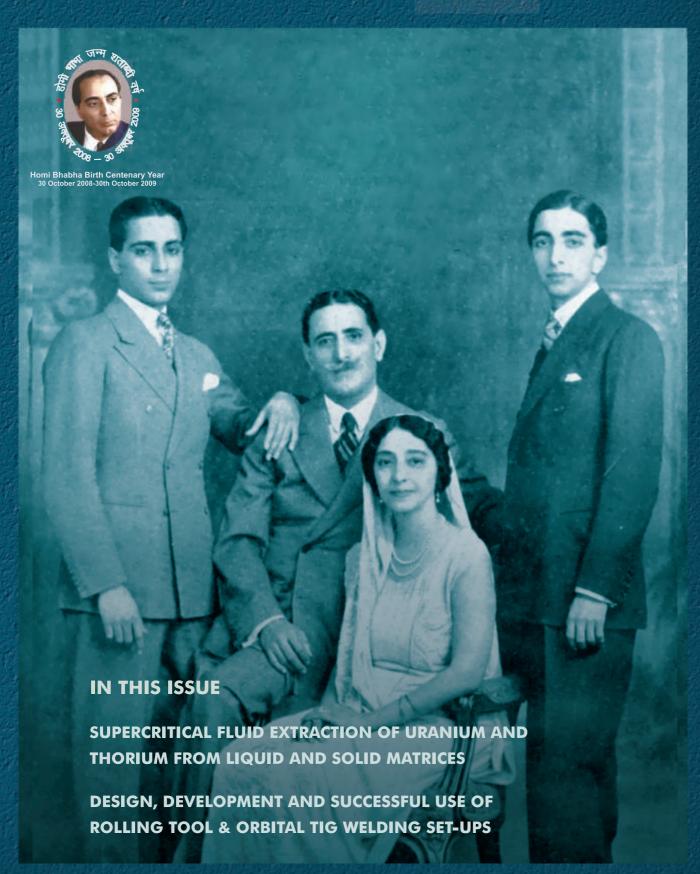


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### In the Next Issue

Development of dispersive Extended X-ray Absorption Fine Structure (EXAFS) beamline at INDUS-2 synchrotron source

The determination of the structure of different types of materials such as amorphous, polycrystalline, polymers, surfaces and solutions, has been made easier and more accurate, due to the advent of synchrotron radiation sources and subsequent developments in synchrotron radiation techniques. The Extended X-ray Absorption Fine Structure (EXAFS) technique, enables the measurement of fine structures in the X-ray absorption spectra, above the absorption edge of the atoms in a material. These EXAFS measurements are carried out in two modes: scanning and dispersive.

The Spectroscopy Division has recently developed and commissioned a dispersive type EXAFS beamline, at INDUS-2 synchrotron source. The optical and mechanical layouts of this beamline and its performance evaluation and calibration, have been described in this article.



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# SUPERCRITICAL FLUID EXTRACTION OF URANIUM AND THORIUM FROM LIQUID AND SOLID MATRICES

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#### Introduction

Extraction and purification of actinides (uranium, thorium, plutonium) from various matrices is of utmost importance to the nuclear industry. Conventional techniques for the separation and purification of actinides from various matrices, largely rely on solvent extraction [1]. In the conventional solvent extraction process, large amounts of liquid volume comprising of used organic solvents and acids is generated. In the recent years, Supercritical Fluid Extraction (SFE) has emerged as a promising alternative to conventional solvent extraction process, owing to its potential to minimize the generation of liquid volume and the simplification of the extraction process. Super Critical Fluids (SCF) have the hybrid characteristics of both liquid as well as that of gas; density, diffusivity, viscosity and surface tension are intermediate to that of liquid and gaseous states. (Table 1). Supercritical fluids offer faster, cleaner and efficient extraction, as liquid-like solvating characteristics enable the dissolution of compounds, whereas gas-like diffusion characteristics provide high degree of extraction in a shorter time duration. SCF can penetrate deep inside the material matrix due to low viscosity and surface tension; extracting the component of interest. Also, the solvating properties can be controlled by tuning pressure / temperature conditions.

In view of the associated advantages of SCFs, the Radioanalytical Chemistry Division procured a supercritical fluid extraction system. This article describes the work carried out on the instrument by the authors.

A substance above critical point is said to exist in a SuperCritical Fluid (SCF) state, when a gas is compressed to a sufficiently high pressure and it becomes liquid. However, if the gas is heated beyond a specific temperature, no amount of compression of the hot gas will cause it to become liquid. This temperature is termed as the critical temperature (T<sub>2</sub>) and the corresponding vapour pressure as the critical pressure (P<sub>2</sub>). The solvating characteristics of SCFs were reported by Hanny and Hogarth [2] as early as 1879. However, its application was suggested by Lovelock [3] in 1958. He suggested the use of SCFs in chromatography. However, Klesper et al [4] in 1962 experimentally demonstrated chromatographic separation of nickel porphyrins. Since then, SCFs have been employed for extraction and recovery of organic compounds from solid materials [5]. Among various other substances, CO, was selected as supercritical fluid, owing to its moderate critical constants (Pc= 72.9 atm, Tc = 31.3 °C) and attractive properties such as being easily available, recyclable, non-toxic, chemically inert, non-inflammable and radiochemically stable.

Direct extraction of metal ions with SC  $\rm CO_2$  is known to be highly inefficient, because of the charge neutralization requirement and the weak solute-solvent interactions. For metal ion extraction by SC  $\rm CO_2$ , an approach suggested the formation of metal complexes



Table 1 : Comparison of physical properties of different states

State	Density (g ml <sup>-1</sup> )	Viscosity (poise)	Diffusivity (cm <sup>2</sup> s <sup>-1</sup> )
Gas	10-3	(0.5-3.5)*10 <sup>-4</sup>	0.01-1.0
Supercritical fluid	0.2-0.9	(0.2-1.0)*10 <sup>-3</sup>	(3.3-0.1)*10 <sup>-4</sup>
Liquid	0.9-1.0	(0.3-2.4)*10 <sup>-2</sup>	(0.5-2.0)*10 <sup>-5</sup>

with organic complexing agents, those metal-complexes could be soluble in SC CO<sub>2</sub>. Wai et al [6] demonstrated the SFE of Cu<sup>2+</sup> from liquid and solid medium by SC CO<sub>2</sub>. Subsequently, SFE of many metal ions was reported [7]. Also, SFE of trivalent lanthanides and uranyl ions from solid material was reported by Lin et al [8,9].

### **Experimental set-up**

A schematic of the supercritical fluid extraction set-up is shown in Fig.1. The set-up mainly consists of CO<sub>2</sub> delivery pump, modifier pump, thermostat, back-pressure regulator and collection



Fig. 1: SFE diagram

vessel [10]. CO, gas from cylinder is fed into the CO, delivery pump where it is liquefied to -10 °C. The liquid (co-solvent) is fed by co-solvent pump into the system. The CO<sub>2</sub> and co-solvent flow rates can be varied from 0.001 to 10 ml / min. The CO<sub>3</sub> and co-solvent streams merge into a single stream by a T-joint, to produce a mixture of CO<sub>2</sub> containing the desired percentage of co-solvent. The spiral coil and mixing vessel are contained in the thermostat. The stream from T-joint is passed through a 5-meter long spiral coil for thorough mixing of CO, and co-solvent. High level of homogeneity is achieved, by passing the stream through a 10 ml capacity cylindrical vessel, containing spherical teflon pebbles. The stream then enters a six-port valve, which has a provision for selecting / bypassing the extraction vessel. The stainless steel cylindrical extraction vessel (10 ml) consists of inlet and outlet at the top. The inlet stainless steel tube (0.5 mm inner diameter), passing through the centre of the extraction vessel from the top, extends upto bottom, for purging the supercritical CO<sub>2</sub> through the sample solution. Back-pressure regulator controls the pressure of the extraction vessel by means of opening / closing of variable stroke needle valve. Pressure can be varied from atmospheric pressure upto 500 atm with a precision of  $\pm$  1 atm. The temperature of thermostat can be varied from room temperature upto 80°C with a precision of  $\pm$  0.1 °C. The extract coming out from the outlet of extraction vessel is collected in a collection tube at atmospheric pressure, where CO<sub>2</sub> escapes as gas. Each unit of the set-up can be independently controlled by its inbuilt microprocessor. Additionally, provision exists for controlling all units collectively (except back-pressure regulator) through a computer network. All the parameters can be set, controlled and monitored by a software programme, which can also control CO, delivery pump rate, modifier pump rate and temperature of the thermostat.

#### Determination of uranium / thorium

Uranium or thorium amount in a sample is determined

spectrophotometrically, employing arsenazo III metal indicator [10]. Required volumes of uranium/thorium solutions are aliquotted in a flask, followed by the addition of 1 ml of 1 M sulphamic acid and 1 ml of arsenazo III (1  $\mu$ g/ml). The volume is then made upto 10 ml using 4M HNO3. Uranium/thorium concentration was calculated from calibration graph between uranium/thorium amount (in  $\mu$ g/ml) versus absorbance at 655 nm. Uranium/thorium extraction efficiency is defined as the percentage ratio of the uranium/thorium amount collected, to initial uranium/thorium amount taken in the extraction vessel.

### Back-extraction of uranium into aqueous phase

The Uranium-TBP complex emerging from the extraction vessel is collected in the collection tube containing chloroform. For carrying out spectrophotometric determination, uranium is back-extracted into aqueous phase by employing 10% ammonium sulphate solution. Back-extraction is performed with ~1:1 volume ratio of organic and aqueous phase. Back-extraction efficiency was obtained by determining the uranium amount left unextracted in extraction vessel and uranium amount present in aqueous phase. The back-extraction efficiency is taken into consideration for calculating the overall uranium extraction efficiency.

