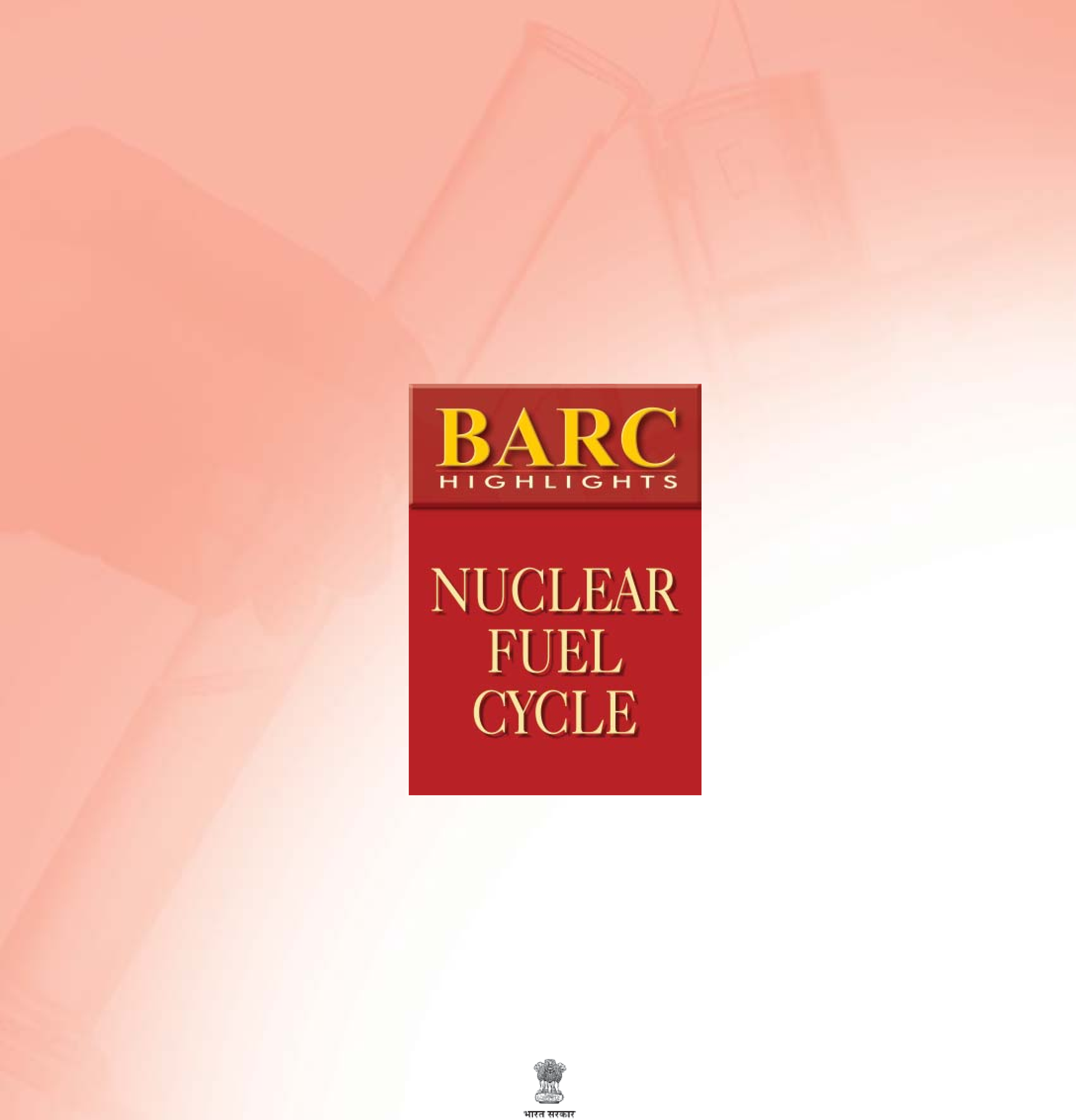

BARC
HIGHLIGHTS

NUCLEAR FUEL CYCLE

भारत सरकार
Government of India

भाभा परमाणु अनुसंधान केंद्र
BHABHA ATOMIC RESEARCH CENTRE

स्वर्ण जयंती वर्ष
GOLDEN JUBILEE YEAR
2006-2007

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FOREWORD

Bhabha Atomic Research Centre (BARC) is celebrating its golden jubilee year during 2006-07. On 20th January, 1956, Pandit Jawaharlal Nehru formally inaugurated the Atomic Energy Establishment Trombay (AEET), which is renamed as Bhabha Atomic Research Centre (BARC) on January 22, 1967. As a premier R&D centre of the Department of Atomic Energy (DAE), BARC has a mandate to provide R&D support to the nuclear power programme, to pursue all activities related to nuclear fuel cycle, to operate research reactors for supporting neutron beam research and supplying radioisotopes for various applications, to conduct frontline basic research in physical, chemical, biological and engineering sciences all of which leading towards improving quality of life of our people. The achievements BARC has made over the last 50 years are well known not only to the scientific community in the country but also to our people at large. Scientific achievements made by this premier research centre are well documented in various publications of DAE including a series named "BARC Highlights". During this golden jubilee year, we have made an effort to bring out some glimpses of recent research and development accomplishments in the form of 8 volumes, highlighting the following areas:

1. Nuclear Fuel Cycle
2. Physical Sciences
3. Chemical Science and Engineering
4. Materials Science and Engineering
5. Life Sciences
6. Reactor Technology and Engineering
7. Electronics, Instrumentation and Computers
8. Environmental Science and Engineering

These volumes will showcase the latest work in the aforementioned areas and will demonstrate how each of these is directed towards achieving the overall goal of using nuclear energy for the benefit of our people.

Nuclear energy programme in India has now reached a level of maturity. Today, India is self-sufficient in building nuclear power stations of 540 MWe capacities and has gained mastery over the entire fuel cycle. We are in the threshold of entering the second stage of nuclear power programme, in which a rapid growth in installed capacity is expected through the fast reactor programme. In the area of basic research in science and engineering, BARC has been maintaining a leading position both in national and international scenario. One of the strongest points of basic research in BARC lies in its capability in building sophisticated research facilities in-house. The core competence of the scientists and engineers in our centre covers a very wide range as is reflected in the 8 companion volumes getting released on the occasion of the golden jubilee year.

BARC is the fountain head of all research and development activities related to complete nuclear fuel cycle. The accomplishments made in the areas pertaining to nuclear fuel, reprocessing and waste management have been discussed in this volume of BARC highlights. BARC meets the fuel requirements of all our research reactors. New plants of higher capacities have been commissioned in BARC facility at Tarapur for MOX fuel fabrication for PFBR and AHWR.

At present major efforts are directed towards development of process and technologies for U-233 based fuel for AHWR and Pu based metallic fuels for future FBRs. In parallel, technology development is going on for fabrication of annular oxide pellets by using rotary press, establishment of welding parameters for D-9 tube and plug, automatic pellet inspection system, microwave dissolution and denitration system, keeping in mind the requirement for production of fuel for PFBR.

Excellent facilities have been created in BARC for evaluation of thermophysical and thermomechanical properties like melting point / solidus temperature, coefficient of thermal expansion, thermal diffusivity / conductivity, hot hardness etc. of various fuels and structural materials used in our nuclear reactors. During the last few years important data have been generated on high plutonia MOX fuel, which is a proposed fuel for FBTR, on Thoria based fuels in the composition range of AHWR fuel and on MK-I and MK-II mixed carbide fuel for FBTR.

Development of Master Sintering Curve (MSC) for AHWR fuel composition, which has provided a new insight into the sintering phenomena and predicted the densification behaviour under a set of arbitrary time temperature excursion, is a good example of this. Molecular dynamic simulation to predict thermophysical properties of Uranium Oxide at temperatures much beyond the experimental capabilities or prediction of properties like shear modulus, bulk modulus, fracture toughness etc. from ultrasonic velocity measurement data are other examples of the usefulness of basic studies.

Candidate materials for advanced nuclear reactor systems are irradiated in research reactor in controlled conditions to evaluate their suitability prior to large-scale deployment in nuclear power reactors. The post irradiation examination data is used by regulatory body for assessment of safety and licensing for continued operation of nuclear power plants.

Reprocessing forms an integral part of the Indian Nuclear Energy Programme which is based on the optimum resource utilization. THOREX process for the recovery of U-233 and thorium from irradiated thoria is in use on a smaller scale and is being developed into a robust process for meeting the challenges of thorium fuel cycle. Spent fuel treatment based on PUREX technology is well entrenched to meet the present and near future challenges. Engineering developments have helped this technology to keep pace with the increasing demands made by the health and safety regulations. Engineering developments have a major role to play in the thorium fuel cycle due to the high energy gamma emitting nuclides associated with this fuel cycle.

India has already demonstrated its capability in design, construction and commissioning of three fuel reprocessing facilities to cater to needs of spent fuel treatment of the first phase of the three stage Indian nuclear energy programme. With acceleration in the programme, the demand of Pu for FBRs necessitated the setting up of more reprocessing facilities and associated ancillary units at a faster pace.

Safe Management of nuclear waste has been accorded high priority right from the inception of our nuclear programme. Low & intermediate level waste streams from the entire fuel cycle have been well characterized and various processes for their treatment, conditioning and disposal are being practiced. Emphasis is on adoption of processes leading to high volume reduction and removal of major radionuclide like Cs-137, Sr-90 etc. Appropriate management techniques are also adopted for organic wastes emanating from the fuel cycle.

Waste isolation system comprising multiple barriers are employed for management of HL waste for their isolation and surveillance for extended periods of time. The vitreous matrix in which these waste are immobilized constitute the primary barrier. Different methods of melting high level waste prior to vitrification have been standardized.

Indigenous development of remote handling equipment is pursued to address the concerns of radioactivity and other hostile environment encountered in the back end of the fuel cycle. Three Piece Manipulator developed in-house is being used in many of the facilities. Remote Inspection Devices, Servo Robot, power manipulators etc. have also been developed for use in radioactive areas. Indigenization of Radiation Shielding Windows has lead to attaining self reliance in the production of RSW glasses. Solid waste management plants in India are equipped with facilities for segregation, repacking, compaction, incineration and embedment of radiation sources.

The present volume gives a flavour of the indigenous technology development to achieve complete self-sufficiency in the entire Nuclear Fuel Cycle.

Srikumar Banerjee
Director

PREFACE

India has adopted an ambitious and technically challenging three stage nuclear power Programme for optimum utilization of its limited uranium resources and large thorium reserves. The 1st stage consist of fuelling a series of indigenously built Pressurized Heavy Water Reactors (PHWRs) with natural uranium for generating nuclear electricity and to produce fissile plutonium as a by-product. In the second stage, the plutonium produced in the PHWRs is utilized to generate more nuclear electricity by using it as fuel in Fast Breeder Reactors and to enhance the fissile fuel base still further by breeding more plutonium and U^{233} from the Uranium and Thorium blankets respectively. Our capability towards the 2nd stage of the programme has been demonstrated by operating the Fast Breeder Test Reactor(FBTR) at Kalpakkam since 1985 and now the commencement of construction of the first prototype unit (PFBR) of a series of 500 MWe fast reactors to be commissioned by 2020 amply demonstrates our confidence in the technology. The 3rd stage would involve utilization of our vast thorium reserves for power generation by constructing Advance Heavy Water Reactors (AHWRs) which will generate almost 65% of the power from Thorium and breed enough U^{233} for a self sustaining cycle.

Thus, it is implied that India has to follow a closed fuel cycle policy to ensure long term energy security. This calls for adopting Reprocessing, Conditioning & Recycle (RCR) option.

India has demonstrated its indigenous capability in the field of reprocessing of spent uranium fuel by designing, constructing and operating three reprocessing plants based on PUREX process located at Trombay, Tarapur and Kalpakkam. Feasibility of reprocessing of irradiated thoria fuel has already been demonstrated by employing the THOREX process and reprocessing of mixed oxide fuels with uranium – plutonium and thorium are being planned. Radioactive Waste management facilities covering the entire range of activities, right from handling, treatment, conditioning, transport to storage, have been set up at all the reactor and reprocessing sites and valuable experience has been gained in design, construction, operation and maintenance of such facilities over a period of 40 years.

Fuel is the heart of a Nuclear Reactor and no indigenous nuclear power programme can sustain without regular and assured fuel supply to the reactors. BARC has mastered the fuel design and fabrication technology of fuels containing U, Pu, Th and U^{233}. BARC produces various fuels for regular operation of CIRUS, DHRUVA, FBTR, KAMINI at its production plants at Trombay. A large plant has been set up at Tarapur for production of MOX fuels for BWR & PHWRs with provisions for mixed (U-Pu) Oxide fuel fabrication for PFBR & FBTR in future. A dedicated fuel cycle centre consisting of reprocessing, fuel fabrication and waste management along with other associated facilities has been planned exclusively for PFBR and future FBRs at Kalpakkam. The facilities of the production plant at Tarapur are being augmented for taking up Thoria based fuel fabrication for AHWR.

In this volume of BARC Highlight, an attempt has been made to present an overview of the activities and the achievements in the field of nuclear fuel cycle during the past few years. A very simple style of writing has been adopted for a wider readership of the volume.

S. Majumdar P.K. Wattal

BARC HIGHLIGHTS

NUCLEAR FUEL CYCLE

CONTENTS

A. NUCLEAR FUELS

B. REPROCESSING

A. NUCLEAR FUELS

1. FUEL FABRICATION/PRODUCTION

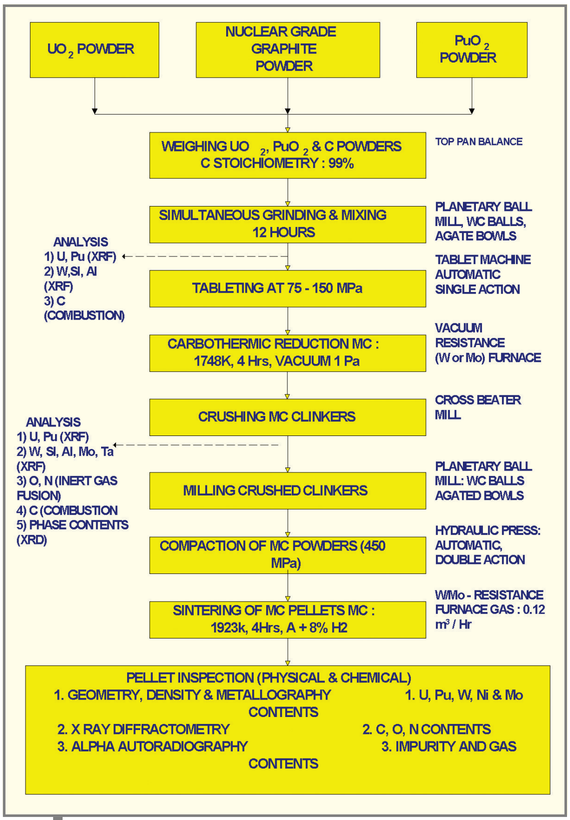
INTRODUCTION

Fuel requirement for regular operation of all our research reactors viz. CIRUS, DHRUVA,KAMINI and FBTR are met by the fuel fabrication / production facilities of BARC. To meet enhanced requirements of fuel in future, the production capacities of these plants are being aurgmented. Automation and remotisation are also being introduced for reduction in manpower and reduction in operator exposure. Large production plants have been commissioned in BARC facility at Tarapur for MOX fuel fabrication for BWRs and PHWRs with provisions for production of MOX fuel for PFBR and AHWR in future.

1.1 PRODUCTION OF FBTR FUEL PINS

Production of mixed (U,Pu) carbide fuel pins for FBTR are carried out by the process of carbide synthesis from the oxide and graphite starting materials, followed by milling of carbide clinkers, compaction of powder to green pellets and sintering of the carbide pellets. Fuel pins are delivered to IGCAR as per requirement. As the existing facility is more than two decades old, a special campaign of cleaning the facility was recently taken up in order to bring down the background radiation levels in the facility. The accumulated carbide scrap was removed from the glove box train and stabilized as oxide by controlled oxidation under He+O_2, taking care of criticality and fire-safety hazards. The broken heaters and reflector shields of the high temperature vacuum furnaces, a major source of high radiation levels due to deposition of plutonium containing vapours, were also removed from the glove box train, oxidized safely and stored separately.

In the mean time, considerable progress was made towards setting–up of a new FBTR fuel production laboratory under a X-Plan project. Several glove boxes of the new line have been commissioned with cold testing of the equipment. A welding chamber complete with vacuum system was set up to carry out Laser welding trials for end-cap welding of the fuel pins, as part of the development of a Laser welding set-up in the new fabrication line. Procurement of a Laser power source and



(U0.3-Pu0.7)C mixed Carbide fuel pellet fabrication flow-sheet

New laboratory facility being set-up for FBTR fuel pin production completely automated mechanical system for remotely operated end-cap welding by laser beam inside glove box is under progress.

1.2 MOX FUEL FOR BWRS

A number of TAPS MOX bundles were fabricated and irradiated in the two Boiling Water Reactors at Tarapur. The technology for fabricating MOX fuel for BWRs was developed by BARC and experimental irradiation of a number of elements was carried out in PWL of CIRUS reactor. MOX fuel with PuO_2 enrichment of 0.9%, 1.55% and 3.25% was used in the bundle.

MOX Fuel Fabrication Line

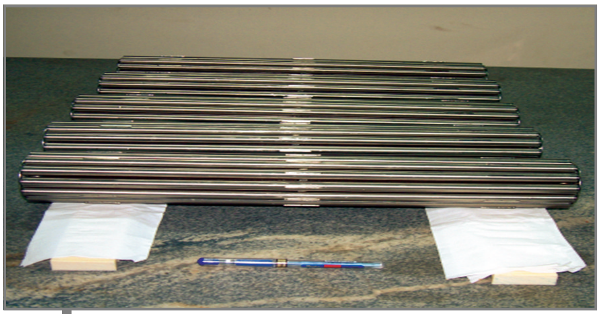
Gamma Scanning of BWR MOX Fuel Pin

Fabrication of the fuel has been carried out in a train of glove boxes specially erected for this purpose in the BARC facilities at Tarapur.

MOX fuel pellets were encapsulated in 4 m long Zircaloy - 2 clad tubes, inspected, characterized and assembled.

1.3 MOX FUEL FOR PHWR

As a part of the work on development of high burn-up fuels for PHWRs, MOX fuel bundles have been fabricated in the BARC facilities at Tarapur. This will permit about 40% higher burn-up as compared to the burn-up achievable in conventional natural UO_2 fuel bundles resulting in conservation of natural uranium. The MOX fuel pellets containing 0.4 wt % of PuO_2 have been used for this purpose. The PHWR MOX bundles consist of two inner rings of MOX fuel pins and an outer ring of 12 Nat UO_2 fuel pins. Technology for TIG welding of end plugs of PHWR MOX fuel pins has also been developed. The end plugs were specially designed to meet the requirement of TIG welding and inspection by X-ray radiography.



PHWR MOX Bundles

1.4 URANIUM METAL FUEL FOR DHRUVA & CIRUS

The fabrication of natural uranium metallic fuel elements for CIRUS/ DHRUVA research reactors involves vacuum induction melting of uranium ingots (received from UED) & casting them into billet, hot rolling and/or hot extrusion to rod shape, β heat treatment, rod straightening, machining to obtain finished dimension, eddy current testing, end threading, aluminium tube cladding, aluminium end plug welding, glycol leak testing, radiography etc. Over the years, metallic uranium fuel assemblies and sub-assemblies and other core components were fabricated and supplied to CIRUS & DHRUVA reactors as required. To achieve the demands of increased fuel requirements and reduction in manpower; manipulators, pick and place system, conveyors and other mechanisation systems have been introduced wherever feasible.

Process Improvements

The emphasis has been on reducing radiation exposure, improving safety aspects and better housekeeping along with increased productivity and yield.

Time saving in rolling & heat treatment

The roll grooves were redesigned with uniform area reduction of 10% per pass to achieve final size in 3 sets of rolls for Dhruva and 2 sets of rolls for CIRUS fuel instead of 4 and 3 sets of rolls. This saved 4 shifts of rolling for every batch of rolling. Efforts are being made to roll CIRUS rods in single stage.

Similarly, β quenching process was made faster by modifying the traverse time of the hoist to suit single dip instead of two. Ultrasonic velocity measurement, metallography and thermal cycling tests as well as XRD tests were found satisfactory.

Active effluent discharge system

During the fuel fabrication processes and other jobs connected with uranium, active waste is generated. As the old settling tanks have become obsolete, a new improved discharge disposal system for AFD/UED is being set up. For this, work on effluent discharge facility comprising of a piping system with storage tanks, delay tanks, filters, pumps etc. is nearing completion.

Autoclave

Autoclave facility was installed to assess clad quality and study the reasons for clad failure. Autoclaving of Dhruva fuel pins was carried out at 7 bars for a duration of one week. No change was observed in the fuel pins.

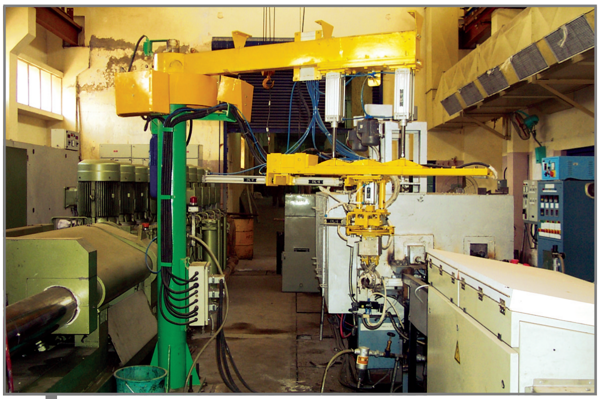
Close circuit TV

CCTV camera has been installed in uranium oxidation room to monitor the safety aspects of the operation.

Mechanisation / Automation

Extrusion Billet Handling System

Pneumatically-operated PLC-based pick & place type hot billet handling system was installed and commissioned for 500 Ton extrusion press. This system picks hot billet from the outlet of continuous furnace and loads it on to billet holder of extrusion press. This has eliminated manual handling of hot billets ensuring better safety.



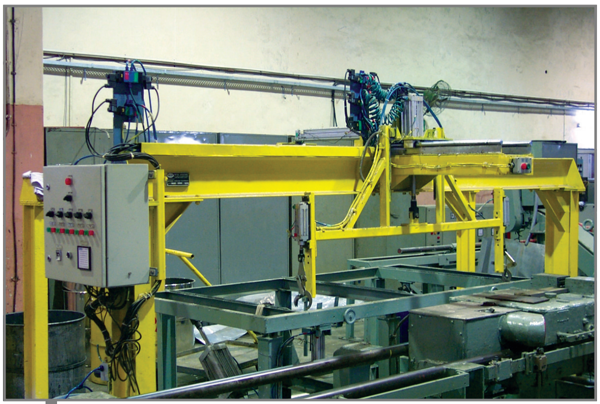
Extrusion Billet Handling System

Roller conveyor system for handling of ingots

For movement of uranium ingots from uranium storage room to band saw machine and back to uranium storage room, a roller conveyor system was procured and commissioned. An ingot-tilting unit provided in the system allows the operator to handle ingots weighing up to 250 kg independently and single handedly.

Mechanisation of Various Machines

Materials handling equipment such as manipulators and pick & place systems were procured & installed for handling uranium rods on rod straightening machine and centreless bar turning



Pick & Place System

machine. The systems work on pneumatic power and PLC control. Rod handling system has also been provided on capstan lathe for end threading of uranium rods. All these systems have reduced manpower requirement for the said operations and have reduced operator fatigue. Retrofitting of capstan lathe is also being planned to carry out the threading operation. This will eliminate requirement of skilled turner for the job.

Mechanised roll change trolley

The existing roll set changing trolley was modified to have the roll table movement by motor with safety features such as limit switches, overload trip, shear pins on coupling etc. A new mechanised roll change trolley has also been procured. Conveyor rolls of the rolling table are also being made power-driven. It will reduce the manual efforts and increase productivity.

Bar cum tube straightening machine

A bar-cum-tube straightening machine for straightening aluminium tubes and rods was procured and successfully commissioned.

■ Qualification of β heat treatment of uranium rods

Ultrasonic testing technique based on velocity, attenuation and back scatter measurement was developed to qualify the β heat treatment non-destructively. The study carried out on samples corresponding to different conditions indicated that the ultrasonic velocity in axial and radial direction for properly heat-treated rod was almost identical, while significant difference was observed in velocity in these two directions if the heat treatment was not satisfactory. This technique has been employed to qualify the heat treatment of few batches of uranium rods as well as to qualify the modified heat treatment process.

A. NUCLEAR FUELS

2. DEVELOPMENT OF FUEL FABRICATION PROCESSES AND TECHNOLOGIES

INTRODUCTION

BARC is the fountainhead of all research and development activities on nuclear fuels. At present major efforts are directed towards development of processes and technologies for U^{233} based fuel for AHWR and Pu-based metallic fuels for future FBRs. In parallel, technology development is going on for fabrication of annular oxide pellets by using rotary press, establishment of welding parameters for D-9 tube and plug, automatic pellet inspection system, microwave dissolution and denitration system, keeping in mind requirement for the production of fuel for PFBR.

2. DEVELOPMENT OF FUEL FABRICATION PROCESSES AND TECHNOLOGIES

Apart from regular production of fuels for operation of research reactors, including FBTR, BARC is engaged in the development of ThO_2/ U^{233} based fuels for Advanced Heavy Water Reactor (AHWR) and Mixed Oxide fuels for Prototype Fast Breeder Reactor(PFBR). It is essential to introduce automation for this fuel fabrication. The fabrication of U^{233} based fuel needs development of remotization in fuel fabrication inside shielded hot cells along with automation. Various activities in the development of fuel fabrication processes and technologies in connection with Th/U^{233} based fuel & PFBR – MOX fuels are briefly highlighted in the following paragraphs.

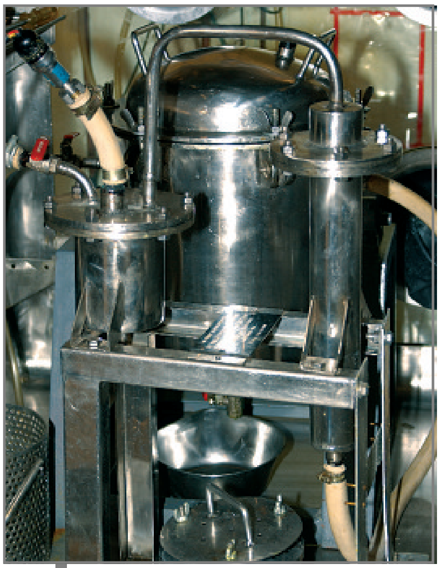
2.1 DEVELOPMENT OF FUEL FOR AHWR

Several technologies for fabrication of (Th-U^{233}) MOX fuel are under development in the Nuclear Fuels Group at BARC. These include Sol-Gel Microsphere Pelletization(SGMP), Impregnation and Coated Pellet Agglomeration (CAP). The SGMP technique has already been demonstrated for fabrication of UO_2 fuel in technological scale. Impregnation technique and CAP techniques which are being actively developed at present are described below:

- Impregnation Technique

Manufacturing of $(Th,U)O_2$ pellets for AHWR by impregnation technique is being developed and the process has been demonstrated in Kilogram scale. This process has the advantage of requiring only a partially shielded facility as compared to completely shielded facility needed for the conventional powder metallurgy process being followed currently for ceramic nuclear fuel fabrication. It is also more amenable to automation and remotisation.

The impregnation technique involves fabrication of low-density ThO_2 pellets having predominantly interconnected open pores, removal of entrapped gases from the pores by application of vacuum and impregnation of these pellets with 1.5M uranyl nitrate solution. Impregnated pellets are then dried and sintered at high temperature to achieve desired specifications. The molarity of the solution has been kept at this level not only for uranium content control in the pellets but also from criticality considerations. Apart from the molarity of the uranyl nitrate solution, the number of impregnation cycles and the time for impregnation are the factors controlling the uranium content and homogeneity of Uranium distribution in $(Th,U)O_2$ pellets. An optimum impregnation cycle has been achieved to produce AHWR fuel pellets to specification.



Impregnation Set-up Inside the Glove Box

$(Th, U)O_2$ Pellet

ThO_2 Pellets

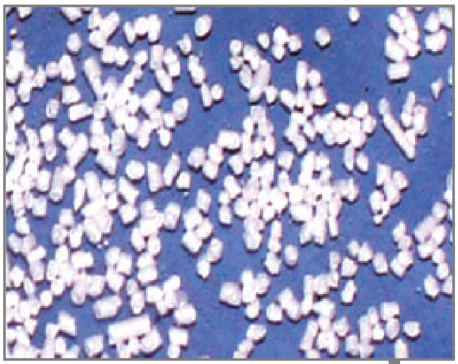
- CAP Technique

Process optimization studies are in an advanced stage of completion for CAP technique for fabrication of (Th-U^{233}) fuel pins for critical facility of AHWR using natural UO_2 to simulate U^{233} oxide. This innovative technique has been successfully demonstrated for the trial fabrication of $(Th-U)O_2$ fuel pellets for AHWR critical facility.

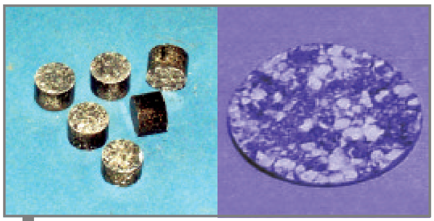
In this process, ThO_2 powder is mixed with organic emulsion of required quantity and extruded through an extruder having perforated rolls. The extrudes are usually of 0.8 mm – 1.0 mm indiameter and 4 – 5 mm in length.

These extrudes are then loaded in spheroidiser where they are broken and rounded by a chequered plate rotating at an optimum speed. The ThO_2 spheroids are then coated with U_3O_8 material of desired percentage in an Universal Mixer. The coated spheroids obtained are then dried in an oven at 100°C for 1 hr and compacted in a Rotary press. The green pellets show network of U_3O_8 in ThO_2 matrix. The green pellets are then sintered in a furnace in an oxidizing atmosphere at 1450° C for 4-6 hours to obtain sintered pellets. The sintered pellets of desired specification show uniform distribution of UO_2 in ThO_2 matrix. The sintered pellets have successfully met the specifications of the fuel and various tests and analysis carried out on these pellets confirm the quality of the pellets.

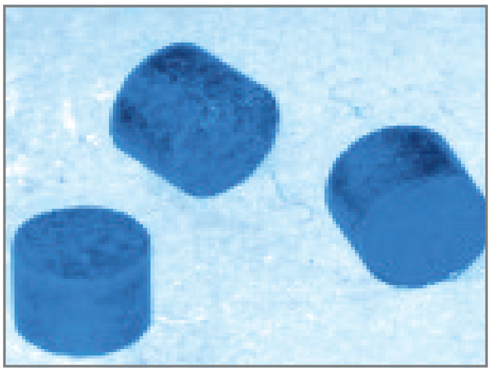
ThO_2 Extrudes



ThO_2 Spheroids



Green $(Th-U)O_2$ Pellets



Sintered $(Th-U)O_2$ Pellets

This technique minimizes a number of operations and bulk material processing in unshielded facility. Handling of controlled quantity for efficient and faster fabrication is an added advantage. The material characteristics improve and offer greater flexibility to exert control on the higher yield of accepted quality pellets.

Fabrication of Th-Pu MOX fuel pins for the critical facility will be taken up shortly. A new glove box train for this purpose is being installed. Development work is also being carried out for making a prototype shielded facility for fabrication of fuel containing U^{233}.

2.2 TECHNOLOGY DEVELOPMENT

■ Annular Pellet Fabrication

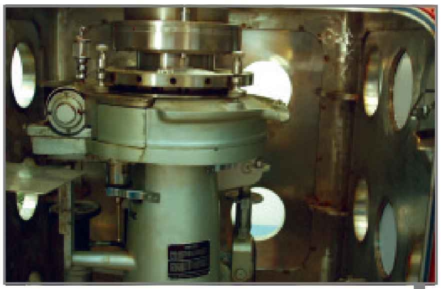
Technology for fabrication of annular pellets using indigenous rotary press has been developed. The necessary design of tooling for making annular pellets for both fast and thermal reactors has been made.

Using this design, MOX pellets containing oxides of natural uranium, U^{233} and Pu required for making the 37 pin PFBR experimental sub assembly have been fabricated. The MOX pellets in these fuel pins are of a diameter of 5.56 mm with a central hole of dimension of1.6 mm. The fuel assembly is undergoing irradiation in FBTR.

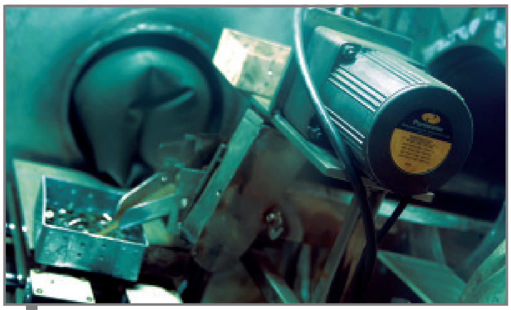
MOX fuel pellets (containing 44% PuO_2) for making MOX fuel pins for the hybrid core of FBTR are being made using this technology. Additional fabrication lines are being installed using advanced process equipment like Attritor, Rotary Press and Sintering Furnace. The fabrication equipment installed is all indigenously developed. A number of automation systems for use in fuel pelletisation line and fuel pin welding line have been developed. The systems are being installed in the new fabrication lines.

Annular MOX Pellets for FBTR

Annular MOX Pellets for PHWR



Installation of Rotary Press in
the New Glove Box Line for PFBR



Automation System in Pellet Fabrication Line

Microwave heating System

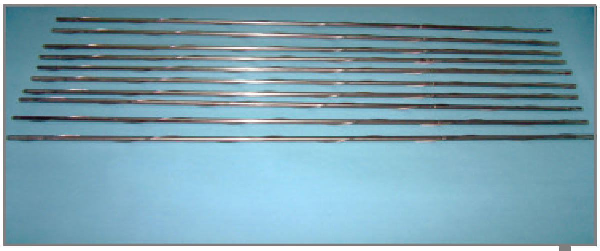
A three KW micro wave heating system has been designed and installed at AFFF based on the experience of the operation of a 700 W stainless steel microwave oven made earlier. Necessary modifications were made to make the system glove box adaptable.

