BARC

NEWSLETTER

Contents

AMIDES AND DIAMIDES AS PROMISING EXTRACTANTS IN THE BACK END OF THE NUCLEAR FUEL CYCLE

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To sustain our nuclear power programme beyond indigenously available uranium resources, it is imperative to follow closed fuel cycle option. Whereas our present PHWR/BWR reactors burn ^{235}U present in naturally occurring U, future of nuclear energy in the country depends on the availability of other man-made isotopes like ^{239}Pu and ^{233}U. These fissile isotopes are produced in nuclear reactors in low concentrations (usually in the range 0.1% to 1%) along with other actinide isotopes and a large number of fission products which cover more than half the elements of the periodic table. The challenging task of recovery and purification of Pu from irradiated U and of ^{233}U from irradiated Th is accomplished presently by the well-known PUREX and THOREX processes, respectively. Both of these processes employ organophosphorous compound, viz. Tri-n-butyl-phosphate (TBP) in long chain aliphatic hydrocarbon, viz. n-dodecane as solvent.

Though TBP based PUREX process has been the workhorse of nuclear fuel reprocessing industry for the last four-and-a-half decades, yet a few drawbacks associated with the use of TBP have caused concern to the separation scientists and technologists. The main problems of TBP are (i) its vulnerability to high radiation field and deleterious nature of its degradation products (mainly H_2MBP and HDBP) affecting the product recovery particularly with respect to fission products like Zr and Ru, retention of Pu in the organic

phase and the rate of separation of the two phases, (ii) relatively lower distribution coefficient of Pu(IV) as compared to that of U(VI), (iii) significant solubility of TBP towards aqueous phase, and (iv) non-incinerable nature of the spent solvent yielding large volumes of secondary radioactive waste. These shortcomings may pose a serious challenge particularly during the reprocessing of short cooled (MOX) thermal reactor fuels, Advanced Heavy Water Reactor fuels as well as fast reactor fuels with the larger Pu content and significantly higher burn up.

The separation of U from irradiated bulk Th, on the other hand, is quite challenging in view of the non-variable oxidation state of Th (unlike that of Pu), poor solubility of $Th(NO_3)_3.3TBP$ species in diluent leading to the third phase during the co-extraction of uranium and thorium. There is also the limitation of the D.F. of U with respect to Th and Pa. In addition, there is a specific problem of the handling of irradiated Th (while reprocessing as well as during fuel fabrication) due to the presence of ^{232}U (precursor of hard gamma emitting decay products), which is a radiological hazard, and the loss of ^{233}Pa (in view of it's long half life) inside the reactor due to neutron absorption. Innovative approaches in fuel reprocessing are called for to overcome at least some of these problems. In this context, it was decided to explore alternate extractants at Radiochemistry Division under IX five year plan.

N, N dialkyl aliphatic amides have received particular attention as alternate potential extractants for the reprocessing of spent nuclear fuels in view of (i) the innocuous nature of their degradation products, viz. carboxylic acids/amines, and (ii) the possibility to incinerate the used solvent leading to reduced volume of secondary waste. In addition, the physico-chemical properties of this class of ligands can be tuned by the judicious choice of alkyl groups. Most of the work reported earlier on amides referred to either aromatic or substituted aliphatic hydrocarbons employed as diluents. These diluents are not suitable for commercial scale reprocessing due to their poor radiation and chemical stability in the presence of

nitric acid as well as their tendency to form a three-phase system. An attempt has been made to investigate (a) linear dialkyl amides as alternate to TBP (as in PUREX process) for the recovery and purification of Pu, and (b) branched dialkyl amides as alternate to TBP (as in THOREX process) for the recovery and purification of U.

Steady growth of global fuel reprocessing activities (6000 tHM/annum) implies a vital role for the radiochemists, not only in developing efficient procedures for the separation and purification of actinides, but also in devising safe procedures for the management of nuclear waste arising at different stages of the PUREX process. High-level liquid waste (HLW) comprising of the concentrate of the raffinate of the co-extraction cycle (with over 95% of the total radioactivity produced in the burn up process in reactor) need to be isolated from the biosphere. There is a consensus among the waste management technologists that the safest route to achieve this is to deposit it in a stable geological formation after its immobilisation in suitable glass / synroc matrix. It ensures that any risk from exposure due to accidental intervention or natural disturbance is minimised.

In view of the high cost involved and the need for continuous surveillance, several countries are considering to modify their reprocessing schemes to partition (isolate) long lived actinides from HLW. Since the volume of the actinide oxides (which retain major fraction of the radio toxicity of HLW) is significantly lower as compared to the other metal oxides present in HLW, such an approach is expected to reduce the cost of immobilization as well as of disposal (in geological repository) and surveillance significantly. Thus, there is a need to develop procedures for the separation of long lived isotopes of minor actinides and fission products from the high active aqueous raffinate streams of co-extraction cycle of PUREX process, commonly referred to as Actinide Partitioning (P). The separated minor actinides need to be kept in retrievable long-term storage facilities as such or in conditioned

thermodynamically stable phase depending on which of the commonly discussed options, viz. trans-mutation-recycle in MOX fuels / transmutation-incineration in special targets or deposition in deep repositories, is proposed to be exercised in future. Duration of the storage for a century is recommended to allow for the decay of ^{244}Cm, which, apart from being an intense heat/neutron source, may lead to the formation of long-lived ^{245}Cm. It is desirable to free the MA fraction from nuclides of high neutron absorption cross section if partitioning is to be followed by transmutation. Possibility of the isolation of some pure radionuclides as valuable by-products makes "actinide partitioning" a further attractive strategy for HLW treatment. Application of universal fuel reprocessing extractant like TBP for actinide partitioning is not possible without producing waste streams with high salt content. Thus, there is a need to develop versatile reagents capable of partitioning actinides under the prevailing conditions of HLW. USA, France, Japan and China are among the leading nations in R&D programmes (in this area) employing different extractants, viz. DHDECMP, CMPO, DMDBTDMA, TRPO and DIDPA. In view of their ability to extract trivalent actinides like Am(III) and Cm(III) from HLW at ~ 3M HNO$_3$, CMPO and DMDBTDMA deserve particular attention. Processes using these reagents are referred to as TRUEX and DIAMEX respectively. TRUEX process was developed by separation chemistry group of Argonne National Laboratory, USA. during the eighties [1]. Salient features of this well investigated process are the strong affinity of extractant towards Am(III) and its high chemical stability. DIAMEX process, on the other hand, is being developed by CEA, France [2]. Salient features of the DIAMEX process are the use of completely incinerable extractant (leading to reduced secondary waste), ease of synthesis and elimination of a step of prior uranium removal. This work has gained momentum in recent years, in view of the support of the European Atomic Energy Community. Extensive work was carried out at BARC on CMPO during the nineties and the work on DMDBTDMA was initiated during IX plan.
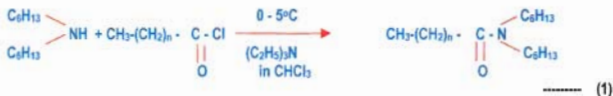
N, N Dialkyl Amides as Alternate Extractants to TBP in Nuclear Fuel Reprocessing

Work was initiated to design, synthesise and characterise dialkyl amides followed by their investigation of the extraction behaviour of U(VI), Pu(IV), Am(III) and fission products like Cs(I), Sr(II), Eu(III), Zr(IV) and Ru(III) from nitric acid medium employing n-dodecane as the diluent. The physical and chemical properties of these amides are influenced strongly by the nature of alkyl groups. N,N-dihexyl derivatives of hexanamide (DHHA), octanamide (DHOA) and decanamide (DHDA) were found to be promising amongst a large number of extractants studied. These ligands readily dissolved in n-dodecane and did not form third phase with nitric acid (up to 7M). The nature of extracted species formed in the organic phase, the corresponding two-phase extraction constants, the influence of U loading on third phase formation and on distribution data and the effect of gamma irradiation as well as of temperature have been investigated. Laboratory batch studies as well as mixer settler studies were performed in further details with DHOA and compared with those of TBP. This is the first ever attempt to evaluate DHOA/n-dodecane system as a process diluent.

