. Plugging run was taken and slow plug was noticed at 200 °C. Then cold trap was put into operation and the sodium in loop and tank was purified up to 105 °C under no-plug condition which corresponds to an oxygen concentration in sodium of < 2 ppm.

An old Mobile Purification sodium Loop at FRTG was re-qualified by carrying out all quality control examinations. All the systems related to the loop were commissioned. Sodium was filled in the loop and operated at 250 °C. Purification of 600 litres of sodium in dump tank was completed by cold trapping. Thus the Mobile Purification Loop was operated and the sodium purification capability has been demonstrated. The performance of the loop is satisfactory and is suitable for purification of sodium in flooding circuit of FBTR.

P. Selvaraj and Colleagues
Fast Reactor Technology Group

Young Officer's FORUM

Computational Studies on Extraction of Actinide Metal Ions

Dr. G. Gopakumar obtained his MSc degree (Physical Chemistry) from School of Chemical Sciences, Mahatma Gandhi University, Kerala. He carried out his doctoral studies at Katholike Universiteit Leuven, Belgium under the supervision of Professor Minh Tho Nguyen. He was awarded the Ph.D in the year 2008 for his thesis work on "Computational Studies of Doped Germanium Nanoclusters". Subsequently, he carried out post-doctoral research works under the guidance of Professor Evert Jan Baerends (Vrije Universiteit, Amsterdam), Professor Walter Thiel (Max-Planck Institut für Kohlenforshung, Mülheim), and Professor Frank Neese (Max-Planck Institut für Chemische Energiekonversion, Mülheim). After spending two years as a visiting scientist at IGCAR, he joined the department as a scientific officer in the year 2016. His research interests focus on modelling of the extraction behaviour of actinides and lanthanides by various ligands.

Nuclear fuel reprocessing is an important step in closing the nuclear fuel cycle. The most preferred method for the separation of actinides from the fission products is by solvent extraction. The versatile solvent tri-*n*-butyl phosphate (TBP) dissolved in a hydrocarbon diluent is commonly used for this purpose. Despite its excellent extraction behavior, TBP shows certain limitations, which affect its performance in fast-reactor fuel reprocessing. The drawbacks of TBP include its tendency to form third-phase in the extraction of tetravalent metal ions & chemical and radiation degradation. These limitations demand development of alternate extractants with improved performance, for the extraction of actinides with better properties than TBP. This requires molecular level understanding of the extracting solvent, metal ions and complex species formed during the extraction process. Structural parameters derived using spectroscopic and X-ray crystallographic techniques are highly useful and often compliment direct experimental observations on solvent extraction. Nevertheless, experimental ligand design for the separation of lanthanide and actinide metal ions from irradiated fuel is a tedious task.

On the other hand, the electronic structure and properties of molecular systems can be well understood by applying quantum chemical methods. This could be accomplished by using computational chemistry which focuses on the applications of quantum mechanics and provides valuable information on the electronic structure of molecular systems and their properties. It becomes an ideal choice for molecular systems and short-lived intermediates that are difficult to study experimentally. The logical set of laws that can be derived by comparing the molecular

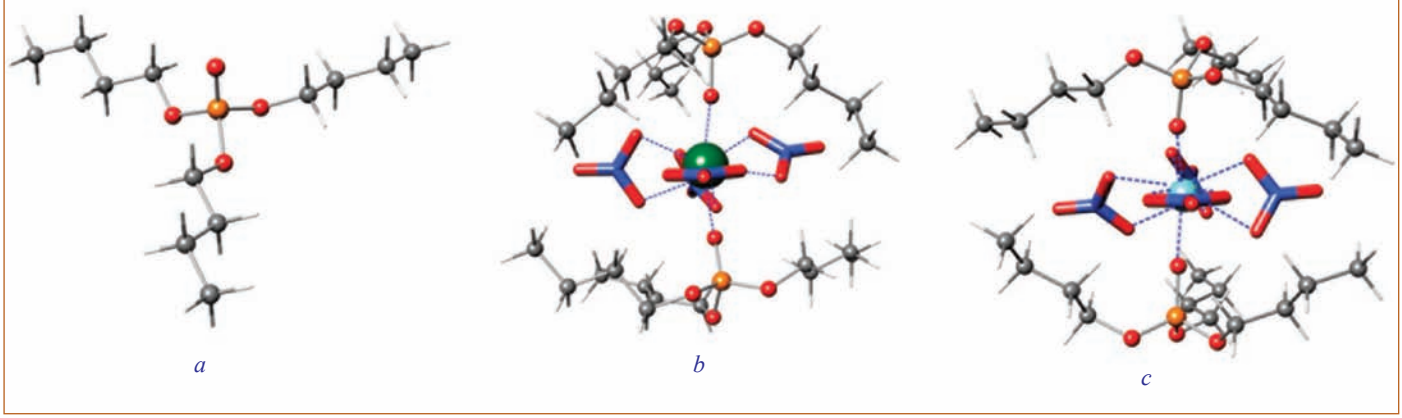

Figure 1: Optimized geometries of (a) TBP, (b) $Pu(NO_3)_4{\cdot}2TBP$ and (c) $Zr(NO_3)_4{\cdot}2TBP$ at RI-BP86/def2-TZVP(-f) level (color code: green ball is plutonium, light blue ball is zirconium, dark blue represents nitrogen, red colour indicates oxygen, orange balls are phosphorus, gray balls are carbon and white colour represents hydrogen atoms

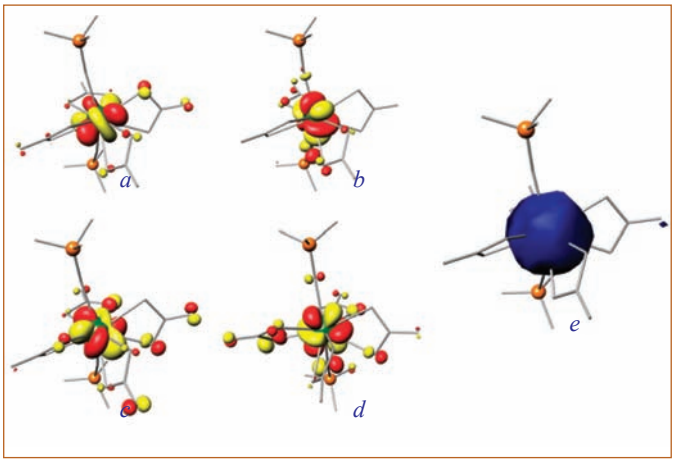

Figure 2: Shapes of singly occupied molecular orbitals (a-d) and spin density isosurface (e) for $Pu(NO_3)_4$·2TBP complex at RI-BP86/def2-TZVP(-f) level. Carbon and hydrogen atoms are omitted from the figure for simplicity

properties resulting from an electronic structure calculation and experiment will be of great importance. This will be useful in predicting the outcome of a future experiment. In this regard, our primary aim is to theoretically address problems relevant to nuclear fuel reprocessing, with a focus on computational ligand design. Depending upon the size of the molecular systems under consideration, this task requires the application of different computational methodologies; ranging from the state-of-the-art computational chemistry techniques to multi-scale modeling. The highlights of our research are reported in subsequent sections.

Methodologies & challenges

Lanthanides and actinides are heavy elements and therefore the applications of quantum chemical method should include relativistic effects. This can be achieved either by using effective core potentials (ECP), thereby reducing the number of electrons treated explicitly or by including scalar relativistic Hamiltonians (example using ZORA or DKH methods) in conjunction with an all electron basis set. In the case of the former, scalar relativistic (quasi-relativistic) ECPs are generally assumed to be sufficient. Depending upon the size of the molecular system under consideration, it is necessary to find a balance between the desired level of accuracy, method, basis sets and resources. For instance, simplification of ligands for calculations (for example, by chopping out large hydrocarbon chains) should be performed with extreme caution considering the electronic and steric factors which affects its extraction/complexation ability. It is worth noting that, density functional theory (DFT) methods provide a very good accuracy/cost ratio. However, the choice of the functional is often system and property dependent. In order to identify a suitable functional for a particular system and/or property, proper benchmark calculations has to be performed against available experimental and/or highly accurate theoretical data. For example, B3LYP hybrid density functional developed in the late 80s was considered as a significant improvement over Hartree-Fock method and is regarded as the most popular functional for predicting and understanding the structure and properties of general organic molecules. However, the application of B3LYP functional for systems containing metal atoms is often debatable owing to the presence of multiple spin states, multireference character of the ground electronic state, etc. Another important challenge is to consider dispersive interactions, which carry significant attractive component as a result of instantaneous dipoles and higher-order multipoles. It is known that dispersion forces are not included in conventional density functional theory and one possibility to consider them will be by applying the atom-pair wise corrections (DFT-D methods). In addition to this, effect of the solvent environment can be considered by employing continuum solvation models (COSMO/PCM). Within the framework of COSMO solvation model, it is also possible to compute solubility of organic substances, activity coefficients, etc., by combining quantum chemistry and thermodynamics. Additional insights on electronic structure can be obtained by applying methodologies such as; atoms-in-molecules (AIM), electron localization function (ELF) and fragment molecular orbital analysis, which are embedded in the wide variety of quantum chemical modeling softwares.