Microwave Heating System

The three KW microwave oven has been commissioned for use inside the glove box. The flow sheets for dry and wet recycling of MOX fuel scrap have been developed. Experimental MOX fuel bundle using micro wave processed feed material has been loaded in PHWRs.

Welding Technique for D9 Tube & Plug

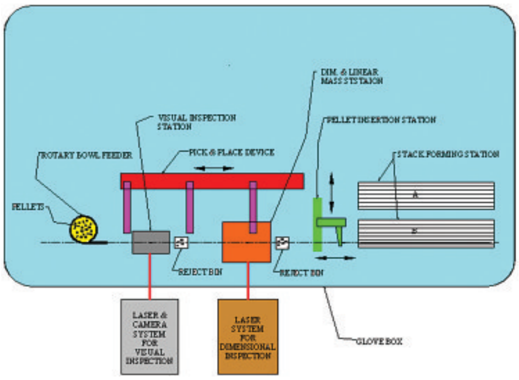
The fuel pins for PFBR use advanced D 9 material for cladding tube. Annular MOX pellets are encapsulated in the thin walled D 9 tubes by TIG welding of end plugs at both the ends. Technology has been developed for welding of the end plugs with the D 9 clad tubes. The fuel pins both for the experimental sub assembly and for the hybrid core for FBTR have been made using this technology. The same technology will be used for welding of three meter long PFBR MOX fuel pins.



MOX Fuel Pins for PFBR Experimental Sub-Assembly

Automatic Pellet Inspection System

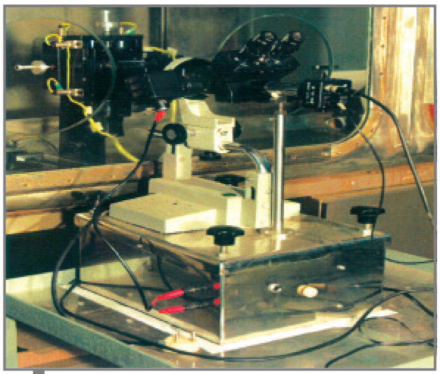
Sintered Uranium / Plutonium / Thorium-based oxide / carbide pellets are used as fuel for thermal and fast reactors. These pellets are radioactive & radiotoxic and give rise to personnel exposure on handling. The stringent specification on variation in diameter, linear mass etc. and very low tolerance of surface defects, make 100% physical inspection of these pellets mandatory and a highly challenging task. A new version of automatic pellet inspection system consisting of automatic vision system and laser metrology system is being developed for convenient, accurate and fast inspection of these pellets. This unit can be used for inspection of sintered pellets needed by all types of nuclear reactors. The schematic layout of the inspection system is shown below. Sintered pellets are loaded in the rotary bowel feeder manually. The bowl feeder arranges the pellets in such a way that the pellet can be picked one by one by pick & place device. The pick and place device places the pellet at the visual inspection station for surface scan. With the help of CCD cameras & laser light, the pellets are classified in visual accept (visual class A_V / visual class B_V) and visual reject categories based on the applicable specification limit for surface defects. The pick and place device places the visual reject pellets (R_V) in reject bin and visual class A (A_V) / visual class B (B_V) pellet at dimensional inspection station for dimensional measurement and calculation of linear mass. Based on the specification limit for dimensional measurement, pellets are classified as dimensional class A (A_D) or dimensional class B (B_D) or dimensional reject (R_D). Dimensionally reject (R_D) pellets are pushed in reject bin. On the basis of both the visual and dimensional classifications, the pellets are finally classified in overall class A / overall class B. Class A and class B pellets are placed at pellet insertion station for stacking in different trays. This process continues until all the pellets are inspected



Schematic Layout of Automatic Pellet Inspection System

Video Microscope Imaging System

Microstructural evaluation of MOX pellets and end plug welds is presently being carried out using special glove box model microscope which has the objective and related optical components inside the glove box. A video microscope imaging system using CCD camera has been developed for glove box use. It consists of CCD camera, monitor, frame grabber and printer. The entire optics is kept outside. The sample is mounted vertically on a special stage inside the glove box but near the glass of the glove box. The system is being used for routine quality control of MOX pellets and active end plug welds at BARC facilities at Tarapur.



Video Microscope Imaging System

Ultrasonic Testing Technique of PFBR Fuel Pin End Plug Welds

The end plug welds for the Fast reactors are currently being evaluated by X-radiography. An ultrasonic immersion technique has been developed for evaluation of these end plug welds.

A five axis weld scanning set up has been developed for positioning the probe precisely and indexing the tube. Angle beam technique has been used for the testing. Experiments have been carried out with standard defects and a large number of experimental welds. Good corelation has been obtained with X radiography and metallography.

Ultrasonic Weld Scanning System for PFBR End Plug Welds

2.3 DEVELOPMENT OF METALLIC FUEL FOR FAST REACTOR

- Physical Metallurgy of Uranium Alloys

U-Zr is a candidate metallic fuel for fast research-reactor. However, U-Pu-Zr can be used in power reactor. In order to develop the U-Pu-Zr fuel, the first judicial step would be to get accustomed with U-Zr system. These alloys are produced by vacuum induction or arc melting technique. Solubility of various alloying elements is different in different phases. α phase can not dissolve any element beyond 0.3%; the extent of dissolution varies from element to element and also with temperature. β phase can dissolve alloying elements to the tune of 1%. Alloying elements, like Mo, Nb, Ti, Zr can form a solid solution with γ phase with a concentration varying from 20% to 100%, while Au, Pd, Pt, Re, Rh, Ru and V are soluble to γ phase in the range of 2% to 10% concentration. In U-Zr system, for example, γ-U can dissolve 100 a/oZr but β phase can dissolve a maximum of 1 a/o Zr at 965 K and alpha phase can dissolve only about 0.6 a/o Zr max. at 935 K. By and large slow cooling permits the γ phase to decompose to two-phase structures morphologically similar to pearlite in steel. Rapid quenching suppresses these diffusional decomposition modes, resulting in various metastable phases. Moreover, quenched structure is quite sensitive to gammatizing temperature and cooling rate, implying that stresses due to quenching, ordering and/or retained vacancy concentrations are important.

RE-EVALUATION OF U-ZR PHASE DIAGRAM:

The following notation is used for the free energy of mixing; in $\Delta G^{\alpha}_{mix}(\delta,\gamma)$, superscript indicates the phase of concern; first term inside the parenthesis indicates the standard state of component *A* and the second one indicates the same for component *B*.

Unfortunately, thermodynamics can not predict the formation of probable phases for a given system. In order to identify the phases, for a given system, there are two available options; either by standard experimental technique (e.g. specific heat capacity measurement, high temperature XRD etc.) or by first principle electronic calculations.

U-Zr system manifests the following phases, excluding the phases of pure components – Liquid (completely miscible), γ(solid solution of γ U and β Zr, bcc), γ' and γ'' (formed due to spinodal decomposition of parent γ phase), β-U (U-rich solid solution, tetragonal), α-U (U-rich solid solution, orthorhombic), α-Zr (Zr-rich solid solution, hcp) and δ (non-stoichiometric intermetallics compound, primitive hexagonal).

The next task is to find the equations for the free energy of mixing. It is of utmost importance that while applying the common tangent construction it must be ensured that for all the phases the designated standard states should be same for individual components. For the present case α-U and α-Zr are chosen as the standard state for U and Zr respectively. Forming the equation of free energy of mixing will be elaborated below only for the liquid phase.

$$\Delta G^{L}(L,L)=\Delta G^{id}(L,L)+\Delta G^{xs}(L,L)$$

The last two terms on the right hand side of the above equation are the changes in free energy when pure U (and pure Zr) melts from its α phase. Basically,

$$\Delta G_U^{0,\alpha\to L}=\Delta G_U^{0,\alpha\to\beta}+\Delta G_U^{0,\beta\to\gamma}+\Delta G_U^{0,\gamma\to L}$$

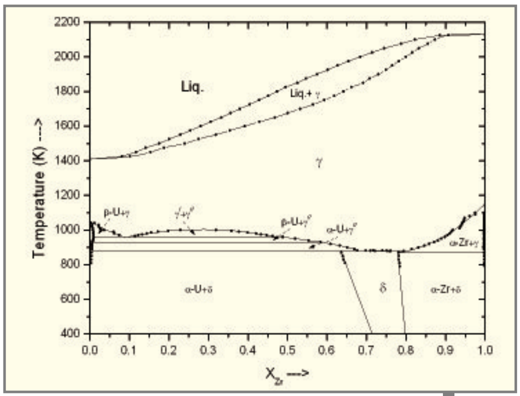
and

$$\Delta G_{Zr}^{0,\alpha\to L}=\Delta G_{Zr}^{0,\alpha\to\beta}+\Delta G_{Zr}^{0,\beta\to L}$$

Clearly, such equations can be written for all the phases –

$$\begin{aligned}
\Delta G^{L}(\alpha,\alpha) &= \Delta G^{L}(L,L) + X_{U}^{L}.\Delta G_{U}^{0,\alpha\to L} + X_{Zr}^{L}.\Delta G_{Zr}^{0,\alpha\to L}\\
\Delta G^{\gamma}(\alpha,\alpha) &= \Delta G^{\gamma}(\gamma,\beta) + X_{U}^{\gamma}.\Delta G_{U}^{0,\alpha\to\gamma} + X_{Zr}^{\gamma}.\Delta G_{Zr}^{0,\alpha\to\beta}\\
\Delta G^{\delta}(\alpha,\alpha) &= \Delta G^{\delta}(\delta,\delta) + X_{U}^{\delta}.\Delta G_{U}^{0,\alpha\to\delta} + X_{Zr}^{\delta}.\Delta G_{Zr}^{0,\alpha\to\delta}\\
\Delta G^{\beta-U}(\alpha,\alpha) &= \Delta G^{\beta-U}(\beta,\beta) + X_{U}^{\beta-U}\,\Delta G_{U}^{0,\alpha\to\beta} + X_{Zr}^{\beta-U}\,\Delta G_{Zr}^{0,\alpha\to\beta}
\end{aligned}$$

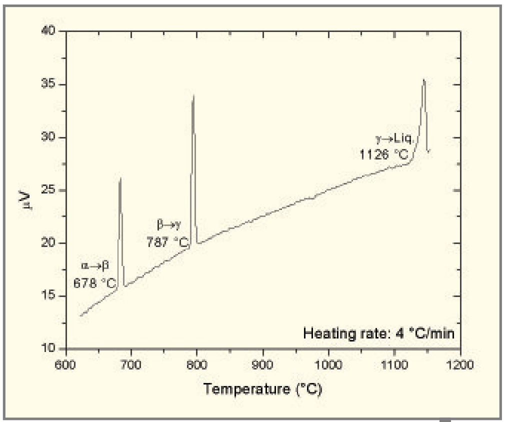
$\Delta G^{\alpha-U}(\alpha,\alpha)$ and $\Delta G^{\alpha-Zr}(\alpha,\alpha)$ are left unmodified. All the coefficients of excess free energy term can be expressed in Redlich-Kister form. U-Zr phase diagram is shown in the following figure -



Calculated U-Zr phase diagram

Differential Thermal Analysis:

So far DTA (Differential Thermal Analysis) experiments have been carried out for pure uranium and U-2%Zr alloy. DTA result of pure uranium shows that the phase transformation temperatures are approximately 10 °C higher for both the alpha to beta and beta to gamma transitions while the melting temperature is lower by around 10 °C. It has also been seen that the rate of heating/ cooling influences the transition temperatures whereas melting temperature remains more or less constant. All the experiments were conducted in high purity flowing argon atmosphere.



DTA result showing the phase transition temperature of pure U

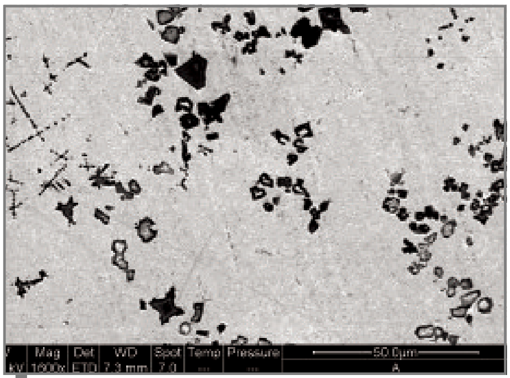
The apparent deviation of the transition temperatures for U are attributed due to the presence of Al in U to the tune of 0.1 wt% which was confirmed by the chemical analysis and supported by the Al-U phase diagram.

Metallographic Techniques:

Pure uranium as well as most of the uranium alloys are highly prone to oxidation. It is not uncommon to observe that metallographically polished sample get tarnished within one to two hours of exposure in air. Moreover polygonization takes place very easily both in pure uranium and in dilute uranium alloys resulting in irregular and massive grain structure; unlike the classical equiaxed grains. Hence apparently there are no high energy regions to response in chemical etching.

The inclusions present in the alloys can readily be seen in polished sample with conventional bright field mode as well as in SEM. The major inclusions present in uranium and its alloys are oxide, carboxinitride, hydride, nitride and carbonitride. The morphology of the inclusions and their chemical nature (i.e. oxide or nitride or hydride etc.) are established and well documented.

For alloys with higher concentration of alloying element, chemical etching can be employed. For U-Zr alloys, there are several chemical etchants listed in literature. A series of microstructures are presented here that are self explanatory.



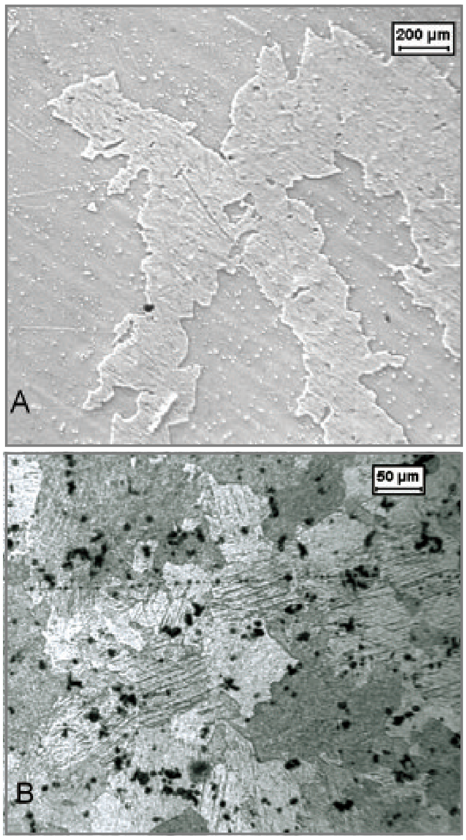
SEM micrograph of inclusions present in pure U

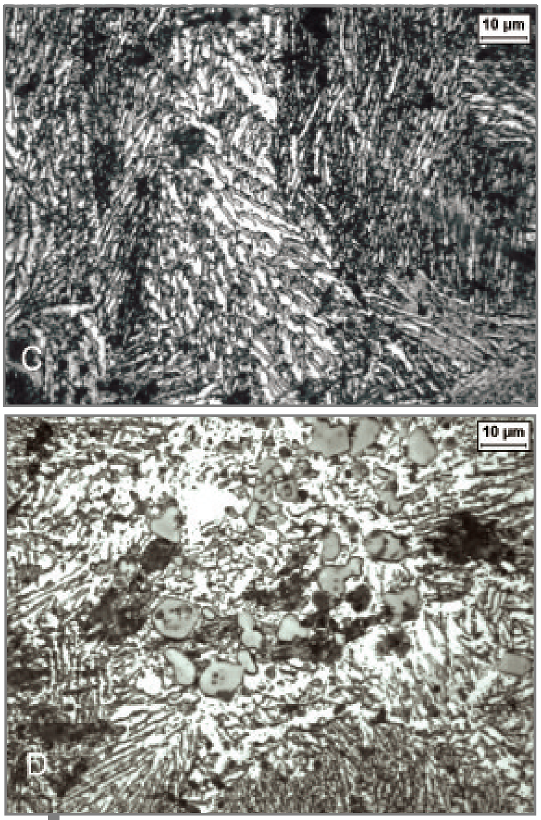
■ Injection Casting Process For Metallic Fuel Pins

It is planned to use metallic fuel for FBR/PFBR reactors due to its short doubling time. Keeping this in view work was initiated in Nuclear Fuels Group, BARC in mid 2004 for development of injection casting process for production of pure uranium and U-Zr alloys rods of 6 mm dia. Injection casting process was chosen due to the following advantages.

- the process is simple and fast
- possibility of multi-mould casting.
- capability of producing precision castings with higher L/D ratio.
- the process can be applied to variety of alloy compositions and
- amenable to remote operation.

In this process, a bunch of one-end closed precision-bore quartz moulds are suspended with open end down, with the help of a suitable fixture above the graphite melting crucible. The furnace is evacuated to the required level of vacuum and the metal is melted and heated to a pre-determined superheat using induction power source. The moulds are lowered to the required depth in the molten metal and the chamber is isolated. The furnace chamber is then pressurized with argon gas to a set pressure for forcing the molten metal in the evacuated moulds. After the castings are solidified, the moulds are raised and removed from the fixture and subsequently, the castings are removed by breaking the quartz moulds.

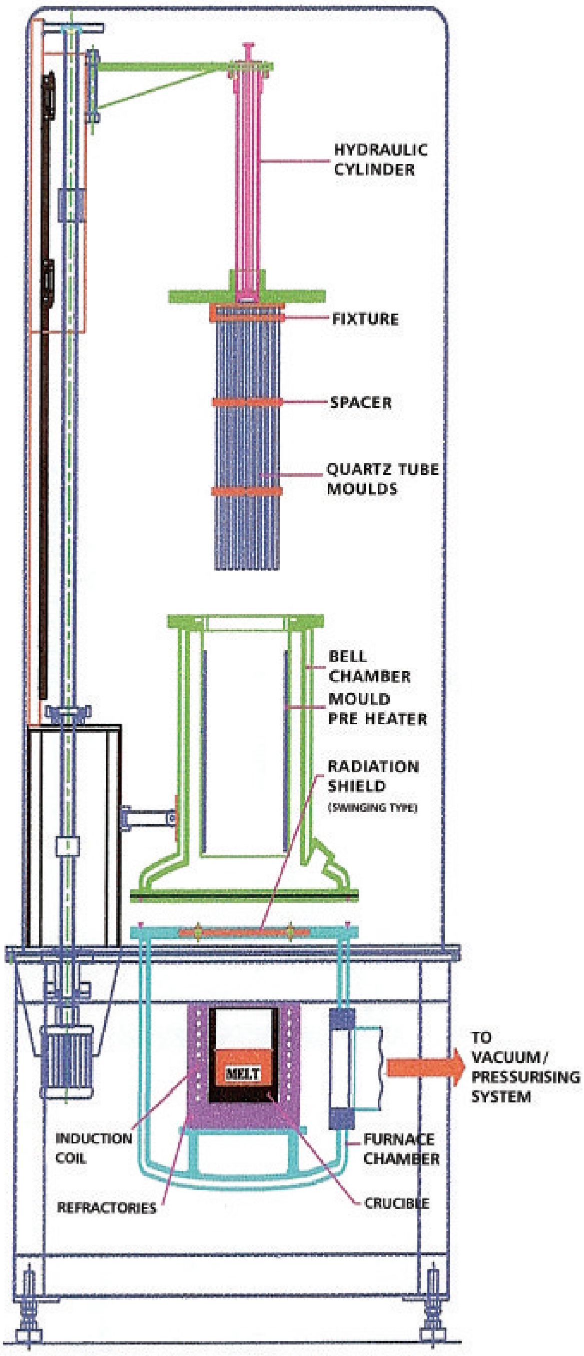




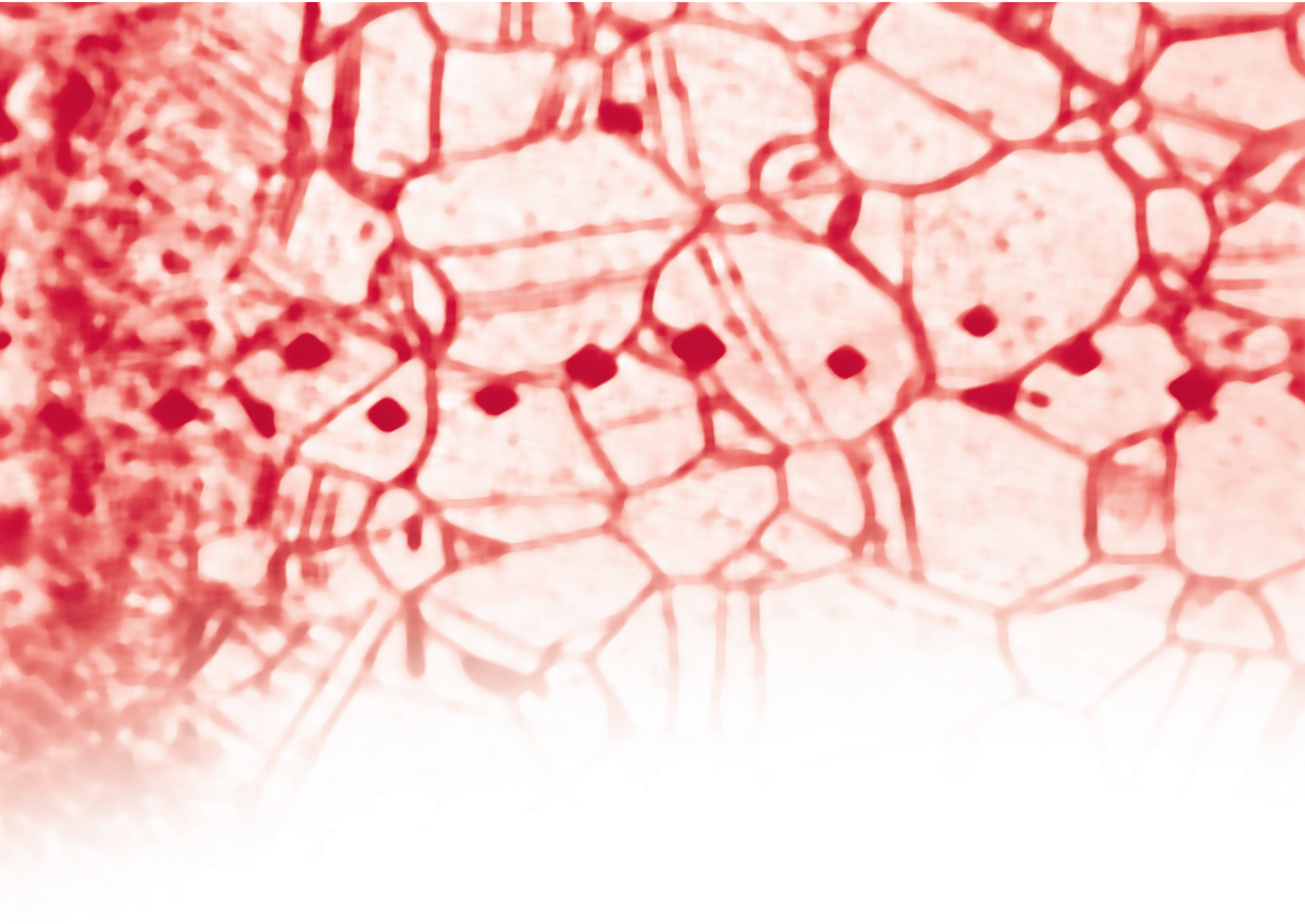
Optical photomicrograph of A) as cast U; B) Beta quenched U; C) as cast U-2%Zr alloy and D) at the center U-2%Zr alloy slug

A suitable set up consisting of graphite crucible integrated with quartz tube moulds was fabricated and installed in the existing vacuum induction melting and casting furnace for experimental purposes. Uranium and uranium zirconium alloy rods of 6 mm dia. and 10 mm dia. and length ranging between 300-350 mm were successfully produced and evaluated.

Procurement of an injection casting set up suitable for being installed in the glove box is in process. After carrying out initial trials with U-Zr alloys, the system will be installed for fabrication of **Pu-U-Zr** alloy fuel pins.



INJECTION CASTING SET-UP FOR DEVELOPMENT OF METALLIC FUEL PINS



A. NUCLEAR FUELS

3. FUEL PROPERTY EVALUATION

INTRODUCTION

Excellent facilities have been created in BARC for evaluation of thermophysical and thermomechanical properties like melting point / solidus temperature, coefficient of thermal expansion, thermal diffusivity / conductivity, hot hardness etc. of various fuels and structural materials used innuclear reactors. This data is very essential for fuel pin design, for predicting in-pile fuel performance, generation of computer codes and for accident analysis. During the last few years important data has been generated on high plutonia MOX fuel, which is the proposed fuel for FBTR, on ThO_2-based fuels in the composition range of AHWR fuel and on MK-I and MK-II mixed carbide fuel for FBTR.

3. FUEL PROPERTY EVALUATION

Thermo-physical and thermo-mechanical properties data of nuclear fuels are very essential for fuel pin design, for predicting in-pile fuel performance, generation of computer codes and for core accident analysis of the reactor system. The most important thermo-physical and thermo-mechanical properties are:

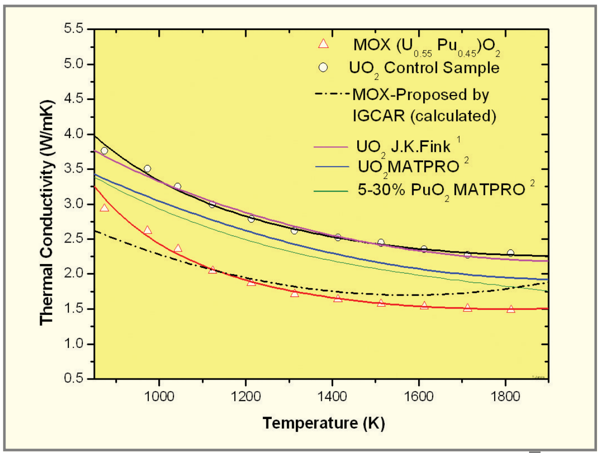
- Melting point / Solidus temperature
- Coefficient of thermal expansion
- Thermal diffusivity/conductivity
- Thermal toughness/creep (Hot hardness)
- Compatibility with clad/coolant

Good facilities exist in BARC for evaluation of thermo-physical & thermo-mechanical properties and an excellent data base has been created for many fuel systems. Some of the recent data generated in this field are elaborated below.

3.1 HIGH PLUTONIA MIXED OXIDE FUEL

As a part of the high plutonia (44% PuO_2) MOX fuel development for FBTR, new thermo-physical property data which is not available in literature has been generated and highlighted in the following paragraphs.

The coefficient of linear thermal expansion data of MOX fuel was generated as a function of temperature (ambient to 1873K) using a dilatometer under flowing Argon gas. The average thermal expansion was found to be 12.52 x 10^{-6}/K (ambient to 1273 K). The same for MOX fuel containing 30% PuO_2 is 10.65 x 10^{-6}/K. Thermal conductivity of the fuel was determined from the experimentally measured thermal diffusivity by laser flash method between 873 – 1773K. At 1273K thermal conductivity of MOX (44% PuO_2) was found to be 1.803 W/m.K which is lower than that of MOX containing 30% PuO_2 (2.3265 W/m.K).



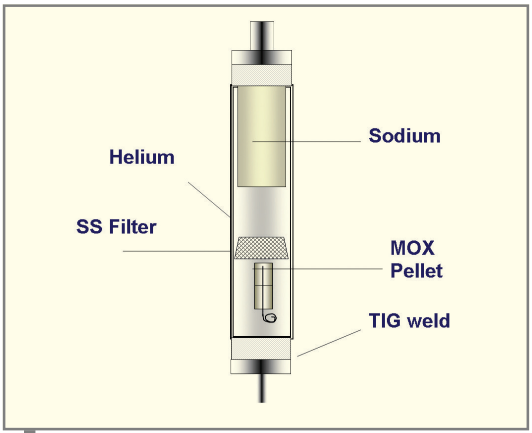
Thermal conductivity of MOX (44% PuO_2) fuel

Fuel coolant chemical compatibility is one of the most important aspects for the safe operation of the fuel inside the reactor. A number of compatibility test capsules containing fuel pellets and sodium were made to simulate different reactor conditions. Different types of test carried out were:

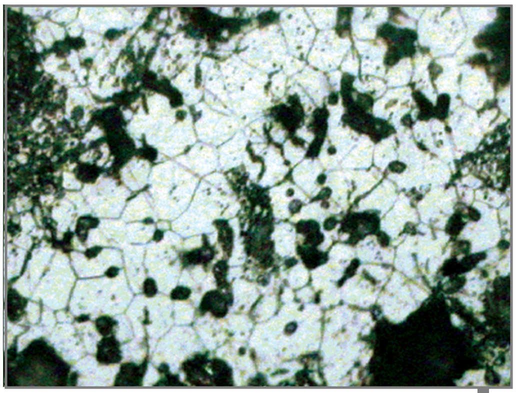
- MOX fuel pellets immersed directly into liquid sodium;
- Precracked fuel pin containing fuel pellets in liquid sodium.

The purity of sodium in terms of 'O' content varied from highly pure, pure and impure sodium. Test capsules, after isothermal annealing at 973-1073K for times varying from 30 hrs. to 500 hrs. were evaluated by visual examination, X-ray radiography, X-ray diffractometry, weight change and metallography. All these examinations indicated that there was no sign of incompatibility between the fuel and sodium and the pellets retained the integrity. The results of these studies have made a very positive impact on the possibility of utilizing this fuel for FBTR.

After approval of the safety committee MOX fuel is expected to be used in the hybrid core of FBTR which will consist of both mixed oxide (44% PuO_2) and mixed carbide fuel (MK I) containing 70% PuC.

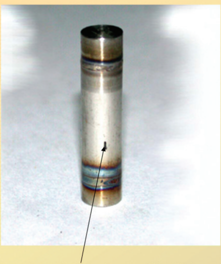


Schematic Diagram of MOX / Sodium compatibility capsule



Microstructure of as-received MOX ($44\%\ PuO_2$ pellet)

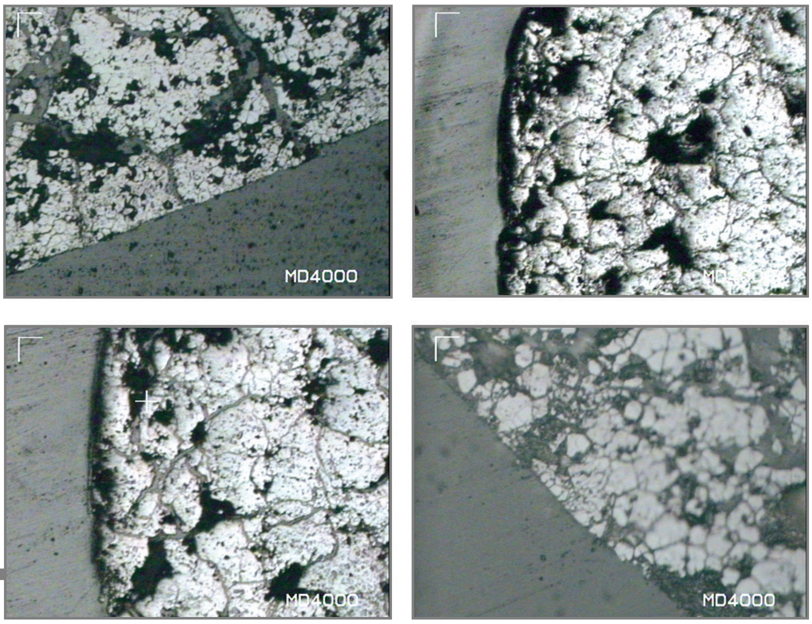
Components of Fuel-clad-coolant compatibility experiments.



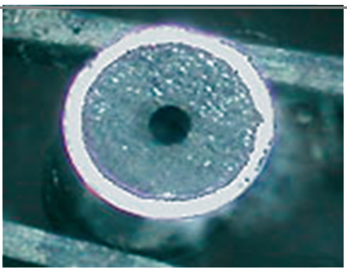
TIG welded D9 tubes with 'C' type defect containing MOX pellets

D9 cladding tube with 1mm width slit

Clad defect of Capsule no. L1C1 showing presence of 'Na' after the experiment (350 hrs at 700°C).



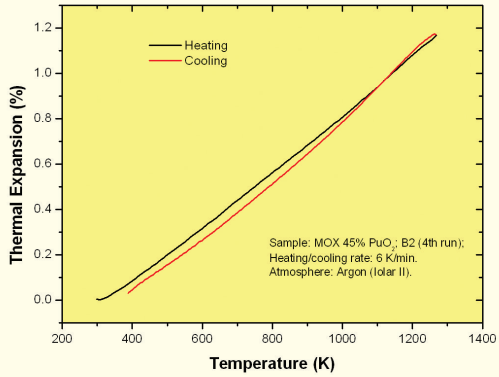
Microstructures of MOX ($44\%\ PuO_2$) at different locations after compatibility test at 973K for 150 hrs. showing no reaction product at the pellet/sodium interface. The grey areas within the pellet are cracks filled with araldite



Cross sectional view of MOX pellet (Capsule no.L1C2, 450hrs at 700 C) in D9 cladding indicating Na throughout the cross section, but no reaction product .

A fuel pin undergoes thermal cycling during power ramp or shut down/restart of a reactor. Any second phase precipitation may lead to dimensional changes which is undesirable.

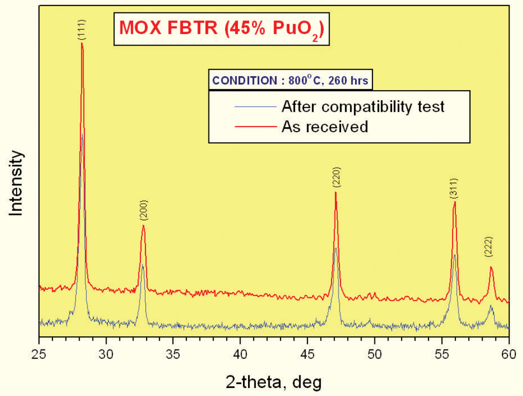
The dimensional stability of the fuel was tested by thermal cycling (ambient to 1473 K) in a push rod type dilatometer under inert cover gas and monitoring the change in length. No abrupt change in the dimension of the pellet could be observed after a number of cycling.