#### Theoretical aspects of uranium SFE

A probable extraction scheme for uranium extraction from nitric acid medium into supercritical  $CO_2$  is depicted in Fig. 2. Uranium extraction process into supercritical  $CO_2$  involves many equilibria processes. Uranium is extracted as  $UO_2(NO_3)_2.2(TBP)$  into supercritical  $CO_2$  phase.

The extraction reaction involves at least three elemental processes: (i) Distribution of TBP between aqueous and supercritical  $CO_2$  phases, (ii) formation of complex  $UO_2(NO_3)_2$  2(TBP) in the aqueous phase and



(iii) distribution of the complex between aqueous and supercritical CO, phases. The overall extraction reaction could be expressed by the following formula:

$$UO_2^{2+}_{aq} + 2 TBP_{SF} + 2 NO_3^{-}_{aq} \stackrel{K_{ex}}{\rightleftharpoons} \{UO_2(NO_3)_{2..}2(TBP)\}_{SF}$$
 (1) Where,  $K_{ex}$  is extraction constant defined by the following equation:

$$K_{ex} = \frac{\left[UO_{2}(NO_{3})_{2}.2(TBP)\right]_{SF}}{\left[UO_{2}^{2+}\right]_{aq}\left[TBP\right]_{SF}^{2}\left[NO_{3}^{-}\right]^{2}_{aq}}$$
(2)

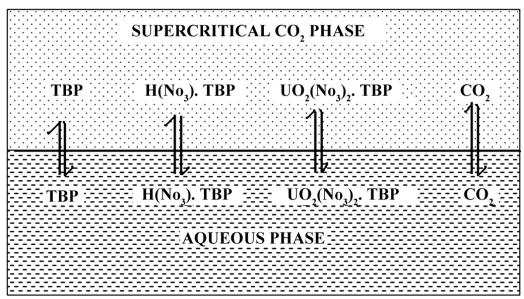


Fig. 2: Extraction scheme of UO<sub>2</sub><sup>2+</sup> from nitric acid into supercritical CO<sub>2</sub> employing TBP as co-solvent

The uranium distribution ratio and extraction constant are related by Eq. (3).

$$\log D_{\rm U} = \log K_{\rm D,U-TBP} + \log K_{\rm f,U-TBP} - 2 \log K_{\rm D,TBP} + 2 \log [NO_3]_{aq}$$
 (3)

Where  $K_{D,TBP}$  and  $K_{D,U-TBP}$  are the phase distribution constants of TBP and U-TBP complex and  $K_{f,U-TBP}$  is the formation constant of U-TBP complex in the acid solution.

Extraction efficiency depends upon solvating power (solubility) of supercritical CO<sub>2</sub>. Chrastil [11] has arrived at a simple empirical correlation relating solubility of the solute 5 'S' with the density 'r' of the supercritical fluid respectively:

$$\ln S = k \ln \rho + C \tag{4}$$

'k' corresponds to the number of CO, molecules solvating around the solute molecule and the constant 'C' is a temperature-dependent term consisting of thermal properties such as the solvation heat, vaporization heat and / or the volatility of the solute. The phase distribution constant K<sub>Di of</sub> substance is related to its solubility and supercritical fluid density by Eq. (5).

$$\log K_{Dj} = k_j \log \rho + C_j - \log S_{j,aq}$$
 (5)

The above equations are valid for equilibrium system. However, in SFE, supercritical fluid phase is continuously flown, overtly extraction efficiency depends on two basic factors: (i) distribution ratio of metal-complex and (ii) kinetics of transport of metal-complex into supercritical CO<sub>2</sub>.

### **Optimization of parameters**

Initially, the SFE of uranium was carried out from acidic medium employing TBP as co-solvent. Various parameters influencing uranium extraction efficiency were identified and a systematic study was carried out [12]. Experimental conditions are listed in Table 2.



Uranium concentration	500.8 μg ml <sup>-1</sup>
Uranium solution in extraction vessel	5 ml
Molarity of uranium solution	4 M
Extraction time	30 minutes
Extraction mode	Dynamic
Complexation mode	Online
Collection liquid (CHCl <sub>3</sub> )	3 ml
CO <sub>2</sub> flow rate	1 ml min <sup>-1</sup>
TBP flow rate	0.1 ml min <sup>-1</sup>

### **Effect of pressure**

Pressure versus extraction efficiency graph (Fig. 3) in the 80-300 atm range at  $60 \, ^{\circ}$ C displays initial steep

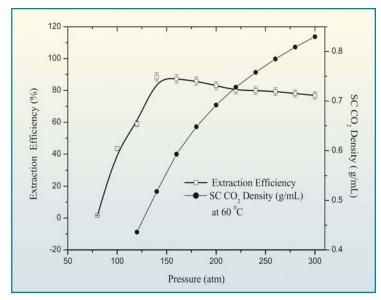


Fig. 3 : Graph of pressure versus uranium extraction efficiency / SC CO<sub>2</sub> density (Error bar is  $\pm$  3% of the value)

rise in extraction efficiency followed by a gradual decline. Under equilibrium conditions, the uranium distribution ratio could be expressed as [13,14].

$$\log D_{U} = \alpha \log \rho + \beta \tag{6}$$

Where  $\alpha = k_{\text{U-TBP}} - 2 k_{\text{TBP}}$ .

As the value of  $\alpha$  is negative ( $k_{TBP}=21.8$ ,  $k_{U-TBP}=40.6$  at 60 °C),  $D_U$  decreases with pressure (in 150-300 atm range). The trend under equilibrium condition is reflected in the variation in the extraction efficiency, in the pressure range of 150-300 atm. Below 150 atm, the trend is not as per predicted trend, this could be due to non-equilibrium nature of the SFE process. The SFE can be visualized as small aqueous droplets immersed in flowing SC  $CO_2$  stream. Eventually any non-equilibrium process progresses towards attaining equilibrium.

#### **Effect of temperature**

Effect of temperature on extraction efficiency and SC CO<sub>2</sub> density is graphically represented in Fig. 4.



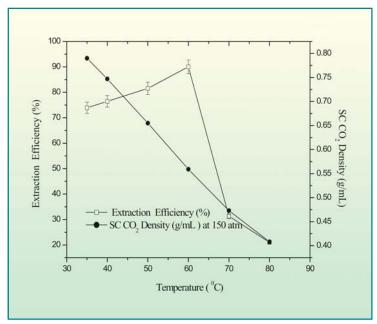


Fig. 4 : Graph of temperature versus uranium extraction efficiency / SC CO, density (Error bar is  $\pm$  3% of the value)

The effect of temperature on the extraction efficiency is the balancing outcome of two opposing factors. On one hand, temperature increase decreases the SC

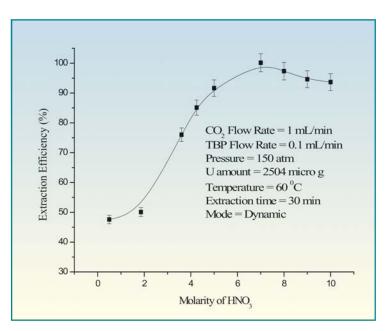


Fig. 5 : Graph of molarity of nitric acid versus uranium extraction efficiency (Error bar is  $\pm$  3% of the value)

CO<sub>2</sub> density, thus diminishing the solvating power and on other hand, it enhances the solute volatility. The observed trend in the 35-60 °C region indicates, that volatility of U-TBP complex increases so sharply, that it compensates for the effect of decrease in density. Steep decrease in extraction efficiency after 60 °C indicates, that the volatility of the U-TBP complex has reached its maximum value and afterwards a decrease in density is the dominating factor.

### **Effect of nitric acid molarity**

Extraction efficiency increases with molarity of nitric acid upto 7 M and decreases afterwards (Fig. 5). From Eq. (1) and (3), as per Le Chatelier rule,

increase in  $NO_3$  concentration in aqueous phase should increase the concentration of  $UO_2(NO_3)_2$ . 2(TBP) complex in the supercritical fluid phase, resulting in

higher uranium distribution ratio and subsequently higher extraction efficiency. The decrease in extraction efficiency after 7 M nitric acid could be attributed to co-extraction of  ${\rm HNO_3}$  into supercritical  ${\rm CO_2}$ .

### Effect of CO, flow rate and % TBP

Extraction efficiency increased with CO<sub>2</sub> flow rate upto 1 ml / min and thereafter reaches saturation. Extraction efficiency linearly increases with %TBP. Since, extraction occurs according to Eq. (1), as per Le Chatelier rule, higher amount of TBP in SC CO<sub>2</sub> should result in increase in U-TBP complex in SC CO<sub>2</sub> phase, leading to higher extraction efficiency.

# Effect of extraction time, modes of extraction and complexation

Fig. 6a reveals that extraction is initially fast but becomes sluggish afterwards, indicating that uranium extraction is a diffusion controlled phenomenon. Equation,  $y=32.24 \ln x-41.58$  (y= extraction efficiency, x= extraction time) has been found to fit into the graph having a correlation coefficient of 0.9943. The graph between logarithm of uranium fraction unextracted and initial uranium amount shows linear decrease with extraction time having a correlation coefficient of -0.9948 (Fig. 6b).