Synthesis

The extractants employed in this work were amongst a score of amides synthesised in our laboratory by the reaction shown in equation (1). Characterisation of the ligands obtained after vacuum distillation was done by elemental analysis and I.R. / P.M.R. spectral analysis. Acid uptake values (K_H) of these amides vary in the order DHHA (0.174) < DHOA (0.181) <DHDA (0.202). The corresponding value of TBP is 0.16. HNO$_3$ concentration at which third phase is formed with 1M amide- n dodecane solution vary in the range 7M (DHHA) to 10M (DHDA).

$$\begin{array}{l} C_6H_{13} \\ \phantom{C_6H_{13}} \end{array} NH + CH_3\text{-}(CH_2)_n - \underset{\underset{O}{\|}}{C} - Cl \xrightarrow[\substack{(C_2H_5)_3N \\ \text{in } CHCl_3}]{0 - 5^\circ C} CH_3\text{-}(CH_2)_n - \underset{\underset{O}{\|}}{C} - N \begin{array}{l} C_6H_{13} \\ C_6H_{13} \end{array}$$

$$\text{-------- (1)}$$

where n =4, DHHA; n=6, DHOA; n=8, DHDA.
5 kg each of DHOA and DHHA were synthesised and employed for the mixer settler runs to investigate their potential as alternate extractants to TBP in the PUREX process.

Nature of extracted species

From moderately acidic solutions, U(VI) and Pu(IV) are extracted by the amides via solvation similar to TBP. The extracted species are identified as $UO_2(NO_3)_2$ 2 Amide and $Pu(NO_3)_4$.2Amide. The log K_{ex} values obtained for these solvated species are 1.43 (DHHA), 1.49 (DHOA) and 1.47 (DHDA) for U(VI) and 3.62 (DHHA), 3.55 (DHOA) and 3.51 (DHDA) for Pu(IV). At higher nitric acid concentrations, the amides undergo protonation $(HAmide)^+$ and extract U(VI) and Pu(IV) as ion-pairs of the type $[UO_2(NO_3)_3^-]$ $[HAmide^+]$ and $[Pu(NO_3)_4^{2-}]$ $[HAmide^-]_2$. Thus, the amides differ from TBP in respect to the nature of extracted species of U(VI) at high acidity.

Comparison of the distribution behaviour of amides and TBP towards U(VI) and Pu(IV)

At trace level concentrations, the distribution coefficients (D) of Pu(IV) with 1M solutions of DHHA, DHOA, DHDA, and TBP in n-dodecane at 3.5M HNO_3 (usual feed acidity in PUREX process) are found to be 41.2, 38.2, 32.6 and 19.2 respectively. At 50% uranium saturation of the organic phase, the corresponding 'D' values of Pu(IV) are 9.2, 7.3, 5.8 and 2.1. It is evident from these data that all the three amides used in the present work extract Pu(IV) more efficiently than TBP, both at trace level concentration as well as under uranium loading conditions. The 'D' values of U(VI) at trace level concentration with 1M solutions of DHHA, DHOA, DHDA and TBP in n-dodecane at 3.5M HNO_3 are found to be 13.5, 13.9,

13.6 and 29.6 respectively. At 50% uranium saturation of the organic phase, the corresponding D values are 4.2, 4.3, 4.0 and 11.4 respectively.
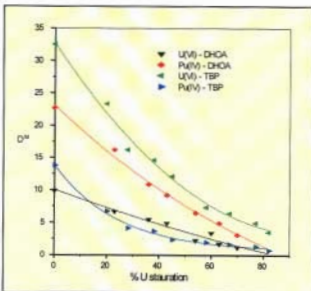

Fig.1 : Variation of distribution coefficients of U(VI) and Pu(IV)from 3M HNO_3 into 1M DHOA / 30% TBP in n-dodecane with uranium saturation at 25ºC

The distribution data of U(VI) and Pu(IV) obtained at 3M HNO_3 as a function of uranium saturation of the organic phase (1M DHOA or 30% TBP in n-dodecane) are plotted in Fig.1. The D values of U(VI) and Pu(IV) decreased continuously with uranium saturation. It is of particular interest to note that at a given value of uranium saturation of the organic phase, D_{Pu} value for DHOA is much higher than the corresponding value for TBP. Distribution ratio values for 60% U saturation (commonly employed in some reprocessing plants at co-extraction stage) for the two solvents are (i) $D_{Pu(IV)}$. $_{DHOA}$: 5.6, (ii) $D_{Pu(IV)}$. $_{TBP}$: 1.8, (iii) $D_{U(VI)}$. $_{DHOA}$: 2.1 and (iv) $D_{U(VI)}$. $_{TBP}$: 7.0. It is obvious that larger number of contacts are needed for the quantitative extraction of Pu(IV) with 30% TBP as compared to 1M DHOA. The 'D' values of Pu(IV) under plutonium loading conditions (5 g/l) are found to be 19.4

(DHHA), 18.6 (DHOA), 14.9 (DHDA) and 8.9 (TBP). It is clear that DHOA is a better extractant of Pu(IV) as compared to TBP under loading conditions of U as well as Pu which may lead to reduced losses of Pu towards the aqueous raffinate stream. The lower D values of U(VI) with the amides as compared to TBP facilitate its easier stripping from the loaded organic phase.

Limiting organic concentration (LOC) of U with amides

Merits of amides over TBP like complete incinerability, benign nature of degradation products and higher extraction of Pu (mentioned above) are partially offset by rather low solubility of uranyl nitrate solvates of amides into aliphatic hydrocarbon- type diluents. The concentration of uranium in the solution, resulting from the dissolution of irradiated thermal reactor fuel in nitric acid, is usually maintained at 300 - 350 g/L, which is much higher as compared to plutonium (~1 g/L). Due to the limited solubility of U(VI) solvates, third phase formation can appear in the amide extraction system under high uranium loading conditions [3]. The LOC data of U(VI) for 1 M DHHA and 1 M DHOA in n-dodecane obtained as a function of equilibrium nitric acid concentration of the aqueous phase (1-8 M) at 26 °C are presented in Fig. 2. It can be seen that the LOC value for both the amides decreases regularly with nitric acid molarity in the aqueous phase. Moreover, the LOC values for DHOA over the entire acidity range studied are significantly higher than those for DHHA. The LOC value ranges from 88.4 g/L (at 1 M HNO₃) to 20.9 g/L (at 6.6 M HNO₃) for DHHA and 103.3 g/L (at 1 M HNO₃) to 40.3 g/L (at 7.7 M HNO₃) for DHOA. The effect of nitric acid on the LOC of uranium was explained as due to the competition of amide for HNO₃ and UO₂(NO₃)₂ molecules. Uranium loading capacities of 1 M solutions of the amides in n-dodecane at 3.0 M HNO₃ are evaluated to be 69.1 g/L for DHHA; 96.1 g/L for DHOA and 62.8 g/L for DHDA. Apart from the influence of nitric acid, the influence of NaNO₃, temperature and ionic strength
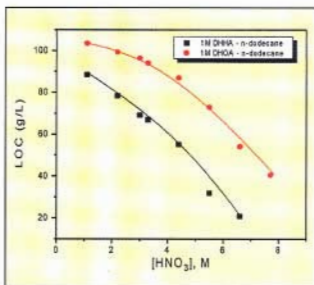

Fig.2 : LOC of U(VI) as a function of HNO₃ concentration; temperature : 26ºC

was also studied on the limiting organic concentration of uranium. The LOC value increases continuously with amide concentration for both DHHA and DHOA. However, considering UO₂(NO₃)₂.2Amide as the extracted species, % U saturation of the organic phase does not change significantly with the ligand concentration. In case of DHHA, it varies between 56.2-59.8% and in the case of DHOA it varies between 80.3-81.3% while varying the ligand concentration in the range 0.5M to 1.25M. In view of the higher LOC value of DHOA, further work was pursued with this ligand only.