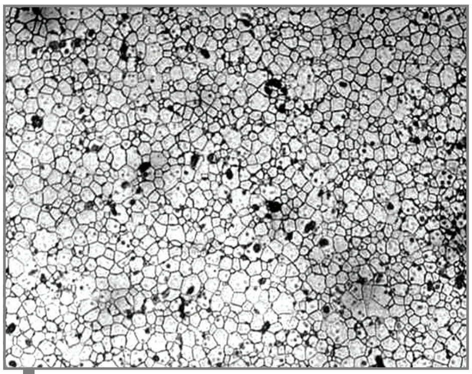
Dimensional Stability of MOX (44% PuO_2) after thermal cycling

3.2 THORIA BASED FUELS

Thoria based fuels like (ThO_2-3%UO_2) and (ThO_2-3%PuO_2) are proposed fuel for AHWR. Hence, efforts were made to generate various thermo physical properties data of these fuels which include thermal expansion, thermal conductivity, density as a function of temperature and UO_2 content. Sintered pellet samples were made by powder metallurgy route. Typical microstructure of ThO_2 and ThO_2-4%UO_2 are shown indicating uniformly distributed grains and pore structure.

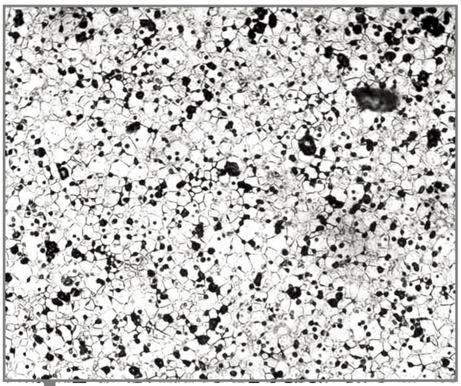


XRD pattern of residue obtained from two different capsules after leaching with ethyl alcohol

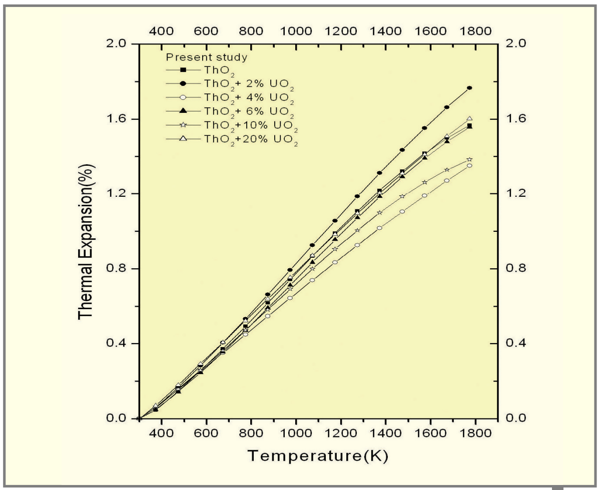


Microstructure of ThO_2 - sintered pellets

Coefficient of thermal expansion of $(Th,U)O_2$ and $(Th,Pu)O_2$ were measured from ambient to 1773 K as a function of



Microstructure of ThO_2 – 4 % UO_2 sintered pellet temperature and UO_2 and PuO_2 content using a horizontal dilatometer. The thermal expansion of these fuels could be expressed as percentage linear increase in length (L / L). The experimental data and that obtained from literature were summarized to obtain the recommended equation. Typical data of ThO_2 with 4% UO_2 and 4% PuO_2 in the temperature may range ($300 \leq T \leq 1773$K) and are given below in the form of equation and figures:



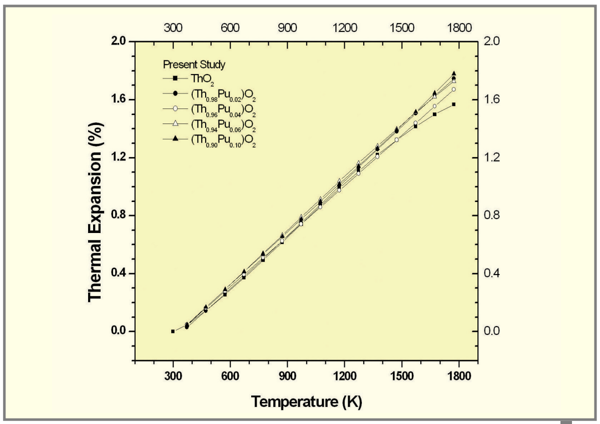
Thermal expansion data of ThO_2 – UO_2 system

ThO_2 + 4% UO_2

$$(L / L) \times 100 = -0.246 + 7.762\,_*10^{-4}.T + 1.206\,_*10^{-7}.T^2 - 4.735\,_*10^{-12}.T^3$$

ThO_2 + 4% PuO_2

$$(L / L) \times 100 = -0.379 + 11.4\,_*10^{-4}.T + 1.872\,_*10^{-8}.T^2 + 5.162\,_*10^{-12}.T^3.$$



Thermal expansion data of ThO_2 –PuO_2 system

Thermal conductivity data was determined from the experimentally measured thermal diffusivity by laser flash method and literature data of heat capacity and density. Measurements were carried out as a function of temperature, UO_2 and PuO_2 content. The recommended equations of thermal conductivity as a function of temperature and UO_2 and PuO_2 content could be summarized as follows:

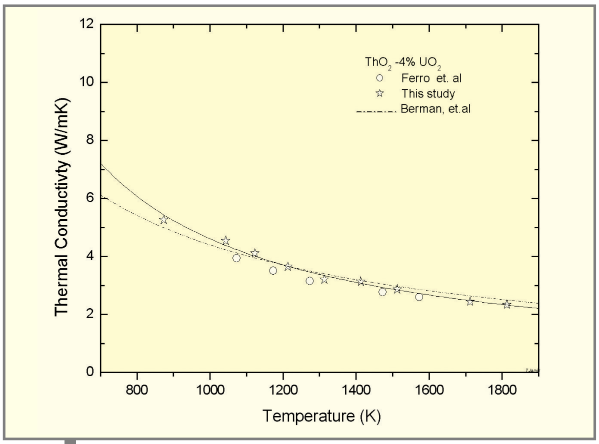
$(Th_yU_{1-y})O_2$

$$k(y,T) = 1 / [-0.0464 + 0.0034.y + (2.518\,_*10^{-4} + 1.0733\,_*10^{-7}.y)\,T] \quad (W/m.K)$$

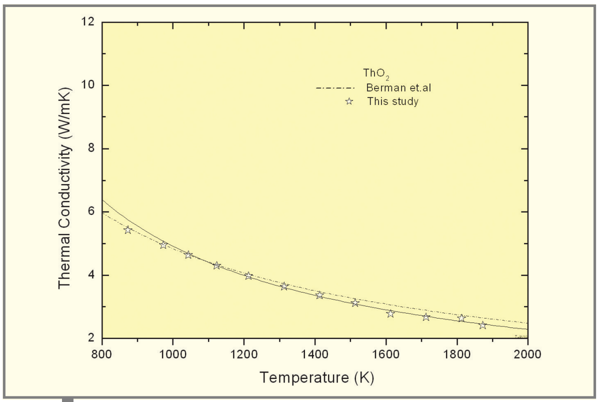
$(Th_yPu_{1-y})O_2$

$$k(y,T) = 1 / [-0.0838 + 1.737.y + (2.625\,_*10^{-4} + 1.740\,_*10^{-4}.y)T] \quad (W/m.K).$$

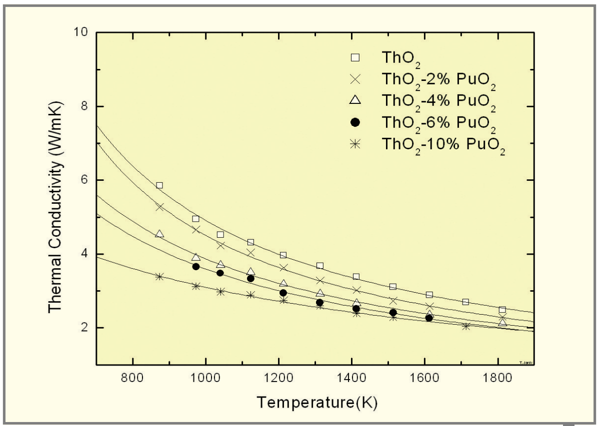
Thermal conductivity of ThO_2, ThO_2-4%UO_2 and ThO_2-4%PuO_2 are shown graphically as a function of temperature.



Thermal conductivity of ThO_2 – 4% UO_2



Thermal conductivity of ThO_2

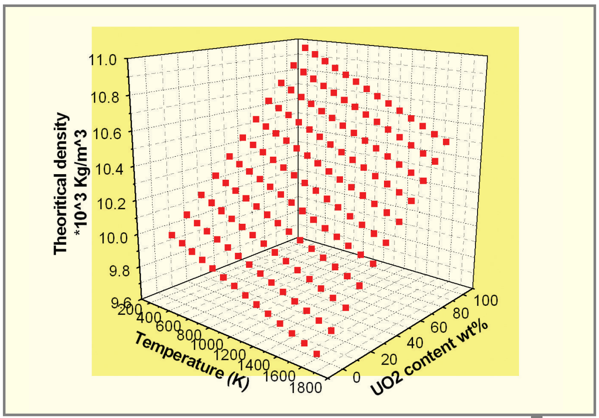


Thermal conductivity of ThO_2- PuO_2 sintered pellets

The recommended equation for theoretical density of ThO_2-UO_2 as a function of UO_2 content (x) and temperature (298 – 1600K) is given by:

$$D = 10.087 - 2.891 \times 10^{-4}.T - 6.354 \times 10^{-7} (x). T + 9.279 \times 10^{-3} (x) + 5.111 \times 10^{-6} (x)^2.$$

The uncertainty of the above equation is ±0.28%. The above equation was generated on the basis of the available data on lattice parameter and average coefficient of thermal expansion. These studies were taken up as IAEA-CRP on “Establishment of a thermophysical properties data base for LWRs and HWRs”. The data generated has been peer reviewed by international experts in the field and will appear in the form of a TECDOC and subsequently in an IAEA-sponsored web-based data bank “THERPRO”.



Variation of Theoretical density of $(Th,U)O_2$ with temperature and composition

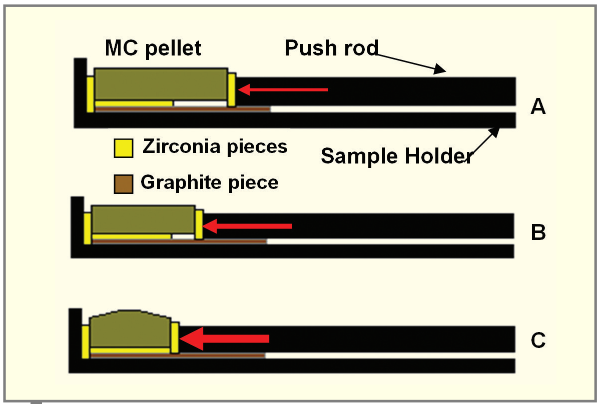
3.3 MIXED CARBIDE FUEL

The Fast Breeder Test Reactor (FBTR) at Kalpakkam, India is the only operating reactor in the world with high plutonium content hyperstoichiometic mixed carbide as driver fuel. The reactor was first made critical with a small core containing $(Pu_{0.7}U_{0.3})C$ fuel (Mark I) and the core is now being progressively enlarged with addition of fuel containing $(Pu_{0.55}U_{0.45})C$ (Mark II).

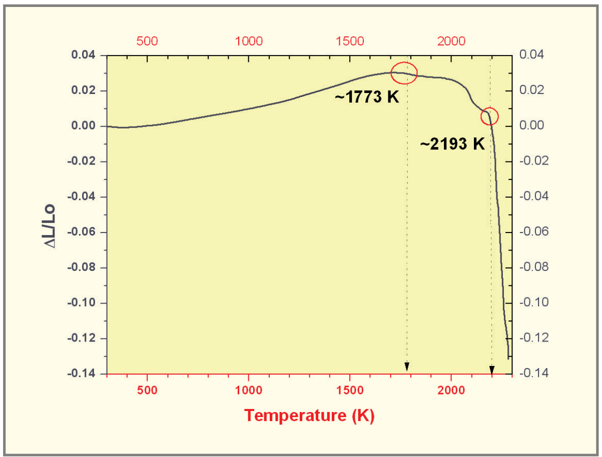
There are several methods of estimating or measuring the melting/ solidus temperature of materials. The melting point can be estimated theoretically by classical molecular dynamic simulation method or experimentally by using a Kundesen cell, DTA technique or by high temperature X-ray analysis. However, the melting/ solidus temperature of (45%UC – 55% PuC) fuel for FBTR has been determined by using a novel and unique technique using a high temperature horizontal dilatometer. Sintered pellet was heated upto 2283 K in flowing argon gas and the change in length was monitored as a function of temperature.

The schematic loading of the pellet using zirconia pieces for separation of the pellet with the graphite sample holder and the push rod inside the dilatometer and the subsequent softening upon heating is shown in the following figure.

A sudden/abrupt change is slope at 2193 K was observed in the shrinkage curve. The solidus temperature of this fuel was thus approximated to be ~ 2193 K. Beyond this temperature a high rate of shrinkage was observed which could be attributed to gradual melting of the pellet.

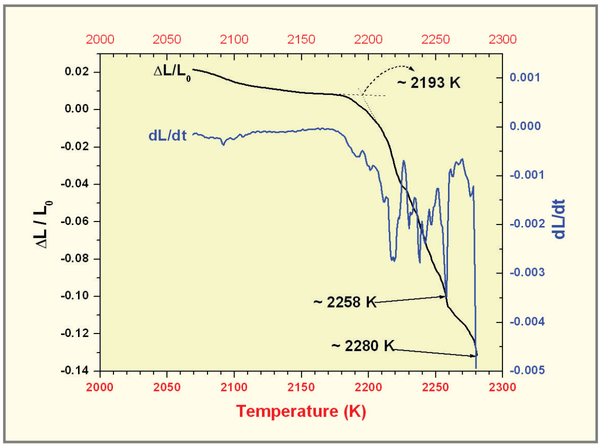


Schematic loading of MC pellet inside dilatometer and its subsequent softening.
(A) 300 K, (B) ~2233 K, (C) ~2249 K



The change in length of MC pellet during heating upto 2283 K

This was confirmed by visual observation of the pellet after cooling to room temperature, which showed the pellet had lost its geometry due to melting. The magnified high temperature region of shrinkage and rate of shrinkage versus temperature plot of the MC pellet is shown below.



Thermal expansion was measured from room temp to 873 K for MK I fuel using a horizontal dilatometer under vacuum of 4.65 x 10^{-3} Pa. The relation between ($\Delta L/Lo$) and T can be expressed by the following equation:

$$(\Delta L/Lo \times 100) = -16.59 \times 10^{-4} + 4.17 \times 10^{-6}\,T + 4.60 \times 10^{-9}\,T^2$$

where ΔL is the net expansion and Lo is the original length at ambient temperature.

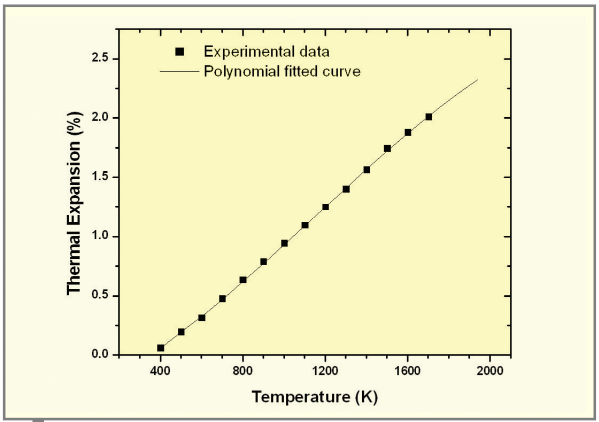
The average linear expansion coefficient between 300 and 873 K calculated is 9.2 x 10^{-6} K^{-1}. Thermal expansion for MK II fuel has been measured in a horizontal dilatometer using graphite sample holders and push rod assembly from ambient to 1773 K in flowing argon atmosphere. The percentage thermal expansion [($\Delta L/Lo$) x 100] at any temperature between 300 and 1800 K can be expressed by

$$[(\Delta L/Lo) \times 100]_T = -0.3333 + 7.1528 \times 10^{-4}.T + 7.6889 \times 10^{-7}.T^2 - 2.249 \times 10^{-10}.T^3.$$

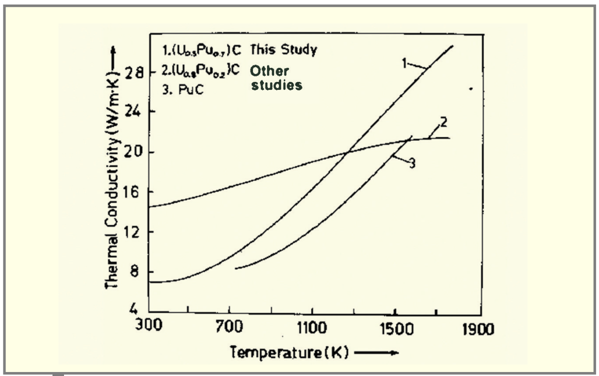
The plot of percent thermal expansion versus temperature for MK II is shown in figure. An average value of coefficient of thermal expansion between 300 – 1800 K has been calculated as 11.6 x $10^{-6}K^{-1}$ for MK II fuel. The thermal conductivity 'k' at any given temperature was calculated using the relation

$$k = \alpha \times \rho \times C_p$$

where α, ρ and C_p are thermal diffusivity, density and specific. heat respectively at the measurement temperature.



Thermal expansion as a function of temperature for hyperstoichiometric sintered ($Pu_{0.55}U_{0.45}$)C



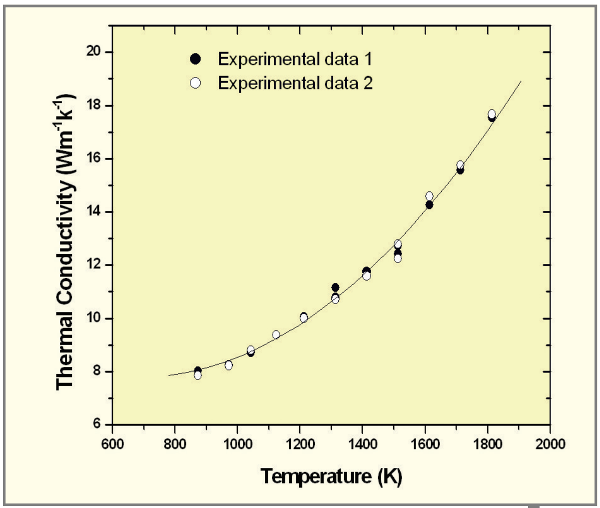
Thermal conductivity of (U-Pu)C (100%T.D.)

Thermal diffusivity (α) was measured by transient laser flash method from ambient to 1773 K in vacuum of 0.133 Pa. The density (ρ) of the MC samples was corrected for temperature using the experimentally determined average coefficient of linear expansion data and the specific heat (C_ρ) was experimentally determined up to 1273 K for MK I fuel and calculated for MK II fuel by adding the sp. heat data available in literature for UC & PuC, proportionate to their weight fraction present in the MC fuel. The thermal conductivity values were corrected to 100% theoretical density by using the following relation

$$k_{TD} = k_m \ (1+p/1-p)$$

where 'p' is the pore volume fraction; k_{TD}, the thermal conductivity value of 100% dense material and k_m is the thermal conductivity of as sintered material. The thermal conductivity of MK I & MK II fuels with temperatures are shown in the figures.

Hot hardness for MK I & II fuels were measured using a high temperature micro hardness tester with Vickers pyramid indenters made of diamond and cubic boron nitride. The accuracy and reproducibility of the equipment was tested at room temperature using standard test pieces JIS – B 7725 and NB5 SRM 1894.



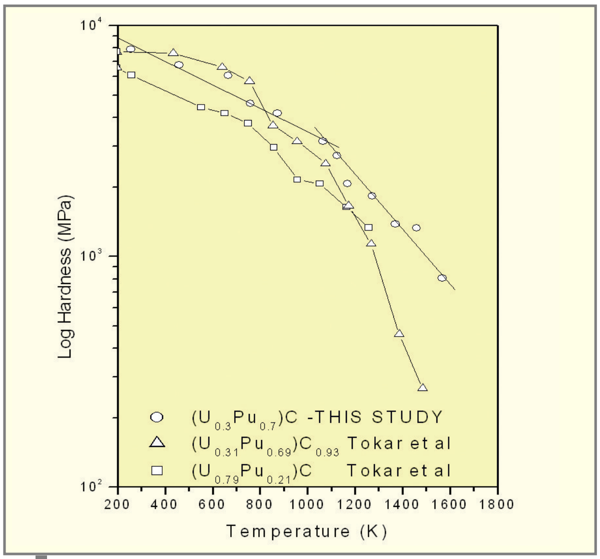
Thermal conductivity of $(Pu_{0.55}U_{0.45})C$ as a function of temperature

The relation between the hardness (H) and temperature (T) is given by

$$H = A \exp(-BT)$$

where A is the intrinsic hardness of the material at absolute zero and B is the softening coefficient. The plot of Log H vs. T for MK I Fuel is shown in the figure.

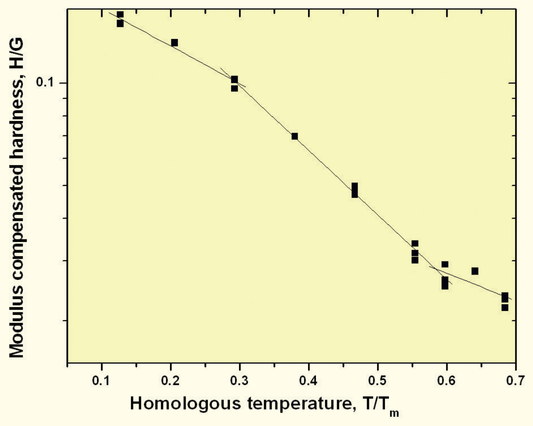
The plot clearly shows a change in slope at around 1123 K (~0.52 T_m; where T_m is the melting point of the material. The change in slope indicates change in deformation mechanism from simple slip to diffusion-controlled processes. The data generated has been compared with that of Tokar et al. They had reported data from experimental measurements for mixed carbide containing 21% and 69% PuC. The data generated by Tokar for 69% PuC are in close agreement with those of the present data containing 70% PuC up to 1100K. The small variation in the hardness could be attributed to difference in composition, second phase sesquicarbide and porosity between the samples.



Variation of hardness with temperature for $(Pu_{0.7}U_{0.3})C$

In more recent experiment with MK II fuel, the hardness values at a particular homologous temperature T/T_m was compensated for the variation of the shear modulus with temperature and the log of modulus compensated hardness (H/G) vs. homologous temperature was plotted in the figure.

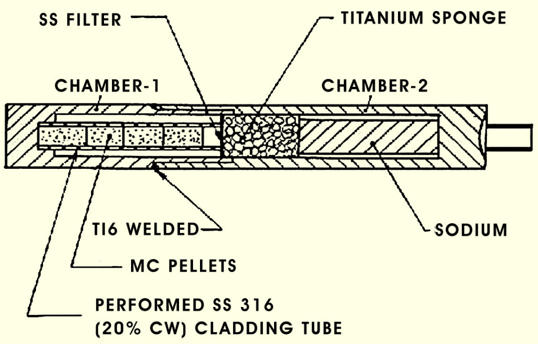
Three regions with change in slope is observed. At low temperature (region I), hardness is found to be a weak function of temperature and deformation is controlled by dislocation interaction with solute impurities. In region II, an appreciable softening is observed involving plastic flow with



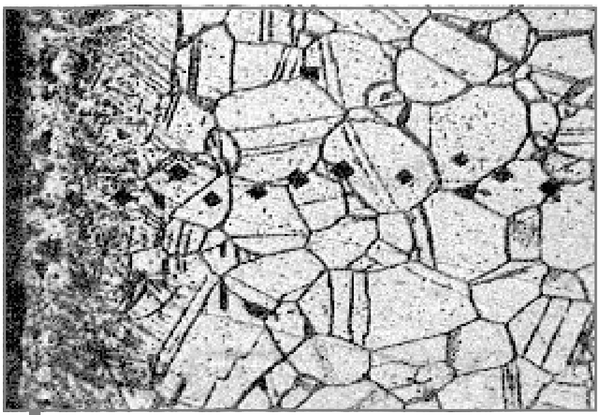
Modulus compensated hardness H/G versus homologous temperature T/Tm for $(Pu_{0.55}U_{0.45})C$

glide and climb with controlled lattice diffusion. In region III, the softening rate decreases because of microstructural changes and appearance of oxide phase due to high temperature oxidation.

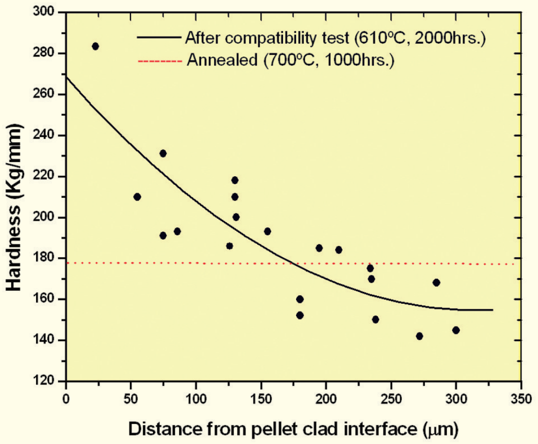
A typical fuel-clad-coolant compatibility capsule design is shown below. The capsules have two chambers, separated by a SS filter. Chamber 1 contains a perforated SS-316 cladding tube, in which four sintered MK I & MK II pellets are loaded. Chamber 2 contains titanium sponge (Oxygen getter) and sodium rod. Sodium is allowed to come in chamber 1 after melting. Capsules were heated in this condition at 883 K upto 2000 hrs. After the experiments, sodium was leached out both from the pellet and the cladding material. The clad and the fuel were observed to be in good physical condition. Metallographic examination revealed very narrow reaction layer near clad-coolant interface. Hardness profile of SS-316 (20% cold worked) cladding material from the fuel clad interface is shown in figure.



Schematic diagram of fuel-clad-coolant compatibility capsule



Photomicrograph of SS-316 (20%CW) showing pellet/clad interface and Vivkers indentations after fuel-clad-coolant compatibility experiment



Hardness profile of SS316 (20% cold worked) cladding from fuel-clad interface

A. NUCLEAR FUELS

4. BASIC STUDIES

INTRODUCTION

Basic studies are sometimes needed for proper understanding of a particular phenomenon. Development of Master Sintering Curve (MSC) for AHWR fuel composition, which provided a new insight into the sintering phenomena and predicted the densification behaviour under a set of arbitrary time-temperature excursion, is a good example of this. Molecular dynamic simulation to predict thermophysical properties of UO_2 at temperatures much beyond the experimental capabilities or prediction of properties like elastic modulus, shear modulus, bulk modulus, fracture toughness etc. by ultrasonic velocity measurement are other examples of the usefulness of basic studies.

4.1 CLASSICAL MOLECULAR DYNAMICS SIMULATION OF UO_2

Thermo-physical and thermo-mechanical properties as well as transport phenomena of nuclear fuels are of special interest to the fuel designers for better understanding and prediction of in reactor fuel performance. Moreover during the loss of coolant accident (LOCA) condition when fuel melt down could occur; the engineering design parameters of the reactor components are of paramount importance. Such a situation also demands the relevant properties to be evaluated at or near melting point.

It is not always possible to determine experimentally various thermophysical and other properties at very high temperature or pressure since majority of the instruments have their own limitations. Hence, computer modeling provides a useful route to simulate such extreme conditions e.g. thermal conductivity of the fuel at LOCA condition. With the advent of modern powerful computers such simulation 'experiments' are gaining popularity.

In recent years a number of studies on Molecular Dynamics (MD) simulation of UO_2 have been published and it was observed that it is quite simple to simulate UO_2 system using classical pair potential in order to get various thermophysical and transport properties. The same could be done with the help of shell model. Non-equilibrium molecular dynamics (NEMD) could play a potential role to get various useful kinetic and transport properties of the system (e.g. thermal conductivity).

It has been seen that for some systems there does not exist any unique set of pair-potential parameters that are able to produce all the thermodynamic properties of that system at all temperature ranges and this is known as the transferability problem. The sustenance of this transferability problem of the pair-potential parameters for various oxides, silicates and some other compounds is still there and so also for the UO_2 system.

In this work emphasis has been given on the selection of the potential model, especially the fitting of the potential parameters and to study the lattice parameter variation, thermal expansion, mean square displacement of cation and anion and isothermal compressibility of UO_2 as a function of temperature with the help of these fitted potential parameters.

■ Potential Model

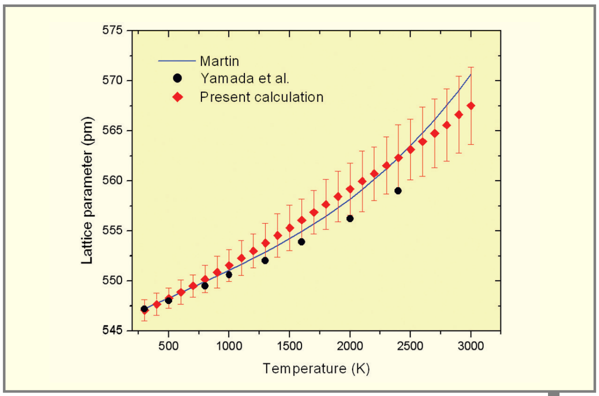
Bushing- Ida type of potential along with Morse type potential model is useful while simulating a semi-ionic system; where the long range Coulomb interactions, core repulsion and the Van dar Wall's weak attraction are considered. Along with that the Morse type potential is also applicable only for anion-cation pair.

■ Simulation Techniques

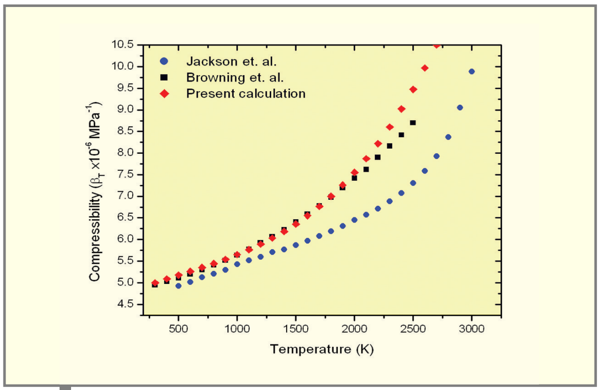
UO_2 holds stable fluorite structure (CaF_2 type) and each unit cell contains 4 U^{4+} ion and 8 O^{2-} ion. The MD cell was constructed with an array of 3X3X3 supercells in three mutually orthogonal directions totaling 108 cations and 216 anions. The size of MD cell was determined by the correctness of Ewald sum technique that was used to calculate the long range Coulombic interaction part.

The initial random velocity was chosen from the Maxwell-Boltzmann distribution at 298K. The equation of motion was integrated using Beeman's algorithm, which is of predictor-corrector type, with the unit time step of $2.0X10^{-15}$s. Only constant pressure-temperature (NPT) simulation was performed using Nosé -Hoover thermostat to control the temperature. Before accumulation of the thermodynamic data, an equilibrium run of $2X10^4$ time steps were made at desired temperature and pressure. During the simulation Parrinello-Rahman constant stress method was applied in order to judge the structural reproducibility of the system along with the required pressure control. The calculation was performed by the popular molecular dynamics code MOLDY in LINUX platform using PC.

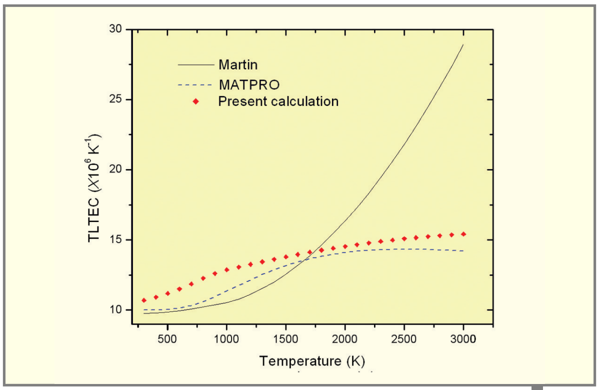
To ensure effective coupling between system and external pressure bath, the extended system mass parameter was approximated using ultrasonic velocity measurement in UO_2 at each temperature. It ensures better pressure control of the concerned system.