As a first step to understand the electronic structure of tri-*n*-butyl phosphate ligand, a detailed computational survey was performed which indicated that the existence of a number of low-energy conformers for TBP within the 5 kcal/mol energy window. This suggests the conformational flexibility of the system under experimental conditions, as the C-C bond rotation is an energetically favorable process. The lowest energy geometry for TBP was characterized as an energy minimum by evaluating real harmonic vibrational frequencies at RI-BP86/def2-TZVP(-f) level. it is to be noted that for better computational efficiency, the f-polarization functions for main group elements were removed from the standard def2-TZVP basis sets and dispersion effects were considered using latest atom-pairwise dispersion correction with Becke-Johnson damping (D3BJ). The P=O and P-O bond lengths were estimated to be 1.48 and 1.60 Å, respectively (cf. Figure 1a) and Mulliken population analysis indicated considerable amount of electron population on the oxygen atom (-0.70 e).

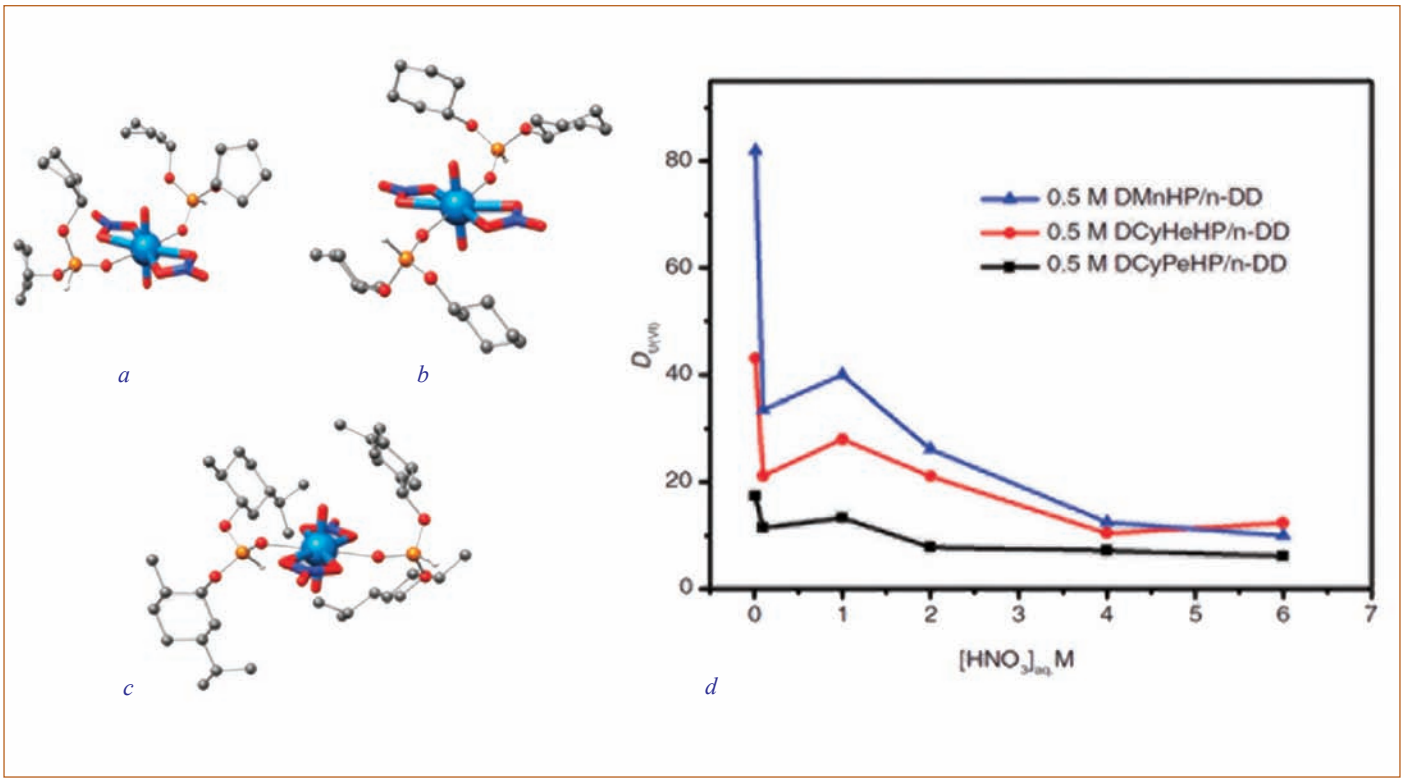

Figure 3: Optimized geometries of (a) $UO_2(NO_3)_2$·2DCyPeHP, (b) $UO_2(NO_3)_2$·2DCyHeHP, (c) $UO_2(NO_3)_2$·2DMnHP and (d) variation of $D_{U(VI)}$ with equilibrium aqueous phase nitric acid for the H-phosphonates at 303 K

After establishing the geometry for TBP, we turned our interest towards the metal complexes of TBP. Along with U, Pu and minor actinides, the dissolver solution of thermal and fast reactor spent nuclear fuels also contain the fission product Zr, which is produced as a major element during U/Pu fission. The experimental studies indicate significantly higher D_{Pu} (24) for TBP compared to D_{Zr} (0.5) at 4M nitric acid medium. This highlights the influence of the nature of the metal ion on the extraction behaviour of TBP. In this context, we set out to investigate the difference in extraction behaviour of plutonium and zirconium nitrate complexes with TBP. The model structures for $Pu(NO_3)_4$·2TBP and $Zr(NO_3)_4$·2TBP were generated by distributing TBP molecules around the metal core in all possible ways. The resulting starting configurations were subjected to geometry optimization at BP86/def2-TZVP(-f) level considering various spin states. The calculations were corrected for relativistic effects using zero-order regular approximation (ZORA) approach and for Pu atom the segmented all-electron relativistically contracted (SARC) basis sets were used. A quintet ground state was derived for Pu(IV) complex while Zr(IV) form singlet species (Figures 1b and 1c). Inspection of the singly occupied molecular orbitals and derived spin population value for Pu (4.21 electrons) suggested that the unpaired electrons are mainly localized on the metal *f* orbitals (cf. Figure 2). In order to provide insights on the chemical bonding, an "atoms in molecules" analysis has been performed on the Pu(IV) and Zr(IV) complexes with TBP. The calculated Laplacian of electron density ($\nabla^2\rho_b$) were positive values which indicated a considerable amount of ionic character for M-O{TBP} and M-O{NO_3} bonds.

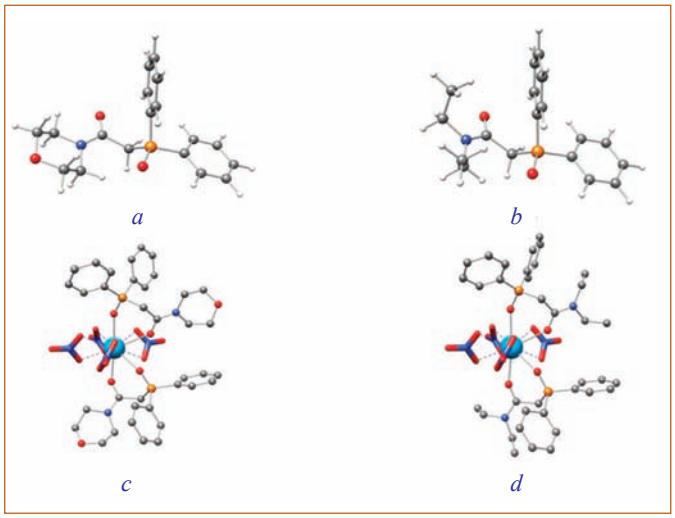

Figure 4: Optimized geometries of (a) diphenyl morpholine CMPO, (b) diphenyl-N,N-diethyl CMPO, and their respective complexes with $Th(NO_3)_2$ (c and d) at PBE0/def2-TZVP-ECP level

In addition to the electronic structure of complexes, one of the

aims of our study was to understand the extraction ability of various ligands. As a first step towards this, we have attempted to model the extraction process computationally by evaluating the extraction energies for TBP-Pu and TBP-Zr systems. The extraction energies were evaluated by considering the solvent environment in DFT calculations by applying COSMO solvation model ($\varepsilon = 80.4$ for aqueous, $\varepsilon = 2$ for n-dodecane and $\varepsilon = 6.2$ for the organic phase). It is to be noted that in the beginning of the extraction, the metal nitrates and TBP are in aqueous and *n*-dodecane medium, respectively. During extraction, TBP complexes with the metal nitrates at the aqueous-organic interface are extracted to the organic medium. After carefully considering these facts, the extraction energies were evaluated by taking the energy balance of equations (1) and (2).

$$Pu(NO_3)_{4(aq)} + 2TBP_{(n\text{-dodecane})} \rightarrow Pu(NO_3)_4.2TBP_{(org)} \quad (1)$$

$$Zr(NO_3)_{4(aq)} + 2TBP_{(n\text{-dodecane})} \rightarrow Zr(NO_3)_4 \cdot 2TBP_{(org)} \quad (2)$$

The calculated large extraction energies for plutonium complex suggests greater selectivity of TBP and this observation is in agreement with the trend established from experimental distribution ratio data.