Effect of uranium saturation of DHOA on the extraction of U(VI), Pu(IV), Am(III) and Zr(IV)

The distribution behaviour of U(VI), Pu(IV), Am(III) and Zr(IV) with 1M DHOA in the presence of 97.3 g/L of uranium in the aqueous phase was also studied as a function of nitric acid concentration [4]. The data presented in Fig.3 shows that both U(VI) and Pu(IV) are extracted efficiently, whereas the extraction of Am(III) and Zr(IV) is very poor throughout the acidity range (1-6M) investigated, suggesting reasonably high separation factors for plutonium and uranium from these two metal ions. Another important observation is that DPu values are higher than the DU values in the nitric acid concentration range of 2.5 - 6 M.
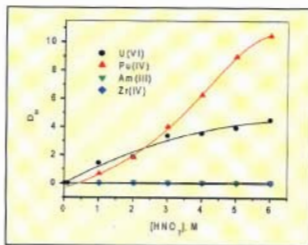
Fig.3 : Variation of D_U with varying concentrations of HNO_3 at macro concentrations of U(VI) (97.3 g/L)

Radiolytic degradation

The infrared investigations have revealed that the main degradation products of the amides are carboxylic acids ($v_{C=O}$ =1720 cm^{-1}) and amines (v_{N-H}= 3420 cm^{-1}). These degradation products are easily washable with dilute acid / water, unlike those of TBP which need alkali wash (1M Na_2CO_3) leading to higher volume of secondary waste.

The decontamination factor (DF) values of U and Pu with respect to Ru(III) employing irradiated amides as extractants are comparable to the corresponding values with TBP. However, amides are found to be particularly promising for their selectivity over Eu(III) and Zr(IV) from irradiated solutions as compared to TBP. Typically the DF values at 3x10^5 Gy with 30% TBP are ~7 (U/Zr) and ~12 (Pu/Zr) which are enhanced about five folds with 1M DHOA.

Effect of temperature on the extraction of macro amounts of uranium

Fig.4 shows the extraction isotherms of the system U(VI) / 3M HNO_3 / 1M DHOA- n-dodecane at 25ºC and 45ºC. As expected, D_U decreases sharply with % U saturation of the organic phase as well as with increase of temperature. D_U value lies in the range 2-3 for 60% U saturation, recommended for process applications in view of the LOC values determined by us earlier. Thus, it appears possible to carry out quantitative extraction of U from PUREX feed

(~ 300 g/L) in 3-4 stages provided suitable volume ratio for organic and aqueous phases is chosen. It was verified in the present work by results given in the following section on mixer settler studies.
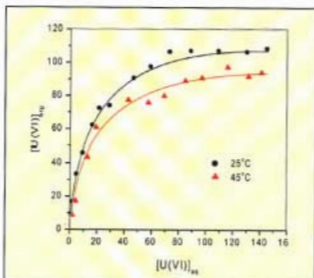

Fig.4 : Distribution isotherms of uranium at 25ºC and 45ºC using 1M DHOA in n-dodecane

Mixer settler studies

To explore the use of DHOA in fuel reprocessing as an alternate to TBP, mixer settler studies were carried out with both the extractants under identical experimental conditions [4].

Extraction Cycle

In the mixer settler studies, concentration of uranium and of nitric acid in the feed for the extraction cycle was maintained close to the conditions prevailing in the PUREX process viz. 260.7 g/L U and 3.07 M HNO_3. Extractant was 1.1 M DHOA in n- paraffin hydrocarbon (NPH). Organic to aqueous phase ratio was 3:1 (Aqueous flow rate: 1.5mL/min; Organic flow rate: 4.5 mL/min.)

Concentration of uranium and HNO_3 in organic EXIT sample at equilibrium (after six bed volumes) was 88.6g/L and 0.43M HNO_3 respectively. On the other hand, aqueous EXIT samples contained <0.1g/L of uranium throughout suggesting quantitative extraction of U even after one bed volume was passed. Acidity of the Aqueous EXIT samples under equilibrium condition was ~1.9M. It is observed that the composition of EXIT organic stream as well as EXIT

Org. EXIT									Org. IN
Stage No.	1	2	3	4	5	6	7	8	
Aq. IN									Aq. EXIT

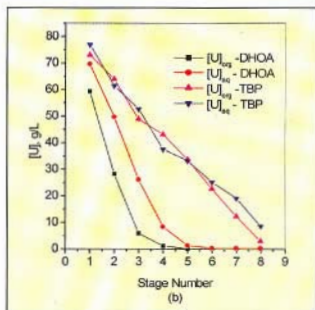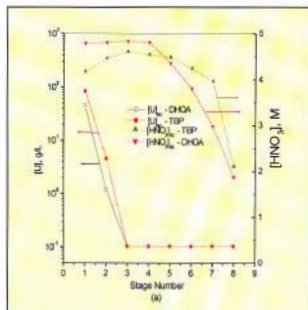Fig.5: Stage analysis data of (a) the aqueous phase for extraction cycle, and (b) the organic phase for stripping cycle for DHOA and TBP

aqueous stream is similar to that of 30% TBP with respect to uranium concentration as well as acid concentration. On the other hand, stage analysis data in Fig. 5(a) depicts some differences in the behaviour of two extractants. Aqueous uranium concentration for DHOA system is lower but acidity is higher as compared to TBP system at stage 1 as well as at stage 2. Whereas approximately 215g/L of uranium is transferred from aqueous phase to organic phase at 1st stage for DHOA, the corresponding figure for TBP is approximately 180 g/L.

Stripping Cycle

Concentration of uranium in feed was maintained as 87.7 g/L and of $[HNO_3]$ as 0.43M and the strippant was 0.01M HNO_3. The organic to aqueous phase ratio was maintained as 1:1.3 for TBP as well as for DHOA system. Flow rate of organic phase was 4.0ml/min. and of aqueous phase was 5.2ml/min. EXIT samples collected after passing three bed volumes showed quantitative stripping of uranium from organic phase and equilibrium was observed after 4 bed volumes were passed. Aqueous uranium

concentration showed a steady value of 68g/L and acidity of approximately 0.4M.

Stage analysis data shows that stripping is more efficient for DHOA system. (Fig.5 (b)). Whereas quantitative stripping (>99.9%) was observed with this ligand at stage 6 only 74 % stripping could be achieved for TBP system for the corresponding stage. After eight stages of mixer settler, <97% of stripping was seen in the case of TBP. About 2.6 g/L of uranium was present in the EXIT organic samples for TBP but < 0.1 g/L for DHOA at equilibrium.

It was, however, observed that the organic phase after extraction cycle is hazy and it turns to clear solution only after prolonged settling periods but there was no difficulty encountered in the flow of the loaded organic phase.

Branched Chain N, N Dialkyl Amides: A Promising Class of Extractants for the Separation of ^{233}U from Irradiated Thorium

In our laboratory, large number of N, N dialkyl

amides were synthesised (following the reaction shown by Eq. (1) and evaluated for their extraction behaviour towards U(VI) and Th(IV) from nitric acid medium (Table 1). Branched chain N, N dialkyl amides (S.N. 1-5 in Table 1) hold great promise towards process applications for the recovery of ^{233}U from irradiated thorium. Branching in the alkyl chain adjacent to the carbonyl group suppresses the thorium extraction considerably due to the steric hindrance exerted by the amide molecules on coordination to Th(IV) surrounded by four nitrate ions.

Attempts were made to arrive at the conditions suitable for the separation of ^{233}U from Th(IV), Pa(V) and fission products employing di(2-ethylhexyl)isobutyramide (D2EHIBA, a typical branched amide). D2EHIBA was chosen in view of it's lower viscosity as compared to the other branched amides. No third phase was observed while equilibrating 1M solution of D2EHIBA in n-dodecane with either 10M HNO$_3$ or with 200g/L Th(IV) solutions at 4M HNO$_3$ (V$_O$/V$_A$:1). The third phase is formed

with 1M TBP even at 1M HNO$_3$ in the presence of 200g/L of Th.

Fig.6 reveals that in the presence of thorium (~220g/L), efficient separation of ^{233}U could be achieved from Th(IV) and Pa(V) in the acidity range 1-4M HNO$_3$. Negligible extraction of fission products (D: ~10^{-3}) such as Zr(IV), Ce(III), Eu(III), Sr(II), Cs(I) and the structural material, Fe(III) over a wide range of nitric acid concentrations (1-6M) suggested that an efficient fission product decontamination of product ^{233}U could be achieved. Preferential extraction of U over Pa, in principle can be employed for the decontamination of ^{233}U from ^{232}U in a two stage extraction cycle. In the first stage (with cooling period sufficient for ^{232}Pa decay, T$_{1/2}$ = 1.3 days), mixture of ^{233}U and ^{232}U can be separated leaving a part of ^{233}Pa, Th and fission products in the raffinate. In the second stage (with cooling period sufficient for ^{233}Pa decay), ^{233}U can be separated from Th and fission products.