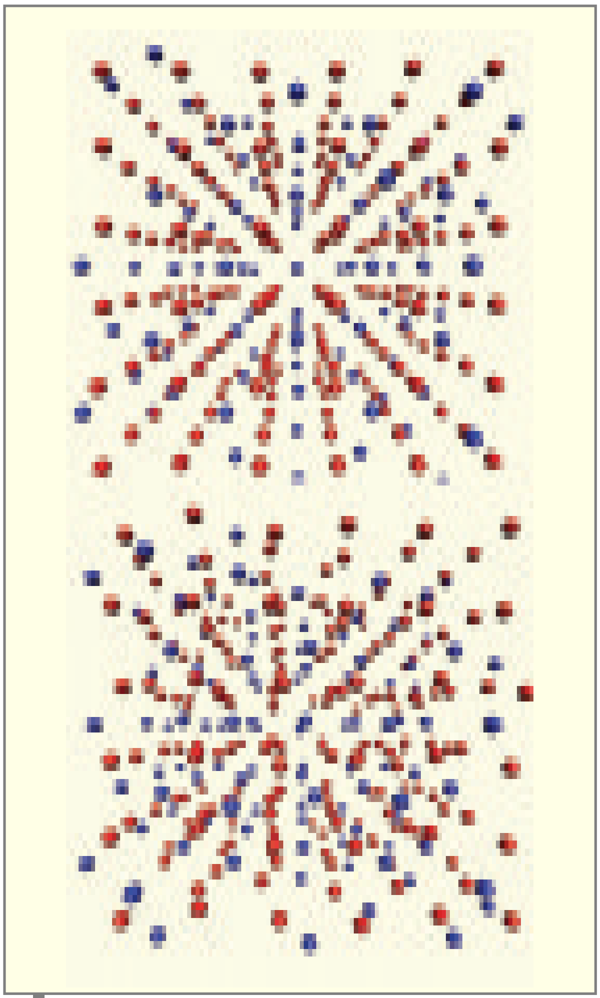
Lattice parameter of UO_2 as a function of temperature

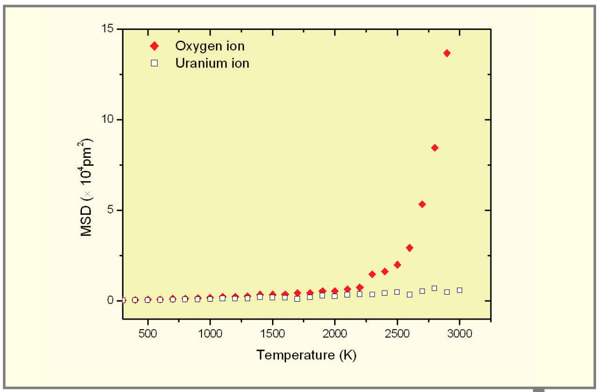


Isothermal compressibility of UO_2 as a function of temperature



True linear thermal expansion coefficient of UO_2 as a function of temperature





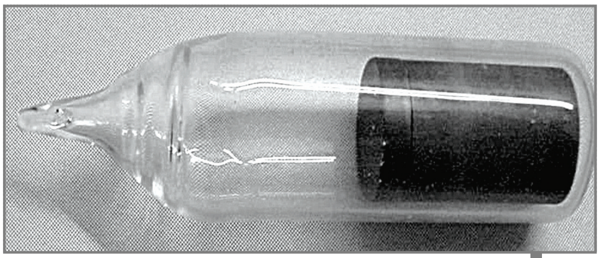
Mean square displacement of U and O ions in UO_2 lattice as a function of temperature : also note the Bredig transition temperature

Ionic arrangements in UO_2 lattice; blue:U and red:O; at 300 and 1500K

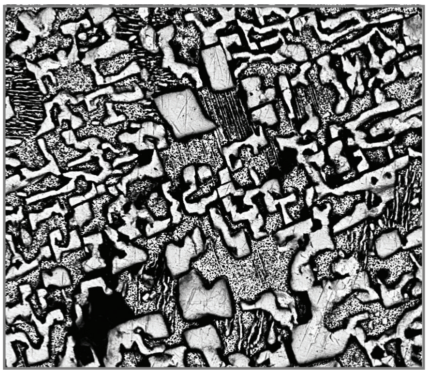
4.2 COMPATIBILITY OF Pb-Bi ALLOY WITH GRAPHITE

High temperature nuclear reactors generally use gas as coolant, however, liquid metal or alloy could be a better alternative because of their higher thermal efficiency which can make the reactor more compact. Lead Bismuth Eutectic (LBE) alloy (Pb: 55.5 wt %, Bi: 44.5 wt %) could be a potential candidate material as coolant for the Compact High Temperature Reactor (CHTR) because of its several favourable properties like high thermal conductivity, high boiling point and low vapour pressure]. While high boiling point (1943 K) eliminates the possibility of over pressurization and prevents boiling and explosion due to over heating of the core, low melting point (397 K) reduces the chances of freezing of the alloy in the primary coolant circuit. It has low chemical activity, which makes it safe against possibility of fires and explosion in the event of coolant leakage. It also act as a shield for high energy 'γ' radiation in the reactor. Besides, LBE has a negative void coefficient of reactivity, which makes the reactor safe in case of loss of coolant accident (LOCA). Apart from these, low vapour pressure and low volume contraction on solidification also makes it attractive as a coolant. However, the compatibility of the coolant with the structural and fuel cladding materials should be explored for the deployment of lead based alloys as coolant for such reactors. Lead bismuth alloy buttons of eutectic composition (Pb: 55.5 wt.%, Bi: 44.5 wt%) were made in an arc furnace.

Pure graphite of density 1.78 gm/cm^3 was taken in the form of crucibles with threaded lid. The crucibles were dedusted and degassed by soaking at 573 K for 1 hr, following quenching in boiling water and then subsequent heat treatment at 573 K for 30 min. Small pieces of the LBE alloy were filled in the graphite crucibles and were encapsulated in quartz capsules under helium atmosphere.



Graphite crucible containing Pb-Bi alloy encapsulated in quartz capsule

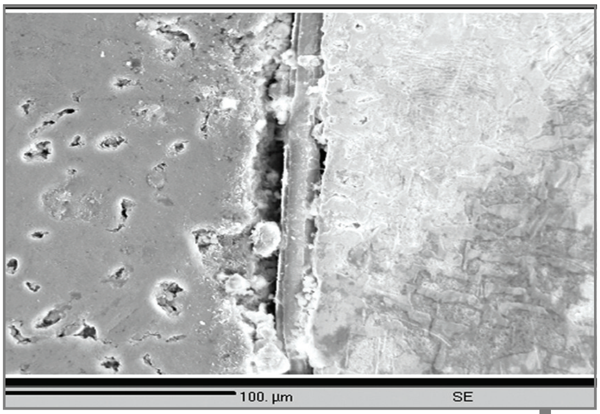


Scanning Electron Micrograph of Pb-Bi alloy of eutectic composition

The graphite crucibles containing the LBE alloy enclosed in quartz capsules were isothermally annealed at 1073 K, 1173 K, 1273 K and 1373 K for various time intervals ranging from 100 to 1000 hours in resistance heating furnace.

After heat treatment for the specified times and temperatures, the graphite crucibles were sectioned longitudinally using a slow speed diamond saw. The surface of the cross-sections was polished using standard metallographic techniques. The samples were characterized using an electron probe micro analyser (EPMA). The EPMA used was equipped with three wavelength dispersive spectrometers (WDS). Line scans of 'Pb', 'Bi', and 'C' and 'Y' were acquired across the interface to determine distribution of each of the elements.

Secondary electron image (SE) of the graphite/LBE interface of the crucible heat treated at 1073 K for 100 hrs indicates a layer of compound along the interface having uniform thickness throughout. The intensity profile of Pb(Lα), Bi(Lα) and C(Kα) X-ray lines were taken across the interface along a line AB and it indicates that the compound basically contains Pb and C. The compound was quantitatively analysed by fixing the beam on it and correcting the intensities of Pb and C. It was also found that the compound was PbC_2. Phase diagram of Pb-C also confirms the presence of PbC_2 in the system. It was also observed that the layer of PbC_2 formed at the interface adhered to the LBE alloy and a gap developed between the graphite and PbC_2 layer when the graphite crucible containing liquid LBE was cooled down to room temperature after the compatibility test. This is essentially due to the differences in coefficient of thermal expansions of LBE alloy, PbC_2 and graphite. Similar reactions



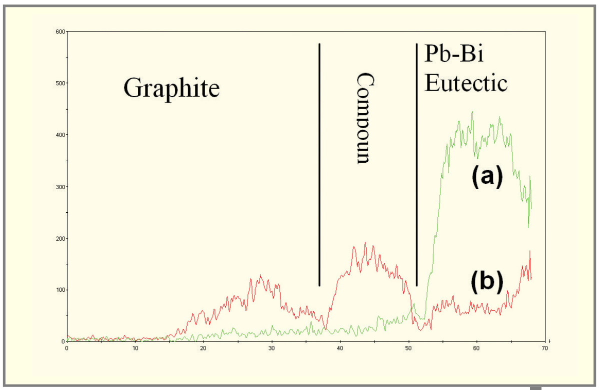
Scanning Electron Micrograph of the Interface of Pb-Bi eutectic alloy showing PbC_2 interface alloy

were also observed in other crucibles heat-treated at various temperatures and time intervals.

The data points were fitted with a straight line using the least square method and can be represented by the following relation,

$$w = 1.29\text{x}10^{-5} + 8.62\text{x}10^{-9}\sqrt{t}.$$

It was estimated that a zone of 61.3 µm wide would develop in 1 year and 121 µm in 5 years. Since the growth is parabolic in nature, initially the reaction layer forms very rapidly but the growth rate decreases after some time and becomes very slow subsequently. The growth of the reaction zone is thus diffusion controlled.



Intensity profile along the line perpendicular to Pb-Bi/graphite interface; (a) Pb(Lα) and (b) Bi(Lα)

4.3 DEVELOPMENT OF N-A FDM BASED CODE TO DETERMINE THE 3-D SIZE DISTRIBUTION OF HOMOGENEOUSLY DISPERSED SPHERICAL SECOND PHASE FROM MICROSTRUCTURE

In the field of powder metallurgy and composite material it is of great interest to know the actual 3-D distribution of porosity and/ or the second phase particles in the matrix. In case of ceramic nuclear fuel the size distribution of pores determines the in-reactor densification behaviour and swelling of the fuel pellet. A classical example is the nodular cast iron, where inoculant is used to allow the graphite particles to grow in spherical shape in ferrite matrix and the size distribution of such nodular graphite particles determines various bulk properties of the material; like elastic modulus, ductility etc.

The present endeavour is to determine the 3-D distribution from its 2-D counterpart by solving an integral equation analytically. However, in order to form an executable code, one needs to have a better insight of this formulation and its overall mathematical behaviour. In the present study, emphasis has been given on the behavioural features of the formulation considering various possible cases and checkpoints. Eventually the algorithm has been implemented for nodular cast iron along with proper experimental verification.

This formulation was based on the following basic assumptions:
i) All Particles are spherical in shape.
ii) Particles are distributed homogeneously in the matrix in non-overlapping manner with continuous size variation.
iii) Maximum diameter of the cross sectional circle (as seen in microstructure) is equal to the diameter of the largest particle.

The probability that a particle of diameter *z* will appear as a circle with a diameter between *x* and *x*+*dx* on a horizontal sectional plane within a cube of unit length can be expressed as

$$p(x) = \frac{x}{\sqrt{z^2 - x^2}}dx \quad \forall x \le z \qquad (1)$$

Since $N_a(x)$ is the sectional number density (i.e. 2-D distribution) in the diametric interval of [*x*,*x*+*dx*] which resulted from the actual particle number density (i.e. 3-D distribution) N_v in the diametric range of [*x*,∞]; so the relation between these two quantities can be expressed as –

$$N_a(x) = \int_x^\infty p(x) \cdot N_v(z)dz \qquad (2)$$

$N_v(z)$ is unknown and $N_a(x)$ is the known quantity, hence Eqn. (2) can be regarded as Volterra equation of the second kind. Solution of this equation for an arbitrary diameter *u* is given by

$$N_v(u) = -\frac{2}{\pi}\cdot\frac{d}{du}\int_u^{\infty}\frac{N_a(x)}{\sqrt{x^2-z^2}}dx \qquad (3)$$

Assuming that the groups are arranged in arithmetic progression with group width (or class interval) of Δ and D_m is the largest diameter observed in the microstructure and also the largest particle diameter (i.e. $D_m = k\Delta$) then applying finite difference method on Eqn. (3) and subsequent integration yields for the jth group

$$N_v(j)\Delta = A(j,j)N_a(j) + \sum_{i=j+1}^{k} A(i,j)N_a(i) \qquad (4)$$

where,

$$A(j,j) = 1 \qquad \text{for } (j=1)$$

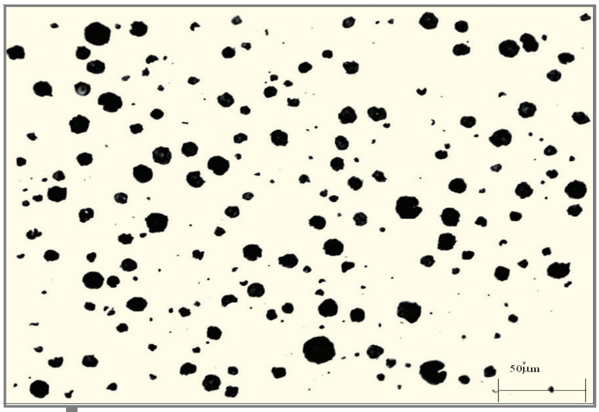
$$= \frac{2}{\pi}\ln\left(\frac{j+\sqrt{j^2-(j-1)^2}}{j-1}\right) \quad \forall(j>1) \qquad (5a)$$

$$A(i,j) =$$

$$\frac{2}{\pi}\ln\left(\frac{i+\sqrt{i^2-(j-1)^2}}{i+\sqrt{i^2-j^2}}\cdot\frac{i-1+\sqrt{(i-1)^2-j^2}}{i-1+\sqrt{(i-1)^2-(j-1)^2}}\right) \quad \forall(i>j) \qquad (5b)$$

■ Experimental Procedure

Nodular cast iron samples were obtained from Electrosteel Casting Ltd., Khardah Works, West Bengal, India. The specimens were cut from a fully annealed spun pipe (nominal diameter 250 mm). A typical optical micrograph is shown below.



Typical photomicrograph of nodular cast iron, after grinding and polishing (contrast enhanced followed by intensity calibration)

After grinding and polishing the 2-D distribution was generated using Image Pro Plus (v 4.1) software. It may be noted that the 2-D distribution has to be scaled down with respect to the area of interest (AOI); because the formulation considers the AOI as a unit area. Scaling up the area instead of scaling down may give erroneous results because of small AOI and hence poor statistical sampling.

Since the present formalism is based on a probabilistic approach a large number of sampling was needed. For the present study the 2-D distribution was made from 20 different places, comprising 5 different places across the thickness from each of the four different sections of the specimens and then merged all of them in order to get a representative 2-D distribution. The final 2-D distribution was fed into the code to generate the desired 3-D distribution of graphite nodule.

In order to validate the model the carbon balance method was used as follows

$$xD_{NCI} = 100\,pD_{Nd} + 0.007(1-p)D_{Fr}$$

where, *x* is wt. % of carbon in the sample and *p* is volume fraction of graphite nodule (obtainable from the model). D_{NCI}, D_{Nd} and D_{Fr} are the specific gravitiy of nodular cast iron, graphite nodule and ferrite respectively. The factor 0.007 denotes the wt % C present in the ferrite. The specific gravity of nodular cast iron (D_{NCI}) was measured and found to be 6.99. Specific gravity of ferrite (D_{Fr}) is taken same as a-iron i.e. 7.87 and the same for nodular graphite is 2.1. Carbon content in the sample was determined using the carbon analyzer where the known amount of milled pieces of the sample is heated under oxygen atmosphere upto 1773 K in an alumina crucible. CO present in the evolved gas is converted to CO_2 which is measured by infrared detector. After four analyses the mean value of carbon wt% was found to be 3.364.

Result and Discussions

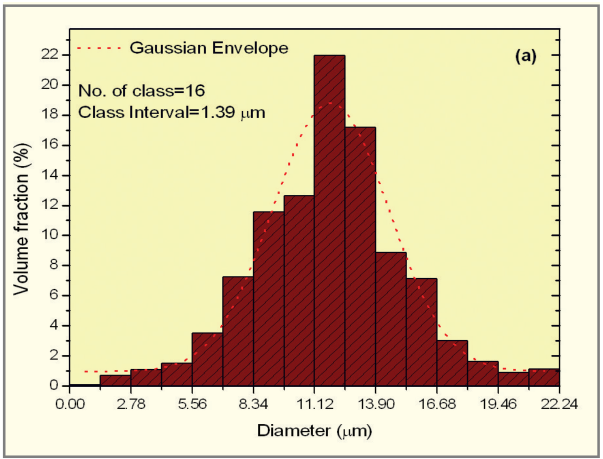
The minimum detectable length being one pixel the spatial calibration gives the resolution of 0.45 µm at 200X. The maximum observed diameter was found to be 22.24 µm. The class interval (Δ) should be high enough to avoid excessive data discretisation and small enough to represent the meaningful classification of data. For the present study we took two values of Δ as 1.39 µm and 0.695 µm generating the number of classes as 16 and 32 respectively to build up two different 2-D distributions.

The sections with aspect ratio greater than 1 were converted to circular section with equal area of that section during the formation of the 2-D distribution. However it has been observed that the value of aspect ratio has never exceeded 1.76.

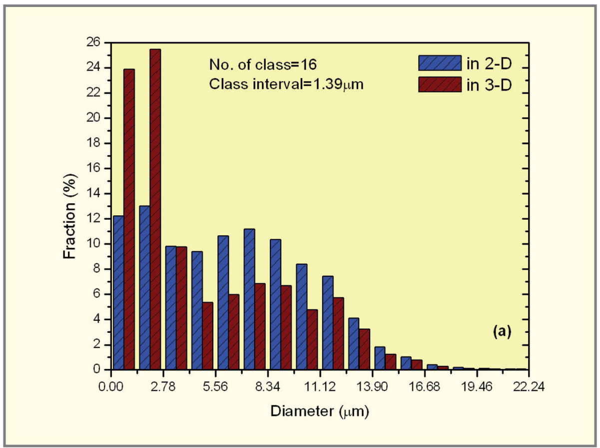
The total volume fraction of graphite nodule is derived using the following equation:

$$V_{total} = \frac{\pi\Delta^3}{12}\sum_{j=1}^{k} N_v(j).[(j-1)^3 + j^3]$$

It is interesting to note that the volume fraction histogram (shown below) shows a trend of a bell-shaped envelope curve that resembles the typical Gaussian type, though the diametric distribution (shown below) does not follow the Normal distribution. The wt% of carbon calculated from the volume fraction of individual class agrees reasonably well with that found from experiments. However, the small deviation of the calculated carbon content from the experimental value could be attributed to the following reasons. Firstly, the area conversion of the nearly circular shapes into the perfect circle will affect the 3- D distribution and hence the total carbon content. Another reason is the limitation in the resolution. Although higher resolution could give rise to better accuracy but number of screen shots required will increase sharply to cover the same AOI in lower resolution e.g. in 400X total 80 screen shots will cover the same AOI as for 20 screen shots in 200X.



Histogram of volume fraction obtained from 3-D diametric distribution with number of class 16



2-D and 3-D diametric distributions with number of class 16

Conclusions

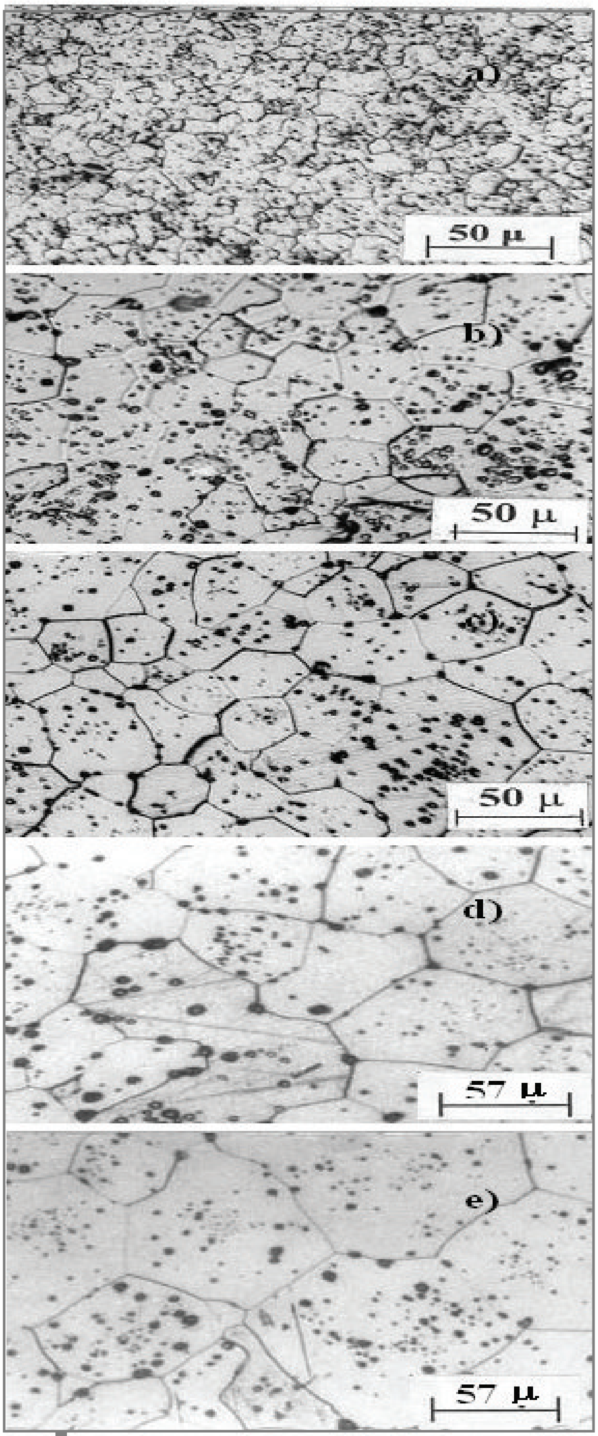
A method is presented here to derive the diameter distribution of 3D homogeneously distributed spheres from measurements of the diameter distribution in random 2D sections through the distributed spheres. The solution of the analytical integral equation is very easy to implement in a computer code. It is possible to predict whether the particles are of uniform size or not. This model predicts the 3-D distribution more accurately than that of Saltykov's model. The future scope of this model is wide; porosity modeling and the effect of it in thermophysical properties can be determined for any material.

4.4 EFFECT OF TITANIA ADDITION ON HOT HARDNESS OF UO_2

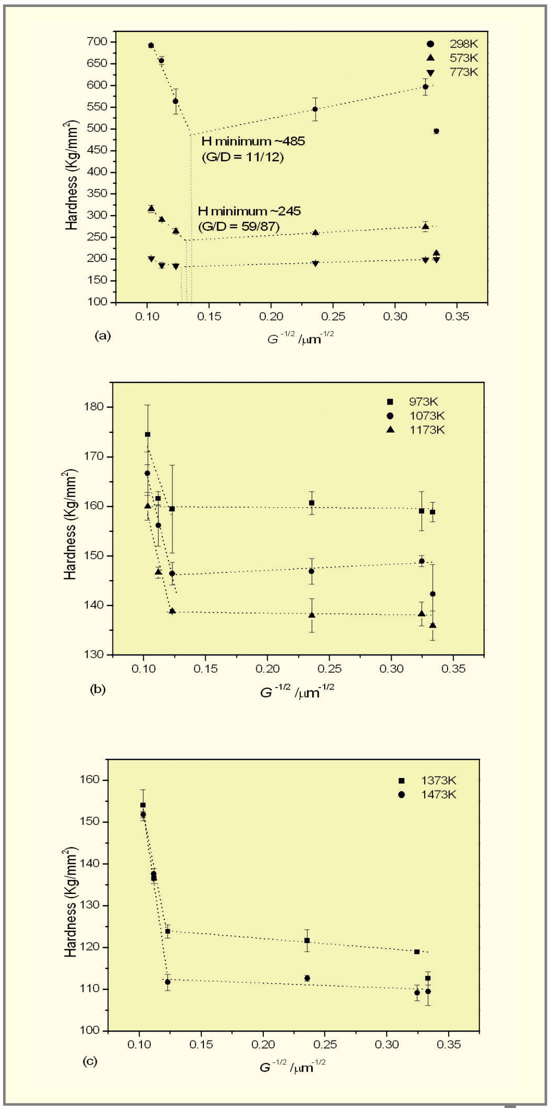
Large-grained UO_2 fuel has been developed as a high burn-up fuel for LWRs. The large grain size increases the path length of the fission gas species for transportation to grain boundaries for coalescence and subsequent release. This helps in retention of the fission gases in the matrix without swelling. Though large grain size UO_2 pellet can be obtained by modifying powder characteristic and by increasing the sintering temperature and time, they are commercially not viable and are normally obtained by addition of dopants like Nb_2O_5, TiO_2, Cr_2O_3, and V_2O_5 etc., which also act as sintering aids. The grain size of UO_2 in the final sintered product, however, depends on the type and amount of dopants added.One of the prerequisites for addition of these dopants to the fuel is that they should not impair any other properties of the fuel. Literature reveals the effect of Nb_2O_5, TiO_2, Cr_2O_3 and V_2O_5 on the sintering behaviour of UO_2 and their effects on other properties. It has been reported that titania addition increases both grain sizes and thermal conductivity of UO_2 by about 10-15%. However, its effect on other material properties, particularly hot hardness has not yet been ascertained. In the present investigation attempts have been made to study the effect of TiO_2 on the hot hardness of sintered UO_2 fuel. This has been achieved by hardness measurements of UO_2 pellets from ambient to 1573 K in vacuum for titania content varying from 0.01w/o TiO_2 to 0.15w/o which resulted in grain size variation from 9.5 µm for UO_2 with 0.01 w/o to 94 µm for UO_2 with 0.15 w/o TiO_2. The grain size of the pure UO_2 pellet (control pellet) was of 9 µm under the same sintering condition.

Results and discussions

Photomicrographs of UO_2 containing different TiO_2 content (0.01- 0.15 w/o) are shown below. The photomicrographs indicate presence of equiaxed grains increasing in size with TiO_2 content with intragranular spherical pores of different sizes. No precipitates of UO_2-TiO_2 eutectic for UO_2 containing 0.15% TiO_2 could however be revealed by optical microscopy at grain boundaries (solubility limit TiO_2 at 1923 K in H_2 atmosphere is 0.13 w/o). The plot of hardness vs inverse square root of grain size at three different temperature ranges and the plot of hardness vs temperature for different grain sizes are shown



Photomicrographs of sintered UO_2 pellets with different TiO_2 content; [% TiO_2, Grain size]
a) (0.01%, 9.5µm; b) (0.05%, 18µm
c) (0.10%, 60µm d) (0.13%, 80µm
e) (0.15%, 94µm)

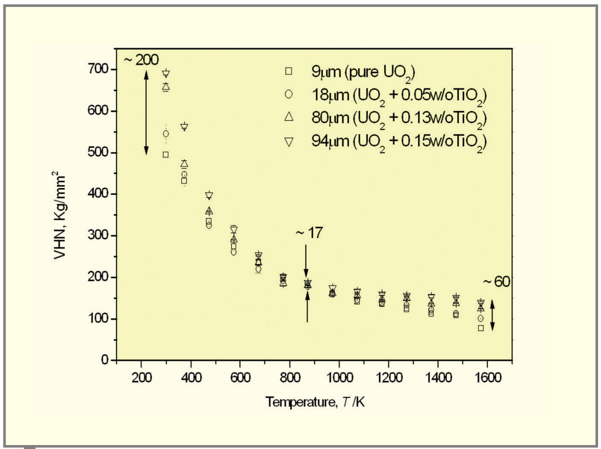


Variation in hardness as a function of 1/ $\sqrt{G}$ at three different temperature zones : fitted lines are indicated by dotted line

in figure. It should be noted that grain size as well as TiO_2 content influence hardness value at any temperature and also they are interrelated. However, the results have been discussed into three categories signifying the effect of TiO_2 content, grain size and temperature.

The effect of TiO_2 content, grain size and temperature on hardness and their complex interrelationship could be explained as follows:

Hardness of UO_2 increases with increase in TiO_2 content at any temperature and hence, the fuel becomes less and less plastic although grain size increases many folds e.g. 9μ to 94μ. This increase in hardness could be attributed to solid solution hardening by increasing amount of lattice strain induced by more and more TiO_2 addition within the solubility range. The hardening effect could also be attributed to the hindrance of the dislocation motion by pinning due to the presence of TiO_2 solute atom in UO_2 or precipitates (at high TiO_2 content, low temperature condition).



Variation in hardness with temperature. dH/dT for high grain size is sharp than that for low grain size in low temperature zone. But at higher temperature it is reversed

It is very difficult to separate the effect of grain size and TiO_2 content on hardness since the grain size and TiO_2 content are interrelated. However, in order to ascertain the dependence of hardness (*H*) variation with grain size (*G*) at various temperatures (*T*), hardness was plotted as a function of inverse square root of G (based on Hall- Petch relationship). The plot of *H* vs. $G^{-1/2}$ shows the same trend like most of the oxide and non-oxide ceramic materials at room temperature i.e. with increasing grain size hardness first decreases, reaches a minimum and then increases. However, the same trend was not observed at higher temperature and in the present study the whole temperature range was divided into three regions, namely lower temperature ($T \leq 773K$), intermediate temperature ($773K < T \leq 1273K$) and high temperature ($T > 1273K$) region to discuss their effects on hardness.

At lower temperatures (T= 773K) hardness decreases sharply with decrease in grain size because of two reasons. Firstly, the diagonal length of indentation becomes comparable to that of grain size (i.e. G/D ratio ≈1) causing grain boundary spalling due to intergranular crack generation. This results in decrease in hardness. The tendency of spalling is often enhanced by the presence of porosity on grain boundary. Secondly, the lower grain size contains lower amount of TiO_2, which in turn reduces the hardness. These two factors together oppose the strengthening effect due to grain fineness (following Hall-Petch relation) and becomep- redominant. Further decease in grain size increases the hardness due to the effect of grain fineness over spalling. Hence a minimum H value is observed due to transition from grain boundary spalling domination to grain fineness domination. It has been observed that in the lower temperature range there is increase in hardness for the sample with grain size of 9.5 µm (UO_2+0.01w/oTiO_2) than that for 9 µm (pure UO_2), which is due to the addition of TiO_2 alone; since the grain size effect is negligible. Hence hardness data corresponding to 9 µm grain size has not been considered for the fit.

At intermediate temperature range (773K< T $\leq$ 1273K) the higher grain size shows similar trend in hardness (as observed at lower temperatures) with the exception that the slope is less due to less grain boundary spalling. However, at lower grain size, hardness does not increase as sharply as in case of lower temperature range. With decreasing grain size, on the contrary, it becomes almost independent of grain size. This could be attributed to lowering of grain boundary strength at this temperature range. Hence, the dislocation piled up stresses generated during indentation is released easily which, in turn, lowers the hardness. As the grain size dependency of hardness at lower grain size is not predominant at this temperature range, H minima is not much pronounced here.

In the higher temperature range (T > 1273K), higher grain size shows similar effect as mentioned above. However, with decrease in grain size, hardness gradually decreases. This is attributed to grain boundary sliding which becomes operative at high temperature. Accordingly, smaller the grain size, more weak it becomes, though, the decrease in hardness with respect to grain size is not much.

From the variation of hardness with temperature for different TiO_2 content, it is seen that the spread in hardness data is maximum at 298K (~ 200 VHN) and minimum at 873K (~17 VHN); whereas at 1573K it is ~60 VHN. The relation between hardness and temperature is given by the following equation:

$$H = A\exp(-BT)$$

where, *H* is Vicker's hardness, *A* is the extrapolated hardness value at 0 K (called intrinsic hardness) and *B* is the softening coefficient of the material. The values of *A* and *B* are dependent on the amount of additives or impurities, grain size etc. The slope of ln*H* vs. *T* gives the softening coefficient (*B*). Since the deformation mechanism, as stated earlier, is different in the lower temperature range than that at higher temperature range; a distinct change in slope (i.e. $d(\ln H)/dT$ or *B*) is expected between lower and higher temperature regimes. The plot of ln*H* vs. *T* for various TiO_2 content conform reasonably well to the exponential relationship between hardness and temperature. It is observed that the change in slope (i.e. $d(\ln H)/dT$) or the transition occurs between 600- 800K; depending upon the TiO_2 content. This transition refers to change in deformation mechanism. Below 700K, the rapid decrease in hardness with the increase of temperature could be attributed to the release of strain energy (due to titanium ion and other interstitials) by lattice dilation. Beyond 700K the rate of decrease in hardness is less due to the pinning of dislocations by the interstitials and fine precipitates of eutectic phase; such mechanism ensures that the variation in hardness is insensitive to temperature at least up to $0.6T_m$; resulting in lower value of $d(\ln H)/dT$ at high temperature regime. As TiO_2 content goes up the misfit strain increases which gives rise to higher intrinsic hardness value whereas with the lattice dilation (i.e. increasing *T*) more strain energy is released that caused higher value of softening coefficients as TiO_2 content increases.

4.5 DEVELOPMENT OF MASTER SINTERING CURVE AND SINTERING KINETICS STUDIES ON (Th-U)O_2 MOX PELLETS

The sintering parameters of many ceramic products are still decided by the ancient method of trial and error basis. The theory of Master Sintering Curve (MSC) provides a new insight into the sintering phenomena. MSC enables the prediction of the densification behaviour under arbitrary time-temperature excursions with the help of a minimum number of preliminary experiments. The procedure for development of a master sintering curve for AHWR fuel of composition ThO_2-3%UO_2 is described below:

Theory of Master Sintering Curve

The master sintering curve is derived from the densification rate equation of the combined-stage sintering model. The parameters in the sintering rate equations can be separated into two parts: (a) those related to the microstructure and (b) those related to time and temperature terms. These parts, which are on the opposite sides of the equation, are then related to each other experimentally. The temperature -dependent side of the equation can be represented by

$$\theta = (1/T) \exp(-Q/RT)dt \qquad (1)$$

where Q is the sintering activation energy, R is the gas constant, t is the instantaneous time and T the absolute temperature. The relationship between density ρ and θ is defined as the master sintering curve. For the construction of MSC, the integral of equation (1) and density should be known.

Activation energy of sintering

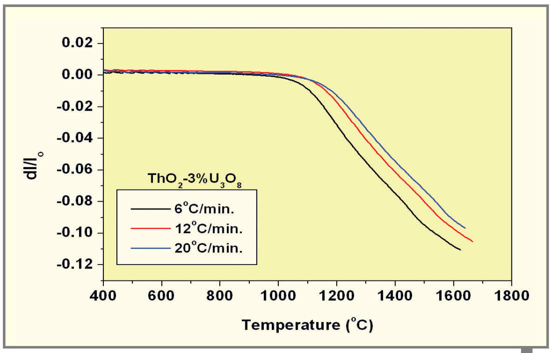
For construction of Master sintering curves (ρ versus θ), correct value of activation energy is required which can be available from literature or can be estimated with good precision from ρ versus θ data. To estimate the activation energy for sintering, firstly, a particular value of activation energy is chosen and ρ versus θ curves are constructed for each heating rate. If the curves fail to converge, a new value of activation energy is chosen and the calculations are repeated. This procedure continues until all the curves converge and the corresponding activation energy is the true activation energy for sintering. If the correct value of Q is chosen, all of the data converges to a single curve. The best estimate of Q will be the value of the minimum in the plot of mean residual squares versus activation energy.