After establishing the correlation between the extraction energies (theory) and trend in distribution ratio data (experiment), we have attempted to further probe the usefulness of these parameters for different ligands/metal ion combinations. The first system we considered was selected alicyclic H-phosphonates ligands (dicyclopentyl H-phosphonate, dicyclohexyl H-phosphonate and dimenthyl H-phosphonate) and $UO_2(NO_3)_2$. The experimental studies indicated the following trend in the distribution ratio data; dicyclopentyl H-phosphonate (7.1) < dicyclohexyl H-phosphonate (10.4) < dimenthyl H-phosphonate (12.5) at 4 M nitric acid concentration (cf. Figure 3). As a preliminary step to computationally model the extraction process, we have identified the lowest energy structures for the respective ligands. The ground electronic states of the corresponding metal complexes were derived by distributing the ligands (after considering the stoichiometric ratio) around the $UO_2(NO_3)_2$ unit (cf. Figure 3). This was carried out by employing the PBE0 functional with 25% of HF exchange in conjunction with def2-TZVP basis sets and D3BJ dispersion corrections. For uranium atom, the 60 inner-shell core electrons were replaced by an effective core potential (ECP) generated for the neutral atom using quasi-relativistic methods and explicitly treated electrons were described by the standard def2-TZVP basis sets. After establishing the ground electronic states, the extraction energies are evaluated by taking the energy difference of the equations (3), (4) and (5)

$$UO_2(NO_3)_{2(aq)} + 2DCyPeHP_{(n\text{-dodecane})} \rightarrow UO_2(NO_3)_2.2DCyPeHP_{(n\text{-dodecane}))} \quad (3)$$

$$UO_2(NO_3)_{2(aq)} + 2DCyHeHP_{(n\text{-dodecane})} \rightarrow UO_2(NO_3)_2.2DCyHeHP_{(n\text{-dodecane})} \quad (4)$$

$$UO_2(NO_3)_{2(aq)} + 2DMnHP_{(n\text{-dodecane})} \rightarrow UO_2(NO_3)_2.2DMnHP_{(n\text{-dodecane})} \quad (5)$$

The calculated extraction energies for the uranium complexes increases in the order dicyclopentyl H-phosphonate (-71.6 kcal/mol) < dicyclohexyl H-phosphonate (-73.6 kcal/mol) < dimenthyl H-phosphonate (-88.4 kcal/mol) and are in agreement with the experimental results.

We have further extended this methodology to systems containing diphenyl morpholine CMPO(L1) and diphenyl-N,N-diethyl CMPO (L2) ligands with $Th(NO_3)_2$. The geometries and electronic structure of the ligands and metal complexes were characterized at DFT level employing PBE0 functional. The extraction energies were evaluated by taking energy difference of the equations (6) and (7)

$$Th(NO_3)_{4(aq)} + 2L1_{(chloroform)} \rightarrow Th(NO_3)_4.2L1_{(chloroform)} \quad (6)$$

$$Th(NO_3)_{4(aq)} + 2L2_{(chloroform)} \rightarrow Th(NO_3)_4.2L2_{(chloroform)} \quad (7)$$

In agreement with the experimental results, the calculated extraction energies indicated a large value for diphenyl-N,N-diethyl CMPO ligands (-77.4 kcal/mol) as compared to diphenyl morpholine CMPO (-69.2 kcal/mol).

In summary, we have applied computational chemistry methodologies to understand the geometric and electronic structures of various actinide metal complexes and their extraction behavior with different types of ligands. The extraction energies calculated by applying quantum chemical methodologies are in good agreement with the trend established by experimental distribution ratio data. In view of the results obtained in the present study, extraction energies can be considered as a useful index in predicting and comparing the complexation ability of different ligands

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Young Researcher's FORUM

Phase Structure of Rare Earth Sesquioxides: Cation Size and Pressure Dependence

Shri K. A. Irshad obtained his Masters degree in physics from Central University of Kerala, Kasaragod. He joined IGCAR as a research fellow in July 2013 and pursued his Ph. D from HBNI under the supervision of Dr. N. V. Chandra Shekar, Condensed Matter Physics Division, Materials Science Group. His prime area of interest is in investigating material properties at extreme conditions of pressure and temperature. He has submitted his doctoral thesis titled "Studies on crystal structure of functional rare earth sesquioxides at high pressures" to HBNI. He has authored eight peer reviewed publications in international journals. Presently he is a Research Associate at IGCAR.

The rare earth sesquioxides (RES) are RE_2O_3 type compounds where RE stands for the rare earth cation. These oxides are widely studied due to their variety of physical, chemical and structural functionality. The functional nature of these oxides is extensively utilized in many of the technologically important fields. Solid state lasers, solid oxide fuel cells, radiation detectors, wave guides, scintillating materials, random access memory (RAM) devices and sensing are few of the areas where these oxides are used. Some of these oxides have potential application as control rods in nuclear reactors and nuclear waste host materials. The fundamental properties of these oxides are further enhanced by fine tuning the specific functionalities through chemical doping, defect creation/ control, nano structuring, fabrication of thin films etc. In addition, hydrostatic pressure is also known to be an excellent tool to fine tune the functionalities of these materials. The crystal structure, electronic structure and lattice properties can get profoundly altered at high pressures. Moreover the chemical reactions taking place at high pressures challenges our present understanding of the reactions at ambient conditions. A promising way to mimic the effect of hydrostatic pressure on materials properties is the chemical substitution/ doping to the crystalline lattice.

The understanding of polymorphism and related phase transitions in the RES is essential to establish more definitive structure-property correlations which would help further exploration of the functional nature of these oxides. Depending on the cation size, RES exhibit three different structure types, C-type (small cations), B-type (medium cations) and A-type (large cations), at Ambient Temperature and Pressure (ATP). As the crystal structure of RES depends on the size of the cation, a systematic investigation on the cation size dependant structural evolution in these RES would be more beneficial in understanding the preference of one structure type over the other. At high pressures, these oxides show different transition sequences depending on which category they belong to. If they belong to the category of small cations then a C→B→A transition is expected, on the other hand a direct C→A transition is expected for RES of medium cation size. There are reports on the phase transition (isostructural or by a distortions to the hexagonal structure) in RES with large cation size, but are debatable due to the contradictory reports from various studies. Also, there are, ambiguities in the high pressure behavior of RES with hexagonal structure (large cation size). The present studies are intended to shed light on the cation size dependent structural evolution, both at ambient and at high pressures, and to gather more understanding about the polymorphic structural phase transitions occurring in the RES. To meet the objectives, simple RES, cubic (small cation size), monoclinic (medium cation size) and hexagonal (large cation size) structures have been investigated at high pressures. The insights from these investigations are used to understand the high pressure behavior of solid solutions of RES.