Table 1: Evaluation of branched chain amides for the separation of ^{233}U from irradiated ^{232}Th; Concentration of the extractant: 1 M; Aqueous phase: 4 M HNO$_3$, Diluent: n-dodecane; Temperature: 25°C; S. F. : D$_U$ / D$_{Th}$ (using ^{233}U / ^{234}Th tracers only)

$$R - \underset{\underset{O}{\|}}{C} - N \overset{R'}{\underset{R'}{\big\backslash}}$$

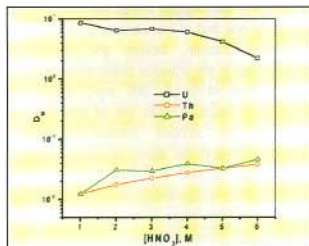| S.N.	Amide	R	R'	D$_U$	D$_{Th}$	S.F.
1	D2EHIBA	(CH$_3$)$_2$CH	C$_4$H$_9$CH(C$_2$H$_5$)CH$_2$	3.70	1.0x10^{-2}	370
2	D2EHPVA	(CH$_3$)$_3$C	C$_4$H$_9$CH(C$_2$H$_5$)CH$_2$	2.85	8.04x10^{-3}	353
3	DIB2EHA	CH$_3$(CH$_2$)$_3$CH (C$_2$H$_5$)	(CH$_3$)$_2$CHCH$_2$	4.70	1.34x10^{-2}	351
4	DOIBA	(CH$_3$)$_2$CH	C$_8$H$_{17}$	5.84	1.42x10^{-2}	411
5	DO2EHA	CH$_3$(CH$_2$)$_3$CH (C$_2$H$_5$)	C$_8$H$_{17}$	6.58	1.85x10^{-2}	356
6	D2EHBA	C$_3$H$_7$	C$_4$H$_9$CH(C$_2$H$_5$)CH$_2$	8.36	6.01x10^{-2}	139
7	D2EHPRA	CH$_2$CH$_2$	C$_4$H$_9$CH(C$_2$H$_5$)CH$_2$	9.7	0.1	97
8	DHOA	C$_7$H$_{15}$	C$_8$H$_{13}$	12.40	0.59	21
9	DHDA	C$_9$H$_{19}$	C$_6$H$_{13}$	11.62	0.45	26
10	DBDA	C$_9$H$_{19}$	C$_4$H$_9$	11.48	0.96	12
11	DHHA	C$_5$H$_{11}$	C$_6$H$_{13}$	12.80	0.80	16
12	TBP	–	–	40	4	10

Fig.6 : Extraction behaviour of Th(IV), Pa(V) and U(VI) as a function of nitric acid concentration : [Th] : ~ 220 g/L; [D2EHIBA] : 1M

Table 2 compares the distribution data of U(VI) and Th(IV) with TBP, TEHP (a branched chain phosphate), DHHA (a linear N, N dialkyl amide) and D2EHIBA (a branched chain N, N dialkyl amide) under identical conditions. S. F. value of 2980 for 0.18M D2EHIBA is significantly larger than the corresponding value of other extractants [5]. However, 0.18M D2EHIBA has a limited process application in view of its low D_U value (1.19). On the other hand, 1M D2EHIBA has a reasonable value of D_U (6.0) but relatively lower S. F. value (220). 0.5M D2EHIBA was chosen as a candidate for process applications in view of the significant enhancement in the S. F. values (D_U / D_{Th}: 1670 at 4 M HNO₃) as well as sufficiently high D_U value (4.0 at 4M HNO₃). Also, density (g/cc) and viscosity (cP) in the case of 0.5M D2EHIBA (0.768, 1.59) compare favourably

Table 2: Extraction behaviour of linear and branched chain extractants towards U-Th separation; [Th]: 220g/L; [U] :~10⁻⁴M; [HNO₃] = 4M

Extractant	[Ligand], M	D_U	D_{Th}	D_U / D_{Th}
TBP	0.18	2.4	2.3x10⁻²	100
TEHP	0.18	6.2	3.5x10⁻²	180
DHHA	0.18	0.4	1.7x10⁻³	240
D2EHIBA	0.18	1.19	4.0x10⁻⁴	2980
	0.5	4.0	2.4x10⁻³	1670
	1.0	6.0	2.7x10⁻²	220

with those of 5% TBP (0.739, 1.40) suggesting that the former could be explored further for process applications [6]. Presence of fluoride ion (used during dissolution step) suppressed the extraction of Th thereby enhancing the S. F. of uranium over thorium.

Degradation behaviour

Acid hydrolysis as well as gamma radiolysis of 0.5M D2EHIBA in *n*-dodecane (pre-equilibrated with 4M HNO₃) was compared with that of 5% (0.18M) TBP.
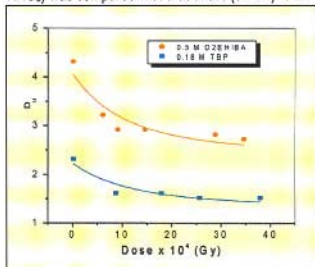

Fig.7 : Effect of radiolytic degradatation on D_U; aqueous phase: ²³³U (~10⁻⁴M) + 200g/L Th at 4 M HNO₃

Whereas no change was observed in the amide content as well as in the distribution data of uranium due to acid hydrolysis, there was a continuous decrease in amide content and D_U value due to radiolytic degradation of D2EHIBA (Fig.7). A similar decrease in D_U was observed in the case of 5% TBP. Stripping behaviour of irradiated 0.5M D2EHIBA was found to be better than that of 5% TBP solution. Whereas three contacts were found to be adequate for quantitative stripping (>99.9%) of U in the former case, a white solid appeared at the interface in the latter case which was confirmed (by IR spectral studies) as due to Th-DBP (dibutyl phosphate) complex.

Mixer settler studies

5kg of D2EHIBA was synthesised and vacuum distilled for mixer settler studies. These runs have

been carried out employing 0.5M D2EHIBA solution in n-dodecane as extractant and feed solution composition during these runs was as: [Th] = 200 g/L, [U] = 210 mg/L, [HNO$_3$] = 4.0M, [HF] = ~0.05M and [Al(NO$_3$)$_3$] = ~0.1M. Flow rate of the organic and aqueous phases was maintained as 4 mL/minute. The aqueous EXIT samples contained 6±1 mg/L U suggesting that uranium concentration in the raffinate is lower as compared to that of 5% TBP (10.3 mg/L) for similar number of extraction stages. Thorium and nitric acid concentrations in the aqueous EXIT samples were 200.0±0.9g/L and 3.60±0.06M respectively. Fig.8(a) shows the stage wise concentration profiles of uranium, thorium and nitric acid in the loaded organic phase as well as in the raffinate. There was a gradual increase in the uranium content of the organic phase with the number of stages. However, thorium and nitric acid concentration remained steady throughout. Final composition of the loaded organic phase was: [U] = ~208 mg/L; [Th] = 180 mg/L and [HNO$_3$] = 0.44 M.

During the stripping cycle, distilled water was used as strippant. The organic phase flow rate was ~4 mL/minute and that of the aqueous phase was ~2 mL/minute. Uranium, thorium and nitric acid concentration in the aqueous phase collected after stripping was ~410mg/L, 360 mg/L and 0.75M respectively. Uranium could not be detected (<1 mg/L) in the stripped organic phase (by spectrophotometry). As shown in Fig. 8(b), stage analysis data showed a gradual increase in the aqueous phase concentration of nitric acid, thorium and uranium from stage 6 to stage 1. Nitric acid concentration increased from 0.16 to 0.79 M. Whereas thorium concentration increased from 0.05 to 0.39 g/L, that of uranium increased from 145 to 475 mg/L. Stripping studies thus suggested that quantitative stripping of uranium could be achieved employing organic-to-aqueous phase ratio of 2. Purification of uranium from thorium in the stripped solution was carried out by cation exchanger Dowex 50x4. Quantitative recovery of uranium could be achieved during purification stage.