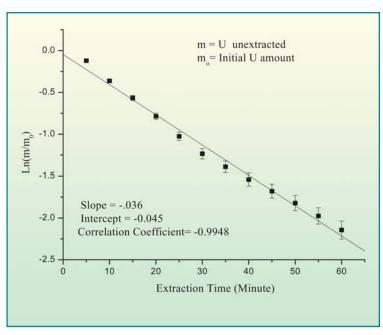


Fig. 6b: Graph of extraction time with time logarithm of fraction of uranium unextracted (Error bar is  $\pm$  3% of the value)

In static mode, under constant pressure and temperature for 20 minutes, followed by 20 minutes

of extraction, was found to be equivalent to 30

minutes extraction in dynamic mode. Online complexation mode was found to be better than the *in-situ* complexation mode.

Reproducibility study of uranium SFE was performed on a set of 5 samples under identical conditions. The mass balance study calculations yielded results acceptable in the range of experimental error (( $100 \pm 1$ )%) giving full credence to the extraction process. From the reproducibility study under optimized conditions (Table 3), the uranium extraction efficiency was found to be ( $98 \pm 2$ )%.

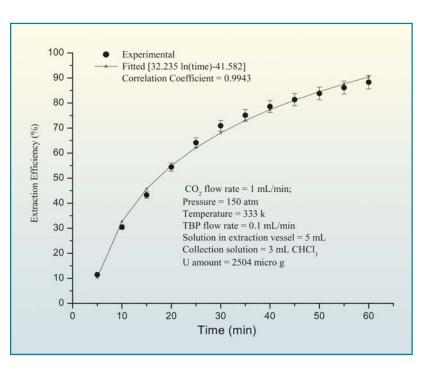


Fig. 6a: Variation in uranium extraction efficiency with time



Table 3: Optimized parameters for SFE of uranium from acidic medium with TBP as co-solvent

Parameter	Optimized Value
Pressure	150 atm
Temperature	60 °C
CO <sub>2</sub> flow rate	1 ml/min
TBP flow rate	0.1 ml/min
HNO <sub>3</sub> molarity	7 M
Extraction time (in-situ, dynamic)	30 min

### SFE of uranium employing TOPO as co-solvent

TOPO is more complexing than TBP. In *in-situ* mode, (1 ml 0.2 M TOPO (in CCl<sub>4</sub>)) 20 minutes static and 20 minutes of extraction, almost complete uranium extraction was achievable at lower pressure (100 atm). The efficiency was found to decrease linearly with pressure.

ion-specific extractants and have gained importance as cation binding agents, due to size selective nature. Uranium gets extracted as ion pair. Pentadecafluoron-octanic acid (HPFOA) was selected as counter ions, as it contains CO<sub>2</sub> phillic C-F bonds [15]. Various crown ethers were evaluated (Table 4(b)) under optimized parameters (Table 4(a)).

The effect of substituents is reflected while comparing the efficiency for crown ethers of the same ring size i.e. 18-crown-6 series:

Ditertbutyldicyclohexano-18-crown-6 > ditertbutyldibenzo-18-crown-6 > dicylohexano-18-crown-6 > dibenzo-18-crown-6.

It is evident that cyclohexyl and / or ditertiary butyl substituents, enhance the extraction efficiency, which could be attributed to the enhancement in basicity of oxygen atoms of the crown ether ring, thereby increasing bonding ability. In fact, the highest extraction efficiency was observed with

Table 4(a): Optimized parameters for SFE of uranium from acidic medium employing crown ethers as co-solvent

Pressure	200 atm	Crown: HPFOA mole ratio	1:10
Temp	50 °C	Uranium: Crown mole ratio	1:10
Steady time	20 minutes	Nitric acid molarity	2 M
Extraction time	20 minutes		

Supercritical carbon dioxide extraction of uranium from acidic solution employing crown ethers as co-solvent

Crown ethers are among the most versatile class of

ditertbutyldiccyclohexano-18-crown-6. However, when two benzo groups were attached to the ring, the extraction efficiency was found to decrease. The observed decrease could be attributed to the electron withdrawing nature of benzo group.

Table 4(b): Various crown ethers studied along with their molecular weight, cavity diameter and extraction efficiency

Crown ether	Mol. Wt.	Cavity diameter (°A)	Extraction efficiency (%)
15-Crown-5	220.20	1.7- 2.2	25.29
Dibenzo-18-Crown-6	360.41	2.7-2.9	32.81
Ditertbutyldibenzo-18-crown-6	424		58.12
Dicylohexano-18-crown-6	372.50	2.7-2.9	48.59
Ditertbutyldiccyclohexano-18- crown-6	484.72		64.93 85.78*
Dibenzo-21-crown-7	404		45.33
Dibenzo-24-crown-8	448.52	4.5-4.8	63.32

The extraction efficiency values are a mean of five repetitions. The standard deviation was  $\pm 3\%$ ,

The basicity of four oxygen atoms in the ring is expected to reduce, thereby decreasing the bonding ability. With 15-crown-5 extractions efficiency is almost the same as without crown ether, indicating no complexation, which could be attributed to smaller cavity size of 15-crown-5 (1.7-2.2  $^{\circ}$ A) than the size of UO $_2^{2+}$  (2.4-2.5  $^{\circ}$ A).

For crown ethers having the same substituents (dibenzo) the following trend in extraction efficiency was observed:

Dibenzo-24-crown-8 > dibenzo-21-crown-7 > dibenzo-18-crown-6.

From the observed trend, efficiency increases with ring size. The enhancement with increasing ring size might be the combined effect of enhanced cavity size as well as the number of ether oxygen atoms.

### SFE of thorium from acidic solution employing TBP/TOPO as co-solvent

Thorium is a fertile material and in a reactor, by

absorbing neutrons, gets converted into fissile <sup>233</sup>U. India's third stage of nuclear programme is based on thorium utilization. The fabrication of thorium-based fuel, reprocessing of irradiated thorium-based fuel and various radiochemical operations in laboratories, result in the generation of significant quantity of liquid and solid matrices containing thorium. Owing to its importance in nuclear industry, it is desirable to recover thorium from various liquid and solid matrices.

With TBP, the extraction efficiency obtained was only 81.87%. However, with more complexing, nearly complete extraction  $\sim$ 99% was achievable.

# SFE from solid matrix : SFE of uranium from tissue paper matrix using TBP / TOPO as co-solvent

Radiochemical operations result in the generation of a lot of solid waste. Tissue paper matrix was chosen as a representative of solid matrix. In the conventional process of uranium extraction, the matrix is completely destroyed in acid dissolution. Synthetic tissue paper waste samples were prepared, by loading known

<sup>\*</sup> With uranium amount =  $100 \, \mu g$ .



Table 5.: Experimental conditions for SFE of uranium from tissue paper matrix

Pressure	200 atm	TBP/TOPO flow rate	0.2 ml/ min
Temperature	60 °C	Steady time	20 min
CO2 flow rate	2 ml/min	Extraction time	20 min

amount of uranium on tissue paper by sprinkling uranyl nitrate solution, containing 1.5 to 3 mg uranium and heating under IR-lamp for 20 minutes. SFE was carried out under conditions as shown in Table 5. After SFE, uranium from tissue paper matrix was leached by heating with 40 ml of 4 M nitric acid for 20 minutes on a hot plate. Extraction efficiency was calculated from the difference in initial uranium loaded and uranium left unextracted. Leaching efficiency was found to be 88%. With TBP uranium extraction efficiency was found to be 66.83  $\pm$  9.80 % only, whereas with TOPO nearly complete uranium extraction was achievable ((98.07  $\pm$  0.80)%).

### SFE of thorium from tissue paper matrix employing various organophosphorus reagents

Similar to uranium, synthetic tissue paper waste samples (3 to 7 mg thorium) were prepared and SFE

was carried out with various organophosphorus reagents [16,17]. The leaching efficiency was found to be (95  $\pm$  2) %. In order to have an understanding of the extraction process from solid matrix, the effect of various parameters as well as various organophosphorus reagents was investigated and optimized values are as shown in Table 6(a).

Among various organophosphorus reagents, the following trend was observed (Table 6(b)):

- 1. Among phosphates, on replacing aliphatic group by aromatic group, extraction efficiency was found to decrease e.g. TBP and TPP.
- 2. Among phosphine oxides, higher the aliphatic chain length, higher was the extraction efficiency e.g. TOPO and TBPO.
- 3. Among phosphine oxides, if phenyl group is attached to P i.e. TPPO then extraction efficiency is intermediate to TOPO and TBPO.

Table 6(a): Optimized parameters for SFE of thorium from tissue paper matrix

Pressure	200 atm	Co-Solvent Flow rate	0.2 ml/ min
Temperature	60 °C	Steady time	20 min
CO <sub>2</sub> flow rate	2 ml/min	Extraction time	20 min



Table 6(b): Thorium extraction efficiency with various organophosphorus reagents (0.2 M in methanol) and TBP plus organophosphorus reagents

Organophosphorus reagent	Structure	Extraction efficiency (%) Organophosphorus reagent	Extraction efficiency (%),TBP+organophosphorus reagent
Tributylphosphate (TBP)	(RO)3-P=O $(R = C_4H_9)$	53	
Triphenylphospahte (TPP)	(RO)3-P=O $(R = C_6H_5)$	39	60
Trioctylphosphine oxide (TOPO)	R3-P=O $(R = C_8H_{17})$	68	68
Triphenylphosphine oxide (TPPO)	$R3-P=O$ $(R=C_6H_5)$	59	55
Tributylphosphine oxide (TBPO)	R3-P=O (R = C <sub>4</sub> H <sub>9</sub> )	50	74

(The extraction efficiency was a mean of five trials. The standard deviation was  $\pm 8\%$ )

4. On comparing phosphates with phosphine oxides, for aliphatic hydrocarbon, the extraction efficiencies are comparable. e.g. TBP and TBPO. For aromatic ring, as in the case of phosphine oxide, extraction efficiency is higher than its phosphate analogue e.g. TPP and TPPO.