Structural stability and compression behaviour of simple RES Tm_2O_3, Eu_2O_3 and La_2O_3 crystallizing in the C-type, B-type and A-type respectively have been investigated at high pressures. High pressure (HP) synchrotron X-ray diffraction and HP Raman scattering studies on Tm_2O_3 revealed a structural phase transition from C-type cubic to A-type hexagonal structure at ~12 GPa (Figure 1a). This transition was associated with a 7.4% volume collapse and are known to be of reconstructive type. Further, the results

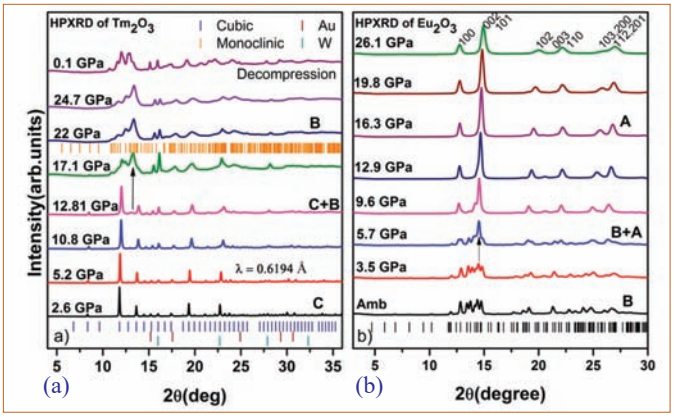

Figure 1: XRD pattern of C-type Tm_2O_3 and B-type Eu_2O_3 collected at various pressure steps showing the C→B and B→A structural phase transitions respectively. The tick marks indicates the reflection positions of different phases present

of ab initio density functional theory (DFT) calculations revealed an increase in the electron density of states (DOS) near the Fermi level at the transition pressure, indicating the structural instability of the cubic phase. On the other hand, a structural phase transition from B-type to A-type has been observed for the Eu_2O_3 sample at a comparatively lower transition pressure of 4.3 GPa (Figure 1b). This transition was accompanied with a volume reduction of 2%, indicating the lower energy barrier of B→A transition which in this case is displacive in nature. Compared to the C-type Tm_2O_3 and B-type Eu_2O_3, the investigation on the A-type La_2O_3 revealed no structural phase transitions at high pressures. These studies show that, the small and medium cation sized RES prefer a transition from C→B and C→A respectively at high pressures whereas, the RES with large cations prefer to be in the A-type structure even at high pressures.

In order to understand the compression behaviour of B-type and A-type structure of RES, lattice compressibility of Eu_2O_3 and La_2O_3 has been examined using the equation of state (EOS) fit to the structural parameters. An axial compressibility of $\beta_a = 3.33(5) \times 10^{-3}$ GPa^{-1}, $\beta_b = 1.18(3) \times 10^{-3}$ GPa^{-1} and $\beta_c = 2.11(4) \times 10^{-3}$ GPa^{-1} along the *a, b* and *c* axes respectively for the B-type structure of Eu_2O_3 is obtained by this method. The low compressibility along the b axis followed by *c* and *a* is attributed to the presence of closely packed edge sharing polyhedral arrangement along the *b* axis and the presence of voids along the *c* and *a* axis. Contrary to the available reports, the high pressure hexagonal structure of Eu_2O_3 shows different lattice compressibility behaviour in the two pressure regimes, 5-15 GPa and 15-25 GPa. This anomolous behaviour is indicated in the Figures 2a and 2b. An axial compressibility of $\beta_{a1} = 1.05(2) \times 10^{-3}$ GPa^{-1} and $\beta_{c1} = 5.23(18) \times 10^{-3}$ GPa^{-1} respectively for a and c axis is obtained in the range 5-15 GPa. In the range 15-25 GPa, the a axis becomes harder and the EOS fitting to the c axis has yielded an axial compressibility of $\beta_{c2} = 11.39(66) \times 10^{-3}$ GPa^{-1}, indicating an increased compressibility of c axis in this range. The compressibility of the c axis is approximately 5 times greater than that of the *a* axis in the 5-15 GPa pressure range. Also, the compressibility of *c* axis in 15-25 GPa range is almost twice as that in the 5-15 GPa pressure range. This indicates the fact that, the observed incompressibility along the *a* axis is compensated by the doubling of the compressibility along the *c* axis. However, this anomaly was not reflected in the unit cell volume compressibility. A more definitive understanding of this anomolous behavior was obtained through a carefull investigation on the lattice compressibility of hexagonal phase of La_2O_3 (Figure 2c). The anomolous lattice compressibility observed in the case of high pressure hexagonal phase of Eu_2O_3 is also present in the A-type La_2O_3 at a comparatively lower pressure of 9.7 GPa. Apart from this, a substantial increase in the intensity of *100* reflection and a corresponding reduction in the intensity of *103* reflection with increasing pressure above 5.6 GPa leads to the conclusion that the cations might have progressively shifted from the 100 to *103* plane (see Figure 3). Moreover, the Rietveld refinement in association with the Stephans anisotropic strain broadening model has shown that, the cations are immobile along the c axis. These lead to the conclusion that, above 5.6 GPa, the cation-oxygen layers in the ab plane of the hexagonal structure glides one over the other in opposite direction as shown in Figure 3. It can be stated that, in the region 5.6-19.8 GPa, the effect of

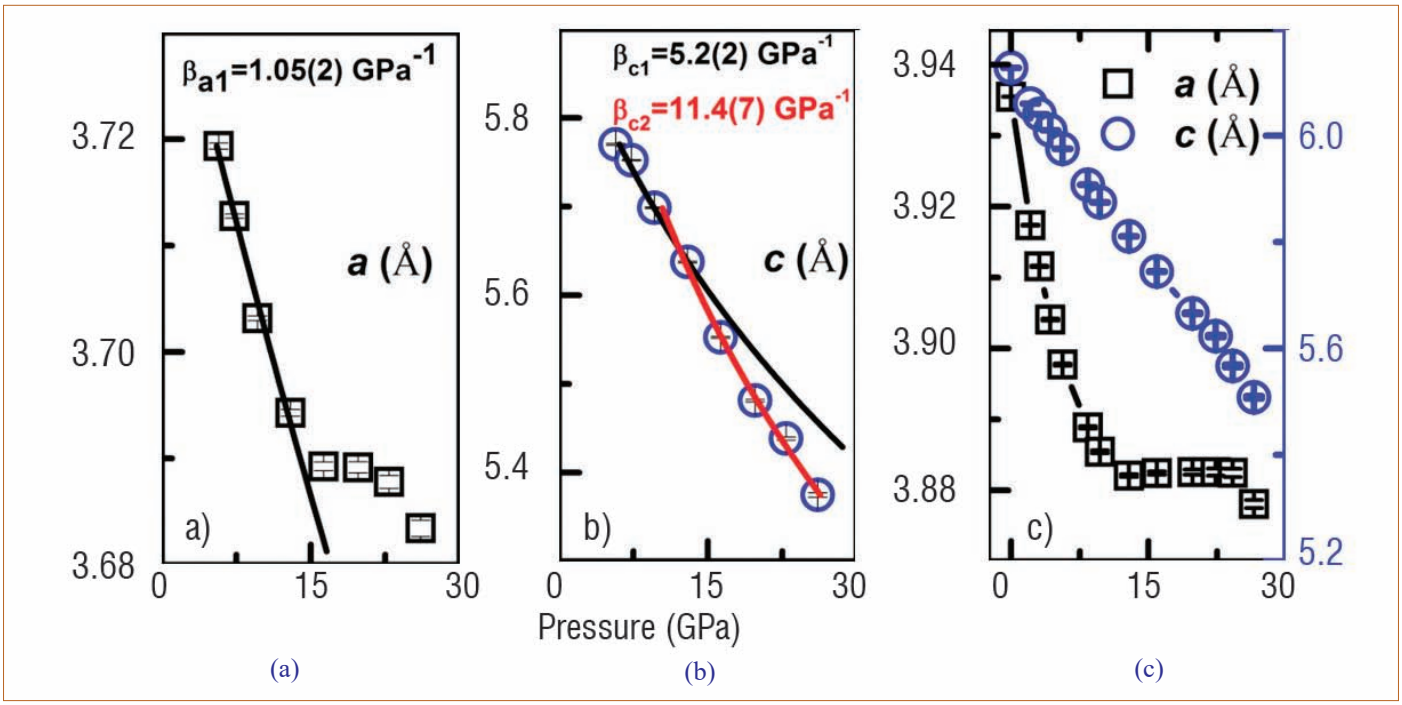

Figure 2: (a&b) The lattice compressibility behaviour of the hexagonal structure of A-type Eu_2O_3 and c) A-type La_2O_3