Experimental

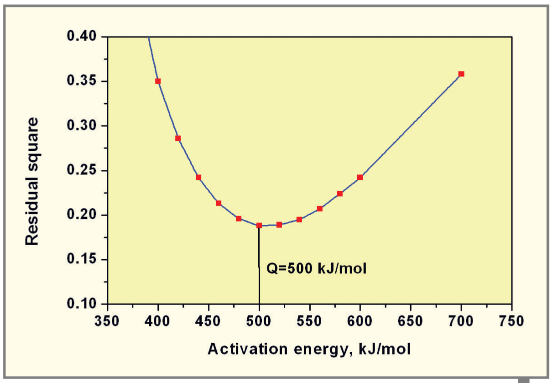
The green pellets of ThO_2-3% UO_2 for this study were prepared by the conventional powder metallurgy route. The procedure adopted for the fabrication of ThO_2-3% UO_2 green pellets are as follows:

a) milling of the as-received ThO_2 powder in a planetary ball mill
b) mixing/milling of the above milled ThO_2 powder with the required quantity of UO_2 powder for 4 h in a planetary ball mill with tungsten carbide balls
c) double precompaction of the above mentioned mixtures at 150 MPa
d) granulation of the precompacts
e) final cold compaction of the granulated powder at 300 MPa into green pellets of about 8 mm diameter and 7mm long.

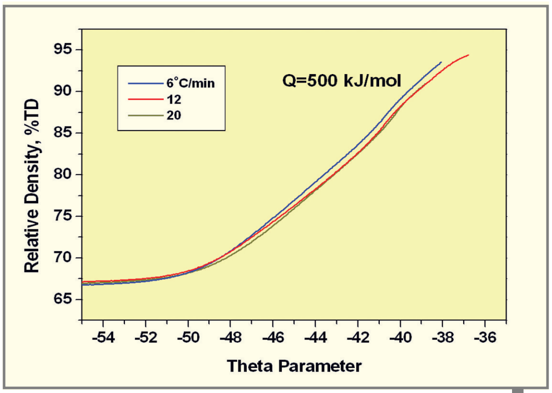
To determine the shrinkage of (Th-U)O_2, a push rod type high temperature horizontal dilatometer was used. The dilatometric experiments were carried out using a flow rate of 18 l/h. The heating rate used for the above studies was 6, 12 and 20°C/min. For the determination of activation energy, the density data for ThO_2-UO_2 compacts obtained from the dilatometric data, and θ values obtained from the equation (1) are employed. A ρ-θ curve is then constructed for all the heating profiles for a chosen value of activation energy. The mean residual squares for the various values of activation energy have been calculated and the minimum has been found to be for 500 kJ/mol.



Shrinkage versus temperature plot for ThO_2-3%UO_2 in air for different heating rates



Mean residual squares for various values of activation energy



Master sintering curve for ThO_2-3%UO_2

From the knowledge of the activation energy, θ values are determined using (1) and are plotted against density (ρ). Such plot (master sintering curve) for ThO_2-3%UO_2 has been shown here.

- Discussion

The following conclusions are drawn from the above study:

The concept of MSC can be used to calculate the activation energy for sintering. The activation energy for sintering for ThO_2-3%UO_2 was found to be 500 kJ/mol. The sinterability of powder compacts made from different powders and fabrication procedures under different thermal histories, can be characterized through the master sintering curve. The MSC curve can also be used as an aid to compare the sinterability of different powders and to know the effects of additives, atmosphere and fabrication procedure of sintering.

4.6 PHYSICAL PROPERTIES OF FUELS BY ULTRASONIC VELOCITY MEASUREMENT

Mechanical properties such as elastic modulus, hardness and yield stress of the fuel are very important for assessment of the Pellet Clad Mechanical Interaction (PCMI). The fracture properties of sintered fuel pellets for thermal reactors play an important role in the formation of stress-induced cracks and fission-gas swelling during reactor operation. Physical property like heat capacity of nuclear fuel is needed for reactor physics and safety calculations.

Some of the properties like Elastic modulus, Shear modulus, Bulk modulus and Poisson's ratio, compressibility, yield stress, yield strain, fracture toughness, fracture surface energy, Debye temperature, heat capacity, Gruneisen parameter and lattice vibrational frequency have been determined /calculated by ultrasonic velocity measurement method. The data generated for $ThO_2+2\%UO_2$ and SIMFUEL based on UO_2 are highlighted.

Elastic constants like Elastic modulus, Shear modules, Bulk modulus and Poisson's ratio were determined from the measured longitudinal and shear wave velocities and density of the sample. Subsequently, using the elastic constants and measured micro hardness data yield stress was calculated. Yield strain was determined from yield stress and measured elastic modules. Fracture toughness was obtained using measured elastic constant and crack length generated at the corner of the indentations. Fracture surface energy and fracture modules were obtained from calculated fracture toughness. Debye temperature was calculated using ultrasonic longitudinal and shear wave velocities and lattice parameter. Debye temperature was used to obtain harmonic contribution to specific heat of the materials. Gruneisen parameter which is an average measure of lattice anharmonicity, is calculated using specific heat. Subsequently lattice vibrational frequencies were calculated using Gruneisen parameter.

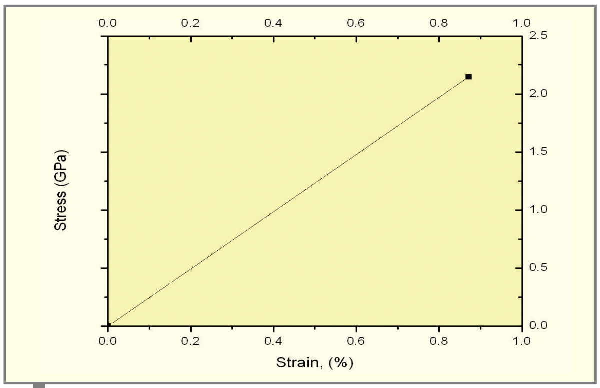
ThO_2 containing 2% UO_2 is the driver fuel for Advanced Heavy Water Reactor (AHWR). Sample pellets were prepared by conventional powder metallurgy route. It had a density of 96%TD.Simulated high burn-up nuclear fuels (SIMFUEL) attempts to replicate the chemical state and microstructure of the solid fission products generated in irradiated fuel so that detailed experiments can be undertaken without intense radiation fields to estimate the extent of degradation in the thermo-physical and mechanical properties of the fuel due to the presence of several fission products. Simulated UO_2 fuel (SIMFUEL) was prepared by adding high purity oxides of 11 different major fission products (Zr, Mo, Ce, Nd, Ru, Ba, La, Pd, Sr, Y and Rh) in UO_2 for an average burn up of 7000 MWd/ton for Indian PHWRs following ORIGEN code. UO_2 and SIMFUEL had densities of 95.72% T.D. and 90 % T.D. respectively.

Some of the properties of ThO_2+2% UO_2 and SIMFUEL based on UO_2 are given in the following tables and the stress/strain diagrams are shown in figures.

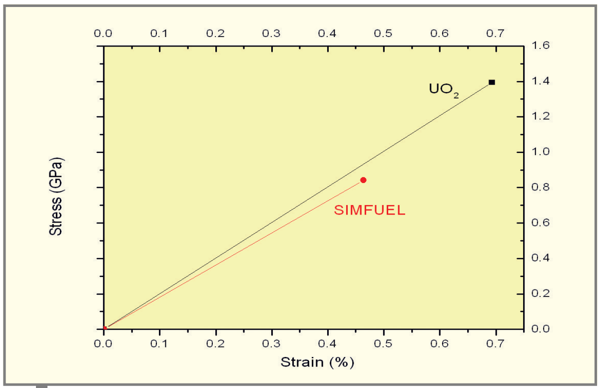
Property	UO_2	SIMFUEL
Shear modulus, G (Gpa)	76.3	70.25
Elastic modulus, E (Gpa)	201.10	181.64
Bulk modulus, K (Gpa)	185.07	147.94
Poison's ratio, γ	0.318	0.294

Heat capacity: C_p at constant pressure can be evaluated from the following relationship,

$$C_p = C_h + C_d + C_{el} + C_{anh} + C_{sch} + C_{SP} + \ldots\ldots$$



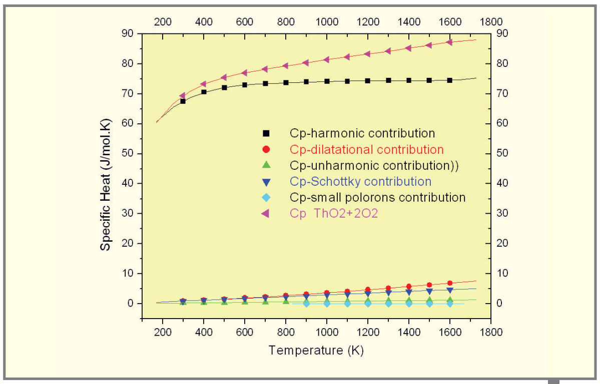
Stress-strain diagram of ThO_2+2%UO_2



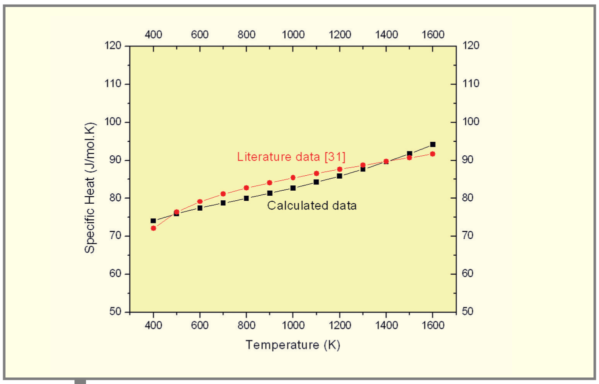
Stress-Strain diagram of UO_2 and SIMFUEL

where different contributions are: C_h is the harmonic due to lattice vibration, C_d is the dilational, C_{el} is the electronic, C_{anh} is the anharmonic, C_{sch} is the Schottky and C_{SP} for the formation of the small polaron to specific heat.

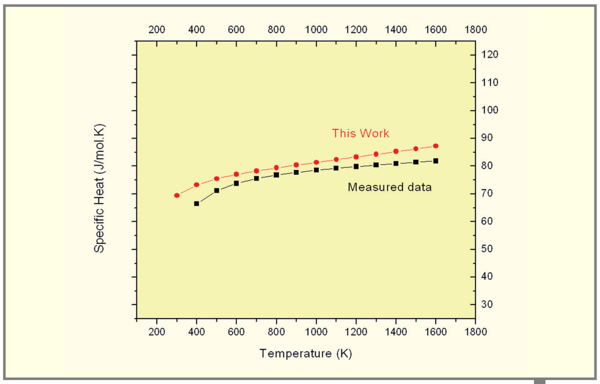
Debye temperature, which is determined by using measured longitudinal and shear wave sound velocities, was used in calculating harmonic contribution to specific heat of the ThO_2+2% UO_2, UO_2 and simulated UO_2 fuel. Other components of the specific heat which are contributing to total specific heat like dilational, anharmonic, schottky and small polaron were calculated from measured bulk modulus and other parameters obtained from literature. Specific heat of UO_2 and SIMFUEL were obtained from the summation of their individual contributions.



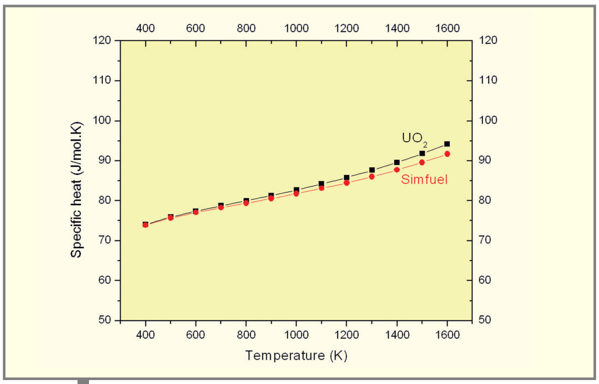
Graphical representation of contribution of each term to Specific heat of ThO_2+2%UO_2



Specific heat of UO_2



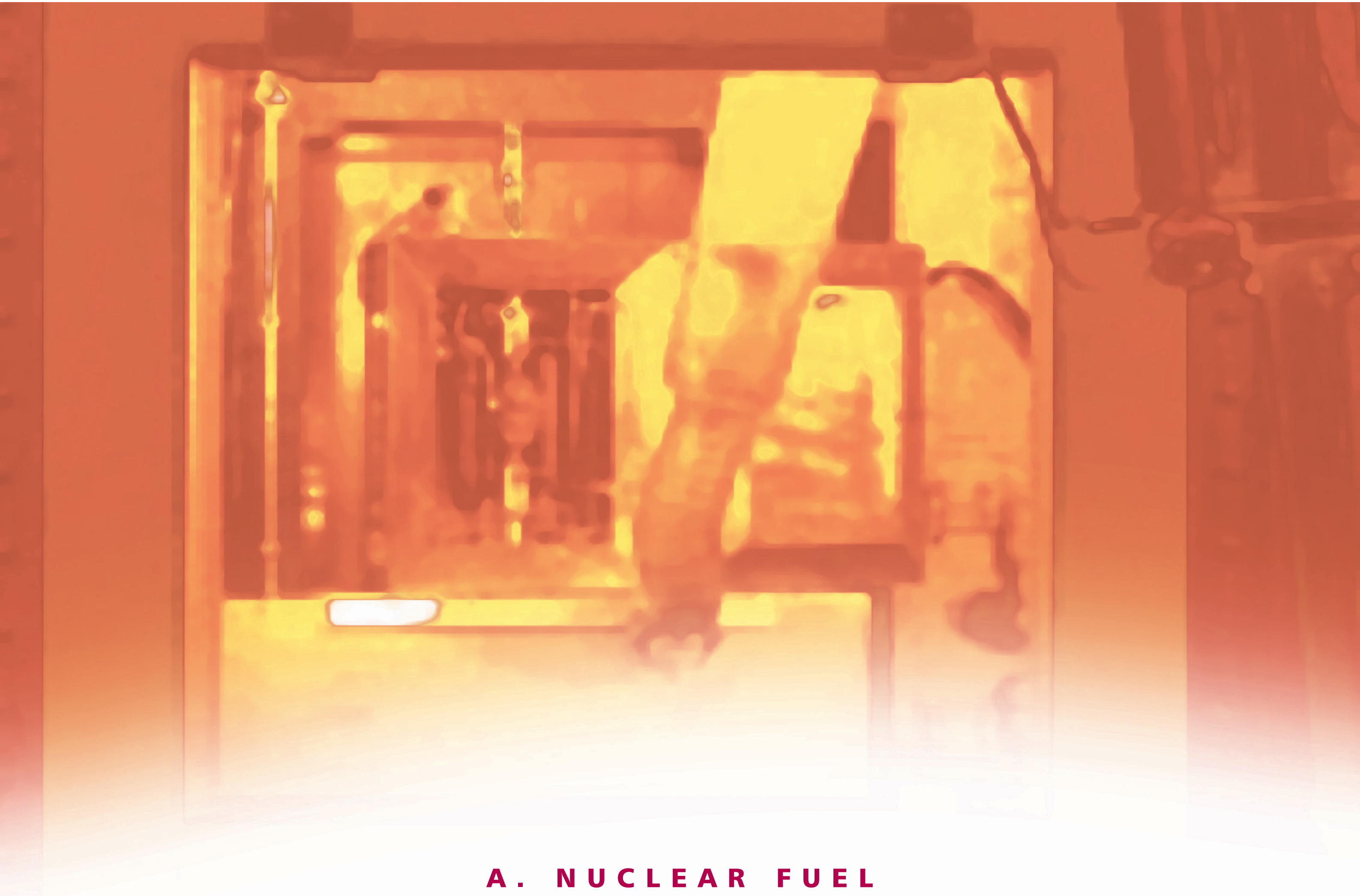
Specific heat of ThO_2+ 2% UO_2



Specific heat of UO_2 and Simfuel

Sr no	Property	Numerical value at 298 K
1	Shear modulus, G GPa	97.899
2	Elastic modulus, E GPa	246.375
3	Bulk modulus, K GPa	169.9
4	Poison's ratio, γ	0.258
5	Compressibility, β Gpa^{-1}	5.898×10^{-3}
6	Micro-hardness (VHN)	787.11
	(Gpa)	7.72
7	Yield stress (Gpa)	2.147
8	Yield strain	0.0087155
	(%)	0.87145
9	Fracture Toughness, K_{1C} ($Mpa*m^{0.5}$)	1.203579
10	Fracture surface energy, J_{IC} (J/M^2)	2.7436
11	Fracture Modulus, E_f ($*10^{12}$) (Nm^{-2})	0.528
12	Debye Temperature, $\Theta_{D,}$ K	432.569
13	Specific heat, C_p (J/mol.K)	67.99
14	Gruneisen parameter	1.88

Physical and mechanical properties of ThO_2 – 2% UO_2 fuel



A. NUCLEAR FUEL

5. POST IRRADIATION EXAMINATION

INTRODUCTION

Nuclear reactor core structural material and nuclear fuels are used in a very hostile environment of high temperature, high pressure and with intense beta, gamma and neutron irradiation. Performance of these materials in critical components of the nuclear reactor need to be assessed for assurance of safe continued operation of Nuclear Power Plants.

Detailed post irradiation examination of the nuclear fuel and critical reactor core components are periodically carried out as a part of surveillance programme to monitor degradation properties for ageing and life management studies.

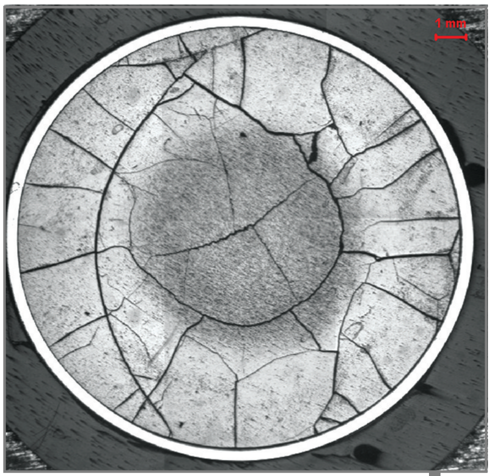
Candidate materials for advanced nuclear reactor systems are irradiated in research reactor in controlled conditions to evaluate their suitability prior to large-scale deployment in nuclear power reactors.

Feedback information generated by post irradiation examination is used by designers, fabricators, reactor operators in improving design, safety & economy of the nuclear plant systems. The post irradiation examination data is used by regulatory body for assessment of safety and licencing continued operation of nuclear power plant.

5.1 POST IRRADIATION EXAMINATION ON FUEL

■ High Burnup PHWR Fuel

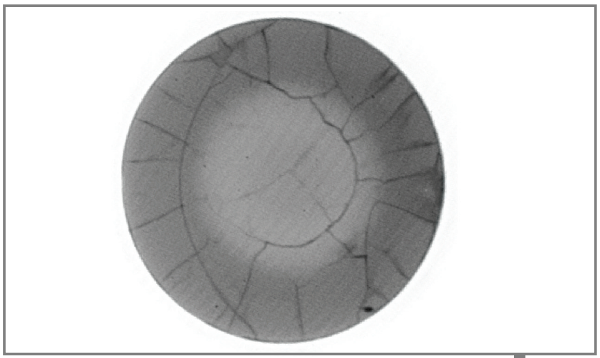
PIE of two fuel bundles with a burn up of ~15,000 MWD/TeU was carried out to give a feedback on the possibility of increasing the discharge burn up. The outer fuel elements had released 15% of the fission gas leading to an internal gas pressure of ~ 20 atmosphere in the cold condition.



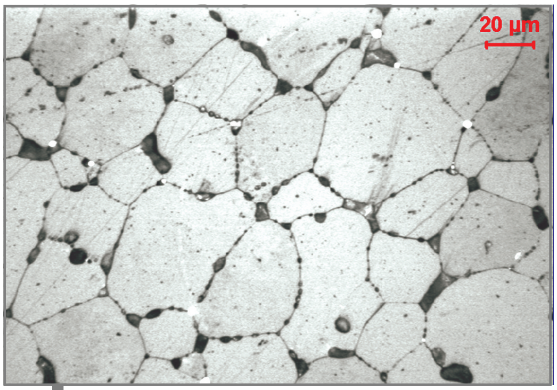
Fuel Cross-section

Detailed metallographic examination and β–γ autoradiography carried out did not show pellet-clad interaction. However significant fission product redistribution was observed.

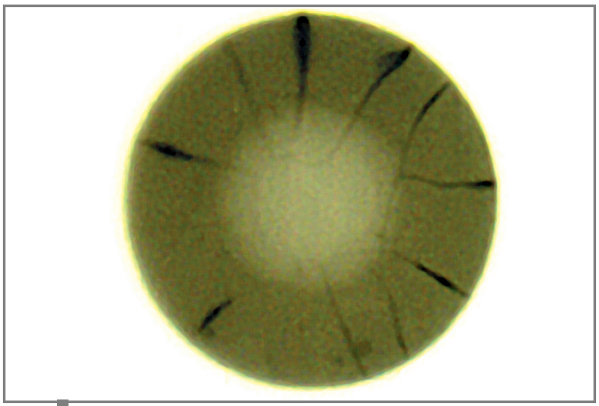
The estimated temperature at the center of the outer fuel pins was about 1600°C. Microstructure of the central zone revealed grain boundary decorated with interconnected porosity leading to higher fission gas release.



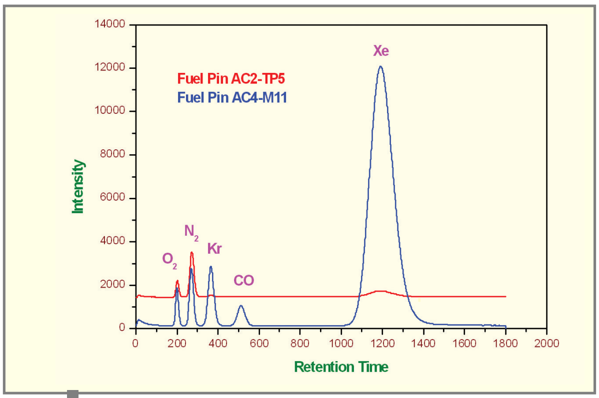
β-γ Autoradiograph



Microstructure at the Central Region



Cs^{137} Redistribution in MOX Fuel



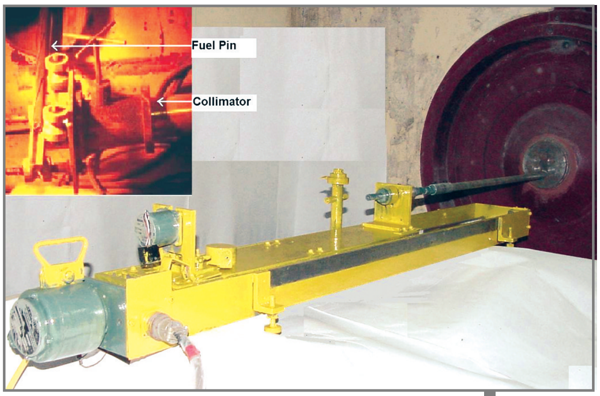
Chromatogram of Fission Gases

■ Irradiated MOX Fuel

PIE was carried out on experimental MOX (UO_2-4%PuO_2) fuel elements of AC-4 cluster, that contained fuel elements pellets produced by different fabrication routes and varying pellet clad gaps and filler gas composition, after test irradiation in pressurised water loop (PWL) of CIRUS.

Fuel pins with controlled porosity pellets and pellets with central hole showed very low fission gas release even at 110 W/cm^2 heat flux.

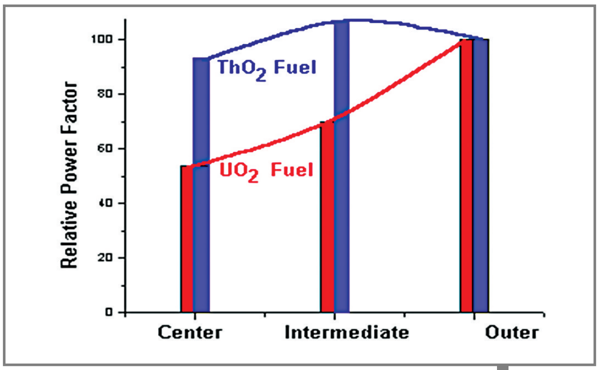
Fuel pin containing low temperature sintered pellets showed abnormal gas release. Presence of CO which was found in the fill gas probably has caused the abnormal behaviour.



Scanning Stage for Fuel.

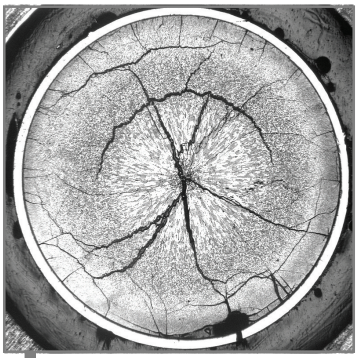
PIE OF ThO_2 FUEL

Post Irradiation Examination (PIE) was carried out on ThO_2 fuel bundles of KAPS irradiated up to 3164 n/Mb, which is equivalent of 11725 MWD/T of burnup. Detailed PIE studies showed excellent behaviour of ThO_2 fuel during reactor operation. Fuel samples cut from one of the outer pins were subjected to radiochemical burn up measurement and isotopic analysis. The results of burn up measurements were close to estimated value. However, the measurement of isotopic content of U^{232} differed significantly from the theoretical estimation. The PIE results are being used for verification and up gradation of the computation code and the cross sectional parameters used for calculations and predictions of ThO_2 fuel. Gamma scanning was carried out on irradiated ThO_2 and UO_2 fuel pins of different burn-up to generate information on axial burn-up distribution and power distribution profile in the fuel bundle using the Cs^{137} as fission monitor.

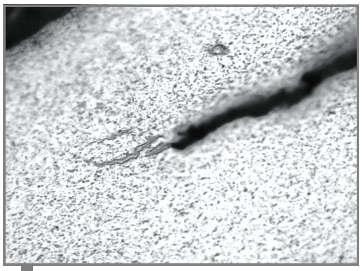


Power Profile In Tho_2 and UO_2 Fuels

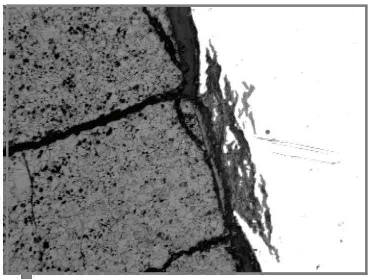
The relative power profile of UO_2 and ThO_2 fuel bundle showed significant difference. The inner ring fuel elements in ThO_2 fuel



Cross Section of Failed Fuel



DHC Crack



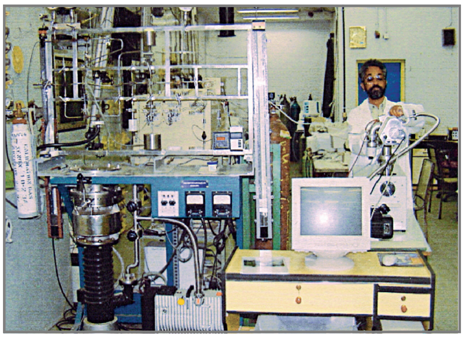
Microblister

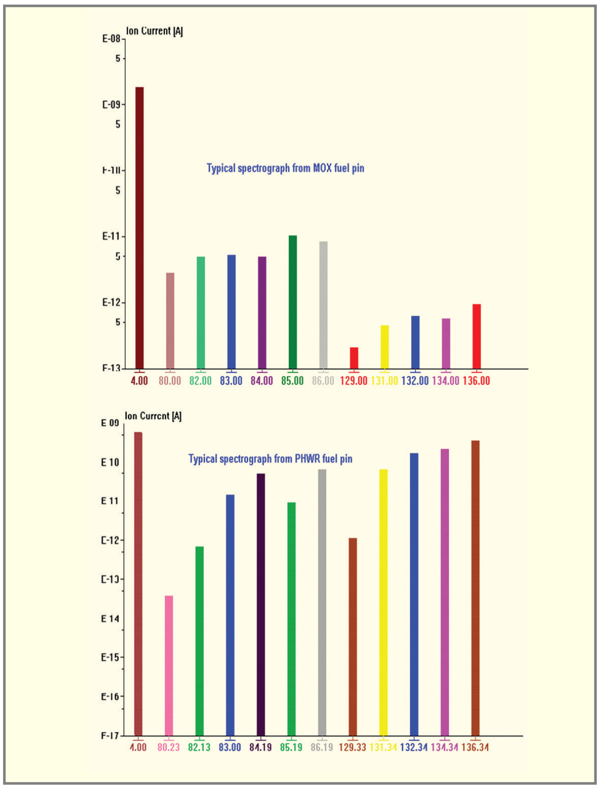
bundle showed higher power than the outer fuel elements in the bundle showing effect of epithermal neutrons.

Low burn up Fuel Failure

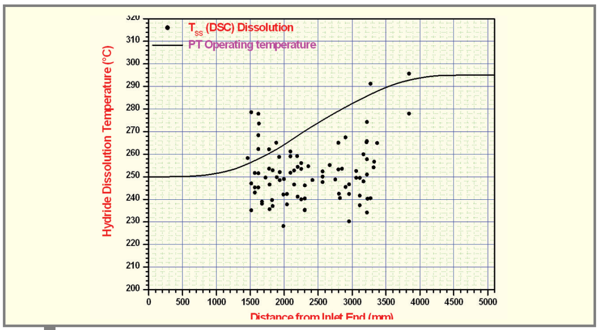
Detailed investigation carried out on low burn up failed PHWR fuel indicated high center temperature of fuel.

The failure has been caused by insitu power ramping leading to pellet clad interaction and internal hydriding of fuel cladding.





Formation of microblisters on inner surface of cladding and through wall clad cracks at multiple locations were observed.



Hydride Dissolution Temperature (TSS)

Analysis of Fission Gases

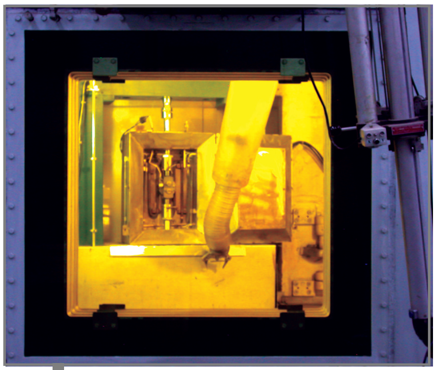
The content of released fission gases and their composition was measured for the MOX, UO_2 and ThO_2 fuels,irradiated in research and power reactors.

The isotopic composition of gases released from the fuels is given below.The irradiated ThO_2 fuel did not release much gas.The PHWR UO_2 fuel released gases, the quantity being dependant on the location of the fuel element in the bundle.

5.2 STUDIES ON PRESSURE TUBES

Life Management of Pressure Tubes

As a part of Life Management of Pressurised Heavy Water reactor, scrape sliver samples were retrieved from operating pressure tubes. The samples were analysed by Differential Scanning Calorimetry (DSC) technique to generate data on total equivalent Hydrogen (H_{eq}) content of the pressure tubes which was used for assessment of safety of pressure tubes in the reactor for continued operation.

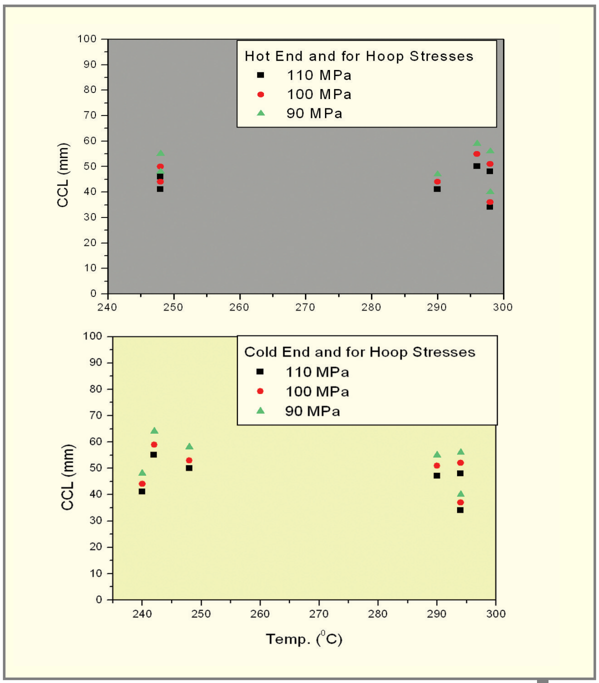


UTM Housed Inside Hotcell

Fracture Toughness of Irradiated Pressure Tube

There is a generic reduction in the pressure tube fracture toughness due to the synergistic contribution of cumulative neutron irradiation and deuterium pick up during in-reactor residence. The degradation in fracture toughness properties from surveillance pressure tubes removed from reactor need to be monitored to estimate the critical crack length (CCL) and assure leak before break (LBB) criterion.

Ring Tension Test Specimen



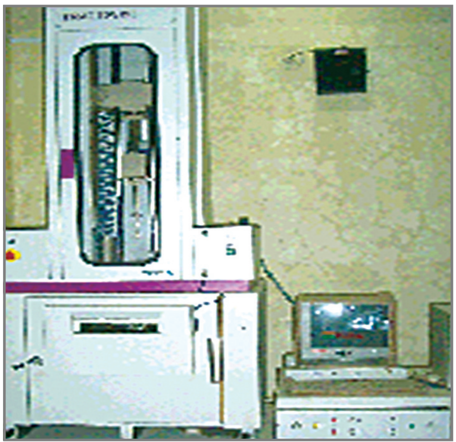
CCL Values of The Pressure Tube
at Inlet and Outlet Ends

Zircaloy pressure tube J-07 from Madras Atomic Power Station (MAPS #1) was subjected to post irradiation examination (PIE). The PT had experienced 9.5 effective full power years (EFPY) of reactor operation and had hydrogen equivalent (Heq) content upto 200 ppm. Fracture toughness and CCL were evaluated from tube sections from inlet end, outlet end and mid length of the irradiated PT using transverse tensile strength and transverse ductility obtained from ring tension test.

The test results indicated that the zircaloy-2 PTs beyond 9.5 EFPY and containing 200 ppm of hydrogen have reached limit of safe operation.