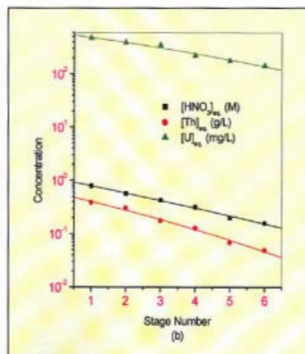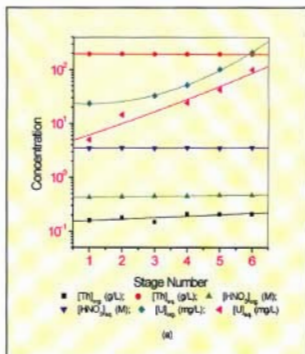| Org. IN							Org. EXIT
Stage No.	1	2	3	4	5	6	
Aq. EXIT							Aq. IN

Fig.8: Stage analysis data for (a) extraction cycle; (b) stripping cycle employing D2EHIBA as extractant

Comparison of mixer settler data of D2EHIBA and TBP

Table 3 shows the comparison of mixer settler data for U / Th separation using 0.5M D2EHIBA and 5% TBP. Extraction data has been compared for six stages of mixer settler. In case of 0.5M D2EHIBA, the organic phase concentration of thorium (0.18 g/L) is significantly lower as compared to that of 5%TBP (7.5 g/L). In addition, loss of uranium in the raffinate during extraction in the present studies is lower than that of 5% TBP. However, extraction cycle shows that nitric acid uptake by 0.5 M D2EHIBA (~0.4 M) is more than that of 5% TBP (~0.1M) which is a disadvantage. As a consequence, for efficient stripping of uranium, organic-to-aqueous (O/A) flow rate ratio of 2 during stripping cycle has been maintained. This is in sharp contrast to O/A of 5 employed for the efficient stripping of uranium in the case of THOREX process (with 5% TBP). D. F. values of U(VI) over fission products viz. Cs(I), Sr(II), Eu(III) and Zr(IV) were significantly larger (~2 times) for D2EHIBA than those of TBP.

Table 3: Comparison of mixer settler data for U / Th separation for six stages in the extraction cycle

Parameter	5% TBP	0.5M D2EHIBA
Volume ratio (O/A)	1	1
[Th]$_{org.}$ (g/L)	7.5	0.18
[U]$_{aq.}$ (mg/L)	10.3	6
[HNO$_3$]$_{org.}$ (M)	0.09	0.4
% U Extraction	95	>97

Results obtained during this work clearly demonstrate the potential of D2EHIBA in meeting the challenges encountered during the reprocessing of irradiated thorium. It offers very selective extraction of uranium over thorium and a large number of fission products. It is of interest to explore the possibility of subjecting the stripped solution of the extraction cycle directly to precipitation cycle (oxalate / ADU) thereby eliminating the ion exchange purification step. In the context of reprocessing of AHWR fuel, branched amides are also under investigation in our laboratory for the separation of ^{233}U from bulk Th after the selective removal of Pu.

Pentaalkyl Malonamides as Promising Extractants in Actinide Partitioning

A number of pentaalkyl malonamides namely N, N, N', N'-tetrabutyl undecyl malonamide (TBUDMA), N,N,N',N'-tetrabutyl dodecyl malonamide (TBDDMA), N,N,N',N'-tetrabutyl tetradecyl malonamide (TBTDMA) and N,N'-dimethyl-N,N'-dibutyl tetradecyl malonamide (DMDBTDMA) were synthesised (as explained elsewhere in this report). Efficacy of these extractants was evaluated for Am(III) from nitric acid medium [7]. Fig. 9 shows that DMDBTDMA is the most promising malonamide at 3-4M HNO$_3$ (acidity at which HLW is usually stored). Therefore, more elaborate work was undertaken to study the distribution behaviour of actinides and fission products using DMDBTDMA under IX plan.
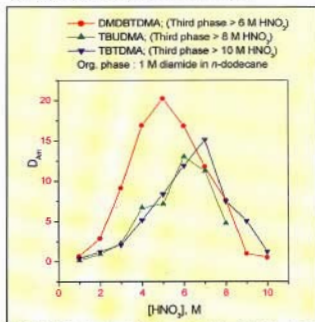

Fig.9 : Distribution ratio of Am(III) as a function of [HNO$_3$]$_{aqu.}$ for various diamides

Extraction of actinides and fission products from nitric acid medium

DMDBTDMA extracts actinide ions including trivalent ions like Am(III) and Eu(III) preferentially

over Cs(I) and Sr(II) in the acidity range 3-5M (Fig.10). D_{Pu} and D_U values increased with acid concentration up to 2 M and were steady thereafter since the enhancement expected due to the law of mass action for increased nitrate concentration is compensated by the decreased free ligand concentration (caused by the HNO_3 –diamide adduct formation). D_{Pu} values were higher than D_U values at all acid concentrations which is attributed to the high ionic potential of Pu(IV) over U(VI). Major fission products like Sr(II) and Cs(I) were poorly extracted at all acid concentrations ($D_{Sr}<10^{-2}$ and $D_{Cs}<10^{-3}$). Tc(VII) showed peculiar distribution behaviour with increase of acidity. While for all other metal cations, D values increased with acidity, interestingly D_{Tc} decreased with increasing acid concentration, which is attributed to the presence of Tc as TcO_4^- anion in acidic solutions. Reverse trend of D values with acidity is due to increasing concentration of NO_3^- ion which competes with TcO_4^-. Reasonably large D_{Tc} value at 3M HNO_3 suggests that ^{99}Tc can be co extracted along with minor actinides from acidic medium. Zr(IV) and Fe(III) are extracted moderately.
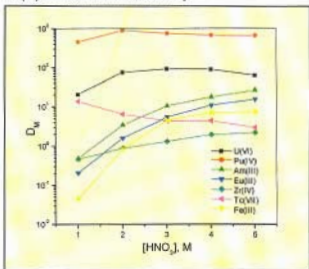
Fig.10 : Variation of D_M with nitric acid concentration; organic phase: 1 M DMDBTDMA in n-dodecane; aqueous phase: pure tracers in varying [HNO₃]

Extraction of actinides and fission products from simulated waste

Fig.11 summarises the extraction behaviour of actinides, fission products and Fe from simulated
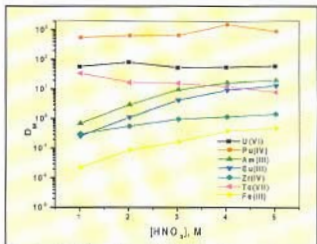
Fig.11 : Variation of D_M with nitric acid concentration in presence of simulated waste; organic phase: 1M DMDBTDMA in n-dodecane; aqueous phase: PHWR simulated waste containing respective tracers at various acidities

PHWR-HLW waste as a function of nitric acid concentration [8]. D_{Tc} increased for simulated waste as compared to the pure tracer throughout the acidity range. On the other hand, D_{Fe} decreased throughout the acidity range in case of simulated waste. For all other metal ions viz. U(VI), Pu(IV), Am(III), Eu(III) and Zr(IV), D_M values are either in the same range or decreased marginally as compared to the corresponding pure tracer values. Relatively low values of D_{Fe} and D_{Zr} and high values of D_{Tc} suggest the possibility of separating Fe and Zr from long lived actinides and fission products at least partially. There are reports indicating the possibility of improved separation of these metal ions in the presence of oxalic acid. D_{Am} (at 3 M HNO_3) of ~9 is sufficient for the quantitative Am(III) separation from HLW in 3-4 contacts ($V_o/V_a = 1$). D_{Sr} and D_{Cs} values varied in the range 10^{-2} to 10^{-3} suggesting efficient separation of these fission products from actinides. The extractant dependence experiments for Pu(IV), U(VI) and Am(III) suggested the stoichiometry of the extracted species as $Pu(NO_3)_4.3L$, $UO_2(NO_3)_2.2L$ and $Am(NO_3)_3.3L$ respectively. On the other hand, Tc extracted as $HTcO_4.2L$ (in the absence of U) and as $UO_2(NO_3)(TcO_4).2L$ (in the presence of U) whereas Fe extracted as $Fe(NO_3)_3.2L$ (where L = DMDBTDMA) .