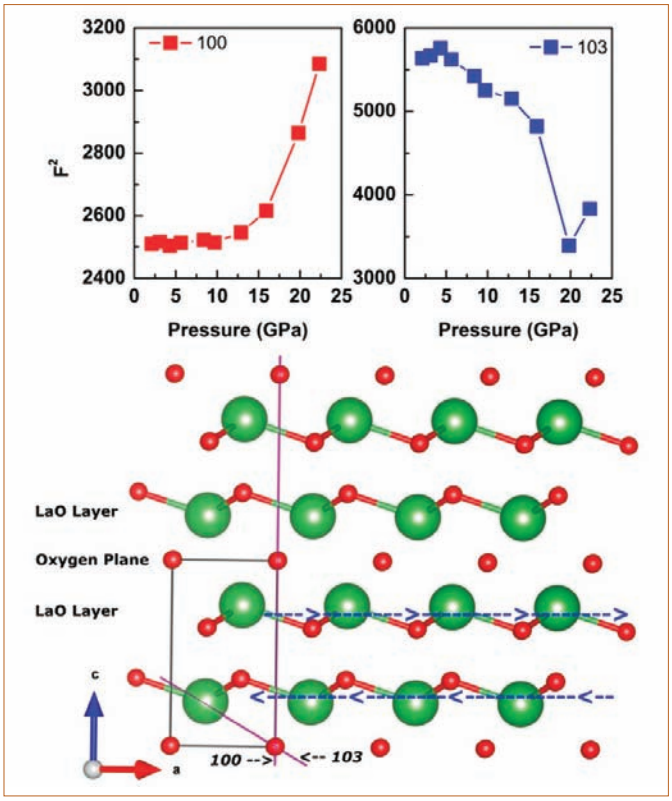

Figure 3: Top portion: Variation of F^2 (Intensity), extracted from the Rietveld refinement of the HPXRD data, the increase and decrease of intensity of *100* and *103* reflections respectively with compression are shown. Bottom portion: Layered structure of La_2O_3, in which a single layer of oxygen atoms is present in between two LaO layers. The blue dotted arrows represent the direction of motion of LaO layers

pressure is to favour the cation-oxygen layer movements rather than the compression along the a axis and hence an anomalous compressibility behaviour is observed in the hexagonal structure of RES.

The bulk modulus is a useful parmeter which describes the elastic properties of a material under pressure. Bulk modulus value of all these simple RES were estimated using the Birch-Murnaghan EOS fitting to the unit cell compressibility data and are shown in Table 1. It can be concluded that, the bulk modulus increases with decreasing cation size within the RES. This is ascribed to the increasing nature of covalent bonding with decreasing cation size of the RES.

Table 1: The bulk moduli of Tm_2O_3 Eu_2O_3 and La_2O_3 estimated from the EOS fitting. The values obtained for the Tm_2O_3 from the ab initio DFT calculation is also shown

RES	Bulk modulus (GPa)		
	C-type	B-type	A-type
Tm_2O_3	149(2) 146 (DFT)	169(2) 151(DFT)	- -
Eu_2O_3		159(9)	165(6)
La_2O_3			102(5)

Though the studies carried out on the simple RES gave an intutive idea about the cation size and pressure dependance on the different structure type, more quantitative understanding can be obtained through a systematic investigation by considering the solid solutions of these oxides which are characterised by a smooth variation in their cation size. In order to understand the dependence of cation size and pressure on the different structure types, solid solutions of Eu_2O_3 and Ho_2O_3, having similar structure (cubic) and small difference in cationic radii, and solid solutions of Eu_2O_3 (cubic) and La_2O_3 (hexagonal), having dissimilar structure and significant difference in cationic radii, were synthesized by chemie douse method and investigated both at ambient and at high pressures.

In the case of $(Eu_{1-x}Ho_x)_2O_3$, a single phase solid solution, crystallising in the C-type cubic structure is obtained in the entire range of compositions. The evolution of crystal structural parameters and vibrational modes have been obtained using the Rietveld structure refinement of the X-ray diffraction data and Raman spectroscopy and are reported for the first time. A decrease in bond lengths and hardening of Raman modes in the high frequency range (>300 cm^{-1}) were obtained as a function of their average cation size, $R_{RE}=(1-x)*R_{Ho}+x*R_{Eu}$. These observations reveal an increase in bond strength, hence an increasing structural rigidity with the decrease of R_{RE}. To understand the cation size effect on the high pressure behaviour of C-type RES, these solid solutions are studied at high pressures. The HPXRD studies show that, for R_{RE} equivalent to or below 0.9164 Å, the system prefers C→B structural transition, whereas for R_{RE} equivalent to or above 0.9220 Å a C→A transition is preferred. The bulk modulus of these solid solutions are estimated through EOS fitting of the

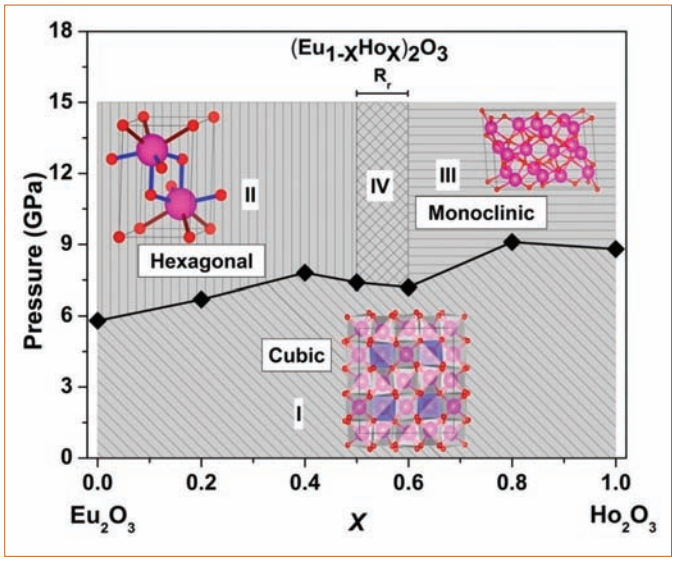

Figure 4: Pressure – concentration (P-x) phase diagram for the solid solution $(Eu_{1-x}Ho_x)_2O_3$. Different crystal structures and their stability regions are marked accordingly. Transition boundary, R_r, is characterized by $0.9164 < R_r < 0.9220$ Å

compressibility data of respective structure types. A decrease in the phase transition pressure and a sudden reduction in bulk modulus is observed in the $0.4 \leq x \leq 0.6$ compositions. This reduction in transition pressure and bulk modulus is ascribed to the manifestation of microstrain, developed by the difference in the size of the rare earth cation, as an internal pressure in the crystal structure. The results obtained from the high pressure structural investigations on $(Eu_{1-x}Ho_x)_2O_3$ are consolidated to a pressure-concentration phase diagram and is shown in Figure 4. The phase boundary between the two high pressure phases namely, A-type hexagonal and B-type monoclinic, is characterised by an average cationic radii $0.9164Å < R_{RE} < 0.9220Å$.

Investigation on the composition and morphology of the solid solutions of Eu_2O_3 and La_2O_3, $(Eu_{1-x}La_x)_2O_3$ using the energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) show the particles are in submicron size and are irregular in shape. Angle dispersive XRD measurements revealed a structural phase transition from cubic (C-type) to monoclinic (B-type) and subsequently to the hexagonal (A-type) structure with an increasing substitution of La. The onset of C→B and B→A transition is at R_{RE}=0.980 Å and 1.025 Å respectively. Due to the difference in the rare earth cation size, as we have seen in the case of Ho:Eu_2O_3, the microstrain was found to be developing in the crystal structures with the increasing R_{RE}. In accordance with this, the overall isothermal parameter, U_{iso}, of the cubic structure is found to be increasing with the increase of R_{RE} whereas the reverse is true in the case of hexagonal structure. The increasing U_{iso} in the cubic structure with an increase of R_{RE} indicates an increasing substitutional disorder in the system. However, the reduction of

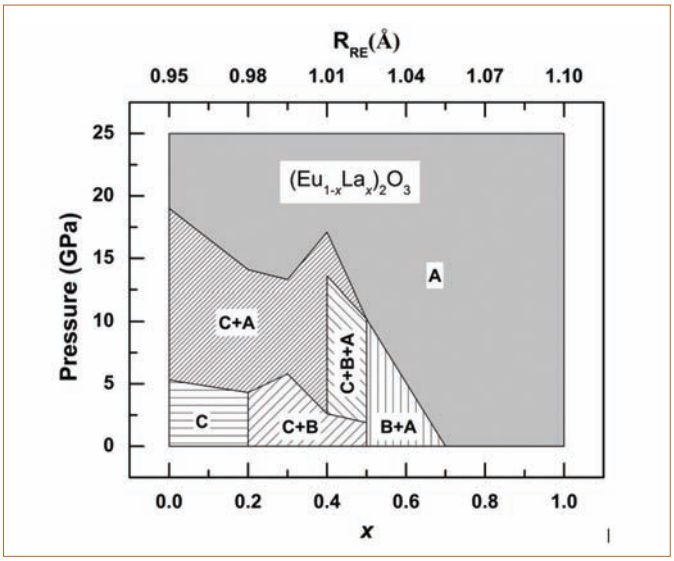

Figure 5 : Pressure – concentration (P-x) phase diagram for the solid solution $(Eu_{1-x}La_x)_2O_3$. Single, di and tri phasic regions of different crystal structures and their stability regions are marked accordingly

U_{iso} in the hexagonal structure with an increasing R_{RE} indicates the progression towards the formation of an ordered structure. This micro strain and the substitutional disorder are considered as a plausible cause for the observed phase transitions in these oxides.