Instrumented Impact Tests

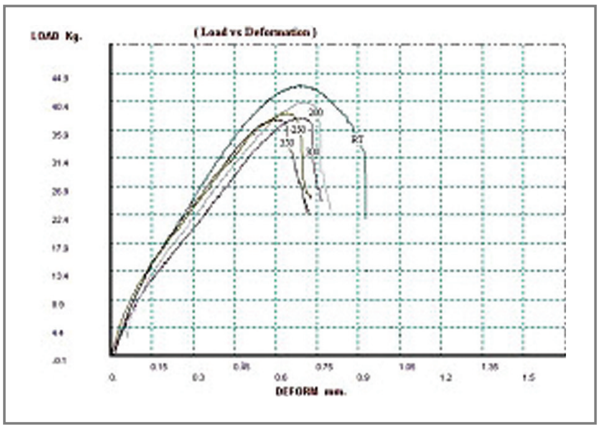
Drop tower impact test machine fitted with a special anvil was used for testing V-notch impact test specimens made out of irradiated Zircaloy-2 pressure tubes, keeping the curvature intact.The equipment has environmental chamber for testing samples from -100^{0}C to 600^{0}C.



Drop Tower Impact Machine

This test offers an alternative conventional method for characterising the irradiation and hydride-induced embrittlement effect in reactor operated of pressure tubes.

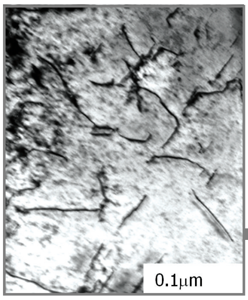
Small Punch Testing System



Miniature Sample Testing:

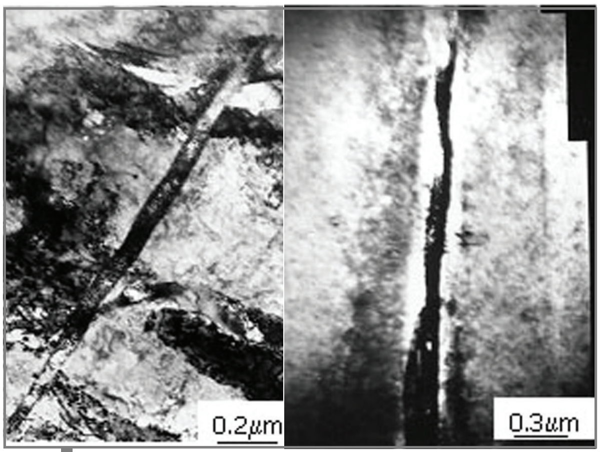
Small Punch Test (SPT)

Small Punch Test (SPT) technique was developed for evaluating tensile and fracture toughness properties using thin disc samples of 3 mm dia x 0.25 mm thick.Miniature sample testing provides the advantage of testing higher radioactive materials with lower person-sievert exposure. The system has an environmental chamber to carry out testing at temperature in the range of –30 to 600°C



Defect Structure In Irradiated Zircalloy-2

The system has been used for estimation of the mechanical properties of A533 RPV Steel and for evaluation of irradiated pressure tube and cladding tube properties.



(a) (b)

Hydrides in Zircaloy–2 Pressure Tube, (a) unirradiated and (b) irradiated

TEM Studies on Irradiated Pressure Tubes

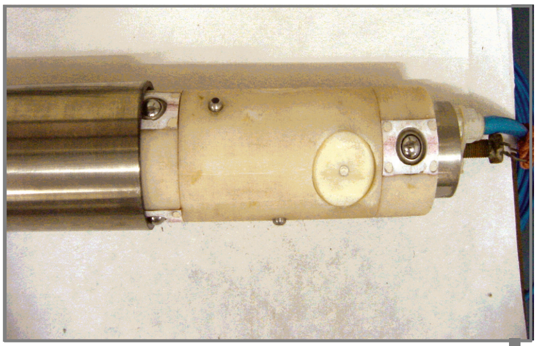
The microstructure of irradiated pressure tube has been examined by transmission electron microscope (TEM). The microstructure and the defect structures of the unirradiated and irradiated material were compared.

Different morphologies of hydrides were observed in the unirradiated and irradiated pressure tube samples. The samples of unirradiated pressure tube showed hydride needles with high aspect ratio and sharp interfaces. The samples of the irradiated pressure tube revealed a large size range of hydrides starting from nucleation stage.

Oxide Layer Thickness Measurement

Non-destructive method based on eddy current technique is developed for the oxide layer thickness measurement of irradiated pressure tubes. The system consists of indigenously developed eddy current lift off measuring probes, probe holding and positioning device and eddy current measuring equipment .

Oxide layer thickness measurements on a pressure tube which had partially operated in dry quarantined condition



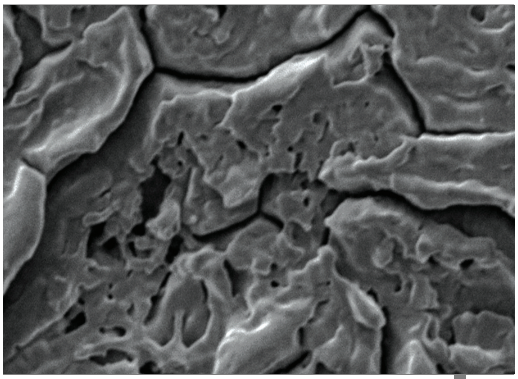
Eddy current Probe for Oxide Thickness

ware carried out. The oxide layer measurements by metallography of pressure tube were compared with eddy current measurements.

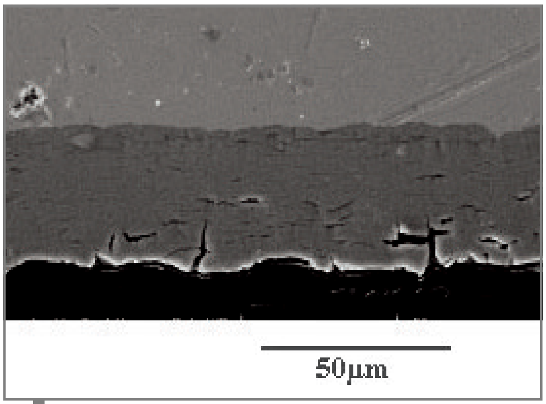
Oxide Morphology

The inside surface of the pressure tubes used in PHWRs is exposed to high temperature coolant water during reactor operation. This causes oxidation of pressure tube leading to hydriding and embrittlement. Initially oxidation rate is slow but later when oxide becomes thick, an accelerated oxidation takes place. The morphology of oxide in irradiated pressure tubes was examined using scanning electron microscopy and optical microscopy.

SEM examination revealed extensive surface cracking along grain boundary and presence of micro-pores and micro-cracks in the oxide of 25 µm thickness. Thin oxide layer (< 15 µm) was comparatively dense, adherent and contained only fine surface cracks.



Micro-cracks and pores in thick oxide



Thick oxide layer in pressure tube

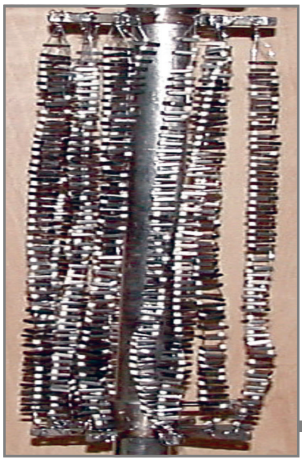
Radiolysis of coolant water trapped in the porous oxide creates highly localized water chemistry near the metal-oxide interface independent of the bulk water chemistry which causes acceleration in the oxidation and hydrogen pickup kinetics.

Long-term Corrosion Test of Zr-2.5%Nb Pressure Tube Offcuts

High temperature water side corrosion of zirconium alloys are sensitive to the chemical composition and microstructure of the alloy. In order to rank the corrosion behaviour, coupons were prepared from the offcuts of 306 pressure tubes of KAPS-2. 10 mm x 10 mm and 4 mm thick curved samples were cut from 612 offcuts from both ends. These samples were numbered by punching serially using a numbering machine. The samples were metallographically prepared and chemically polished to remove the surface deformed layer to produce shining surface.

Strands of 50 samples each were made using stainless steel wire with ceramic beads sandwitched between two samples as spacer. Strands were fixed on the specimen hanger.

Long term autoclaving of the samples are being carried out at 400°C and 10.3 MPa steam pressure.



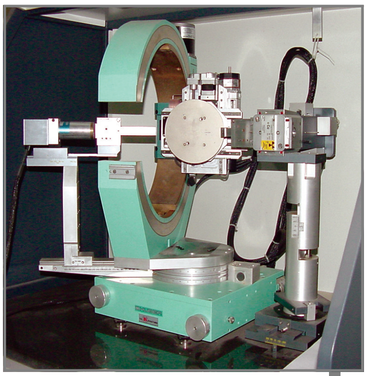
Hanger Rod with the coupons

Texture Analysis of Zr-2.5% Nb Pressure Tubes

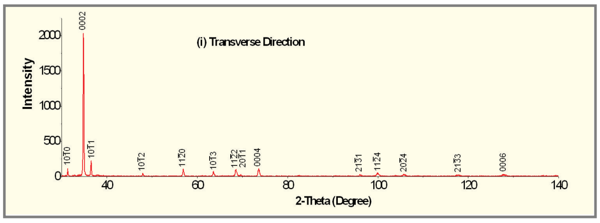
Crystallographic texture has significant influence on mechanical properties, creep, irradiation growth, orientation of zirconium hydride precipitates and delayed hydride cracking of the pressure tube in reactor operation.

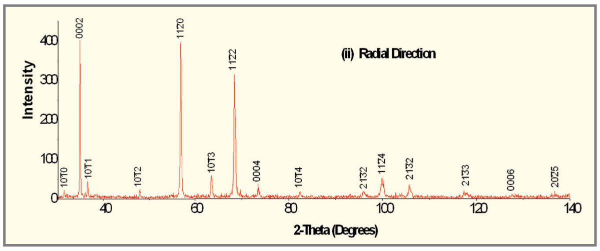
A X-Ray Diffractometer with a large Eulerian cradle has been used for the texture analysis. 155 samples out of 306 offcut samples of first generation Zr-2.5% Nb pressure tubes of KAPS-2 have been analyzed.

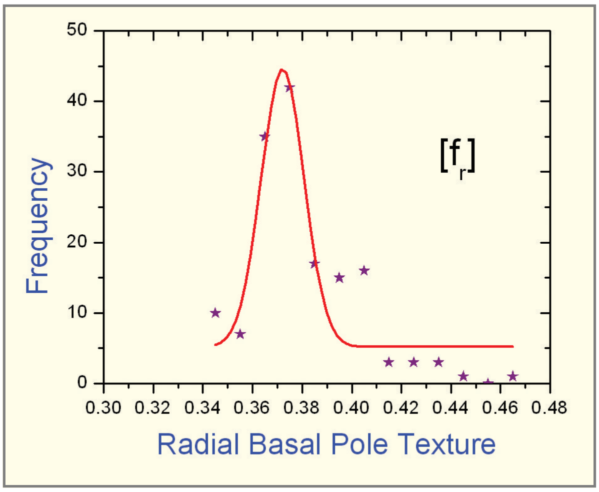
For texture measurement, samples were taken from transverse, radial and axial directions of the pressure tube in such a way that the reflection surfaces were normal to the selected directions. The XRD patterns were recorded on the samples in the 2θ range 30°-140°, on a X-Ray Diffractometer. XRD pattern of zirconium powder sample was also recorded to represent a random sample. Diffractograms of pressure tube offcut samples from transverse and radial directions using Cu Kα radiation are shown in the figures. Preferred orientation factors for basal poles f_t, f_r and f_a using Kearns method, were determined from the intensity data of 2θ, X-Ray Diffractometer scan of the samples. A computer program was developed and used to calculate orientation factors. Variations in the transverse (f_t) and radial (f_r) texture parameters observed in the different pressure tubes are shown below.

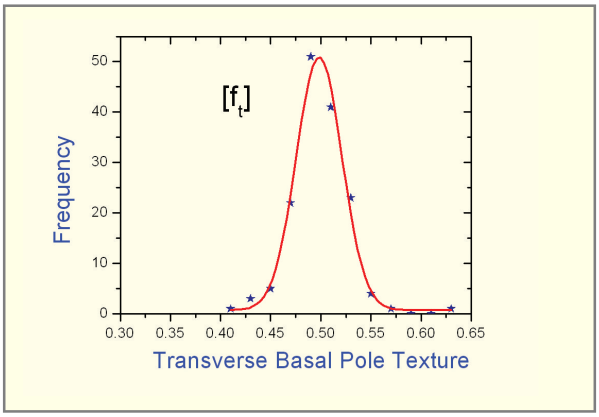


Eulerian Cradle for XRD

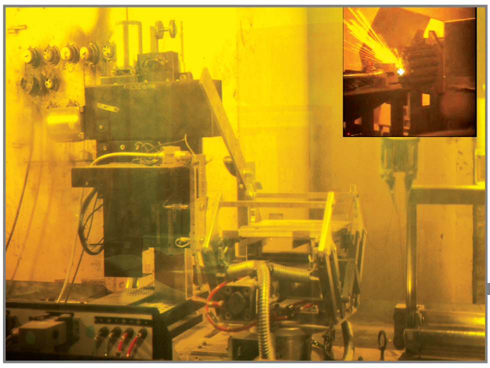








5.3 LASER BASED DISMANTLING SYSTEM



Irradiated Bundle Dismantling Using Nd-YAG LASER

A LASER based system for dismantling of PHWR fuel bundles using Nd-YAG beam has been developed through collaborative effort of BARC and CAT. The system was installed in the hot cells using an optical fiber and LASER head was manipulated using computer numerical control for accurate positioning and cutting operation. The system was successfully used for dismantling of 12 irradiated PHWR fuel bundles received for PIE in the recent campaign.

5.4 CASK FOR IRRADIATED PHWR FUEL

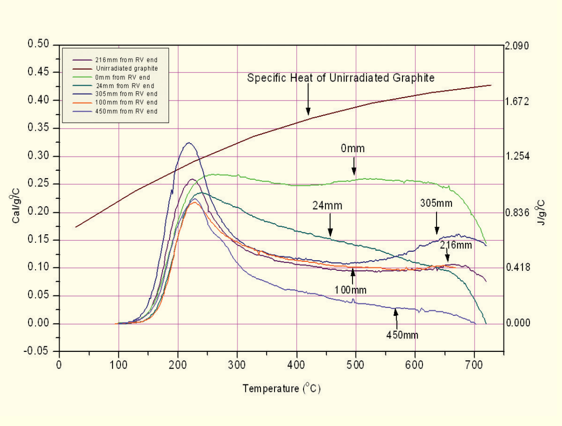
As a part of safety demonstration, prototype double PHWR bundle transport cask was subjected to 9 M drop test, punch test and fire test. The feedback information was used to modify the cask design. Two double bundle PHWR fuel transport cum storage casks of modified design has been fabricated.

These casks will be used for transportation of irradiated UO_2 and ThO_2 fuels from reactor site to the hot cells facility for PIE studies.

5.5 WIGNER ENERGY STUDIES ON CARBON MATERIALS

■ Wigner Energy in Graphite Reflector

The Wigner energy storage and release behaviour of the graphite reflector was evaluated after 30 years of operation. The irradiated graphite plug was sampled and subjected to different annealing cycles. Graphite samples from one location, at 305 mm from the reactor vessel end, showed that rapid



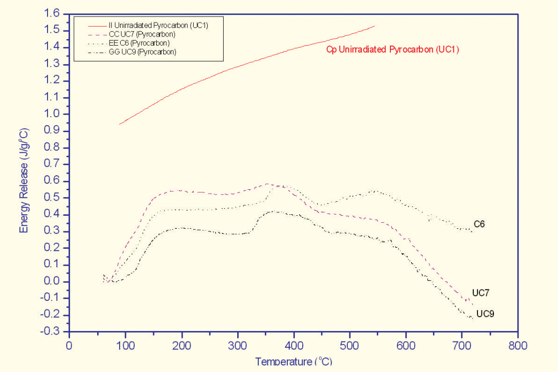
Wigner Energy in CIRUS Graphite

Wigner energy release during annealing is possible which could lead to sudden temperature increase from 189°C to 290°C. The conditions for safe annealing of the stored Wigner energy were established experimentally using differential scanning calorimetry (DSC).

The reactor was taken to high power operation under controlled cooling conditions to allow an operating temperature of 120°C for the graphite. The stored energy in the graphite after the high power operation was estimated by sampling from another graphite plug removed from the east thermal column, which showed residual Wigner energy in safe levels.

■ Wigner Energy of Pyrocarbon Scattering Material for AHWR

Developmental work is being carried out for obtaining non-crystalline high density pyrocarbon as the scatterer material of AHWR with joint effort of BARC and NPL, Delhi. The pyrocarbon material developed by BARC was characterized to obtain the porosity and density of the compacts. The pellets prepared were irradiated in DHRUVA reactor. Wigner energy storage characteristics of the irradiated pellets were measured by DSC technique. The pyrocarbon pellets showed crystallinity and storage of considerable Wigner energy after irradiation.

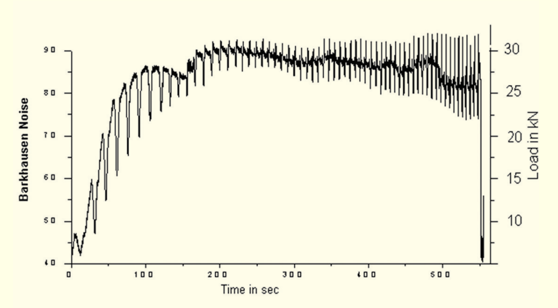


Wigner Energy in Pyrocarbon

5.6 BARKHAUSEN NOISE MEASUREMENT

Magnetic Barkhausen Noise (MBN) probe was interfaced to a Laptop PC and a user friendly software was developed for online data acquisition, display and storage for analysis.

Fatigue Test of PHT Piping

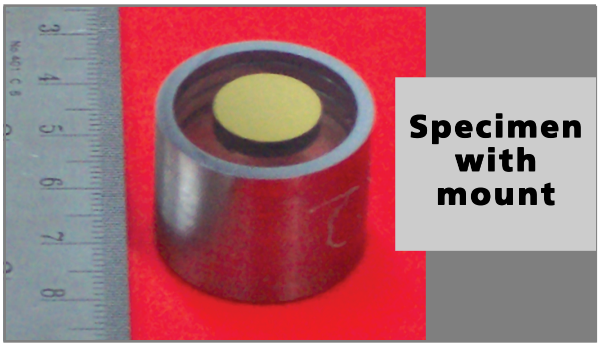


J-integral Test on CT Specimen

The system was used during fracture toughness test on compact Tension (CT) specimen and PHT piping subjected to monotonic as well as fatigue loading conditions.

5.7 AUTOMATED METALLOGRAPHIC SAMPLE PREPARATION SYSTEM

Surface preparation of specimens for Metallographic studies on irradiated material involves skilled manpower and lot of remote handling of radioactive specimens. Being a labour and person-sievert intensive activity, it puts limitations on number of samples that can be prepared for the studies. In view of this, automated systems have been developed for surface preparation of specimens.

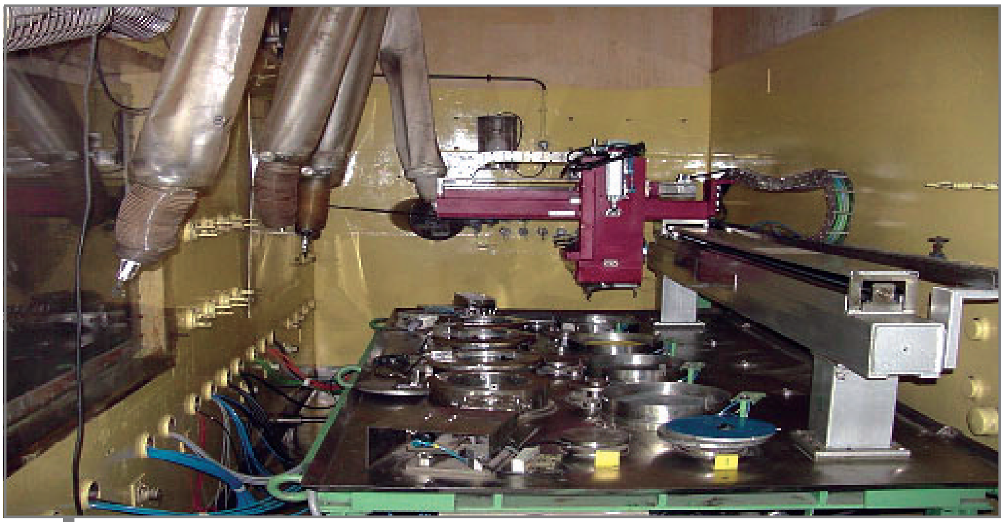


The system includes grinding and polishing stations, water jet cleaning station, ultrasonic cleaning stations, drying station, sample loading and unloading station, automated head for movement of the sample holder disc from one station to other spare disc locations.

The systems offer facility to change sequence of operations and remote changing of grinding/ polishing discs from the stations.

The systems have been installed and commissioned for PIE of irradiated structural components and fuels. This development has increased the throughput and the person-sievert budgeting.

Disc Changing Operation



Automated Metallographic Sample preparation system in Hot Cell

B. REPROCESSING

6. INDIAN PROGRAMME ON REPROCESSING

INTRODUCTION

Reprocessing forms an integral part of the Indian Nuclear Energy Programme which is based on the optimum resource utilization. Aqueous reprocessing based on PUREX technology is in use for more than 40 years and has reached a matured status. THOREX process for the recovery of ^{233}U and thorium from irradiated thoria is also in use on a smaller scale and is being developed into a robust process for meeting the challenges of thorium fuel cycle.

6. INDIAN PROGRAMME ON REPROCESSING

India has chosen to follow a closed fuel cycle policy to ensure long term energy security. This calls for adopting reprocessing, conditioning and recycle (RCR) option. Having low reserves of uranium and high reserves of thorium, this strategy of reprocessing and recycle of uranium and plutonium would lead to optimum resource utilization. Thus, in the Indian context spent fuel is a vital resource material and not a waste to be disposed off.

Indian reprocessing journey started way back in 1964 with the commissioning of a reprocessing plant at Trombay, serving to demonstrate the indigenous capability and expertise in this vital area of technological importance. Currently, India has three operating reprocessing plants based on PUREX technology – one each at Trombay, Tarapur & Kalpakkam. While the Trombay facility reprocesses spent fuel from research reactors, the plants at Tarapur and Kalpakkam process the oxide fuels from PHWRs. Operating experiences over the years have contributed to the mastering of the PUREX technology, leading to higher recoveries, lower exposures and reduced environmental discharges.

Standardization of the designs has been achieved. Additional reprocessing facilities are being setup with the active participation of Indian industry to accelerate the programme.

Reprocessing of irradiated thoria has been carried out by employing the THOREX process. The challenges in reprocessing of mixed oxide fuel with uranium, plutonium and thorium are being addressed.

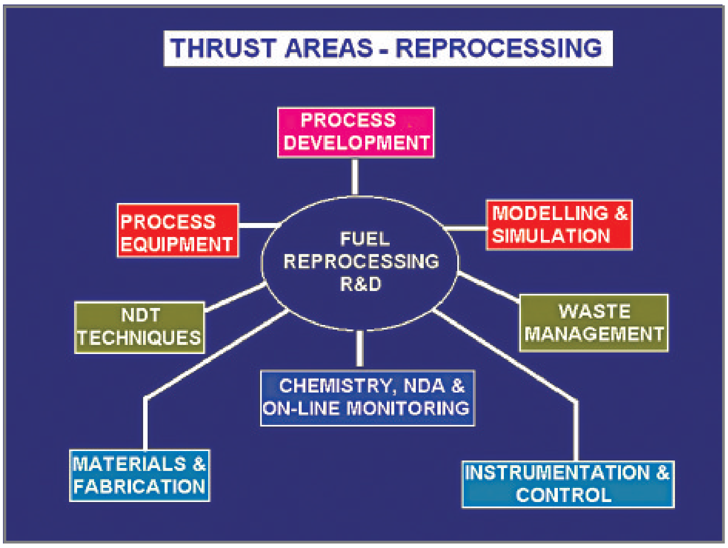
6.1 OPERATING PLANTS AND THEIR PERFORMANCE

The first Plutonium Plant at Trombay reprocesses research reactor spent fuel with a capacity of 60 tons per year. The second and third plants are located at Tarapur and Kalpakkam and reprocess spent fuel from power reactors. Each of these plants has an operating capacity of 100 tons per year. Reprocessing capacities are being augmented in a phased manner to match the Pu requirement.

The planning of reprocessing capacity has to match with the requirement of Pu and U-233 by fast breeder reactors (FBRs) and advanced pressurized heavy water reactors (AHWRs).

The Trombay plant, commissioned in 1964, reprocesses natural Uranium, Aluminium clad metallic fuel. The head end process involves chemical de-jacketting and dissolution in concentrated nitric acid under reflux conditions. This is followed by a decontamination cycle, a partition cycle and two separate parallel cycles for the purification of uranium and plutonium based on PUREX process

The successful operations of this plant not only provided the required Plutonium but also gave sufficient impetus for acquisition of skills in the domain of reprocessing. These included, optimization of process parameters for improved performance,



Reprocessing Plant, Trombay

operational safety, waste minimization, development of equipment and systems for higher plant throughput, techniques for representative sampling and their analyses, on-line instrumentation and data acquisition etc.

The second plant located at Tarapur and commissioned in 1975 reprocesses zircaloy clad oxide spent fuel using chop-leach technique for the head end.

Besides providing the required Plutonium, several campaigns of reprocessing have also been carried out under international safeguards in this plant, thereby, providing valuable experience in material accounting practices adhering to the international standards.

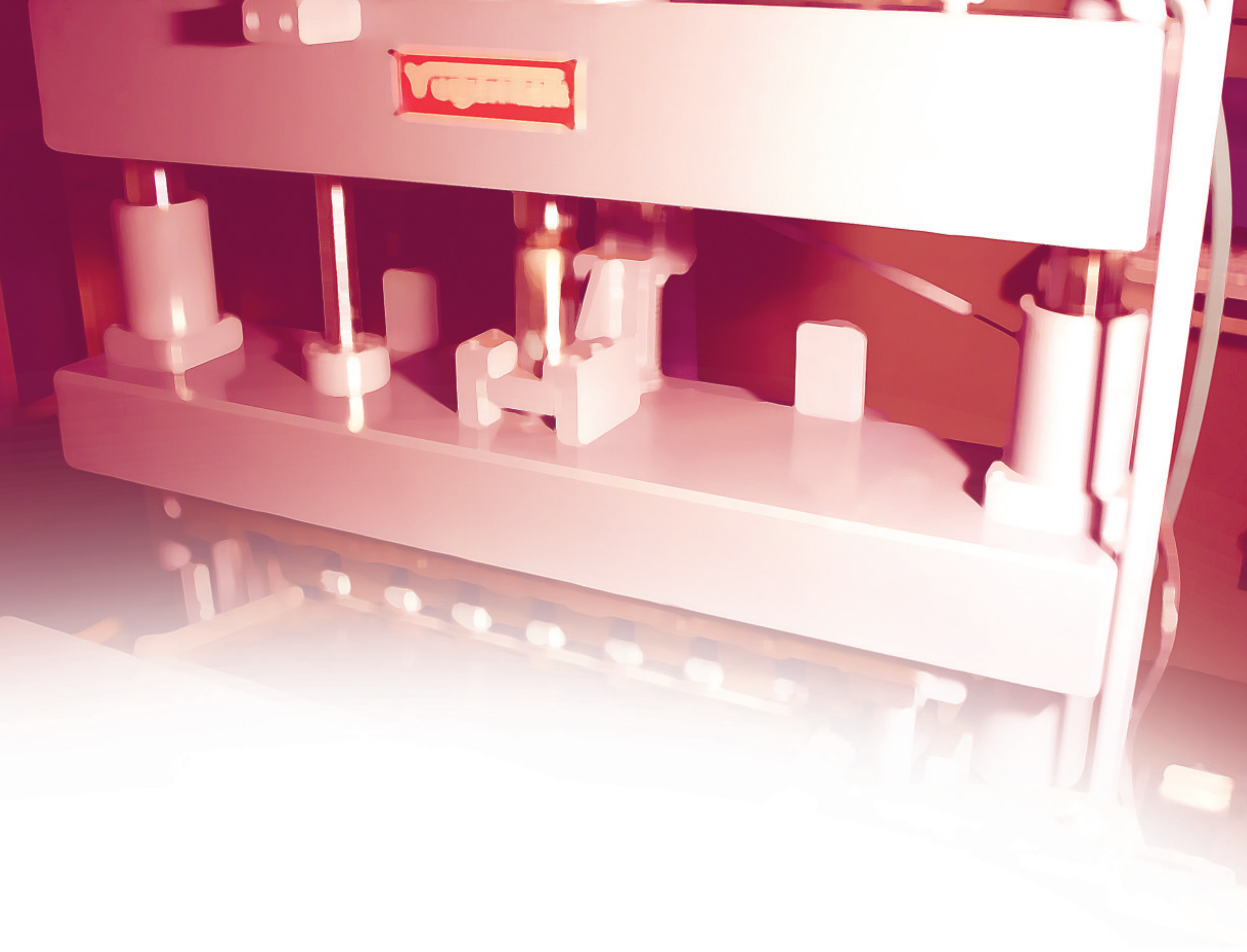
The third plant at Kalpakkam caters to the needs of reprocessing zircaloy clad natural uranium oxide spent fuel from PHWRs. This plant serves as a standard design for future plants aiming at attaining the nameplate capacity with sustained operations.

PREFRE Plant, Tarapur

In view of the inherent corrosive environment and due to the poor choice of materials in the initial days, it was imperative to decontaminate and decommission (D&D) the Plutonium plant, Trombay for effecting the necessary replacements to extend its life. This opportunity was also utilized to modify and enhance the capacity of the plant. The entire decommissioning programme was meticulously planned and successfully carried out. The success of the decommissioning operations could be gauged from the insignificantly low background levels of radiation fields ultimately achieved, the absence of transferable contamination on cell surfaces, and the fact that personnel exposures were well within the prescribed limits. Extent of D&D of the cells permitted almost unrestricted access into the cells for carrying out fresh installation. The decommissioned and augmented plant started operating from 1983 onwards.

Kalpakkam Reprocessing Plant

Around 40 years of experience in the spent fuel reprocessing based on PUREX process has given the confidence that this technology can be successfully employed for the recovery of both U and Pu with yield exceeding 99.5%. Substantial reduction in waste volume has been achieved over the years by resorting to salt free reagents. Evaporation followed by acid reduction by formaldehyde is used to reduce the high level waste volume. The overall decontamination factors for the Pu and U products from fission products exceed 10^6 and are handled subsequently with minimum radiation protection.



B. REPROCESSING

7. ENGINEERING DEVELOPMENT

INTRODUCTION

Spent fuel treatment based on PUREX technology is well entrenched to meet the present and near future challenges. Developments taking place elsewhere in the frontiers of Science and Technology are being absorbed into this field to improve recovery, to reduce exposure and to reduce waste volume generation. Engineering developments have helped this technology to keep pace with the increasing demands made by health and safety regulations. Developments continue to take this technology to further heights. Engineering developments have a major role to play in the thorium fuel cycle due to high energy gamma nuclides associated with this fuel cycle.

7. ENGINEERING DEVELOPMENTS

Reprocessing plants are being built with a high degree of remotisation and automation. Elaborate safety features are incorporated in the design to obviate criticality incidents and to minimise radiation exposure. Over the years, improved practices have brought down the environmental discharges to much lower levels than the stipulated values.

Developments taking place elsewhere in the science and technology frontier had also its impact on the PUREX process. Equipment design, computerised data logging and control, robotics and automation, material development etc. have taken this technology to further heights by reducing direct maintenance, providing automatic built-in safety features, reducing radiation exposure to the working personnel, improving the project management with reduced construction time.

Head-end systems have undergone major engineering developments. An indigenous shearing machine was developed and installed at KARP incorporating many design improvements. The design of shearing machine and clapper assembly is being standardised for subsequent reprocessing plants.

Laser-assisted dismantling of the fuel bundle followed by single pin chopping is also being developed. Developments are under way to design and fabricate indexing casks and automated charging of the fuel bundles into the shearing machine magazine.

Homogeneous sampling of key measurement points is vital to the nuclear material management strategy. Vacuum assisted airlift operated sampling design has been developed and tested thoroughly during the IAEA safeguarded campaigns at Tarapur. Further efforts are on to automate the sampling system to minimize exposure.

The operating life of a reprocessing plant is determined by the corrosion resistance of the material of construction. With a better understanding of the corrosion of austenitic stainless steel in nitric acid environments, tighter specifications have been formulated. These challenges have led to the development of nitric acid grade(NAG) type 304 L stainless steel in the country with corrosion resistance rate as low as 10 mpy.

Currently PUREX process is a multi-cycle process and is being continuously developed to change into a single cycle process. Some of the features needed are computer control of extraction column with on-line monitoring and automated control of process parameters. Maintenance-free short residence contactors and annular pulse columns which are safe with respect to criticality with provisions for near real time accountancy and *in-situ* electrochemical, photolytic or other Pu and Np reduction and partitioning techniques for an ultimate salt-free process. Minimization of losses to waste, improvements in solvent quality, crystallization of uranyl nitrate, direct denitration of products to oxide, co-processing and co-conversion for fuel development, recovery of useful isotopes, separation of long-lived actinides and fission products under P&T option are some of the challenging R&D tasks ahead.

Irradiated thorium processing also needs developmental efforts for better head-end techniques for mechanical dejacketing of zircaloy or stainless steel cladding and dissolution of Thoria, corrosion-resistant materials of construction, modifications in process to deal with ThO_2-PuO_2 fuels, behaviour of ^{231}Pa in the process and its long term impact in waste, radiological safety in handling $^{233}U/^{232}U$. The state-of-the-art remote handling technology and robotics will have maximum application because of the associated activity of ^{232}U daughter products.