Stripping Studies

Based on the extensive work carried out with several stripping agents, following scheme was proposed for individual stripping of Am, Pu and U from the extract of simulated waste. Two contacts of 0.05M HNO_3 which stripped >99.9% Am and <25% U; three contacts of 0.3M $NH_2OH.HCl/0.5M\ HNO_3$ to strip >95% Pu and finally three contacts of 0.1M oxalic acid to recover residual U and Pu. No reagent employed in the present study could strip quantitatively all the three actinides together. Nevertheless, three contacts of 0.05M $HF/0.05M$ HNO_3 effected stripping of >99.9% Am, ~91% U and >99.9% Pu.

Comparison of DIAMEX Process with TRUEX Process

Table 4 summarises the salient features of the two processes commonly employed for the partitioning of actinides from HLW. From synthesis

consideration, it is rather convenient to prepare DMDBTDMA as it involves two steps. First step is simply the sub ambient condensation reaction between a secondary amine and an acyl chloride. Second step requires somewhat extra care in view of the use of NaH for the alkylation of middle carbon atom of tetralkylmalonamides. Overall yield is ~70%. On the other hand, synthesis of CMPO is carried out in three steps. First step is the esterification of phenyl phosphinic acid using triethyl phosphate resulting in the formation of ethyl phenyl phosphinate. Second step involves reaction between Grignard reagent (n-octyl magnesium bromide) with ethyl phenyl phosphinate. The product so obtained was treated with N,N -diisobutyl - 2- chloroacetamide to give CMPO. Overall yield of the product is ~ 40% . It is possible to dissolve 1.5 M of DMDBTDMA in n-dodecane, which does not form any third phase upto 10 M HNO_3. Usually 0.5 M or 1.0 M of DMDBTDMA in NPH has been employed as solvent in the DIAMEX process.

Table 4 : Comparison of DIAMEX and TRUEX solvents

Point of comparison	DIAMEX (1M DMDBTDMA in n-dodecane)	TRUEX (0.2 M CMPO + 1.2 M TBP in n-dodecane)
Synthesis and purification	2 stage (simple)	3 stage (cumbersome)
Phase modifier	Optional (D2EHAA)	Mandatory ($\geq$ 1.2 M TBP)
Viscosity	7.91cP	1.67cP
Additional cycle for prior U separation	Optional	Mandatory
$[HNO_3]$ for D_{Am} > 3	$\geq$ 3M	$\geq$ 0.5 M
$[HNO_3]$ for D_{Am} < 0.01	~ 0.1 M	< 0.01 M
No. of contact for quantitative stripping	2	7
Extraction capability for various metal ions : Excellent (D > 100): Good (100 > D > 10): Moderate (10 > D > 0.5): Poor (D ≤ 0.01):	Pu(IV), Np(IV) U(VI) Am(III), Eu(III),Tc(VII), Zr(IV), Fe(III) Cs(I), Sr(II)	Pu(IV), U(VI), Np(VI) Am(III), Eu(III) Zr(IV), Fe(III), Tc(VII) Cs(I), Sr(II)

On the other hand, 1.2 M or 1.4 M TBP as phase modifier is employed while using 0.2 M CMPO as solvent in the TRUEX process. This is done to avoid third phase formation when the solvent is equilibrated with HLW solution. In spite of using phase modifier, it was observed that the third phase appeared when the TRUEX solvent is contacted with an aqueous solution containing 10 g/L of Nd or 11g/L of U at 3M HNO_3. PHWR high level waste solution involves U concentration up to 18 g/L. It was found, therefore, essential to have an additional cycle of 30 % TBP to diminish the U concentration in the range of mg/L. In the DIAMEX process, third phase did not form either with 10 g/L of Nd or with a mixture of 2 g/L of Nd and 18 g/L of U but it does occur in case of simulated waste $(V_o / V_a = 1)$. Third phase can be eliminated by employing $V_o / V_a = 1.5$.
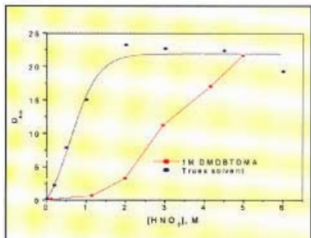

Fig.12 : D_{Am} as a function of nitric acid concentration

Fig.12 shows the extraction behaviour of Am(III) for these two solvents in n-dodecane. Whereas D_{Am} gradually increases with increasing nitric acid for DMDBTDMA, the value for TRUEX solvent increases sharply initially and reaches a maxima at 2M HNO_3. As a consequence, the TRUEX solvent could treat solutions varying widely in acidity (0.75-6M HNO_3). On the other hand, DIAMEX solvent showed significant variation in D_{Am} in the acidity range 0.1 M – 5 M.

Therefore, for efficient extraction of Am(III), ~ 3.0 M HNO_3 concentration was required in the DIAMEX process. On the other hand, a multistage stripping

process involving diamide is expected to be efficient and help in reducing the number of contacts needed to strip Am quantitatively from the extract containing actinides. Various metal ions investigated for their distribution behaviour were classified in four groups, viz. excellent (D> 100), good (100 > D > 10), moderate (10 > D > 0.5) and poor (D≤ 0.01), employing the two solvents. Table 4 shows that, whereas TRUEX solvent extracts both tetravalent and hexavalent actinides excellently, DIAMEX solvent extracts only tetravalent ions with D values of the same order. Distribution ratio value of U(VI) is, however, larger for DIAMEX process as compared to those of Am(III), Eu(III) and Tc(VII). DIAMEX solvent has larger D_{Tc} (4.07) as compared to D_{Tc} (0.42) observed for TRUEX solvent. Comparable extraction of Zr(IV) and Fe(III) and poor extraction of Cs(I) and Sr(II) is obtained with both solvents. The most important criterion to be used in ranking different methods is the overall Decontamination Factors (DF's) obtained during actinide partitioning of HLW. According to the hot cell tests carried out at JRC-ITO at Karlsruhe, the DIAMEX process represents the best compromise where DF's of ~1000 have been reported for the minor actinides from 3.5 M acid concentrated HLW.

Partitioning of Zr and Tc along with minor actinides is desirable considering the long half-lives of isotopes like ^{93}Zr (1.5 x 10^6 y) and ^{99}Tc (2.1 x 10^5y) and potential radiological toxicity of these radionuclides. On the other hand, it is desirable to leave structural elements like Fe and Ni and short lived fission products including lanthanides, Cs and Sr in the aqueous raffinate as they contribute unnecessarily towards the volume of waste to be vitrified and deposited in deep repositories. It is possible to achieve good D.F values of minor actinides from Fe by choosing suitable contact time or by adding desired concentration of oxalic acid. DIAMEX flow sheet was found to be similar, but somewhat simpler than TRUEX process flow sheet. Whereas extensive hydrolytic and radiolytic degradation of process solvent reduced the stripping efficiency of TRUEX solvent, no significant
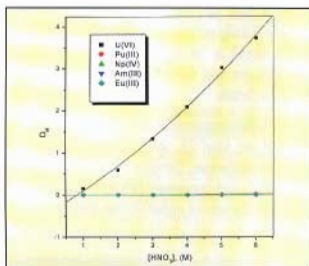
Fig. 13 : Distribution data of metal ions as a function of nitric acid concentration in presence of SHLW; reducing agent : 0.3M HAN + 0.8 MHN; organic phase : 1M D2EHPVA

problem was encountered in case of DIAMEX solvent. Therefore, no involved periodic solvent cleanup step would be required, as with TRUEX solvent. In contrast to the TRUEX solvent, the DIAMEX solvent was completely incinerable leading to lesser secondary waste volumes. However, very high viscosity of diamide may necessitate high pressure for achieving the desired flow rate of the organic stream and larger settling time for phase separation.