In order to figure out the structural stability and compression behaviour, these solid solutions have been investigated at high pressures. Cubic structure is found to be stable for $0.95 Å \leq R_{RE} < 0.98 Å$ at ambient temperature and pressure and transform to hexagonal structure at high pressures. A biphasic region of cubic and monoclinic structure is stable for $0.98 Å \leq R_{RE} < 1.025 Å$ at ambient temperature and pressure and a C/B→A transition is preferred under pressure. Further, a biphasic region of monoclinic and hexagonal structure is favoured for $1.025 Å \leq R_{RE} < 1.055 Å$ and the B phase progresses towrds the hexagonal A phase under pressure. A pure A phase has been obtained for $1.055 Å \leq R_{RE} \leq 1.10 Å$ and the system is structurally stable at high pressures. As in the case of hexagonal La_2O_3, the presence of anomalous lattice compressibility along the a axis of the A-type structure is confirmed in all the compositions and is considered as the intrinsic feature of the hexagonal structure of RES. The estimated bulk modulus of hexagonal structure show a monotonous decrease with the increasing R_{RE} except for x=0.2 and 0.6 compositions. This reduction is again due to the increased internal pressure in the crystal structure as similar to that observed in $(Eu_{1-x}Ho_x)_2O_3$. Using the results obtained from the HPXRD investigation on $(Eu_{1-x}La_x)_2O_3$, a pressure-concentration (P-x) phase diagram upto a pressure of 25 GPa is constructed and is shown in Figure 5. The phase diagram illustrates the dependance of different structure types on the cation size and pressures.

In summary, the polymorphism in RES are systematically investigated both at ambient and at high pressures. High pressure studies on Tm_2O_3 and Eu_2O_3 indicate the C→B and B→A phase transition of small and medium cation sized RES. On the other hand, the HP studies on the hexagonal La_2O_3 revealed that, the structure is stable even at high pressures. Though the structure is found to be stable, the pressure induced cation-oxygen layer motion occurs at high pressures which in turn leads to an anomolous lattice compressibility along the a axis of the hexagonal structure. The two pressure concentration phase diagrams, one representing the pressure dependence of solid solutions of RES with similar structure and small difference in cation size and the other representing the pressure dependence of solid solutions of RES with dissimilar structure and significant difference in cation size, constructed for $(Eu_{1-x}Ho_x)_2O_3$ and $(Eu_{1-x}La_x)_2O_3$ helps in advancement of the basic knowledge and understandings of the polymorphism in rare earth sesquioxides.

K. A. Irshad
Materials Science Group

Conference and Meeting Highlights

BITS Practice School-1

May 22 - July 14, 2018

Students from BITS Practice School with Dr. Arun Kumar Bhaduri, Director, IGCAR and senior colleagues of the Centre during inaugural function

Fifty students from BITS Pilani, Hyderabad and Goa Campuses underwent summer practice school at IGCAR during May 22 to July 14, 2018. The programme is aimed at exposing the students to industrial and research environment, how the organizations work, maintaining work ethics, and completing the projects given to them in time by effectively making use of the guidance, scientific information resources, hard work and creativity. Dr. Arun Kumar Bhaduri, Distinguished Scientist, Director, IGCAR inaugurated the practice school programme and interacted with the students. Dr. B. Harihara Venkatraman from Hyderabad campus was the program coordinator from BITS. The students were from various disciplines like Chemical Engineering, Computer Science & Engineering, Electrical & Electronics Engineering, Electronics & Instrumentation Engineering, Mechanical Engineering, Civil Engineering and a few with the combination of engineering discipline with basic sciences such as Biology, Physics, Chemistry, Mathematics and Economics. Students carried out challenging projects in various groups of the Centre according to their discipline under the able guidance of scientists and engineers in IGCAR. During the period of their stay, they visited facilities at IGCAR, FBTR, BHAVINI and MAPS. As a part of the curriculum, quiz, project work presentations, group discussions and report writing and viva were conducted. The valedictory function was held on July 12, 2018 and the students were given certificates.

Organising Team
BITS-Practice School

Conference and Meeting Highlights

Summer Training in Physics & Chemistry (STIPAC-2018)

May 28 to July 6, 2018

Chief Guest Dr. D.K. Aswal, Director, NPL, New Delhi, Dr. Arun Kumar Bhaduri, Director, IGCAR along with senior colleagues and students of STIPAC during the inaugural function

Summer training in physics and chemistry (STIPAC) is a prestigious flagship programme conducted by IGCAR every year since 1995, for M.Sc. 1st year students. This program motivates and encourages young students to take up scientific research as a career. STIPAC has evolved over the years to train the pre-final PG Physics & Chemistry students from across the country both in theoretical & experimental expertise available at IGCAR. Like every year, the course was structured around a theme common to both physics and chemistry.

Theme chosen for this year's programme was "Applications of Electromagnetic radiation in Physics and Chemistry" and students were asked to submit a one page write up on "Electromagnetic Radiation and their use in Scientific Research". For the first time, applications were also invited online. Around 500 applications for Physics and 400 applications for Chemistry were received, representing about 100 universities across the country, from which 25 students in each discipline were selected, based on their academic credentials, quality of their write-up (Physics) and telephonic interview (Chemistry).

The STIPAC-18 programme was inaugurated on May 28, 2018 by the Chief Guest Dr. D. K. Aswal, Director, National Physical Laboratory (NPL), New Delhi and Dr. Arun Kumar Bhaduri, Distinguished Scientist, Director IGCAR gave his presidential address. Dr. D. K. Aswal gave a special lecture on "Metrology: The Pillar of India's Quality Infrastructure".

Duration of the program was for six weeks consisting of about 100 hours of lectures in theory and about 50 hours of experiments. Theoretical courses were held in forenoons. In the afternoons, the students were encouraged to have a hands on learning experience by either doing project works or carrying out experiments on various topics. Towards the end of the course, the students gave a presentation on the project work, which was evaluated by senior scientists of the Centre. Site visits to MAPS and BHAVINI were also organised. In the course of the programme, six special lectures were organised in the evening by inviting professors from premier institutions. In particular, the special lecture by Prof. D. Indumathi from IMSc, Chennai on "How the sun shines: shedding light on neutrino" was well received by students.

The valedictory program was held on July 6, 2018. Prof. Surajit Sengupta, Dean, TIFR, Hyderabad was the Chief Guest and he addressed the students and distributed the certificates. He also gave a special lecture on "Are Solids Rigid?". An online feedback form was also made and the students were encouraged to submit their feedback about the course. Overall feedback received from the students was positive and appreciative of the range and depth of the course content.

Reported by
Dr. K. Prabakar, STIPAC-2018

Conference and Meeting Highlights

Graduation Function of the 12th Batch of Trainee Scientific Officers of BARC Training School at IGCAR

July 26, 2018

Dr. Arun Kumar Bhaduri, Director, IGCAR, Professor M. K. Surappa, Vice-Chancellor, Anna University, Dr. B. Venkatraman, Director, RM&PAG & HSEG and Dr. Vidya Sundararajan, Head, P&HRMD during the release of souvenir at the Graduation function of OCES

12th batch of Twenty nine 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, 2018. Professor M. K. Surappa, Vice-Chancellor, Anna University, Chennai was the Chief Guest. Dr. B. Venkatraman, Director, Resources Management and Public Awareness Group (RM&PAG) & HSEG, welcomed the gathering. Dr. Vidya Sundararajan, Head, P&HRMD briefed the audience about Orientation Course in Engineering and Sciences programme. Dr. Arun Kumar. Bhaduri, Distinguished Scientist and Director, IGCAR delivered the presidential address. Professor M.K. Surappa released the souvenir featuring the training school programme in the previous academic year. He also gave away the prestigious 'Homi Bhabha Prizes' comprising of a medallion and books worth Rs.5000 to the toppers from each discipline and addressed the gathering. He also gave away the course completion certificates to all the graduates passing out. A few of the Trainee Scientific Officers passing out shared their experience, gave feedback on the academic programme and their stay at the hostel. Dr. N. Madurai Meenachi, Head, OCES-Training Section, Resources Management Group, proposed the vote of thanks.