Organophosphorus reagents are known to form coordinatively solvated compounds with actinides through P=O group. The more electronegative alkoxy group decreases the availability of electrons on the phosphoryl oxygen, thus making the molecule the weaker extractant. Electron donating group attached to phosphorus increases availability of electrons on the phosphoryl oxygen, the molecule becomes a stronger extractant. A phenyl group linked through oxygen to phosphorus, reduces the extractive capacity as compared to direct carbon-to-phosphorus bond.

Effect of combination was studied by taking TBP and other organophosphorus reagent (0.2 M in methanol) in 1:1 volume ratio (Table 6(b)). In case of TOPO and TPPO, there is no enhancement in extraction efficiency. Both TBPO and TPP show higher extraction efficiency.

### SFE of thorium from tissue paper matrix employing $\beta$ -diketones

Since complete thorium extraction from tissue paper could not be achieved by organophosphorus reagents as co-solvent,  $\beta$ -diketones were evaluated [18]. Online chelation and *in-situ* chelation mode were evaluated (Table 7). The following trend in thorium extraction efficiency was observed in both the chelation modes for the various  $\beta$ -diketones and also in TBP+  $\beta$ -diketone in 1:1 volume ratio.



### TTA > FOD > HFA > TFA > AA

The observed trend indicates a correlation between extraction efficiency and fluorination in the side arm of the  $\beta$ -diketone. The graph between number of fluorine atoms in the side arm of  $\beta$ -diketone versus extraction efficiency shows high linearity as seen in Fig. 7.

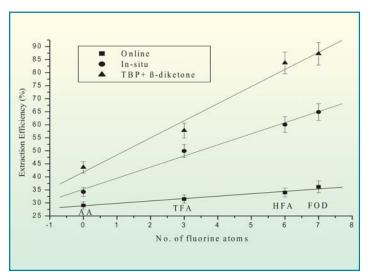


Fig. 7: Correlation graphs between thorium extraction efficiency and no. of fluorine atoms in the side ram of  $\beta$ -diketone for various modes. (Error bar is  $\pm$  5% of the value)

The extraction efficiency is expected to be governed by three factors:

(i) Solubility and stability of  $\beta$ -diketones in SC CO<sub>2</sub>, (ii) efficiency of Th-chelate formation and (iii) solubility and stability of Th-chelate in SC CO<sub>2</sub>. The  $\beta$ -diketones are assumed to be stable, as they do not decompose under SC CO<sub>2</sub> conditions. Fluorination in side arm enhances the solubility of  $\beta$ -diketones in SC CO<sub>2</sub> [19]

by several orders of magnitude. Due to tautomerism, β diketones exist as equilibrium mixture of keto and enol forms. On dissociation, enol form yields enolate ion, which chelates with thorium. The extent of enolate ion formation would depend upon the extent of enol form present and extent of dissociation in supercritical CO<sub>2</sub>. From NMR study, the enol content of AA and TFA were found to be 77% and 98.3% respectively in SC CO<sub>3</sub> (Table 8) whereas HFA, TTA were found to be exclusively in the enol form (~100% enol form). The increased stability of enol form in SC CO<sub>2</sub> with increasing fluorination could be assigned to stabilization by electron-withdrawing fluorine substituents, through enhanced electron delocalization in the intermolecular Resonance-Assisted Hydrogen Bonding (RAHB).

Table 7: Thorium extraction efficiencies with various β-diketones in different modes

Complexing agent	Extraction Efficiency (%) On line Mode	Extraction Efficiency (%) In-situ Mode	Extraction Efficiency (%) TBP+β-diketone
AA	29.05	34.25	43.63
TFA	31.48	49.93	57.76
HFA	34.01	60.06	83.71
FOD	36.21	64.87	87.24
TTA	52.78	76.52	89.45

(The extraction efficiency was a mean of five trials. The standard deviation was  $\pm 5\%$ )



Table 8: Structure  $\bigcap_{R_1 - C = CH_1 - C = R_1}^{O}$  of  $\beta$ -diketones, Mol Wt, enol Content in SC CO $_2$  and pKa values

β-Diketone	Abbreviation	$R_1$	$R_2$	Mol. Wt.	Enol content (%) in SC CO <sub>2</sub>	pKa
Acetylacetone	AA	CH <sub>3</sub>	CH <sub>3</sub>	100.12	77	8.67
Trifluoroacetylacetone	TFA	CH <sub>3</sub>	CF <sub>3</sub>	154.09	98	6-6.5
Hexafluoroacetylacetone	HFA	CF <sub>3</sub>	CF <sub>3</sub>	208.06	~100	4.46
Thenoyltrifluoroacetone	TTA	s	CF <sub>3</sub>	222.18	~100	6.5
Heptaflurobutanoyl pivaroylmethane	FOD	C(CH <sub>3</sub> ) <sub>3</sub>	C <sub>3</sub> F <sub>7</sub>	296.18		6.7

The extent of thorium chelation with enolate ion will depend upon pKa value. Substitution by two CF<sub>3</sub> groups into the AA, increases the acidity by four orders of magnitude e.g. pKa of AA is 8.67 whereas that of HFA is 4.46. Lower pKa enables HFA towards higher chelation. Data on solubility of thorium-chelate with  $\beta$ -diketones in SC CO<sub>2</sub> is lacking. However, reported data on solubility of transition metal-chelates with various  $\beta$ -diketones, reveals that, fluorination in side arm of  $\beta$ -diketone increases the solubility of metal-chelate in SC CO<sub>2</sub>. Hence, it is expected that solubility of thorium-chelate (with  $\beta$ -diketones) would increase with fluorination in the side arm of  $\beta$ -diketone.

# Direct dissolution and uranium extraction from solid uranium compounds (UO<sub>2,</sub> U<sub>3</sub>O<sub>8</sub>, U metal, U-Al alloy) employing supercritical CO<sub>2</sub>

In the nuclear fuel fabrication, lot of solid waste is being generated. It is desirable to extract valuable uranium from this solid waste. The conventional method consists of dissolution of solid matrix in nitric acid, followed by solvent extraction of uranium, which results in generation of copious amount of liquid waste. In the present study, we have carried out direct

dissolution and uranium extraction from solid uranium compounds viz. UO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, U metal, U-Al alloy employing supercritical CO<sub>2</sub>. UO<sub>2</sub> of various formspowder, granules, green pellets and sintered pelletswere studied. For dissolution, TBP-HNO<sub>3</sub> complex was employed. Thus, free acid usage could be avoided.

The TBP-HNO<sub>3</sub> complex used in the study was prepared by stirring TBP and conc. HNO<sub>3</sub> taken in 1:1 volume ratio, for one hour on a magnetic stirrer [20]. The organic phase was separated and employed for experiments.

Before carrying out SFE, knowledge of dissolution time is essential. Dissolution study was first carried out under atmospheric condition, by taking uranium compounds and TBP-HNO $_3$  complex and keeping in thermostat for certain time period. Dissolution status was examined visually.  $UO_2$  powder, granules and  $U_3O_8$  powder are easy to dissolve as they were completely dissolvable within 15 minutes at 50 °C. (Table 9).

UO<sub>2</sub> green pellets, sintered pellets, U metal, U-Al alloy could only be partially dissolved even in 50 minutes at 50 °C. Hence, dissolution study was carried out at



Table 9: Dissolution study (under atmospheric pressure conditions)

	Dissol	n. temp. 50 °C	Dissoln. te	mp. 80 °C
Compd.	Dissoln. time (min)	Dissoln. status	Dissoln. time (min)	Dissoln. status
UO <sub>2</sub> powder	5	Complete		
UO <sub>2</sub> Granule	15	Complete		
UO <sub>2</sub> Green pellet	50	Partial	20	Complete
UO <sub>2</sub> Sintered pellet	50	Partial	30	Complete
U <sub>3</sub> O <sub>8</sub> powder	5	Complete		
U metal	50	Partial	30	Complete
U-Al alloy	50	Partial	50	Partial

Table 10: Optimized conditions for extraction

Pressure	150 atm
Temperature	50 °C
TBP-HNO <sub>3</sub> amount	1 ml
CO <sub>2</sub> flowrate	1 ml/min
TBP/TTA %	2.5% of CO <sub>2</sub> (0.025 ml/min)
Extraction time	30 min
Flushing time	10 min

elevated temperature.  $UO_2$  green, sintered pellets and U metal could be completely dissolved in 30 minutes at 80 °C, whereas U-Alloy was only partially dissolvable.

On dissolution of solid compound, uranium exists as  ${\rm UO_2}^{++}$  ion, irrespective of the nature of solid compound. Hence, after dissolution, extraction time should be the same for all compounds. Various parameters for extraction were optimized with  ${\rm UO_2}$  powder. The optimized values are listed in Table 10. SFE was carried out for all uranium compounds initially with SC  ${\rm CO_2}$  alone and later with TBP/TTA for improving efficiency.

As shown in Table 11, for  $\rm UO_2$  powder,  $\rm U_3O_8$  powder and U metal,  $\sim 70\%$  extraction efficiency was achievable with SC  $\rm CO_2$  alone. Presence of higher amount of TBP in SC  $\rm CO_2$  should enhance the formation of  $\rm UO_2$  ( $\rm NO_3$ )<sub>2</sub> (TBP)<sub>2</sub> complex and hence enhance the extraction efficiency. With supercritical fluid mixture of  $\rm CO_2 + 2.5\%$  TBP, the efficiency enhanced to  $\sim 93\%$ . Nearly complete extraction ( $\sim 98\%$ ) was achievable with SC  $\rm CO_2 + 2.5\%$  TTA.