7.1 DEMONSTRATION FACILITY FOR ^{233}U SEPARATION FROM IRRADIATED THORIA

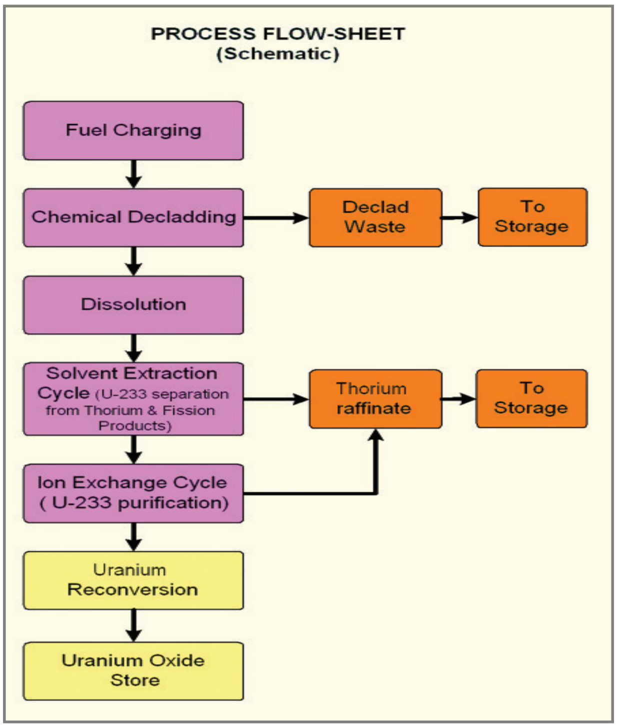
Based on the pilot plant experience in the recovery of ^{233}U from Al clad ThO_2 irradiated in the J annulus of CIRUS, an engineering facility, UTSF, was designed, fabricated and commissioned in the old Evaporation Plant at Plutonium Plant.

3% Tributyl Phosphate in dodecane was used as the solvent. CALMIX, developed in-house, was used as the contacting equipment for the counter current extraction.

Tail end purification of the ^{233}U product was achieved by a cation exchange column. The uranyl nitrate product obtained after cation exchange was further purified by a series of sequential precipitation techniques to decontaminate the product from thorium and iron to less than 100 ppm level.

CAL-MIX Mixer Settler

The final U_3O_8 product was obtained by igniting the ammonium diuranate precipitate. This facility successfully operated for a period of six months and processed all the available J rods.



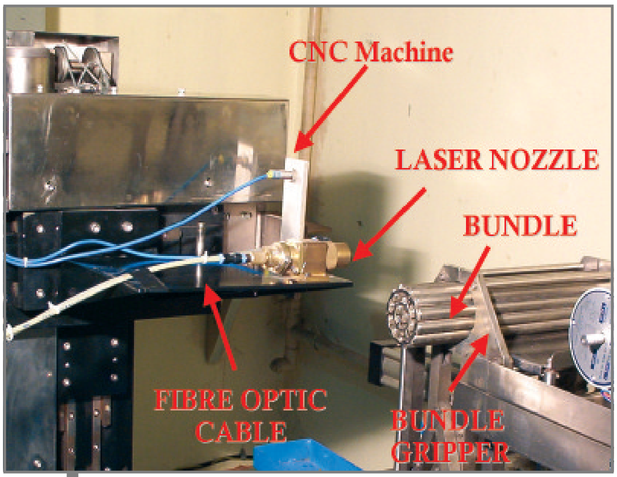
7.2 LASER-ASSISTED SINGLE PIN CHOPPER SYSTEM FOR THORIA BUNDLES

A Laser--assisted single pin chopping system has been developed for de-cladding of 19-pin PHWR Thoria bundles. This is a part of head-end system for Thoria bundle reprocessing at Trombay.

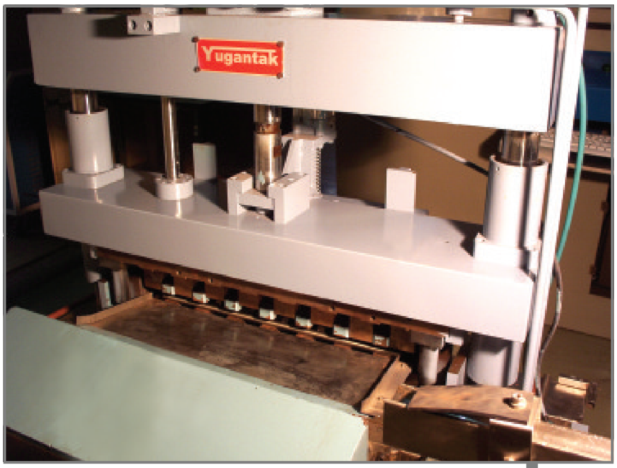
The system basically consists of a bundle gripper, sensor mechanism for detection of bundle orientation, laser nozzle mounted on CNC machine, pin transfer system and hydraulic press for single pin chopping. Thoria fuel bundles will be charged through charging cask and transferred to bundle gripper through transfer port assembly inside the hot cell.

The principle of operation of this system is bundle dismantling by laser cutting of both end plates of fuel bundle and chopping of individual pins employing a hydraulic shear. Nd-YaG laser beam of 200 Watt is used for cutting of 1.57 mm thick Zircaloy end plate. The laser is optically pumped by two flash Krypton flash lamp.

Fibre optics cable is used for laser beam delivery system. Argon gas has been used during cutting to melt blow the molten metal. The separated pins are transferred one by one to shearing machine by specially developed pin transfer mechanism. These individual pins are then chopped to thirteen pieces in one stroke by 10 T hydraulic shear. The complete system is remotely operated through PC interface. The whole operation can be viewed through CCTV system.



3 Axis CNC for Laser Nozzle & Bundle Gripper



Single Pin Hydraulic Chopper

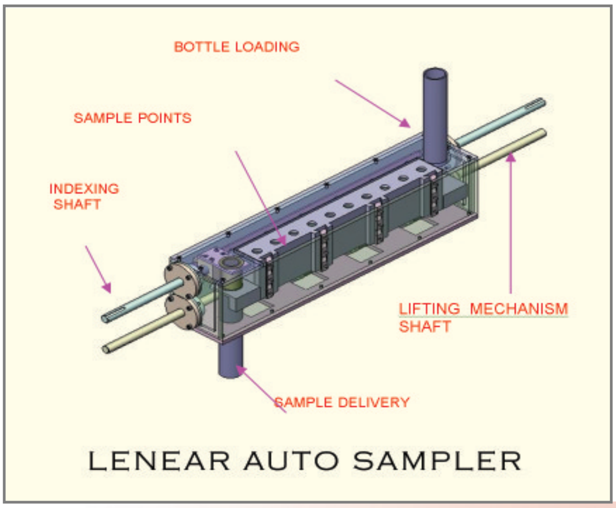
The first version of this system has been designed, developed, manufactured and installed at PP complex, Trombay.

Based on this design, the modified version of this chopper is being employed in the new plant for reprocessing of PHWR thoria bundles at Trombay. This system will have features like remotely operable assemblies/sub-assemblies with manual overrides in case of power failures.

7.3 LINEAR AUTO SAMPLER

Fuel Reprocessing Plants use vacuum-assisted airlift operated sampling system to achieve representative samples. The system is reliable and has built in safety features. Development of a Linear Auto Sampler has led to total automation of sampling operations. An Auto Sampler unit caters to 10 sample points. A single button operation leads to bottle loading, alignment with the desired sample point, drawing of sample and delivery of sample bottle to the laboratory. The Auto Sampler uses lead screw mechanism for indexing and alignment and cam operated mechanism for engaging/ disengaging a bottle with the sample point. The sampling operation is controlled by a PLC. Built-in safety features & interlocks have been incorporated in the Linear Auto Sampler system. This design has been tested rigorously for more than 1000 operations and is further being put on test loop. This system is being adopted in the ongoing Project at Trombay.

The design is expected to eliminate human errors in sampling and reduce exposure to O&M personnel.

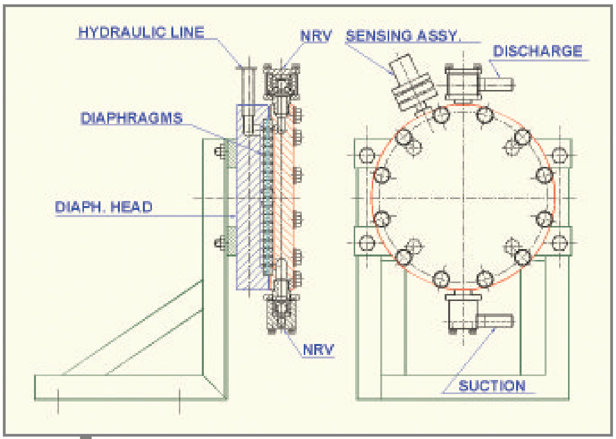


V.K. Savarkar / T.L. Rao, <vksavar0@hotmail.com>

7.4 INDIGENISATION OF METERING PUMPS AND BELLOW SEAL BELLOW-OPERATED VALVES

Reprocessing Plants use a large number of Remote Head Metering Pumps and bellow Seal Bellow Operated Valves. These special purpose items were not manufactured in India and were imported until recently.

Design and development efforts were directed towards indigenisation of these items.



Metering Pump Remote Head

Remote Head Metering Pumps: Special efforts were taken for designing Non Return Valves, Vacuum Compensating Valve and achieving proper contours in the remote heads. Metering accuracies of ± 1%, with Repeatability & Linearity within ±3% have been achieved. Pumps have been tested for endurance under simulated conditions successfully.

Bellow Seal Bellow Operated Valves: Compact Valves with Soft Plugs and Bubble tight Class-VI leakage have been developed. These valves are tested rigorously and have with stood endurance testing of 25000 cycles of continuous operation with 7 bar pressure successfully.

These items are being adopted in our ongoing projects at Trombay, Tarapur & Kalpakkam.


Hydraulic Pulse Dissolver Scale-Up Model

7.5 PROCESS DEVELOPMENTS - R&D

Reprocessing Chemistry is constantly under development to achieve higher recovery and reduced waste volumes. Along side developments in chemistry, implementation of the chemical understanding on an engineering scale requires the development of equipment for optimum performance. Enhancing the dissolution rate of spent fuel, handling the zircaloy fines from chopping, designing of different counter current contactors for solvent extraction, development of electrode materials for *in-situ* partitioning etc. are some of the challenging tasks under active development to improve the recovery of Pu and U. Development of suitable models with experimental validation is essential for optimum process performance. Engineering scale test facilities form an integral part of this R&D to try out various concepts, to generate basic data for modeling and subsequent design of the equipment. Multi-cycle PUREX process has already crossed the recovery mark of 99.5% and further developments are aimed at improving the recovery to almost 99.9% with fewer number of cycles.

■ Hydraulic Pulse Dissolver

The developments in the dissolver systems are being undertaken with the objective of enhancing recovery of nuclear materials, improving dissolution rates and addressing the problem of fines accumulation in dissolver during chop-leach process of spent fuel dissolution from Power Reactors. The required phenomenon of high turbulence and fuel bed upheaval for completion of dissolution and enhancing dissolution rate has been achieved and demonstrated on a bench scale model. This was followed by design development and construction of scale up model in transparent acrylic material. The hydraulic phenomenon for turbulence, upheaval of hull bed and removal of fines have been demonstrated on scale up model.

■ Power Fluidic Mixers

Development of Air Operated Power Fluidic Mixers for treatment of degraded solvent, NO_2 gas conditioning and homogenisation of tank contents in fuel reprocessing plants is in progress. Working of the mixer was demonstrated on bench scale model.

A Plant scale Mixer for treatment of degraded solvent for ROP, Tarapur was designed, fabricated and tested successfully for homogenized mixing of solvent and wash solution under varying conditions of levels of the two phases simulating plant application.

Power Fluidic Mixer

This design is being incorporated in project ROP. The work on development and design of Air Operated Power Fluidic Mixers for Plutonium cycle feed conditioning by NO_2 gas, homogenisation of process tank contents etc. is in progress.

Improved Contactors for SX

Test Set-up for Improved Pulse Column

Development of improved pulse columns for solvent extraction for use in reprocessing plants is in progress. Different cartridges will be evaluated for improving mass transfer efficiencies. Radial mixing phenomenon for improved mass transfer was successfully achieved using Krimz plate cartridge and demonstrated by constructing acrylic model of the column. Work was initiated to further study the performance in stainless steel columns and fabrication of 2.4 meter SS column is in progress.

Development of Static Mixer CALMIX and CALmsu Contactor

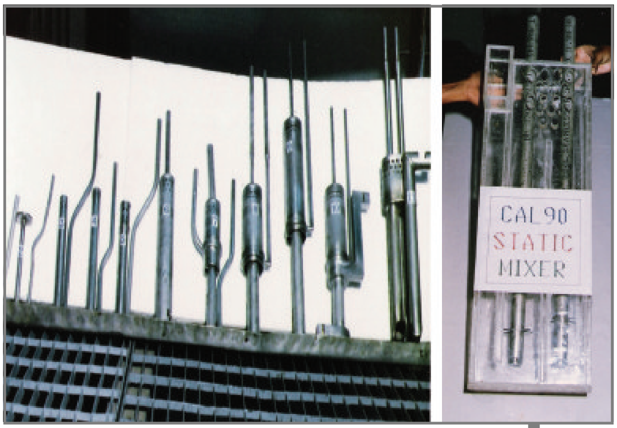
Nuclear industry uses solvent extraction based operation extensively both in the front end and the back end of the fuel cycle for heavy metal extraction. Both these applications call for contacting devices with high reliability, operational flexibility and good overall process performance.

Development of the Combined Air Lift based mixer settler contactor (CALmsu) has been carried out to meet these requirements of the nuclear fuel cycle. The air-lift based mixing element of CALmsu eliminates all moving/ maintainable parts rendering it suitable for in-cell use.

Intimate mixing of the aqueous and organic phases are ensured by appropriate design of the nozzle size of the mixing element and optimized flow of motive air inside the same. These units are provided with end-settlers to take care of any entrained phases in the terminal streams.

Unlike conventional mixer-settlers CALmsu units have hydrodynamically linked mixer and settler making it amenable for control of interphase & complete draining. Suitable design of air inlet header to these units can provide flexibility of operation when required.

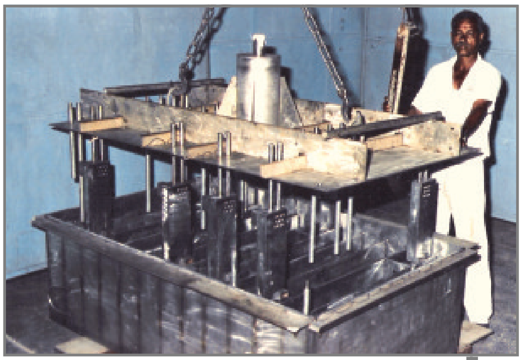
The CALmsu has been put to use in many of the facilities both in the front-end and the back-end. Depending on the end use these units have been designed to operate from 10 L/Hr to 50 L/min with a separation efficiency >99.5%. These units have been operating successfully at IRE (Front-end) and at Uranium Thorium Separation Facility (Back-end). Based on these operational feed backs



Development of Static Mixer: CALMIX

the CALmsu is being considered for other facilities such as Prototype Thorium Reprocessing Facility, Trombay and the Actinide Separation demonstration Facility, Tarapur.

In line with the philosophy of having no moving parts the feed to the contacting devices could ideally be the Air Lift Pump. The horizontal foot piece with on-line cleaning feature is an innovation in airlift pump devices that has improved reliability of this equipment. Low capacity metering using ALP has been achieved by the use of hybrid systems. These innovations as a whole have resulted in high reliability of extraction systems used in the nuclear fuel cycle.



KARP Integrated Spent Solvent Treatment Unit of 200 LPH capacity

B.V. Shah <bvshah@barc.gov.in>

■ Electrochemical Process

Purex process extensively utilizes Pu & U reduction and oxidation processes in separation and purification stages in different solvent extraction cycles. These processes can be conveniently and effectively carried out by electrochemical means. Integrated Development program is undertaken for these processes and equipment requirements. In the direction of development of a suitable equipment for use in radio-chemical plant for in-situ reduction, in-line electrolysis and for production of uranous nitrate, a lab scale Filter Press Type of electrolyser (on the lines of ICI cell) was designed, fabricated and validated for electro-chemical processes. Engineering design development work for this equipment is in progress. To obtain a long life, robust and economical anode for use in radio-chemical plants, platinum-plated electrodes of varying coating thickness have been procured and are being subjected to quality tests.

7.6 UPGRADATION OF THE INSTRUMENTATION AND CONTROL SYSTEM

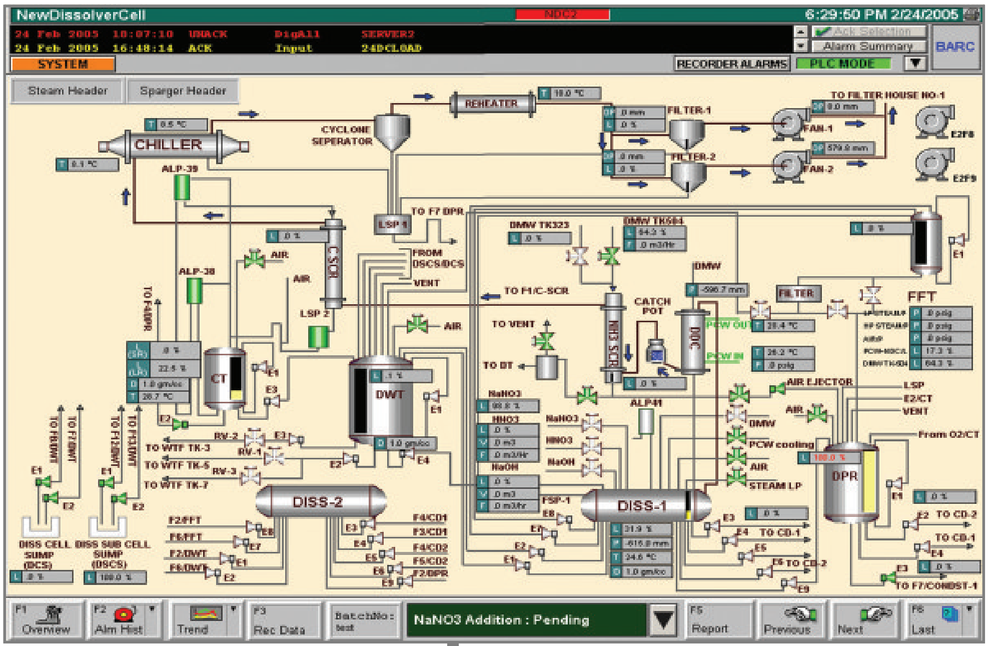
The upgradation of the Instrumentation and control system at Plutonium Plant, Trombay has been completed. The work included the replacement of pneumatic transmitters and recorders with electronic instruments, replacement of manually-operated steam valves with air-operated valves and introduction of a CDACS to monitor and control the process operations. The CDACS has been designed and programmed to carry out the following functions.

1. Monitoring and control of various process parameters like Level, Density, Temperature, Pressure etc.

2. Implementation of the logics required to operate and control various transfer devices like Steam Jets, Air Lift Pots, Remote Valves, Air Spargers, Process pumps etc.

3. Implementing trips, cut-offs and safety interlocks.

4. Providing dynamic mimics and versatile HMI on computer-based operator stations.



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24 Feb 2005  10:07:10  UNACK   DigAll   SERVER2
24 Feb 2005  16:48:14  ACK     Input    24DCLOAD
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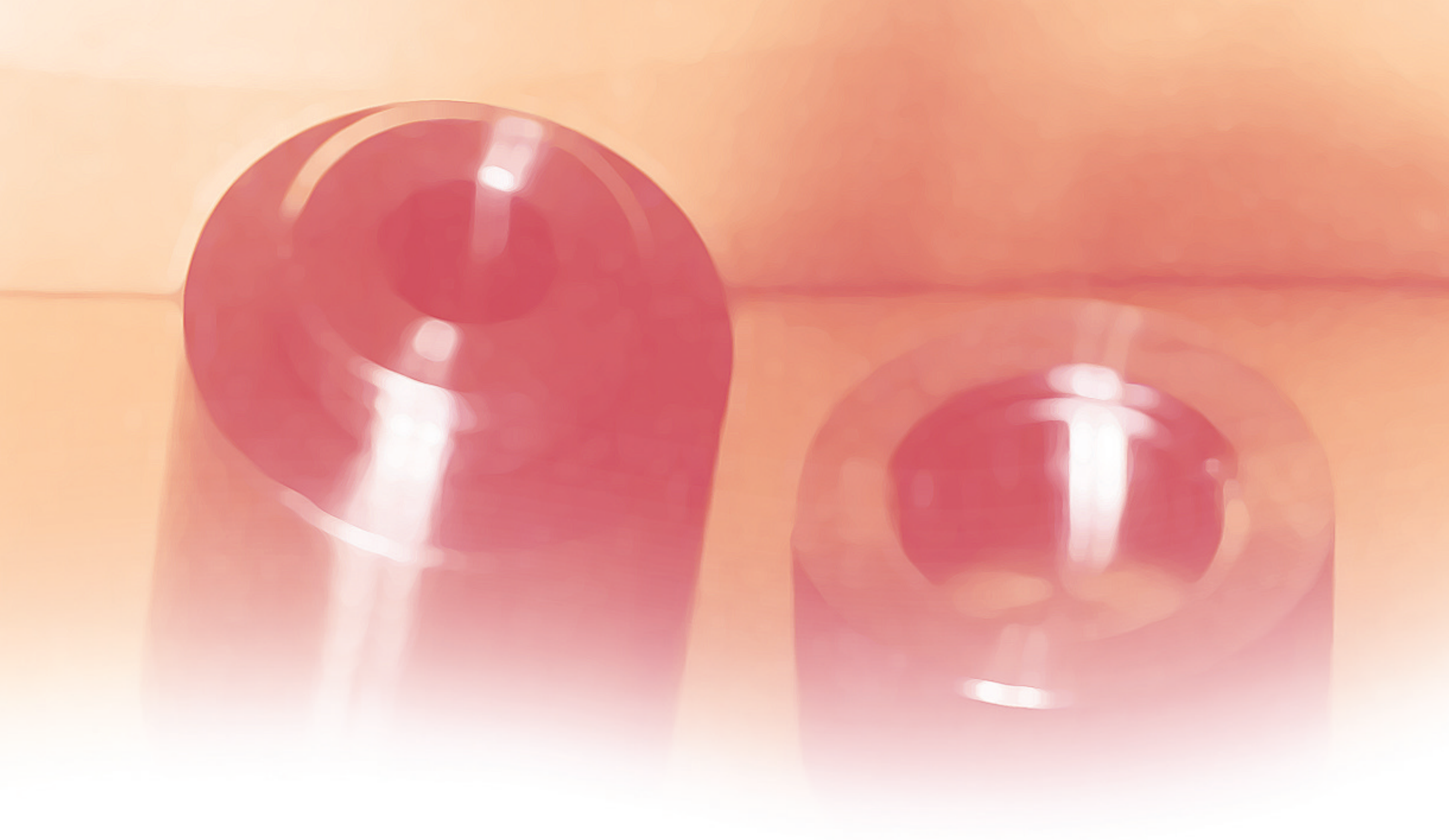
A Sample Mimic Flow Sheet

5. Computer based Data Acquisition, logging, archival and report generation

6. Aiding the operator in processing the acquired data.

Upgradation and retrofitting of the instrumentation and controls in the reprocessing plant at Trombay include induction of programmable logic controllers, videographic recorders, SCADA servers / operator stations to monitor and control the process operations from the control room The HMI is implemented by E-suite SCADA software package. The PLC, operator stations and the videographic recorders communicate each other through Ethernet network.



B. REPROCESSING

8. LABORATORY DEVELOPMENT - PROCESS CHEMISTRY

INTRODUCTION

Reprocessing chemistry has made fast strides during the past few decades. Recovery of U and Pu has reached more than 99.5% and the waste volume generation has considerably reduced. Even under the stringent regulations of environmental discharges and personnel exposure, the reprocessing industry could perform well largely due to the chemistry improvements. Further improvements in chemistry are expected to make this process more efficient, economic and environmental friendly.

8. LABORATORY DEVELOPMENT - PROCESS CHEMISTRY

Even though PUREX Process has developed into a matured process over the years, it is being continuously developed to meet higher and higher goals of recovery to reduce the environment burden arising from the left out radionuclides in the high level waste. Currently the technology is well poised to cross the barrier of 99.9% recovery. Developments are underway to extend the extractive power of TBP to take care of a few more nuclides of environmental concern. A better understanding of the solvent behaviour in the extraction equipment has resulted in improving the process performance. Resorting to salt-free reagents for conditioning has helped in drastic reduction in waste volume generation.

Developments are underway to enhance the partitioning efficiency of Pu from U. The uranous production by electrolysis has been standardised to optimum current efficiency and conversion by resorting to new electrode material like titanium substrate insoluble anode and titanium cathode. Catalytic reduction of uranium(VI) to uranium(IV) over finely divided platinum dust is also being developed as another effective method of U(IV) production.

The *in-situ* reduction of U(VI) to U(IV) for the partitioning of Pu using specially designed mixer settlers and pulsed columns have also been demonstrated on a pilot plant scale using titanium cathode and titanium substrate insoluble anode. The operating experience gained from these pilot studies will be used for firming up the design of such systems for future reprocessing plants.

PUREX streams are rich sources of many valuable nuclides. Recovery of some valuable nuclides has been demonstrated on laboratory scale from different streams. Developments of extractants and sorbants suitable for selective uptake of various nuclides are also in progress.

Over the years, the environmental discharge limits have been brought down drastically. Advanced PUREX process could address some of the challenges posed by these stringent limits.

Process chemistry is continuously under development to meet the following objectives:

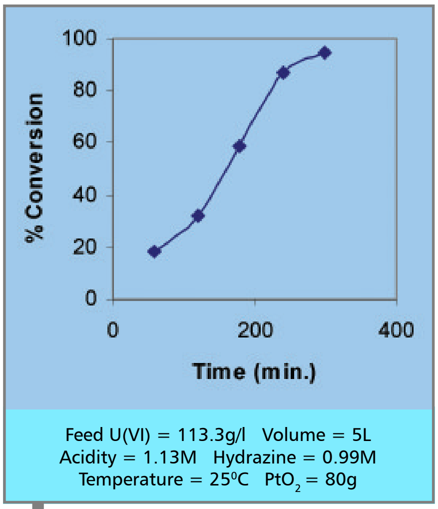
1. Improve the recoveries of Pu & U and decontamination factors
2. Reduce the waste volume generation
3. Reduce the number of cycles
4. Recover nuclides of commercial value
5. Separate long lived actinides and fission products to reduce environmental hazard
6. Develop alternate extractants.

8.1 CATALYTIC REDUCTION OF URANYL NITRATE

Partitioning of plutonium from uranium in the PUREX process involves the reduction of Pu(IV) to Pu(III). Uranous nitrate, the widely accepted reductant for partitioning presently, is prepared by electrolytic reduction of uranyl nitrate using TSIA (Titanium Substrate Insoluble Anode) as anode and titanium as cathode. Degradation of the TSIA electrode needing periodic recoating is a major operational concern. An alternate process has been developed for the preparation of uranous nitrate by reduction of uranyl nitrate using hydrazine nitrate as reductant in the presence of platinum catalyst.

Detailed laboratory studies in batch and continuous mode were carried out to standardise various parameters like uranium concentration, reduction rate acidity, hydrazine concentration, catalyst quantity, temperature etc. for this conversion. Near 100% conversion has been achieved.

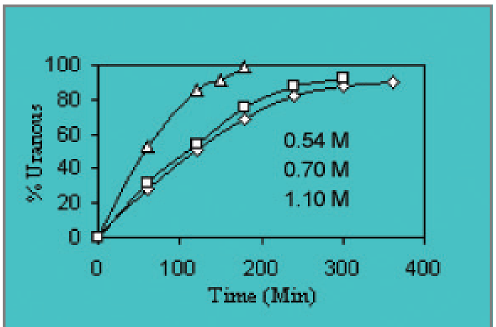
A pilot plant scale reduction column was operated under optimized conditions with a uranous nitrate production



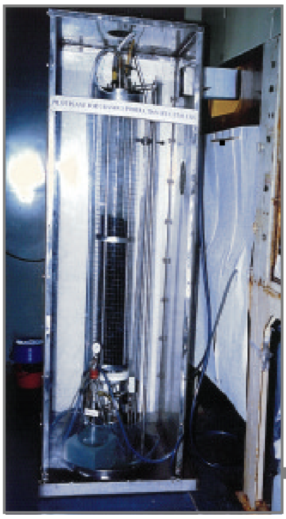
Feed U(VI) = 113.3g/l Volume = 5L
Acidity = 1.13M Hydrazine = 0.99M
Temperature = 25°C PtO_2 = 80g

Rate of Reduction

of 1.75 kg in five hours in a single batch using 80 g platinum catalyst.



Effect of hydrazine on U(VI) reduction



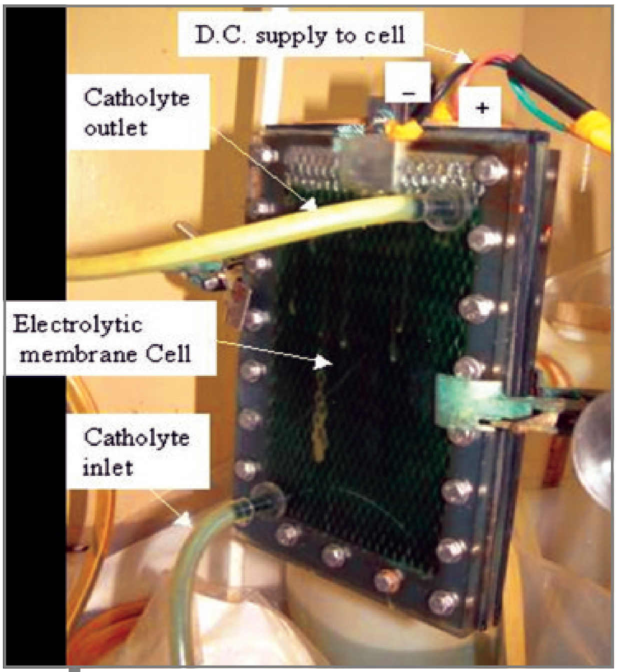
Pilot Plant for U(IV) Production

K. Sreenivasa Rao et.al., "Uranous nitrate production for Purex process- applications using PtO_2 catalyst and hydrazine nitrate as reductant, BARC Reprot : BARC/2003/009

8.2 ELECTROLYTIC REDUCTION OF URANYL NITRATE USING MEMBRANE CELL

In an undivided electrolytic cell, part of the uranous produced at the cathode gets oxidised by the oxygen generated at anode. To prevent this, the catholyte should be separated from the anolyte by a suitable diaphragm. Porous plastic diaphragm does not give very satisfactory result since the catholyte and anolyte can get mixed together by diffusion. Cation exchange membranes which are impermeable to liquids but permeable to cations are used as a barrier to separate catholyte from anolyte.

Cells with cation exchange membrane to separate catholyte from anolyte were fabricated. In all the cells TSIA (Titanium Substrate Insoluble Anode) was used as anode. A thin cation exchange membrane of 50 cm^2 area was used. Titanium was used as the cathode.



Side view of membrane cell for 100% U(IV) production using NAFION membrane

Basic requirement of a membrane for efficient operation of the cell can be summarised as: i) high capacity ii) high degree of selectivity for cations iii) low electrical resistance iv) good chemical stability v) good physical strength vi) low rate of osmosis viii) high transfer rate for counter ion ix) high thermal stability x) low cost and xi) resistance to fouling.

In an electrolytic cell, separating the catholyte from anolyte by cation exchange membrane makes it possible to produce cent percent uranous nitrate. Pilot Plant Operation has confirmed the production of 12 kg of uranous per day in continuous runs.

Uranium Conc. = 232 g/L
Acidity = 2.2 M HNO_3
Hydrazine = 1.4 M
Catholyte Volume = 3 liters
Cathode Current Density = 55 mA/cm^2
Diaphragm = Cation Exch. Membrane

Hours	% Conversion
1	13.9
2	33.8
3	42.3
4	54.6
5	71.8
6	77.6
7	84.2
8	100.0

8.3 QUALITY ASSESSMENT OF PUREX SOLVENT-GAS LIQUID CHROMATOGRAPHY (GLC) FINGERPRINTING TECHNIQUE

The quality of the PUREX solvent dictates the extent of recovery and the purity/quality of the product.

With the objective of understanding the mechanism of solvent degradation and its remedial measures, detailed study on the phenomenon of solvent degradation has been carried out under simulated PUREX conditions. Systematic Gas Liquid Chromatographic (GLC) studies using element selective (N-P detector) and mass specific detector (GC-MS) has led to identification and characterization of the signatures of these hydrophobic degradation products, both for the diluent & TBPs termed as Diluent Degradation Products (DDP) and High Molecular organophosphates (HMP) respectively.

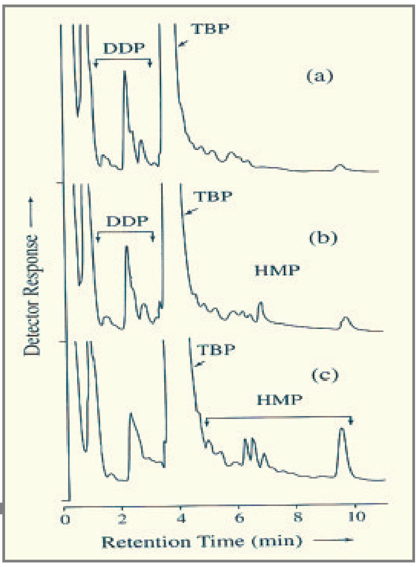
GLC fingerprinting of PUREX solvent has been established as a potential tool to monitor the status of degradation in recycled PUREX solvent. The recycled solvent, at the critical stage of rejection as waste has been found to have several demerits like increased viscosity, poor phase disengagement behaviour and formation of interfacial cruds reflecting the solvent performance.