Reported by
Dr. Vidya Sundararajan, RMPAG

Graduates of BARC Training School, Professor M. K. Surappa, Vice-Chancellor, Anna University and Dr. Arun Kumar Bhaduri, Director, IGCAR and senior colleagues of the Centre

Conference and Meeting Highlights

11th National Conference on Recent Advances in Information Technology

08-09 August 2018

Dr. Venkatraman Chairman, READIT , Director, RMPAG & HSEG, Dr. Arun Kumar Bhaduri, Director, IGCAR, Prof.Partha Pratim Das, Joint Principal Investigator, National Digital Library of India Project, Ms. S. Rajeswari and Shri E. Soundararajan during the release of souvenir

Scientific Information Resource Division, IGCAR in association with Madras Library Association - Kalpakkam Chapter (MALA- KC) organized the 11th Biennial National Conference on Recent Advances in Information Technology (READIT) during August 08-09, 2018 at Sarabhai Auditorium, IGCAR, Kalpakkam, with the theme 'Reinventing Libraries: Digital Innovations & Technologies.'About one hundred and eighty delegates including Librarians from the academic and public domain, Information Technology Professionals and Research scholars attended the conference.

In the inaugural function, Dr. B. Venkatraman, Chairman, READIT, Director, RMPAG & HSEG delivered the welcome address. Smt. S. Rajeswari, Convener READIT & Head SIRD briefed about READIT and MALA- KC. The function was presided over by Dr. Arun Kumar Bhaduri, Distinguished Scientist, Director, IGCAR. In his presidential address, Dr. Arun Kumar Bhaduri, emphasised the importance of visiting libraries and the need for relevant information access in an R&D environment. The Chief Guest of the inaugural event, Prof. Partha Pratim Das, Joint Principal Investigator, National Digital Library of India Project, IIT Kharagpur delivered the keynote address on the topic "National Digital Library of India (NDLI): Innovations in Technology Enhanced Learning" and highlighted the features of NDLI and the need to share the digital repositories across India. The Conference Proceedings with ISBN was released by Prof. Partha Pratim Das. Shri E. Soundararajan, organising secretary READIT proposed the vote of thanks. Dr. Arun Kumar Bhaduri inaugurated the exhibition stalls of publishers and vendors.

The conference included invited talks by domain experts in Information Science & Technology and oral/poster presentations by Research Scholars & Professionals. The topics included various aspects of Digital Innovations & Technologies in Libraries, Personalisation of Digital Library Services: Issues & Solutions, Smart Libraries based on Cloud Computing & Internet of Things, Semantic Web Technologies for Library and Information Sharing in Consortia & Virtual Private Networks. Experts from Pondicherry, Tripura and Anna Universities, DAE units, IT sectors and other reputed institutions delivered the invited lectures.

Special technical sessions were organised for the contributed presentations by Research Scholars which included oral and poster presentations. The conference facilitated good interactions among young researchers, students, professionals and well-known speakers in the area of modern digital technologies.

Dr. Arun Kumar Bhaduri delivered the valedictory address, highlighting the importance of innovations in technologies for information sharing and also distributed the best paper awards. Dr. B. Venkatraman honoured the retired colleagues of SIRD. Dr. S. Velmurugan, Facility Director, BARCF honoured the various sponsors of READIT 2018.

Reported by

Ms. S. Rajeswari, Convener, READIT-2018

Conference and Meeting Highlights

Review of Collaborative Projects on Advanced Ultra Super Critical (AUSC) Project with Academic Institutes and National Laboratories

August 20-21, 2018

Shri. S.C. Chetal, Mission Director, AUSC & Former Director, IGCAR (left) and Dr. A.K. Bhaduri, Director, IGCAR (right) addressing the participants.

A National Mission to design an Advanced Ultra Super Critical (AUSC) power plant with higher efficiency based on clean coal technology has been set up by Ministry of Heavy Industries (MHI), Government of India. An important task of this mission is to demonstrate the technology and indigenously develop the materials and fabrication technologies, with necessary R&D inputs from BHEL, NTPC and IGCAR, the three partners participating in this mission. Materials selection for several components like boiler tubes, super-heaters, re-heaters, rotor and rotor casings poses challenges due to the high temperature of operations (~ 720 °C) and pressure (~ 310 bar). A wide variety of materials from Ni based super alloys to advanced steels are being developed in various product forms including joints and evaluated with respect to their long term properties under service conditions. As the materials are indigenously produced and availability of literature is limited, a round robin testing program has been established with IGCAR as the nodal agency in collaboration with academic institutes such as IITs, NITs, Jadavpur University and national laboratories such as NML, Jamshedpur.

The first meeting to review the progress of the collaborative projects was held at SRI Auditorium, Anupuram during August 20-21, 2018. It was attended by all the Principal Investigators of the projects from various academic institutes and NML. Shri S.C. Chetal, Mission Director, AUSC Mission Directorate, New Delhi & Former Director, IGCAR in his inaugural address, brought forth the significance of the AUSC program and the need for self reliance. Dr. A. K. Bhaduri, Director, IGCAR emphasised the importance of timely deliverables to accomplish this mission, within identified time frame by the Government. Dr. G. Amarendra, Director, Metallurgy and Materials Group, IGCAR, highlighted the scope of the 33 projects, which form part of the round robin program of materials testing and evaluation under AUSC project. There were intense deliberations on technological milestones, procurement issues, manpower deployment and financial progress, during the two days of the meeting. This review meeting provided a very effective forum not only for exchange of scientific information but also for clarifications regarding methodologies to be adopted to meet the time lines. Shri Chetal expressed his satisfaction and appreciation for the focused review meeting and the next meeting is proposed after a period of six months.

Reported by Dr. G. Amarendra, Chairman PEC-AUSC, IGCAR

The participants from various institutes and IGCAR with Shri. S.C. Chetal and Dr. G. Amarendra, Director, Metallurgy & Materials Group and Chairman, AUSC Project Execution Committee, IGCAR

Conference and Meeting Highlights

Quality Circle Annual Meet (QCAM) - 2018

September 11, 2018

Quality Circle Annual Meet (QCAM) was conducted on September 11, 2018 at IGCAR. In the inaugural function, Dr B. P. C Rao, Chairman, Apex Steering Committee on Quality Circles (ASCQC) and chief Project Engineer, FRFCF welcomed the QC teams, facilitators, jury and chief guests on the dais and thanked Dr. Arun Kumar Bhaduri, Director, IGCAR for providing necessary financial support and encouragement. Dr G. Amarendra, Director, MMG & MSG, IGCAR delivered the Presidential Address. He highlighted the role of quality circles and how QCAM is being conducted for the past 20 years in IGCAR and particularly, lauded the participating student delegates for utilising this opportunity to know about quality at an early age. Dr. A. Sanjeeva Rao, Regional Director & Chairman QCFI, Chennai delivered Keynote Address and highlighted the ways to reduce costs, increase productivity, and improve employee morale through QC meets. Shri M. Krishnamoorthy, Head, Fabrication Section, CWD presented the vote of thanks.

Lighting of lamp by Dr. A. Sanjeeva Rao Regional Director & Chairman QCFI, Chennai

Winners Receiving the Awards

QC case studies were presented by the QC teams in two parallel sessions conducted at Sarabhai Auditorium and Raja Ramanna Auditorium. Twenty four QC teams and nominated delegates from all groups of IGCAR (about 300 members), MAPS and Schools around Kalpakkam presented the QC case studies in a wide spectrum of topics covering Technical, Research & Development, Services, and Education. Six professional judges from QCFI, Chennai chaired the QC case study presentations. Under 'Mechanical & Manufacturing' category, PLUTONIUM team from MC&MFCG bagged 'Dr Placid Rodriguez Memorial Trophy', while FERMI team from MC&MFCG bagged the 'Shri M. K. Ramamurthy Memorial Trophy' for the 'Technical Services' category. As part of QCAM-2018, Slogan and Poster competitions were conducted on theme titled "Role of Quality Circle in Digital India Mission". The winners and runners were selected by the professional jury.

In the valedictory function, Dr B.P.C Rao welcomed the Chief Guest Dr. A. Ravisankar, Director, RpG & Project Director, FRFCF and thanked the judges for accepting invitation and sparing their time for QCAM-2018. In his valedictory address, Dr. A. Ravisankar praised the efforts of quality engineers in large engineering projects such as DFRP and FRFCF and highlighted the example of 'Total Quality Management' success by Japan. Shri T.V. Maran, Head, Zonal Workshop Section, FRTG summed up the events of QCAM-2018. Dr. Ravisankar distributed prizes to winners and runners of the three QC categories as well as Slogan and Poster contests. Shri V Suresh Kumar, Head, RFS, MC&MFCG presented the vote of thanks. Top six QC teams including the winners and runners of each category took part in Chennai Chapter Quality Circle Convention (CCQCC-2018) held in Chennai during September 22-23, 2018 and four teams won GOLD awards and two teams won SILVER awards, obtaining eligibility to attend the National Convention.