Table 11: Extraction efficiencies for different uranium compounds

Compd.	Dissolun. temp. (°C)	Dissolun. time (min)	Extraction efficiency (%)		
			SC CO <sub>2</sub>	SC CO <sub>2</sub> +TBP	SC CO <sub>2</sub> +TTA
UO <sub>2</sub> powder	50 °C	10	70.41	94.20	98.10
UO <sub>2</sub> granule	50 °C	20		94.92	98.44
UO <sub>2</sub> green pellet	80 °C	30	1	91.80	99.26
UO <sub>2</sub> sintered pellet	80 °C	40		94.56	98.90
U <sub>3</sub> O <sub>8</sub> powder	50 °C	10	72.11	91.18	98.74
U metal	80 °C	30	73.35	93.48	
U-Al-Si alloy	80 °C	50	32.57		

(Results are a mean of 3 experiments, avg. std. deviation = 4.71)

### **Conclusions**

Supercritical fluid extraction of uranium and thorium from acidic solution and solid medium was successfully demonstrated. Also, direct dissolution and extraction of uranium from various uranium compounds was demonstrated. CO<sub>2</sub> was employed for supercritical fluid preparation. The main highlights of the study are as follows:

- (i) Nearly complete extraction of uranium (98  $\pm$  2 %), from nitric acid medium was achievable employing TBP as co-solvent.
- (ii) To understand extraction mechanism, effect of various factors viz. pressure, temperature, nitric acid molarity, CO<sub>2</sub> flow rate, % of TBP, extraction time, online and in-situ complexation mode were studied. Pressure of 150 atm,



- $60 \, ^{\circ}\text{C}$  temperature, 1 ml/min  $\text{CO}_2$  flow rate, 10% TBP, 7 M nitric acid, 30 minute extraction time were found to be optimum.
- (iii) Detailed investigations were carried out, for SFE of uranium employing various crown ethers. Effect of pressure, temperature, nitric acid molarity, uranium amount, extraction time was investigated. Under optimized conditions (200 atm, 50° C)with ditertiary butyldicyclohexano-18-crown-6 the efficiency was found to be (86  $\pm$  5)%. Efficiency was found to increase with ring size. Electron donating substituents increased extraction efficiency whereas electron withdrawing substituents decreased extraction efficiency.
- (iv) From tissue paper matrix,  $\sim$ 66% uranium extraction was observed with TBP as co-solvent at 200 atm and 60 °C. However with TOPO nearly complete ( $\sim$ 98 %) extraction was achievable
- (v) Direct dissolution and uranium extraction from solid uranium compounds (UO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, U metal, U-Al alloy) was carried out, employing TBP-HNO<sub>3</sub> complex. Under optimized conditions (150 atm and 60 °C), for UO<sub>2</sub> powder, U<sub>3</sub>O<sub>8</sub> powder and U metal, ~70% extraction efficiency was observed with SC CO<sub>2</sub> alone, with addition of 2.5 %TBP, efficiency enhanced to ~93%. Nearly complete extraction (~98%) was achievable with SC CO<sub>2</sub> +2.5% TTA. UO<sub>2</sub> powder, granules and U<sub>2</sub>O<sub>6</sub> powder were completely dissolvable within 15 minutes at 50 °C under atmospheric pressure. UO, green, sintered pellets and U metal could be completely dissolved in 30 minutes at 80 °C whereas U-Al alloy was only partially dissolvable.

- (vi) Nearly complete thorium extraction ( $\sim$ 99%) from nitric acid medium was achievable with 1 ml of 0.2 M TOPO at 100 atm pressure in the *in-situ* mode. With TBP  $\sim$  80% extraction was observed.
- (vii) Various organophosphorus reagents were evaluated for thorium SFE from tissue paper matrix. Effect of pressure, temperature,  $\mathrm{CO}_2$  flow rate and extraction time was investigated. Under optimized conditions(200 atm, 60 °C),  $\sim$  70 % extraction efficiency was achievable with TOPO.
- (viii) Various  $\beta$ -diketones were evaluated for thorium SFE from tissue paper matrix and the trend observed was TTA > FOD > HFA > TFA > AA. $\sim$ 90% extraction efficiency was observed with TTA + TBP. A correlation was observed between extraction efficiency and degree of fluorination in the side arm of  $\beta$ -diketone.

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# USE OF ROLLING TOOL AND ORBITAL TIG WELDING SET-UPS

The Centre for Design and Manufacture (CDM) has designed and developed a large diameter Rolling Tool and an Orbital Welding set-up and which has been tested and successfully used, in carrying out Rolling and Welding of an Inconel thin Can (04.mm thick shell) at its two ends. The Can is part of a Canned motor being manufactured at CDM.

Large diameter Rolling Tool is not available in the market as a standard item. CDM has specially designed and developed it for the specific operation.

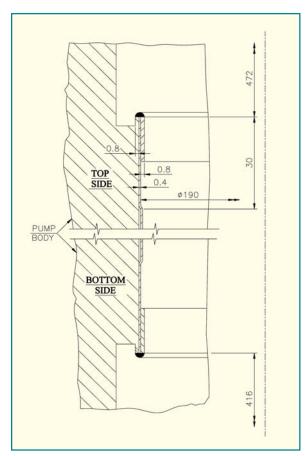


Fig. 1 : Detail of LIP joint for orbital welding

The location of the Rolled joint and Welding of three parts (lip on the body of Canned motor, the Inconel Can and the internal stiffening ring, (Fig. 1), does not allow access and visibility to the welder (due to narrow well size, diameter 190 mm and 472 mm depth) for carrying out manual welding operation, using a standard TIG welding torch.

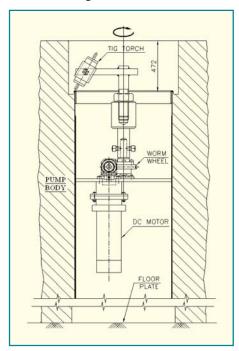


Fig. 2: Orbital Welding Set-up

An Orbital Welding set-up was designed, manufactured, (Fig. 2) and tested on an identical size/shape mock-up to ensure satisfactory operations and to finalize welding parameters (Arc gap, welding voltage / current, Welding speed, etc). to obtain acceptable quality welds before execution of welding on the actual Canned Motor. Welds on both ends of the Can have been successfully carried out on the Canned motor.



### WORKSHOP ON THE LAUNCH OF THE NATIONAL KNOWLEDGE NETWORK

A two-day Workshop on the "Launch of the National Knowledge Network", was organized jointly by the Computer Division, BARC and the National Informatics Center, New Delhi on the 10<sup>th</sup> and 11<sup>th</sup> of December 2008 and was held at the Auditorium, Supercomputing facility building, BARC.

The objective of the National Knowledge Network (NKN) was to bring together all stakeholders in science, technology, higher education, research and development and governance, with speeds of the order of 10s of Gigabits coupled with extremely low latencies. NKN will enable scientists, researchers and students from different backgrounds and diverse geographies of our country, to work in unison, conduct experiments, share knowledge and expertise. NKN would enable use of specialized applications which would allow sharing of high performance computing facilities, e-libraries, Virtual classrooms and very large databases. In the run-up for launching this network, this workshop was organized to impart training to the network administrators, responsible for setting up the network.

The Inauguration function was graced by Dr. R. Chidambaram, Principal Scientific Advisor to the Government of India. Mr. G.P. Srivastava, Director, E&I Group, BARC, Mr. P.S. Dhekne, Raja Ramanna Fellow and Mr. A.G. Apte, Head, Computer Division, BARC were also present. Mr. G.P. Srivastava welcomed the participants to the workshop. Dr. R. Chidambaram, in his presidential address said, that a project like the National Knowledge Network, was essential for a country like India. He also said that modeling of Climate change that requires both High-End computation and faster communication, would benefit from such a network. In addition to

discussing scientific applications, Dr. Chidambaram also dwelt on the societal benefits that NKN would provide, in terms of enabling countrywide virtual classroom concepts, making timely expert-medical advice available to the populace located in remote areas etc.

This was followed by a talk by Mr. P.S. Dhekne. Mr. Dhekne described the architecture of NKN and the different phases in which NKN would be extended to encompass the whole country. In this workshop, the concepts of Network Security, Virtual Private Networks and Information Security were discussed in great detail. Further, the participants were exposed to bandwidth guzzling applications like Video Conferencing, Web Streaming, Collaborative design, Drug Discovery and Grid Computing. The speakers were drawn from National Informatics Centre, New Delhi, Bhabha Atomic Research Centre, Mumbai, Jawaharlal Nehru University, New Delhi and IGIB, New Delhi. All the lectures were supplemented with Live Demonstrations to reinforce the concepts. These practical demonstrations were arranged by engineers from Computer Division, BARC.

About 60 participants from BARC and other institutes like NIC-New Delhi, CDAC-Bangalore, Ministry of Information Technology-New Delhi, IIT-Chennai, IIT-Hyderabad, IIT-Guwahati, IIT-Mumbai, TIFR-Mumbai, HRI-Allahabad, JNU-New Delhi, IGIB-New Delhi, RRCAT-Indore, IGCAR-Kalpakkam, VECC-Kolkata, CSIR-Headquarters Delhi, ECIL-Hyderabad, NPCIL-Mumbai attended the workshop. The participants were provided with Workshop kits that contained detailed documentation about the topics discussed and the demonstration set-ups.