Alternate Approach

Since uranium is the major actinide present in HLW, it influences both actinide partitioning as well as vitrification process. Work has been initiated in our laboratory to develop a scheme for the preferential separation of uranium over Np, Pu and Am using di(2-ethylhexyl)pivalamide, and very encouraging results have been obtained in recent past (Fig.13). DIAMEX / TRUEX solvent can be subsequently employed conveniently to reduce the alpha activity (transuranics concentration) of the HLW to the desired level. In view of the millimolar concentration of residual actinides, the potential of extraction chromatography / membrane separation for the separation of transuranics from short lived / inactive components of high level waste is also being explored [9,10].

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BARC DEVELOPS SLEEVE CUTTING MACHINE

Centre for Design and Manufacture (CDM), BARC, has designed and developed a Special Purpose Machine (SPM) for cutting hardened (HRC-62) Guide Sleeve of Fuelling Machine from a distance of 10 metres. This SPM is required as an emergency tooling to detach the fuelling machine from the other end of the reactor channel, in case the Guide Sleeve bridging the end-fitting and the fuelling machine gets jammed and cannot be retracted, thereby holding up the fuelling machine itself. The Guide Sleeve is having 83 mm internal diameter and 5.75 mm wall thickness. The attached figures show the details.

The final demonstration of the SPM was carried out at CDM on May 23, 2002, in the presence of Mr G. Govindarajan, Director, A&M Group, BARC, Head, RTD and concerned NPCIL engineers. This work was carried out under IX Plan Project of RTD, BARC.

Fig 1. Assembly of Guide Sleeve Cutting Machine with a 10 metre long mock-up structure

Fig 2. Guide Sleeve Cutting Machine, its control panel and vacuum suction pump

Fig 3. Finishing cut in progress on actual, hardened, Guide Sleeve

Fig 4. Close up of Tool Head Guide after separation of the Guide Sleeve

SEMINAR ON 'DIABETES MANAGEMENT'

Medical Division, BARC, organised a seminar on "New Horizons in Diabetes Management" which was held on April 24, 2002 at Atomic Energy Regulatory Board (AERB) Conference room. Dr Anil Kakodkar, Chairman, Atomic Energy Commission & Secretary, Department of Atomic Energy, inaugurated the seminar. He released a compact disc on "New Horizons in Diabetes Education" written by Dr (Ms) Anjali R. Kulkarni, Medical Division, BARC, and prepared by Dr Sharad P. Kale, Nuclear Agriculture and Biotechnology Division (NABTD), BARC, on this occasion. He also released a booklet in Marathi on diabetes written by Dr (Ms) A. R. Kulkarni for public awareness on diabetes. He expressed the hope that these efforts would help in combating the menace of diabetes in the coming years.

Dr Anil Kakodkar, Chairman AEC releasing a compact disc on 'New Horizons in Diabetes Education'

Mr B. Bhattacharjee, Director, BARC, stressed the need for more research on the subject while speaking on this occasion. Dr Mehetalia from Raheja Hospital gave an insight on "Pathophysiology of Type II Diabetes".

Dr P. T.V. Nair, Head, Medical Unit, BARC Hospital, delivered a talk on "Emerging Trends in Risk Factors of Coronary Heart Diseases". Dr R. K. Kulkarni, Head, Pathology Unit, BARC Hospital,

spoke on "New Horizons in Diabetes Research". He reviewed newer concepts in diagnostics and urged the scientists and doctors to work together for developing cheaper and indigenous methods.

Dr Anil Kakodkar, Chairman AEC a booklet in Marathi on diabetes written by Dr (Ms) Anjali Kulkarni of Medical Division

Dr (Ms) A. R. Kulkarni, while giving the glimpses of the compact disc, narrated the importance of proper educative strategies to avoid complications after the onset of diabetes. She expressed her thoughts on "New Horizons in Diabetes Management" in coming years and possible research avenues, which could be tried in BARC. Dr Shankar, Head, Medical Division, BARC, in his concluding remarks, expressed the hope that many more such seminars from different units of Hospital would be organised.

DAE-BRNS SYMPOSIUM AND WORKSHOP ON 'THERMAL ANALYSIS (THERMANS-2002)'

The DAE-BRNS Thirteenth National Symposium and Workshop on 'Thermal Analysis (THERMANS 2002)', organised by Indian Thermal Analysis Society, Mumbai, and sponsored by Board of Research in Nuclear Sciences, Department of Atomic Energy, was held in Multipurpose Hall, Training School Hostel, Anushaktinagar, during January 21-25, 2002. Dr J.P. Mittal, Director, Chemistry & Isotope Group, BARC, presided over

the inaugural function, and Mr D.S.C. Purushotham, Director, Nuclear Fuels Group, BARC, inaugurated the symposium and workshop attended by over 150 delegates. Dr C.G.S. Pillai, NM&SC Division, BARC and Convener of the symposium and workshop, welcomed the delegates and invitees and highlighted the focal theme of the symposium - 'Role of Thermal Analysis in Nuclear Industry'. Dr V. Venugopal, Chairman, National Organising Committee and Head, Fuel Chemistry Division, BARC, spoke on the significant contribution by Indian Thermal Analysis Society and various units of DAE to the development of the science of Thermal Analysis in India. Dr J.P. Mittal, in his presidential address, paid tributes to Dr M.D. Karkhanavala who established a strong Thermal Methods Group in BARC and recalled the contributions of several other prominent scientists of DAE to the research and development efforts in the field. Mr D.S.C. Purushotham referred in his inaugural address to the significant volume of thermal data generated by High Temperature Thermodynamics Section in Nuclear Fuels Group and the various research groups in Indira Gandhi Centre for Atomic Research and their relevance to the development of nuclear fuels. The Netzsch-ITAS Award for outstanding contributions in the field of thermal analysis, and Rheometric Scientific - ITAS Award for young thermal analyst were presented to Prof. N.B. Singh, Chemistry Department, DDU Gorakhpur University, and Dr. A.K. Tyagi, Applied Chemistry Division, BARC, respectively, during the inaugural function. Mr Yogesh Satpute, Institute of Science, Mumbai, was awarded the winner's prize for 'Dr. M.D. Karkhanavala Memorial Essay Competition, 2002'. Dr P.V. Ravindran, Secretary, Indian Thermal Analysis Society, gave a vote of thanks.

The symposium was conducted over the first three days and covered papers on 'Thermochemical and Thermophysical Properties of Fuel Systems, especially Thoria based Fuels', 'Thermochemical Aspects of Corrosion of Structural Materials', 'High Temperature Phase Equilibria relevant to Waste Immobilization', 'Solid State Reactions and

Dr V. Venugopal giving the introductory remarks during the inauguration of Thirteenth National Symposium and Workshop on Thermal Analsyis. Seated on the dais are (from left to right) Dr P.V. Ravindran, Mr D.S.C. Purushotham, Dr J.P. Mittal and Dr C.G.S. Pillai

Kinetics', 'Preparation and Characterization of Novel and Strategic Materials', 'Characterization of Polymers and Composites', 'Assessment of High Temperature Equilibria in Glasses ceramics and minerals', and 'Recent Advances in Instrumentation in Thermal Analysis'. Eight invited lectures on the topic of the symposium were presented by experts in the field. Best papers presented in both oral and poster sessions were awarded. A preprint volume incorporating the papers accepted for presentation and the extended abstracts of the invited lectures was brought out and distributed to the delegates at the time of registration.

A panel discussion was conducted at the end of the symposium and the panelists were Dr V. Venugopal (Head, Fuel Chemistry Division, BARC), Dr. H. Kleykamp (Institute for Materials Research, Karlsruhe, Germany), Prof. N.S. Gajbhiye (Indian Institute of Technology, Kanpur), Dr. M.Sudersanan (Head, Analytical Chemistry Division, BARC) and Dr K. Krishnan (Dy. Head, Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre, Trivandrum). The panelists recommended advanced research in the field of nanotechnology by tailoring reactivity to the properties of the end product, extension of work in the areas of biotechnology, high energy materials and composites as well as improvement of instrumentation to enhance sensitivity of detection and

facilitate low temperature measurements. The panelists appreciated the effort of the organisers to attract young talent for participation.