Reported by
Shri T. V. Maran, FRTG

Dr. A. Ravisankar, Director, RpG & Project Director, FRFCF delivering the Valedictory address

Conference and Meeting Highlights

Radiation Awareness Programme

September 29, 2018

Dr. R. Baskaran, Associate Director, RESG, HSEG delivering the inaugural address

Radiation awareness program, for homemakers residing in Anupuram, on nuclear energy and radiation safety was organized by HSEG, IGCAR, in association with Indian Women Scientist's Association (Kalpakkam), IWSA (K) on September 29, 2018 at Convention Centre, Anupuram.

In the Inaugural function, Dr. S. Kalavathi, Convener, IWSA welcomed the gathering. Dr. R. Baskaran, Associate Director, RESG, HSEG was the chief guest and he elaborated the purpose of such awareness programmes and also quoted great Nobel laureates who worked in the field of radiation physics. Exhibits from MAPS, BHAVINI, ESL, RESG and TCPAS, IGCAR showcased various activities of Nuclear Power Plants (NPP) and DAE. Mrs Jalaja Madan Mohan, Head, TC& PAS coordinated the exhibition arrangements. Mrs Indirani Bhaduri, a keen supporter of IWSA activities formally inaugurated the Exhibition.

Following the inauguration, Dr. M. Manohari, RESG delivered a lecture on Radiation Awareness in English to the audience.

Mrs Indirani Bhaduri inaugurating the exhibition

MAPS Exhibitions

Shri R. Mathiyarasu addressing the participants

There were 106 registered women participants for English Session from Anupuram. The interactive session was lively with various questions raised by participants about radiation safety, use of radiation in food and agriculture and so on. A team lead by Shri R. Mathiyarasu, Dr. V. Subramanian and Dr. O. Annalakshmi clarified their doubts. Further, a game event with quiz and connection round of questions related to radiation and nuclear energy was conducted and participants actively interacted. Visit to the exhibits provided further interaction between the scientists and the participants.

The awareness programme in Tamil followed subsequently and 88 women residents attended this programme. Radiation awareness lecture in Tamil was delivered by Shri R. Mathiyarasu, Head, RBDS, RSEG. The audience interacted with keen interest and energetically participated in the game session revealing their focus and reception of the programme. The programme ended with vote of thanks by Dr. S. Padma, Treasurer, IWSA. Overall, the programme was a grand success in creating Radiation Awareness among women residents of Anupuram.

Reported by Dr. R. Baskaran, RESG

Colleagues from our department demonstrating the exhibits to the participants

HBNI-IGCAR Corner

Ph.D thesis defense

Name	Title	Date	Discipline
Mr. R. Bala Krishnan	Studies on Information Hiding Techniques in Word Processor Documents	20/09/2018	Engineering Sciences
Mr. M. Naveen Raj	CFD Investigations of Thermal Hydraulic Characteristics and Consequences of Flow Blockage in Fast reactor Fuel subassembly	20/09/2018	Engineering Sciences

Awards and Honours

Ms. Alphy George, PMD, MMG received the "FSM-YSA (International Federation of Societies for Microscopy – Young Scientist) Award" in IMC-19 (19th International Microscopy Congress) held during September 9-14, 2018, at International Convention Centre (ICC), Sydney, Australia.

Ms. Alphy George, PMD, MMG received the "Micrography Contest Award" in International Conference on Microscope and XXXIX Annual Meeting of Electron Microscope Society of India held during July 18 - 20, 2018 at Mayfair Convention Center, Bhubaneswar, Odisha (EMSI-2018).

Ms. S. Rajeswari Head, SIRD, RMPAG has been awarded the Best Organiser Award-2018 by the Madras Library Association (MALA), Chennai

Best Paper/Poster Awards

Theoretical and experimental study of Structural Characteristics in Equiatomic CrFeMoV Alloy

Shri. A. Saikumaran, Dr. R. Mythili, Dr. S. Saroja, Dr. Rajesh Ganesan

International Conference on Microscope and XXXIX Annual Meeting of Electron Microscope Society of India, 18 - 20 July, 2018 at Mayfair Convention Center, Bhubaneswar, Odisha (EMSI-2018)

Best Poster Award

Effect of Nitrogen on Precipitation in SS 316LN during Long Term Thermal Ageing

Ms. Alphy George, Dr. R. Mythili, Dr. Arup Dasgupta, Dr. J. Ganesh Kumar and Dr. G.V. Prasad Reddy

International Conference on Microscope and XXXIX Annual Meeting of Electron Microscope Society of India, 18 - 20 July, 2018 at Mayfair Convention Center, Bhubaneswar, Odisha (EMSI-2018)

Best Poster Award

Effect of cold working on corrosion fatigue behavior of austenitic stainless steel in acidified chloride medium

Ms. A. Poonguzhali, Dr. S. Ningshen, and Dr. G. Amarendra

Second International Conference on Structural Integrity Conference & Exhibition 2018 organised by DMRL, Hyderabad and Indian Structural Integrity Society held at Hyderabad during July 25 - 27, 2018

Best Paper Award

Causal Factor Mining of Publication Data: A Case Study

Ms. K. Bharathi Manjula, Dr. N. Madurai Meenachi, Dr. G. Sivakumar, Dr. B. Venkatraman and Dr. M. Sai Baba

11th National Conference on Recent Advances in Information Technology (READIT 2018), Indira Gandhi Centre for Atomic Research, Kalpakkam, August 8-9, 2018

Best Paper Award

Smart RFID Access Control for IGCAR Library

Shri S. Lakshmi Prasad, Shri T. Sathishkumar, Shri J. Immanuel, Shri P. Balaji, Shri P. Arumugam and Shri G. Prabhakara Rao

11th National Conference on Recent Advances in Information Technology (READIT 2018), Indira Gandhi Centre for Atomic Research, Kalpakkam, August 8-9, 2018

Best Paper Award

Challenges in Documenting Biodiversity of DAE Kalpakkam Campus, Kalpakkam

Shri E. Premkumar, Shri E.Soundararajan and Ms. S. Rajeswari

11th National Conference on Recent Advances in Information Technology (READIT 2018), Indira Gandhi Centre for Atomic Research, Kalpakkam, August 8-9, 2018

Best Poster Award

Evaluating Research Output in the Field of “Nuclear Fuel Reprocessing” with Scifinder Database – A Case Study

Shri G. Pentaiah

11th National Conference on Recent Advances in Information Technology (READIT 2018), Indira Gandhi Centre for Atomic Research, Kalpakkam, August 8-9, 2018

Best Poster Award

A Novel Chitosan/Ag/Go Composite Coating with Enhanced Antibacterial Activity and Improved Corrosion Resistance

Shri Geetisubhra Jena, Shri B. Anand kumar, Ms. S.C Vanithakumari, Dr. Rani.P. George, Dr. John Philip and Dr. G. Amarendra

CORCON 2018, held during September 30 - October 3, 2018 at Jaipur

Best Poster Award

High Performance Green Concrete with Improved Biodeterioration Resistance Against Fungus Fusarium.

Shri Manu Harilal, Ms. Sudha Uthaman, Shri B, Anand kumar, Dr. Rani.P. George, Dr. John Philip and Dr. G. Amarendra

CORCON 2018, held during September 30 - October 3, 2018 at Jaipur

Best Poster Award

Self - Healing Plasma Spray Coatings on Graphite for High Temperature Applications

Ms. B. Madhura, Shri E. Vetrivendan, Dr. Ch. Jagadeeshwara Rao and Dr. S. Ningshen

CORCON 2018, held during September 30 - October 3, 2018 at Jaipur

Best Paper Award

Development of Pulsed Eddy Current Instrument and Probe for Detection of Sub-Surface Flaws in Thick Materials

Shri K. Samba Siva Rao, Dr. B. Purna Chandra Rao and Dr. S. Thirunavukkarasu

IETE Technical Review Mar-Apr 2017 awarded during October, 2018

Best Paper Award

Biodiversity Basket - Avian Fauna

Spotted Owlets are the small owls with large round head, curved white eyebrows and straight forward yellow eyes. This is one of the most common owls found in DAE Complex at Kalpakkam.

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