# SYMPOSIUM ON OPERATIONAL AND ENVIRONMENTAL ISSUES CONCERNING USE OF WATER AS COOLANT IN POWER PLANTS AND INDUSTRIES (OPENWAC-2008)

Water is one of the most essential commodities for any industrial activity. Among the various industrial uses of water, its use as a coolant is of utmost importance. Thermoelectric generation alone accounts for more than 50% of all water use. As the coming decades are likely to see rapid growth in power generation in the country, adequate availability of cooling water - fresh or saline - will play a key role in locating the plants. Utilities, in their attempt to economize power production, are increasingly paying more attention to improving the operating efficiency. The availability and capacity factor achieved in power plants and other industries are closely linked to the performance of the coolant systems. Efforts are continuously made to optimize the chemistry conditions of the coolant water, so that, operational problems such as corrosion, scaling, biofouling, poor heat transfer efficiency and radiation field build-up are minimized and operation efficiency is enhanced. However, in spite of efforts, power plants and other industrial plants continue to suffer from many of the above problems, often resulting in economic losses that run into hundreds of crores of rupees.

The cooling water / discharged water often has its physical and chemical properties altered, during its passage through the cooling system of the plant. The impact of such discharges on the environment is a subject of great concern to the general public, plant operators and lawmakers. Environmental effects caused by discharge of heated effluents from power plants have attracted the attention of the scientific community. In this context, work has been going on at Kalpakkam, to understand environmental effects

arising out of discharge of heated water containing chemical additives, on the ambient water quality and ecology of coastal waters.

The Water and Steam Chemistry Division (BARC), located at Kalpakkam, has been engaged over the past 20 years, in research related to both operational and environmental issues, concerning the use of water as a coolant in nuclear power plants. The focus of research over the years has been in areas such as chemical decontamination, minimization of radioactivity build-up in coolant circuits, flow accelerated corrosion, water quality of natural water bodies, biofouling, biocorrosion and environmental effects of condenser discharges into coastal areas. Similarly, a number of groups in BARC have been working on chemical and metallurgical problems related to coolant systems. Significant research work has been carried out on the development of new methods, to resolve the problems related to chemical, biological and environmental milieu of coolant systems employing water. Ultimately, the objective should be to translate the fruits of such efforts to industrial systems. However, percolation of the outcome of R&D efforts, to personnel operating the plants, has been suboptimal. On the other hand, there is limited access to the research community, to the operating experience gained by the industry. There is a need for a healthy synergism between the R&D scientists and the operating personnel, for effective utilization and implementation of newer technologies. The OPENWAC-2008 was organized, to provide a crossdisciplinary forum for discussing and debating key operational and environmental issues, related to the



use of water as a coolant, in industrial systems. The target audience was chemists, biologists, environmental scientists, power plant operating engineers and plant designers. Accordingly, the participants were mostly from the power industry (nuclear and thermal), research institutes, academic centres and regulatory bodies.

The symposium, sponsored by BRNS and INS (Kalpakkam Chapter), was held at the Sarabhai Auditorium in IGCAR, Kalpakkam during 15<sup>th</sup> & 16<sup>th</sup> December, 2008. It was in continuation with the previous meetings; Specialists Meeting on Marine Biofouling and Power Plants held in Kalpakkam (1989), DAE Symposium on Current Trends in Water Chemistry of Nuclear and Thermal Power Plants and Other Related Units (CURTWAC), held in BARC, Mumbai (1995), Discussion Meeting on Natural Waters as Heat Sink of Electric Power Plants, held in Kalpakkam (1997), National Symposium on Water and Steam Chemistry in Power Plants and Industrial Units (SWASCH) held in BARC, Mumbai (2000) and Special Workshop on Water Chemistry held in Kalpakkam (2001).

Dr. T. Mukherjee welcomed the gathering and highlighted the key role played by WSCD over the years, in the area of reactor water chemistry. Dr. S.V. Narasimhan, Chairman, Organizing Committee and Head, WSCD gave a brief introduction about the symposium. Dr. Anil Kakodkar, Chairman, AEC, inaugurated the symposium. He emphasized the contribution of COSWAC in providing advisory services to the nuclear power industry, in terms of chemistry control in various reactor cooling systems. It was mentioned that plant operators could take home the ideas being discussed at the meeting and COSWAC was urged to provide definitive guidelines for their implementation. Dr. Kakodkar also urged COSWAC to come up with standards in the realm of reactor water chemistry. Dr. V. Venugopal, Vice President, INS delivered the presidential address. Dr. S. Rangarajan proposed a vote of thanks.

There were about 150 registered delegates from different units of DAE and universities. The presentations were divided into three sections: invited lectures (9), oral papers (28) and poster papers (62).



Dr. Anil Kakodkar, Chairman AEC, speaking at the inauguration of OPENWAC-2008



Three special lectures were also included that dealt with overview of latest developments in the areas of corrosion and biofouling control, in power plant coolant systems. The three papers showcased advanced technologies, which are not yet practised in India but are likely to have an impact on the Indian nuclear power industry, if implemented in future. Full texts of papers were compiled into proceedings (printed and CD versions) and distributed before the beginning of the symposium.

The following points emerged from the presentations and deliberations held during the symposium:

- 1. In primary heat transport circuits of water-cooled NPPs, one problem of significance is radiation field build-up, on out-of-core surfaces. Novel methods of improving the protective nature of high temperature oxide layer by mending the water chemistry regime should be pursued. Theoretical modelling, laboratory and reactor-based experimental work and possible application in a typical reactor should be pursued.
- 2. Flow accelerated corrosion in both Primary (feeder / PHWR) and secondary should be investigated more intensely. Improved methods of reliable field measurements with better accuracy and precision should be developed. Field measurements should be model based and for this, a model should be evolved. The model should be validated by simulated experiments and feedback from station data.
- 3. In the tertiary circuit, biofouling control is being practiced based mostly on past experience. The treatment mostly involves bulk treatment of the cooling water, while biofouling is essentially an

interfacial problem. Treatment strategy to effectively deal with biofilm is a better option in future. Several options like choice of biocides, improved penetration and reach of biocide, inhibition of biofilm growth, surface coatings etc. should be investigated, depending on type of fouling (micro- or macro-fouling), severity of fouling and the system being fouled. Plant application should be part of these investigations and operator training is essential for ultimate success of the programme. Though complete exclusion of biofouling is not possible without seriously endangering the environment, efforts should be made to control it within allowable limits.

- 4. Several reliable and rugged online chemical instrumentation and biofilm monitors are now available and are being used in NPPs abroad and also in NTPC plants. Efforts should be made to adopt such technologies in Indian NPPs. A specialist group can be entrusted with this job, to study various aspects and to install the instruments in NPPs. The data from such instrumentation should be evaluated / validated by the same team during normal, off-normal and shut down conditions.
- 5. Laboratory studies and simulated loop investigations are being pursued by the research wings of DAE. After regulatory clearance, such procedures can be implemented in chosen plants to validate the procedure under plant conditions. Such an approach will be useful for future plants as well.

As part of the symposium, a function was held to honour veteran scientists and technologists, who have made significant contributions to the area of water chemistry and cooling water research.



## DAE - BRNS SYMPOSIUM ON NUCLEAR PHYSICS - 2008 : A REPORT

The 53<sup>rd</sup> annual DAE Symposium on Nuclear Physics -2008 was held at the Indian Institute of Technology, Roorkee, Uttarakhand, during December 22-26, 2008. This year has a special significance as it coincides with the birth centenary year of Dr. Homi Bhabha. It was with the initiative of Dr. Bhabha that the annual DAE Nuclear Physics Symposium was started in the early 1950s. The aim of this series of symposia has been to provide a scientific platform to the nuclear physics community, to present their research work and to interact with the researchers in this area. This year, there was a very enthusiastic response in terms of the number of papers (281 contributed papers as compared to the last year number of 233) and theses (16) submitted for presentation at the symposium. In addition to this, there were 26 invited talks delivered by distinguished speakers from India and abroad. The symposium covered key areas of nuclear physics: a) Nuclear structure, b) Low and medium energy nuclear reactions, c) Physics with radioactive ion beams, d) Intermediate energy nuclear physics, e) Physics of hadrons and QCD, f) Relativistic nuclear collisions and QGP, g) Nuclear astrophysics and nuclear matter, h) Accelerators and instrumentation for Nuclear Physics. The conference proceedings, which included the writeups of invited talks and two page abstracts of contributed papers were published in advance, to facilitate discussion among the participants, on different topics, covered during the conference.

The symposium was inaugurated by Prof. S.S. Kapoor, Honorary INSA Scientist and Ex-DAE Homi Bhabha Chair Professor. Dr. Kapoor also gave a keynote address describing the overall nuclear physics research scenario and its spin offs to applications for society. Dr. R.K Choudhury, Head, Nuclear Physics Division, BARC and Chairman, Organizing Committee gave the introductory remarks, where he emphasized the



Inauguration of the DAE Nuclear Physics Symposium at IIT, Roorkee, Uttarakhand





Prof. M.G.K. Menon delivering the Special evening lecture on "Dr. Homi Bhabha: the Scientist and Visionary"

importance of the series of symposia for the growth and development of nuclear physics research in India. Prof. H.K. Verma, Dy. Director, IIT, Roorkee presided over the inauguration function. Dr. Alok Saxena, Convener, gave the highlights of the symposium and Prof. A.K. Jain, Local Convener, proposed the vote of thanks.