A two-day workshop on the 'Role of Thermal Analysis in Research and Industry and its Application to the Development of Novel Materials', held subsequently to the symposium during January 24-25, 2002, was attended by seventy seven participants from different parts of the country. Nine invited lectures on `Interpretation of Thermogravimetric and Differential Thermal Analysis Curves', `Instrumentation in Thermal Analysis', `Modulated Differential Scanning Calorimetry', `Understanding Precursor Chemistry through Thermoanalytical Techniques for the Synthesis and Processing of Ceramics', `Thermal Analysis in the Assessment of Polymers and Composites', `X-ray Diffraction as a Complementary Technique for Thermal Analysis', `Assessment of Phase Equilibria from Thermal Analysis', `Thermal Analysis in Research and Development of Pharmaceuticals', and `Solid State reaction - a Non-isothermal Approach' were delivered during the workshop by eminent scientists in the respective field. The programme of the workshop included demonstration experiments. The texts of the invited lectures were brought out in printed form and distributed to the delegates of the workshop. A feedback session was conducted at the end of the workshop. The participants appreciated the programme and wanted more frequent similar interactions.

भाभा परमाणु अनुसंधान केंद्र के वैज्ञानिकों को सम्मान

• श्री सुखेंदु नाथ, विकिरण रसायनिकी एवं रसायन गतिकी प्रभाग (RCCDD), भाभा केंद्र को भारतीय राष्ट्रीय विज्ञान अकादमी, नई दिल्ली द्वारा युवा वैज्ञानिक (२००२), भारतीय राष्ट्रीय विज्ञान अकादमी पदक से सम्मानित किया गया । उन्हें पुरस्कार में

कांस्य पदक के साथ रु. २५,०००/- नकद और निकट भविष्य में उत्कृष्ट अनुसंधान कार्य के लिए अन्य अनेक प्रोत्साहन मिलेंगे । उन्हें दिनांक २४ अक्तूबर, २००२ को नई दिल्ली में आयोजित होने वाली अकादमी की वार्षिक आम सभा के दौरान पुरस्कार दिया जाएगा । श्री नाथ मुंबई विश्वविद्यालय में अपना पी.एचडी शोध पत्र प्रस्तुत कर चुके हैं । यह RCCDD को दूसरा युवा वैज्ञानिक पुरस्कार है ।

• डॉ. जे. पद्मा निलय लेसर एवं प्लास्मा प्रौद्योगिकी प्रभाग, भाभा केंद्र ने "उत्कृष्ट शोध पत्र प्रस्तुति पुरस्कार" प्राप्त किया है । इन्हें यह पुरस्कार दिनांक १८-२० दिसंबर, २००१ को इंदौर में आयोजित राष्ट्रीय लेसर सम्मेलन २००१ में दिया गया । इन्होंने "डेवलपमेंट ऑफ ए रिपिटेटिव वाइडली ट्यूनेबल सिंगल लॉंगिट्यूडनल मोड TEA CO₂ लेसर तथा इसके NH₃ लेसर पर अनुप्रयोग एवं संबंधित विषय अध्ययन पर अपना शोध पत्र प्रस्तुत किया है । उन्हें भारतीय लेसर संघ द्वारा प्रदत्त इस पुरस्कार में प्रमाण पत्र के साथ रु. ५,०००/- की नकद राशि दी गयी ।

• डॉ. ए.के. त्यागी, अध्यक्ष, ठोस अवस्था रसायनिकी अनुभाग, अनुप्रयुक्त रसायनिकी प्रभाग, भाभा केंद्र को Rheometric Scientific Corporation, ITAS पुरस्कार प्रदान किया गया । उन्हें यह पुरस्कार Rheometric Scientific Corporation संयुक्त राष्ट्र अमरीका और Indian Thermal Analysis Society (ITAS) द्वारा भाभा केंद्र में जनवरी २००२ को आयोजित द्विवार्षिक सम्मेलन में प्रदान किया गया था । तापीय विश्लेषण के क्षेत्र में उनके अद्भुत योगदान के लिए उन्हें यह पुरस्कार दिया गया है । डॉ. त्यागी का महत्वपूर्ण योगदान प्रायः भारी पानी रिएक्टरों से संबंधित थोरिया आधारित ईंधन एवं संबंधित प्रणालियों के तापीय विस्तार पर है । उन्हें इसमें प्रशस्ति पत्र एवं रु.७५००/- नकद पुरस्कार से सम्मानित किया गया ।

• अंत सम्मेलन में श्री संदीप वी. चक्राण को सर्वश्री चक्राण, पटवे एवं डॉ. त्यागी द्वारा लिखित लेख "Lattice Thermal Expansion of Ce₁₋ₓ Srₓ O₁₋ₓ (X=०=०, ०.५, ०.०७५, ०.१)" की उत्कृष्ट मौखिक प्रस्तुति के लिए प्रथम पुरस्कार दिया गया । उन्हें पुरस्कार में प्रशस्ति पत्र के साथ रु.१,०००/- नकद राशि प्रदान की गयी । वे डॉ. ए.के. त्यागी के मार्गदर्शन में भाभा केंद्र, मुंबई विश्वविद्यालय सहयोग योजना के अंतर्गत अनुप्रयुक्त रसायनिकी प्रभाग में पीएचडी कर रहे हैं ।

डॉ. सुश्री नीता ए. साल्वी, जैव कार्बनिक प्रभाग, भाभा केंद्र को मॉकोलॉजिकल सोसाइटी ऑफ इंडिया द्वारा उनके लेख "Decontamination of Radioactive Effluents by Rizopus arrhizus Biomass" के लिए एम.जे. तिरुमलाबार पुरस्कार से सम्मानित किया गया । पुरस्कार में प्रमाण पत्र और पदक प्रदान किया गया ।

BARC SCIENTISTS HONOURED

• Mr Sukhendu Nath, Radiation Chemistry & Chemical Dynamics Division (RCCDD), BARC, has been awarded the INSA Medal for Young Scientists (2002) by the Indian National Science Academy, New Delhi. The award carries a bronze medal and a cash prize of Rs. 25,000/- and several other incentives to carry out excellent research in the immediate future. The award will be presented during the Annual General Meeting of the Academy, scheduled at New Delhi on October 24, 2002. Mr Nath has submitted his Ph.D. thesis to the University of Mumbai and is awaiting the award of the degree. This is the second INSA Young Scientist award coming to RCCDD.

• Dr J. Padma Nilaya of Laser and Plasma Technology Division, BARC, has received the "Best Thesis Presentation Award" in the National Laser Symposium 2001 held in Indore during December 18-20, 2001. She presented her thesis entitled, "Development of a Repetitive Widely Tunable Single Longitudinal Mode TEA CO_2 Laser, its Application on NH_3 Laser and Related Studies". The award, given by the Indian Laser Association, consists of a certificate and a cash prize of Rs. 5000/-.

• Dr A.K. Tyagi, Head, Solid State Chemistry Section, Applied Chemistry Division, BARC, was presented Rheometric Scientific-ITAS Award by Rheometric Scientific Corporation, USA, and Indian Thermal Analysis Society (ITAS) at the latter's biennial conference held at BARC in January 2002. This award was conferred on him in recognition of his contribution in the area of Thermal Analysis. A noteworthy contribution of Dr Tyagi is in the field of 'Thermal Expansion of Thoria-based Fuels and related systems, having a direct relevance to AHWRs'. The award consists of a citation and a cash incentive of Rs. 7500/-.

In the same conference, Mr Sandeep V. Chavan got the first prize for the best oral presentation for the paper, "Lattice Thermal Expansion of $Ce_{1-x}Sr_xO_{2-x}$ (x = 0.0, 0.5, 0.075, 0.1)", authored by Chavan, Patwe and Tyagi. This work deals with the simulation of thermal expansion behaviour of $Pu_{1-x}Sr_xO_{2-x}$ using ceria as a surrogate material for Plutonia. The award consists of a citation and a cash incentive of Rs. 1,000/-. Mr Chavan is doing Ph.D. at Applied Chemistry Division under the BARC-Mumbai University collaboration scheme, under the guidance of Dr A.K. Tyagi.

• Dr (Ms) Neeta A. Salvi of Bio-Organic Division, BARC, has received the M.J. Thirumalachar Award from the Mycological Society of India for her paper entitled, "Decontamination of Radioactive Effluents by Rhizopus arrhizus Biomass", presented at the 28th Annual Meeting and National Conference on Fungal Biotechnology and Biodiversity, held in Mumbai. The award carries a medal and a certificate.