There were 242 registered delegates out of which 75 were from DAE institutions, 64 faculty members from universities and affiliated institutions, 90 students and 13 scientists from abroad. The invited talks covered a wide range of topics such as fundamental neutron physics, decay and structure of nuclei beyond the proton drip-line, Giant resonances, fusion-fission dynamics, Hadron Physics with Polarized Photon Beams at SP ring-8/LEPS, latest results from RHIC experiments, QGP, Positron Double Beta Decay, Physics Possibilities with Atmospheric Neutrinos. Two special seminars were organized to discuss the results from the Indian National Gamma Array facility and another to discuss upcoming facilities such as the superconducting cyclotron at Kolkata, the Large Hadron Collider at CERN and Indian participation in CMS and ALICE experiments. There was an evening

lecture on "Dr. Homi Bhabha – the Scientist and Visionary" by Prof. M.G.K. Menon to commemorate the birth centenary year of Dr. Bhabha.

There was a special evening session on Future Generation Facilities for Nuclear Spectroscopy which was chaired by Prof. V.S. Ramamurthy. This session generated many new ideas about the upcoming gamma ray arrays in the country. There was also a proposal to establish a theoretical nuclear physics center in the country. There was good participation from the students. A one day orientation course on Exotic Radioactive Decay and Shell Model was given by experts in this field and was coordinated by Prof. A.K Jain. About 50 students attended this course which was held a day before the symposium started.

A total of eleven theses were presented in the poster session, out of which three theses were shortlisted for oral presentation based on the recommendation of a panel of judges. The best thesis award, named after late Prof. C.V.K. Baba, was given to Pushpendra P. Singh of Aligarh Muslim University for his work on "Probing of Incomplete Fusion Dynamics at E/A H" 4-7 MeV". The award will be given to him by the Indian Physics Association. Three posters out of 220 posters were selected for prize distribution by another panel of judges. The first prize for the best poster was given to Mr. Deeepak Pandit and his collaborators for their work on "Signature of Jacobi shape transition and Coriollis Splitting in GDR Lineshape for <sup>47</sup>V".

The local arrangements at IIT, Roorkee were excellently organized by Prof. A.K.Jain and his colleagues. The symposium organizing committee is thankful to BRNS, DAE for the full financial support for conducting the symposium. There was also a presentation on BRNS activities by Mr. S.G. Markandeya, Head, Planning and Co-ordination Division and Scientific Secretary, BRNS.



#### **New Publication**

Nuclear Tribology: Understanding friction, wear and lubrication

Edited by: N.L. Soni and P.K. Limaye

2008

ISBN:978-81-903899-9-0

Nuclear Tribology is a narrow specialized discipline, that deals with mechanical engineering issues covering friction, wear and lubrication of materials and components, used in the operation of nuclear power plants.

This publication is a compilation of lectures and presentations by DAE and non-DAE experts, working in the field of Tribology. The compilation covers various issues in Nuclear Tribology such as its significance, its various applications, tribological studies related to metallurgical coatings, high-temperature synthetic grease, high performance radiation-resistant lubricants, development of special turbo-materials and testing, evaluation and optimization of materials and components used in nuclear power plants.

### भा.प.अ. केंद्र के वैज्ञानिकों को सम्मान BARC SCIENTISTS HONOURED

विद्या ए. कांबले, तथा हरि एस. मिश्रा, मोलिक्यूलर बायोलोजी प्रभाग, द्वारा लिखित "रिवर्सिबल प्रोटीन फोसफोरिलेशन कन्ट्रोल्स दि न्युक्लियोलिटिक डीएनए डिग्रेडेशन इन ए रेडियोरेजिस्टंट बेक्टीरियम, डायनोकोकस रेडियोड्यूरंज़" नामक शोध-पत्र को दिसंबर 18-20, 2008 के दौरान आयोजित इन्डियन इंस्टिट्यूट ऑफ बायोटेक्नॉलोजी, चेन्नई के डिपार्टमेंट ऑफ बायोटेक्नॉलोजी में सोसाइटी ऑफ बायोलोजिकल केमिस्टस इंडिया (एसबीसी (1)) एन्ड "इम्पेक्ट ऑफ बेसिक एन्ड ट्रान्सलेशनल रिसर्च ऑन मेडिसिन, एग्रिकल्चर एन्ड इंडस्ट्री" के "सेल सिगनलिंग एन्ड एपोटोसिस" के 77वें वार्षिक वैज्ञानिक सत्रों के दौरान बी.एस.नरसिंहा राव श्रेष्ठ पोस्टर पुरस्कार से सम्मानित किया गया।

A paper entitled, "Reversible protein phosphorylation controls the nucleolytic DNA degradation in a radioresistant bacterium, *Deinococcus radiodurans*" by Vidya A. Kamble and Hari S. Misra of Molecular Biology Division, was awarded the B.S. Narasinga Rao Best Poster award at the Scientific Session of "Cell Signaling and Apotosis" during the "77<sup>th</sup> Annual Meeting of the Society of Biological Chemists (India) (SBC(I)) and symposium on "Impact of Basic and Translational Research on Medicine, Agriculture and Industry", held during December 18-20, 2008, at the Department of Biotechnology, Indian Institute of Biotechnology, Chennai.

डॉ. हिर एस. मिश्रा ने भाभा परमाणु अनुसंधान केंद्र में वर्ष 1990 से कार्यारंभ किया। तत्पश्चात् आप मोलिक्यूलर जेनेटिक्स ऑफ बेक्टीरियल रेसपोन्स टु एबायोटिक स्ट्रेस एवं इन्सेक्ट रेज़िस्टन्ट ट्रान्सजिनक प्लान्टस के विकास पर कार्यरत हैं। डॉ. मिश्रा इस समय विकसित आणिवक जीव- विज्ञान संबंधी उपकरणों के उपयोग से जीव- विज्ञान प्रणाली के आधार पर विकिरण प्रतिक्रिया से





आणविक प्रणाली के स्पष्टीकरण हेतु काम कर रहें हैं। इन्होंने पहली बार बेक्टीरिया में डीएनए की लडी में ट्रासडक्शन घटक के संकेत का विवरण दिया है। डॉ. मिश्रा आइएनएस पदक 2004 के प्राप्तकर्ता हैं एवं आप महाराष्ट्र अकादमी ऑफ साइन्सिस, 2003 के निर्वाचित सदस्य भी हैं।

Dr. Hari S. Misra joined BARC in 1990. Since then he was been working on molecular genetics of bacterial response to abiotic stress and the development of insect-resistant transgenic plants. Dr. Misra is currently working on the elucidation of molecular mechanisms underlying the radiation response to biological system, by employing advanced molecular biology tools. His group reports for the first time, the involvement of a signal trasduction component in DNA strand break repair in bacteria. Dr. Misra is the recipient of the INS Medal 2004 and is an elected Fellow of the Maharashtra Academy of Sciences, 2003.



Mr. B.K. Shah

श्री बी. के. शाह, अध्यक्ष, गुणवत्ता आश्वासन प्रभाग, भाभा परमाणु अनुसंधान केंद्र को साइन्स एन्ड टेक्नॉलोजी ऑफ नान -डिस्ट्रक्टिव टेंस्टिंग एन्ड इवेलुएशन (आइएसएनटी) में विशेष योगदान को मान्यता देने हेतु ऑनरेरी फेलोशिप इन्डियन सोसाइटी फॉर नान-डिस्ट्रक्टिव टेस्टिंग की प्रदान की गई। यह फेलोशिप प्रमाण-पत्र

इन्हें भाभा परमाणु अनुसंधान केंद्र के निदेशक डॉ. एस. बॅनर्जी के द्वारा 1 दिसंबर, 2008 को लोनावला में आयोजित "चेलेंजिज़ एन्ड इनोवेशन्ज़ इन एनडीटी (एनडीई - 2008)" की राष्ट्रीय गोष्ठी में प्रदान किया गया। श्री बी.के.शाह ने एम.टेक (कोरोजन साइन्स एन्ड इंजीनियरिंग) इंडियन इन्सिटट्यूट ऑफ टेक्नॉलोजी, मुंबई से किया है। आप भाभा परमाणु अनुसंधान केंद्र के प्रशिक्षण

विद्यालय के 17वें बैच से हैं। नाभिकीय ईंधन एवं रियक्टर कोर कम्पोनंटस के उत्पादन में गुणवत्ता आश्वासन, धातुकी विश्लेषनात्मक असफलता इनके कार्यक्षेत्र में शामिल हैं। इनके 200 से अधिक तकनीकी शोध-पत्र प्रकाशित हुए हैं। इन्होंने विभिन्न पुरस्कार प्राप्त किये हैं जिनमें नैशनल एनडीटी पुरस्कार (1998) भी शामिल हैं। इन्होंने कोरोजन साइंस (2005) में श्रेष्ठता हेतु एनएसीई पुरस्कार (1998) एवं 8 तकनीकी प्रकाशनों में सर्वश्रेष्ठ शोध-पत्र पुरस्कार भी प्राप्त किये हैं।

Mr. B.K. Shah, Head, Quality Assurance Division (QAD), BARC has been conferred the "Honorary Fellowship' of the Indian Society for Non-Destructive Testing (ISNT), in recognition of his significant contribution to the Science and Technology of Non-destructive testing and evaluation. This Fellowship Certificate was presented to him by Dr. S. Banerjee, Director, BARC during the National Seminar on Challenges and Innovations in NDT (NDE-2008)" held at Lonavala on December 1, 2008. Mr. B.K. Shah has done M. Tech. (Corrosion Sc. & Engg.) from Indian Institute of Technology (IIT) Mumbai. He belongs to the 17th Batch of BARC Training School. His field of work includes Quality Assurance (OA) in the manufacture of Nuclear Fuels and Reactor Core Components, Metallurgical Failure etc. He has published more than 200 technical papers. He has received many awards which include National NDT Award (1998), NACE Award for Excellence in Corrosion Science (2005) and the Best Paper Award for 8 technical publications.



Mr. Arbind Kumar

श्री अरबिंद कुमार, गुणवत्ता आश्वासन प्रभाग, भाभा परमाणु अनुसंधान केंद्र को "डिज़ाइन ऑफ एडी करंट टेस्ट कॉइल्स एन्ड डेवलपमेंट ऑफ टेक्नीक्स फॉर इन- सर्विस इन्स्पेक्शन ऑफ पीएचडब्ल्यूआर कूलन्ट चेनल्स एन्ड हीट एक्सचेंजर ट्यूब्स" में विशिष्ठ योगदान को मान्यता देने हेतू इन्डियन सोसाइटी फॉर नान-डिस्ट्रक्टिव टेस्टिंग (आइएसएनटी), मुंबई शाखा के द्वारा आर एन्ड डी श्रेणी का "एनडीटी अचीवमेंट अवार्ड" प्रदान किया गया। यह पुरस्कार इन्हें भाभा परमाणु अनुसंधान केंद्र के निदेशक, डॉ. एस. बॅनर्जी के द्वारा 1 दिसंबर, 2008, को लोनावला में आयोजित "चेलेंजिज़ एन्ड इनोवेशंज़ इन एनडीटी (एनडीई - 2008)" की राष्ट्रीय गोष्ठी में प्रदान किया गया। श्री अरिबंद कुमार आइआइटी, कानपुर से धातुकी विज्ञान के स्नात्कोत्तर हैं। इन्होने भाभा परमाणु अनुसंधान केंद्र के प्रशिक्षण विद्यालय के 39वें बैच से प्रशिक्षण प्राप्तकर परमाणु ईंधन प्रभाग में कार्यारंभ किया। इस समय आप गुणवत्ता आश्वासन प्रभाग के एडी करंट टेस्टिंग के क्षेत्र में कार्यरत्त हैं।

Mr. Arbind Kumar, Quality Assurance Division, BARC has been conferred the 'NDT Achievement Award' in the R&D category for the year 2008, by the Indian Society for Non-Destructive Testing (ISNT), Mumbai Chapter in recognition of his significant contribution towards Design of Eddy Current Test coils and development of techniques for In-Service Inspection of PHWR Coolant Channels and Heat Exchanger tubes. This Award was presented to him by Dr. S. Banerjee, Director, BARC during the National Seminar on "Challenges and Innovations in NDT (NDE-2008)" held at Lonavala on December 1, 2008. Mr. Arbind Kumar is a Postgraduate in Metallurgy from IIT, Kanpur. He joined the Atomic Fuels Division, BARC from the 39th batch of BARC Training School. Presently, he is working in the Quality Assurance Division, BARC in the field of Eddy Current Testing.



Dr. H.S. Sharma

डॉ. एच.एस. शर्मा इस समय भाभा परमाणु अनुसंघान केंद्र के ईंधन रसायनिकी प्रभाग के इलेक्ट्रोके मिस्ट्री अनुभाग के अध्यक्ष हैं। डॉ. शर्मा ने अलाहाबाद विश्वविद्यालय से पीएच.डी प्राप्त करने के पश्चात् भाभा परमाणु अनुसंघान केंद्र के रेडियोरसायनिकी प्रभाग में कार्यारंभ किया। इनकी रुचि के क्षेत्र मे मुख्यत: नाभिकीय ईंधन पदार्थों में एन्टिनाइडस का सही तथा यथार्थ निर्धारण हेत् विश्लेशनात्मक क्रिया पद्धति का विकास एवं (बहुलक) पोलिमर्स का कार्य संचालन एवं नेनो - स्केल पदार्थों का विश्लेशन तथा इलेक्ट्रोरसायन संयोजन शामिल है। डॉ. शर्मा ने पोहांग युनिवर्सिटी ऑफ साइन्स एन्ड टेक्नॉलोजी, साउथ कोरिया में इलेक्ट्रोरसायन संयोजन एवं फलोरंस आधारित बहुलक कार्य संचालन के चरित्रांकन पर अतिथि विद्वान की हेसियत से काम किया। डॉ. शर्मा विभिन्न भारतीय विश्वविद्यालयों के परीक्षार्थी मंडल में पीएच.डी शोध-पत्रों का मुल्यांकन कर रहें हैं तथा सीसीएस युनिवर्सिटी, मेरठ में अनुसंधान निर्देशक भी हैं। डॉ. शर्मा ने डीएसटी, डीआरडीओ एवं डीएइ - बीआरएनएस अनुसंधान प्रस्तावों के मृल्यांकन विशेषज्ञ की हेसियत से कार्य किया है तथा बीआरएनएस परियोजना के मुख्य सहयोगी हैं। इन्हें इलेक्ट्रोरसायन अनुसंधान के क्षेत्र में उत्कृष्ट योगथन को मान्यता देने हेतृ इन्डियन केमिकल सोसाइटी के द्वारा "प्रोफैसर एस.एस. सिद्धु" (2007-08) नामक पुरस्कार से सम्मानित किया गया ।

Dr. H.S. Sharma is presently Head, Electrochemistry Section, Fuel Chemistry Division, BARC. Dr. Sharma joined Radiochemistry Division, BARC in 1978, after completing Ph.D. from University of Allahabad. His major fields of interest includes development of analytical methodologies for precise and accurate determination of actinides in nuclear fuel materials and electrochemical synthesis and characterization of nano-scale materials and conducting polymers. Dr. Sharma worked as a "Visiting Scholar" at Pohang University of Science and Technology, South Korea on electrochemical synthesis and characterization of fluorene based conducting polymers. Dr. Sharma is serving on the board of examiners for evaluating Ph.D. thesis at different Indian universities and is a research guide of CCS University, Meerut. Dr. Sharma has served as expert for evaluating/reviewing DST, DRDO and DAE-BRNS Research Proposals and is a Principal Collaborator to BRNS project. Dr. Sharma has been recently awarded, "Prof. S. S. Sandhu Award" (2007-08) by Indian Chemical Society for his outstanding contributions in the area of Electrochemical Research.





Dr. B.N. Jagatap

डॉ. बी. एन. जगताप, लेजुर एवं प्लाज्मा टेक्नॉलोजी प्रभाग के एक उत्कृष्ट वैज्ञानिक, को (आइएसीएस) इन्डियन एसोसिएशन फॉर दि कल्टिवेशन ऑफ साइन्स, कोलकत्ता में स्पेक्ट्रोस्कॉपी के क्षेत्र में प्रतिष्ठापूर्ण टी.के .रॉय.दस्तीदार मेमोरियल लेक्चर ऑफ 2009 हेत आमंत्रित किया गया था। डॉ.जगताप ने 18 फरवरी, 2009

को " कंट्रोलिंग एटम्ज़ एन्ड मोलिक्यूल्ज़ विथ फोटाँज़" नामक विषय पर भाषण दिया। वक्ता को सम्मानित करने हेतु रजत स्मृतिपट दिया गया ।

Dr. B.N. Jagatap, Outstanding Scientist in Laser & Plasma Technology Division, was invited by the Indian Association for the Cultivation of Science (IACS), Kolkata, to deliver the prestigious Prof. T.K. Rai Dastidar Memorial Lecture of 2009 in the field of spectroscopy. Dr. Jagatap delivered the lecture entitled "Controlling Atoms and Molecules with Photons" on February 18, 2009. The honour included presentation of a silver plaque to the speaker.

डॉ.जय पाल मित्तल, डीएई राजा रमन्ना मंडल के सदस्य, केमिस्ट्री एन्ड आइसोटोप ग्रुप के पूर्व-निदेशक, भाभा परमाण अनुसंघान केंद्र को हाल में ही केमिकल साइन्सिज़ के क्षेत्र में अनुसंधान एवं अध्यापन की उपलब्धियों को मान्यता देने हेत् इन्डियन केमिकल



Dr. Jai Pal Mittal

सोसाइटी के द्वारा "लाइफ टाइम अवार्ड" प्रदान किया गया। यह सोसाइटी वर्ष 1924 में प्रसिद्ध भारतीय रसायनिक आचार्या प्रफुल्ला चंद्र रॉय द्वारा स्थापित की हुई पुरातन भारतीय व्यावसायिक वैज्ञानिक सोसाइटी है। डॉ.जय पाल मित्तल अकादमी ऑफ डेवलोपिंग वर्ल्ड के सदस्य होने के अतिरिक्त तीनों नैशनल साइन्स अकादिमयों

(आइएनएसए, आइएएसई, एनएएससी) के सदस्य हैं। आप नैशनल अकादमी ऑफ साइन्सिज़, इन्डिया (2003-04) के भी अध्यक्ष थे।

Dr. Jai Pal Mittal, DAE Raja Ramanna Fellow, Ex-Director, Chemistry & Isotope Group, BARC was recently conferred the prestigious "Lifetime Achievement Award" by the Indian Chemical Society, as a recognition of his lifetime achievements in research and teaching in the field of Chemical Sciences. It is one of the oldest Professional Scientific Society of India founded by the illustrious Chemist of India, Acharya Prafulla Chandra Ray in 1924. Dr. Jai Pal Mittal is a Fellow of all the three National Science Academies (INSA; IASe, NASc) besides the fellow of the Academy of Developing World, TWAS. He was the President of the National Academy of Sciences, India (2003-04).



Portrait sketched by Dr. Homi J. Bhabha

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