Quantitative correlation between measured concentration of any single degradation species and its impact leading to rejection of the solvent would be rather difficult. Thus, a comprehensive criterion for rejection of solvent has to be evolved, comprising of determination of a threshold GLC concentration profiles of harmful markers in degraded solvent, its viscosity and interfacial tension. Standardisation of GLC fingerprinting method has led to several remarkable applications such as:

(i) Correlation of dose-dependent degradation of PUREX solvent with corresponding adversity in the extraction performance and deviation in hydrodynamic behaviour of the solvent during plant operation.

(ii) Screening the various additives for protection of solvent against radiolytic degradation.

(iii) Standardisation of indigenous method for the production of nuclear grade TBP on plant scale by Heavy Water Board.



Typical gas chromatogram of
(a) diluent phase, (b) Radiolysed solvent
(absorbed dose = 3.5 x 10^5 Gy) and
(c) Middle phase

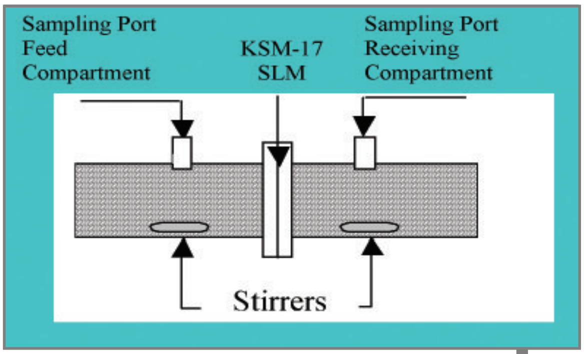
The technique of GLC fingerprinting is emerging as a versatile tool for studying radiation viability of novel solvents in the field of radiochemical separation.

S.C. Tripathi et. al, Separation Science and Technology, 38(10),2307,2003.

8.4 SEPARATION OF CARRIER-FREE ^{90}Y

^{90}Y is obtained by the radioactive decay of ^{90}Sr. ^{90}Sr separation from PUREX HLW in milli curie level was achieved by a series of chemical separation techniques using natural strontium carrier. ^{90}Sr separated in carbonate form was dissolved in nitric acid and served as the feed stream for carrier free ^{90}Y generation. Separation of ^{90}Y from ^{90}Sr was achieved by supported liquid membrane (SLM).

A compact generator is developed for this separation using commercially available polytetrafluoroethylene (PTFE) membrane, impregnated with 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (KSM-17). The ^{90}Y obtained by this technique is pure and in chloride form suitable for complexation with various ligands for medical applications. Three lots of about 10-15 mCi per lot are being regularly supplied per month to Radiopharmaceuticals Division of BARC for their research.



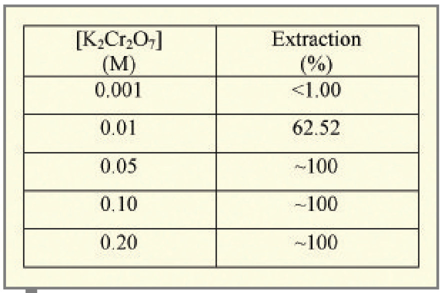
Schematic Diagram of ^{90}Sr-^{90}Y

M. Venkatesh et. al. Radiochim. Acta, 89 (2001) 413.

8.5 SEPARATION OF ^{144}Ce

^{144}Ce with $T_{1/2}$ = 285 days finds wider applications in nuclear research. Gamma energy ($E\gamma \approx 133.5$ keV) of ^{144}Ce is ideal for the excitation of $K\alpha$ X-rays of heavy elements like thorium, uranium, plutonium, etc. and also as a useful source for gamma-induced X-ray analysis. Among other applications it is used as a standard for calibration of detectors, as a monitor for the determination of burn-up of nuclear fuel and for the assay of leached hulls.

Radiochemical separation and purification of ^{144}Ce has been achieved from Purex high level waste (HLW). Granulated ammonium molybdophosphate (AMP) was used for the selective removal of cesium. Uranium and plutonium were removed quantitatively using 20% 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (KSM-17) in dodecane. The tri-valent cerium was oxidised to its tetravalent state using $K_2Cr_2O_7$ and extracted into KSM-17 and stripped with 0.5 M nitric acid.



$[K_2Cr_2O_7]$ (M)	Extraction (%)
0.001	<1.00
0.01	62.52
0.05	~100
0.10	~100
0.20	~100

Effect of Dichromate on Extraction

P.S. Dhami, N.L. Dudwadkar, P.V. Achuthan, U.Jambunathan and P.K. Dey, Sep. Sci. Technol.,39(2004)3143.

8.6 SEPARATION OF ^{241}Am

Power reactor fuel which has undergone more irradiation contains appreciable amount (2-3%) of ^{241}Pu, which on emission of beta with a half life of 14.35 years forms ^{241}Am. ^{241}Am has a half life of 431 years which emits both alpha and gamma (60 KeV, 35%). As the build up of ^{241}Am increases, it will become necessary to purify the PuO_2 for safe handling. Uranium present in this oxide is leached selectively with concentrated nitric acid. The residue left after leaching is dissolved in hot concentrated nitric acid containing traces of fluoride ions. Plutonium is separated by anion exchanger. The loading effluent and washing were collected together and the americium present in this solution is precipitated as americium oxalate under controlled acidity. The oxalate is ignited to get AmO_2.

K.M.Michael et. al., Proc. Of DAE-BRNS meeting in Sepn. Sci. & Tech July 2004, 154.

SPECIALLY DESIGNED S.S. STORAGE CAPSULE FOR AMERICUM OXIDE

8.7 DEVELOPMENT & TESTING OF INDIGENOUS ANION EXCHANGER

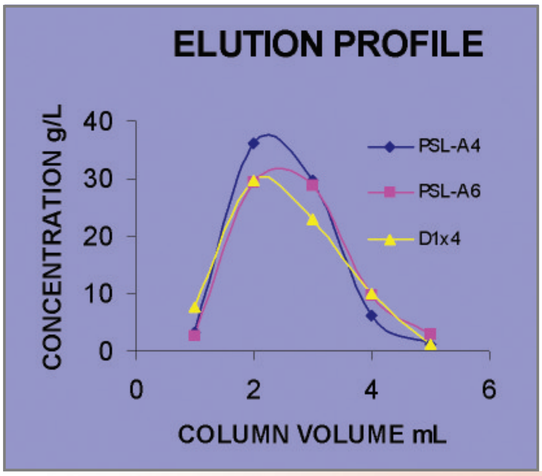
The final purification and concentration of plutonium is carried out by an anion exchange method in nitric acid medium. The inability of many elements to form anionic complexes makes it possible to separate plutonium from many impurities and thus makes this process superior to other purification procedures. In this process the plutonium is sorbed as hexanitrato species at 7.2M HNO_3. The loaded plutonium is washed with solution of same acidity and then eluted with 0.5M HNO_3.

At present Dowex 1x 4 (D1x4), 50-100 mesh, a strong base gel type resin with quarternary ammonium functional group in a polystyrene-divinyl benzene copolymer backbone is used and this has to be imported. Tulsion A-PSL 4 and Tulsion A-PSL 6 are also strong base gel type resins of 4% and 6% cross-linkage respectively with 50-100 mesh synthesised indigenously. The total exchange capacity of Tulsion A-PSL 4 resin is 1.38 meq/ml and for Tulsion A- PSL 6 resin is 1.33 meq/ml. Glass columns of 1.8 cm diameter, height of 18 cm were used for the study. A feed solution containing 1g/l of purified plutonium (IV) in 7.2M HNO_3 was prepared and passed through preconditioned columns at 2BV/hour. The effluent samples collected at regular intervals were analyzed for plutonium. The resin bed was then washed with 5 bed volumes of 7.2M HNO_3 at 100 ml/hour. Column was eluted with 0.5M HNO_3 at 10 ml per hour flow rate.

Effluent volume(mL)	% Breakthrough		
	PSL-A4	PSL-A6	D1**x**4
1000	0.18	0.10	0.28
2500	0.20	0.12	0.28
3000	0.26	0.15	0.31
3500	0.34	0.20	0.52
4000	0.52	0.31	0.52

Comparative Loading Performance Data

The loading behaviour of PSL 4 & PSL 6 was found to be same and were comparable to Dowex 1**x**4 (the performance of Dowex studied in earlier runs) under identical condition. The results indicate that due to its higher cross-linkage, PSL 6 shows tailing in elution compared to PSL 4 and Dowex 1**x**4. On the other hand elution behaviour of PSL 4 was found to be comparable with Dowex 1**x**4.

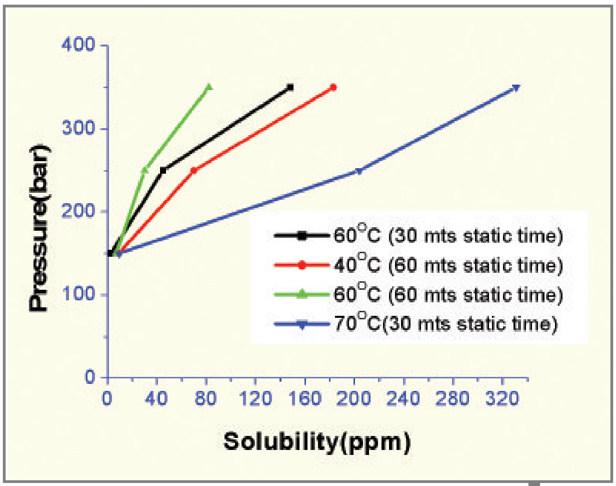


R. Kumaresan et. al. Proc. Of DAE-BRNS meeting in Sepn. Sci. & Tech July 2004, 121.

8.8 SUPERCRITICAL FLUID EXTRACTION (SCFE)

As technology advances, use of Supercritical fluids is explored worldwide for metal–ion separations. Feasibility studies on SCFE have been initiated with the long term objective of extracting heavy metal ions from spent oxide fuel.

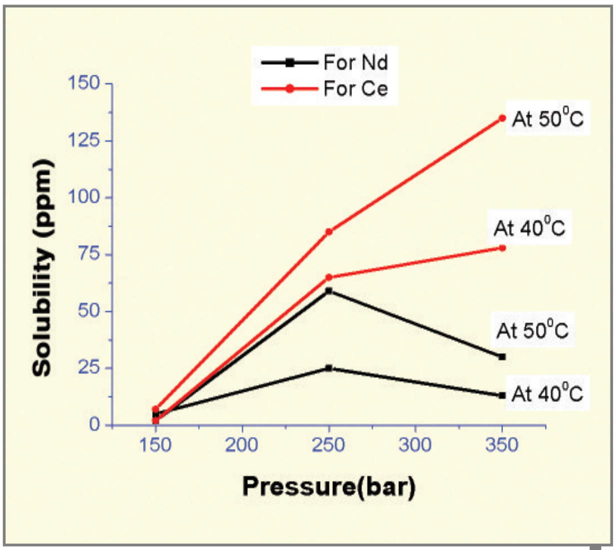
Solubility behaviour of lanthanide chelates have been investigated in supercritical CO_2 medium in the pressure range of 150-350 bar at 40-80^{0}C. Cerium-TTA chelate solubility was



Solubility isotherms for Nd-TTA-CO_2 system

observed to be low (< 70 ppm) as against neodymium-TTA chelate (>300 ppm).

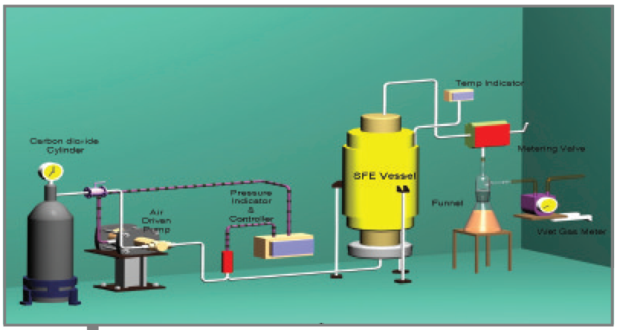
In case of mixed solutes, solubility of Ce- chelate was enhanced (~150 ppm) in the presence of Nd-chelate at 350 bar. For enhanced solubility leading to improved extraction, a mixed ligand approach was tried. SCFE using TTA-TBP system has increased the percentage extraction from 2 to 65% for Nd from its oxide (30 mins under static conditions followed by 150 mins of dynamic extraction at 350 bar and 60°C).



Solubility behaviour of Ce and Nd TTA chelates at different supercritical conditions

In order to explore the SCF technology for decontamination purposes, extraction studies have been carried out with different lanthanide nitrates. Percentage chelation obtained for Nd was nearly 50% under static conditions lasting for 1 hour at 350 bar and 50°C.

Further work on extraction of heavy metals using TBP-HNO_3 complex containing supercritical CO_2 is being taken up.



Experimental Set up for Supercritical Fluid Extraction

B. REPROCESSING

9. REPROCESSING OF THORIA-BASED FUELS - PROCESS CHEMISTRY

INTRODUCTION

THOREX process is still in the developmental stages and needs extensive modifications prior to achieving industrial status. In the Indian context, THOREX has a major role to play as the nuclear programme envisages the utilization of vast resources of thorium in its third and final stage. AHWR and its associated fuel cycle is designed to accelerate the induction of thorium into the power programme. R&D activities are in progress to meet the challenges of this fuel cycle.

9. REPROCESSING OF THORIA-BASED FUELS – PROCESS CHEMISTRY

Even though THOREX process can claim a more or less similar history of PUREX, it cannot claim the same robustness as that of the latter. Most of the experience in THOREX domain has come from the recovery of low amounts of ^{233}U bred in irradiated ThO_2. Even the basic data needs augmentation to achieve industrial scale maturity for the process. Indian experience is based on the reprocessing campaigns of irradiated ThO_2, irradiated in the J annulus of CIRUS. Further studies are required to deal with the reprocessing of irradiated ThO_2 bundles used in the initial flux flattening of PHWRs. These bundles had contributed to the power during its stay in the reactor and the ^{233}U bred had undergone fission to a significant extent. The radioactivity from fission products will be considerable and the ^{232}U concentrations are also expected to be much higher. This will necessitate finetuning of some of the process parameters.

Studies for developing a flow-sheet for the processing of thoria irradiated in power reactors for ^{233}U separation have already been completed. With 5% TBP, ^{233}U is preferentially extracted leaving the bulk of thorium in the raffinate. The extraction was carried out in the presence of fluoride and aluminium ions to simulate feed conditions. Based on the process development studies and on the experience gained during the recovery of ^{233}U from research reactor, a facility to recover ^{233}U from thoria irradiated in power reactors is under construction.

The (n,2n) reactions encountered during the irradiation of thorium lead to the formation of long lived ^{231}Pa and relatively short lived (68.9 yrs.) ^{232}U with its hard beta, gamma emitting daughter products. Thus the ^{233}U produced in the reactor is contaminated with ^{232}U and the level of contamination depends on the isotopic composition of initial thorium fuel, the burn-up and the neutron spectrum encountered in the reactor. The radioactive contamination from ^{232}U in the separated ^{233}U product and from ^{229}Th and ^{228}Th in the separated thorium product will have to be taken into consideration while handling these products. ^{231}Pa is the main long-lived actinide that needs to be assessed for its long-term environmental impact in THOREX High Level Waste.

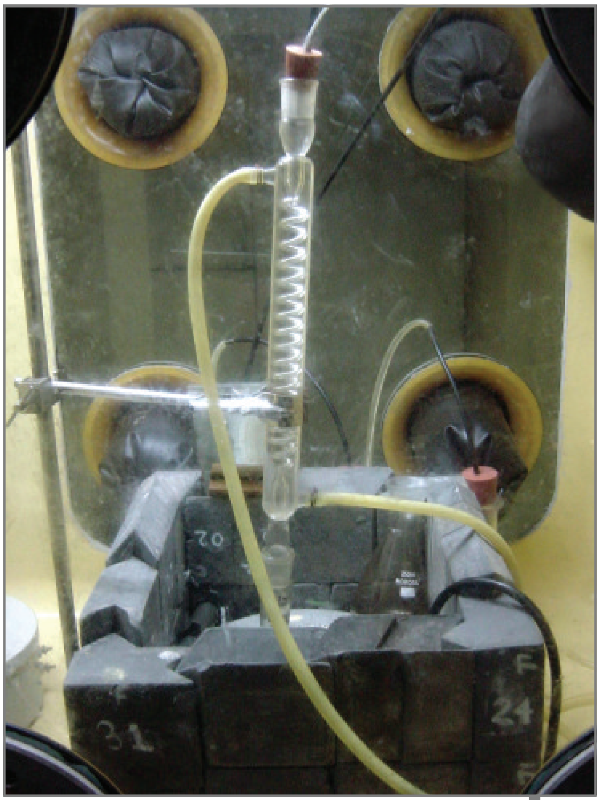
Development of alternate materials for dissolver and evaporators will play a vital role in determining the life of the Thorex plant as this process employs fluoride catalyst in thoria dissolution.

Advanced heavy water reactor(AHWR) is designed with the dual objectives of exploiting the expertise acquired from the PHWR operation and to gain all-round experience in the thorium fuel cycle. This reactor will serve as a predecessor to the third stage reactors which will be based on thorium-^{233}U fuel cycle and will provide the much needed vital information to initiate this fuel cycle.

AHWR spent fuel adds one more dimension to reprocessing by the presence of Pu in the spent fuel. Due to the breeding of ^{233}U in the Pu-Th fuel, a three component product separation is necessary for this spent fuel and suitable flow-sheet development is required to achieve this. This will necessitate the integration of the well known Purex process with Thorex process in some combination. Large amounts of basic and process-related data are required to be generated to master the entire fuel cycle operations.

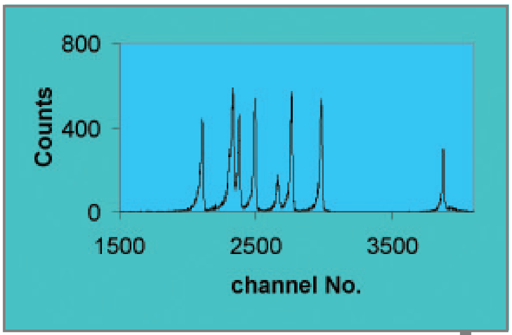
9.1 DISSOLUTION OF IRRADIATED THORIA

India's nuclear power programme envisages the use of vast sources of thorium in its third and final phase of nuclear energy programme. In order to achieve a high through put for industrial scale reprocessing, the first and foremost impediment of thorium fuel cycle, viz., the poor dissolution of thoria, will have to be overcome. Dissolution studies of unirradiated thoria pellets and 4 % PuO_2- Thoria pellets have been conducted in the laboratory. Based on these studies, a standard Thorex dissolvent of 13 M HNO_3, 0.03 M HF and 0.1 M $Al(NO_3)_3$ was recommended to achieve reasonable dissolution rate. Using this reagent studies were carried out for the first time on the rate of dissolution of thoria irradiated at KAPS for 508 full power days and cooled for approximately 4.5 years. Adequate shielding arrangements and remote sampling techniques were made for reducing exposure to the operator. The dissolved sample was analysed by various chemical techniques to estimate the concentration of different constituents.



Dissolution Setup housed in a Glove Box

Measurement of ^{232}U content in the irradiated thoria is of great significance as its daughter products contribute to high gamma dose during processing. Alpha spectrometry and isotope dilution mass spectrometry were employed in the isotopic assay of uranium. High resolution gamma spectrometry was used to calculate the fission product activity as well as the burnup of the sample. This study provided data with respect to the yield of ^{233}U, ^{232}U,Fission Products etc. to validate the physics codes and also gave vital data for the design of reprocessing facilities to reprocess those rods.



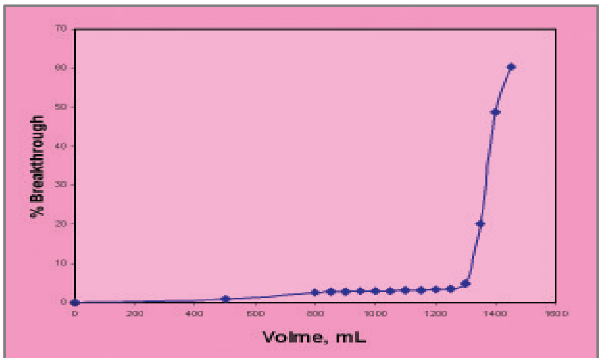
Alpha Spectra of Dissolved Thoria

S. Mukherjee, et.al. "Theoretical and Experimental Analysis of Irradiated Thorium Bundle from KAPS-2." 8th International CNS CANDU Fuel Conference, Muskoka, September 22 - 24, 2003

9.2 RECOVERY OF ^{233}U FROM ADU WASTE

Recent studies have established the use of phosphorus based exchangers in the recovery of actinides from complex reprocessing waste. A recent study from our laboratory using a commercial phosphonic acid exchanger, Bio Rex 63, has revealed the superior kinetic performance of the resin when it is used in Na form. This resin was used in the recovery of ^{233}U from reconversion waste.

Based on the distribution ratio low acid feed (0.25 M) was selected for column studies. Around 1450 ml solution of actual waste solution was passed through a column (id = 3 mm, height = 8 cm) loaded with 0.76 g of resin and around 60% breakthrough was obtained. The inflation of the plot was sharp indicating a fast kinetics of exchange. The column was washed with 0.25M HNO_3 and eluted with 2% ammonium carbonate solution. Total elution could be achieved in less than 40 ml giving a volume reduction factor of more than 35. The effluent from the column showed an alpha activity within the discharge limits.



Breakthrough Curve

K.K.Gupta, et, al. NUCAR 2005,March 15-18, Amritsar, India.

9.3 $(Th,U)O_2$ MOX CO-PRECIPITATION

Co-precipitation of uranium and thorium is an attractive route in which uranium after its reduction to uranous is precipitated along with thorium by oxalate precipitation method. The quantitative reduction of uranyl nitrate has been demonstrated by catalytic reduction using hydrazine over platinum catalyst.

Precipitation was carried out in 2 litre capacity batch precipitator maintaining the acidity at ~ 0.5 M. 10% oxalic acid (0.79 M) was used as precipitant. 0.1 M of stochiometrically excess oxalic acid was added at room temperature.

Composition-1, (50% Th – 50% U): In these precipitation experiments the concentration of thorium and uranium was maintained at 50 g/L each.

Composition-2, (70% Th – 30% U): The concentration of thorium and uranium was kept at 70 g/L and 30 g/L respectively in these precipitation experiments.

The precipitate was allowed to settle for about 2 Hrs. and filtered through SS frit. Precipitate was washed with distilled water and calcined at the following temperature profile,

1. Room temperature to 200 °C 1 Hr.
2. Soaking at 200 °C 1 Hr.
3. 200°C to 700 °C 2 Hrs.
4. Soaking at 700 °C 3 Hrs

Two kg of the mixed oxide of the above two compositions were prepared. The MOX powder was supplied to the Metallurgy Division for fabrication tests and the results are encouraging.

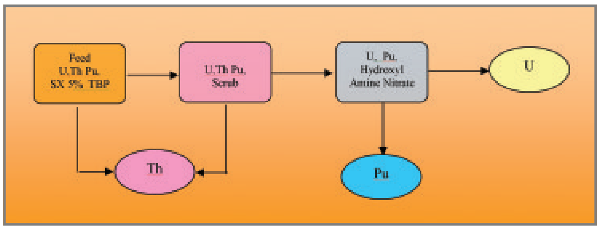
P.S.Dhami, et. al. NUCAR 2005, March 15-18, Amritsar, India.

9.4 REPROCESSING OF AHWR FUEL - FLOW SHEET DEVELOPMENT

AHWR, a hybrid reactor, is an innovative reactor design meeting the dual objective of interim utilisation of the PHWR produced Pu and utilization of vast resources of Thorium for power generation. This reactor uses Th-Pu fuel bundles along with Th-^{233}U fuel bundles. The in-bred ^{233}U from the Th-Pu bundles will necessitate the development of a flow sheet for the separation of each of these three components. India has expertise in acid Thorex Process which is well entrenched to deal with the Th-^{233}U bundles.

Current R&D efforts aim at the development of multi-component processing methods by aqueous route to treat Th-U-Pu bearing fuels based on 5% TBP as extractant. The studies will lead to the development of a complete flow-sheet for the processing of Th-U-Pu including efficient fuel dissolution techniques. Initially, it is proposed to recover only ^{233}U and Pu after a short cooling of two years with a delayed recovery of Th after the decay of ^{228}Th.

The alpha radiolysis aspects of the "dirty" Pu due to enhanced burn-up are also being looked into. The recovered Pu is expected to be recycled in FBRs. The separated ^{233}U may require remote fuel fabrication for recycle. To meet this challenge, co-processing facilities with integrated fuel fabrication capabilities are also envisaged. Since fissile elements are recovered at an early stage, the left over thorium can be processed at a later stage in large through put plants. The extent of ^{228}Th and ^{229}Th contamination in the Th product and its significance during recycle is also being assessed. Segregated processing of Th-Pu-^{233}U and Th-^{233}U fuels is contemplated to restrict the minor actinide problems to selected streams.



Batch equilibrium data and counter current data are being generated. Reductive stripping was achieved by hydroxyl amine nitrate. Based on these studies a scheme for the three component processing is proposed.

P.S. Dhami et. al. Proc. NUCAR 2003 (2003)121.

B. REPROCESSING

10. ONGOING REPROCESSING PROJECTS

INTRODUCTION

India has already demonstrated its capability in design, construction and commissioning of three fuel reprocessing facilities to cater to needs of spent fuel treatment of the first phase of the three-stage Indian nuclear energy programme. With acceleration in the programme, the demand for Pu for FBRs of second stage, necessitated the setting up of more reprocessing facilities and associated ancillary units at a faster pace. This is being achieved by the involvement of the Indian industry in various stages of project execution.

10. ONGOING REPROCESSING PROJECTS

Nuclear Power generation programme of the country has undergone a sea change during last 2 decades. New advanced designs of the future power plants envisage the use of Plutonium with Thorium in the reactor core. To ensure the continued availability of Plutonium, Nuclear Recycle Group of BARC has undertaken construction of a number of new fuel reprocessing plants.

Recently, the Group has also developed the process flow sheet for separation of Uranium from Thorium rods irradiated in a research reactor. Designs of the plant for power reactor rods are in progress.

During the last few years significant progress has been made towards execution of the projects undertaken by the Group. These projects receive feed back from the existing operating plants which has resulted in bringing about a large number of improvements in designs to achieve enhanced safety in operation along with increased output.

In the past, the execution of the projects has been done employing in-house technical manpower. With an increase in the size and expanse of the projects active participation of Engineering Consultants available within the country was felt necessary. The projects are being executed in Engineering Service Consultancy and Procurement & Construction mode. This mode of execution has facilitated faster progress along with development of engineering expertise required for such projects within the country Salient features of the projects are 1. Designs are based on the latest international codes involving highest standards of safety and quality assurance. 2. Massive concrete construction. 3. Large volume of stainless steel piping housed in highly optimized in cell space.

■ Some of the major projects under execution are:

1. Project Revamping of Prefre (ROP)
2. Project Prefre 3A
3. Additional Waste Tank Farms at Tarapur & Trombay:

Project Revamping of Prefre (ROP)

ROP Plant under Construction

The Project Revamping of Prefre (ROP) under construction at Tarapur is a challenge in view of the fact that the construction of this facility is undertaken by the side of a plant under operation. The close proximity of an operating plant necessitated a very cautious approach during the construction of the foundation. Generally the mechanical construction activities commence towards the end of civil construction activity, however with a novel method of providing a false metal roofing in the cell areas, the work of erection of equipment support structure and stainless steel lining of the cell walls could continue concurrently with civil construction work.

Project Prefre 3A

Project Prefre 3A is under execution at Kalpakkam. The project objective is to augment the present reprocessing capacity of existing plant, by equipping already constructed hot cells. This plant being constructed by the side of an operating plant, isolation of the construction areas from the operation areas has been successfully implemented. The project is being executed under Engineering Services Consultancy and Procurement & Construction mode.

Additional Waste Tank Farms at Tarapur & Trombay

The new waste tank farms, designed to withstand the postulated seismic activity will ensure safe storage of high level waste before it is taken up for processing. Currently these facilities are under construction at Tarapur & Trombay.

C. WASTE MANAGEMENT

11. INDIAN PROGRAMME ON WASTE MANAGEMENT

INTRODUCTION

Safe Management of nuclear waste has been accorded high priority right from the inception of our nuclear programme. An Integrated approach, along with adoption of appropriate technology has been the key factor in the successful implementation of the waste management strategy. Although it is recognized that the technologies currently adopted are adequate, waste management being a sustainable development, sufficient scope exists for improvisation of technology to enhance process performance and meet future requirements.

11. INDIAN PROGRAMME ON WASTE MANAGEMENT

Safe & effective management of radioactive waste is vital for the successful implementation of Indian Nuclear Programme. Management of radioactive waste in the Indian context includes all types of radioactive wastes generated from the entire nuclear fuel cycle and also from installations using radio nuclides in medicine, industry and research. Management of these wastes covers the entire range of activities right from handling, treatment, conditioning, transport, storage and disposal.

Waste management facilities have been set up and are operational at various sites all over the country. Decades of safe operations have given valuable experience in the design, construction, operation and maintenance of such facilities.

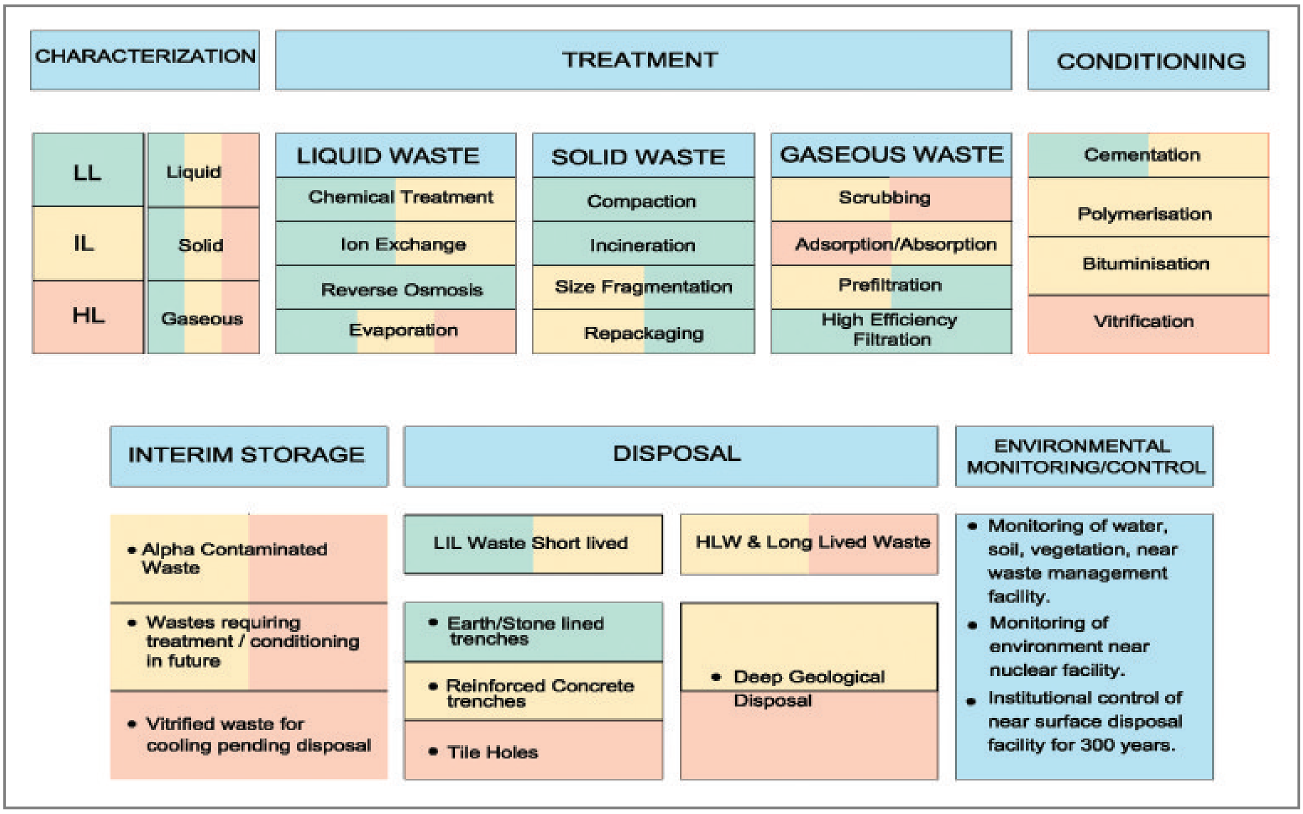
Utmost emphasis is given to waste minimization and volume reduction is the key factor, in the choice of processes and technologies adopted in radioactive waste management plants.

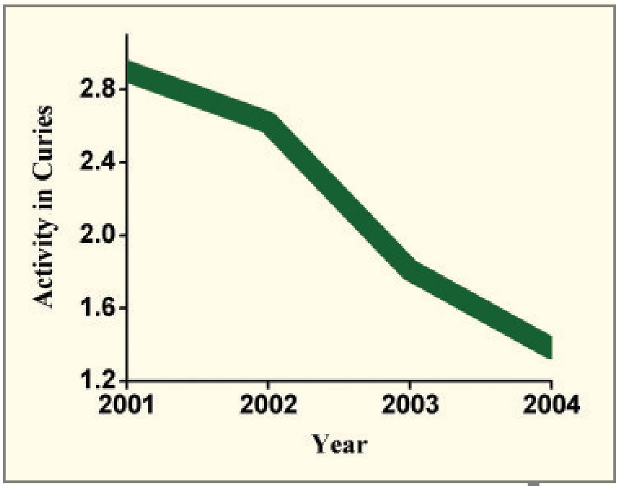
As a waste management philosophy, no waste in any physical form is released to the environment unless the same is cleared, exempted or excluded from regulations.

A comprehensive radioactive waste management system is established taking into account the operational capability for the management of radioactive waste and an independent regulatory capability for its overview.

It is well recognized that the technologies currently adopted are adequate. However, waste management, being a sustainable development, sufficient scope exists for improvisation of these technologies so as to enhance process performance and meet future requirements. Development & induction of cross-cutting technology are being adopted to address recycle & recovery of valuable resources from these wastes leading to a positive impact on the environment.

Waste Management Facilities at Trombay, Tarapur and Kalpakkam have been providing safe management for collection, segregation, conditioning, treatment and

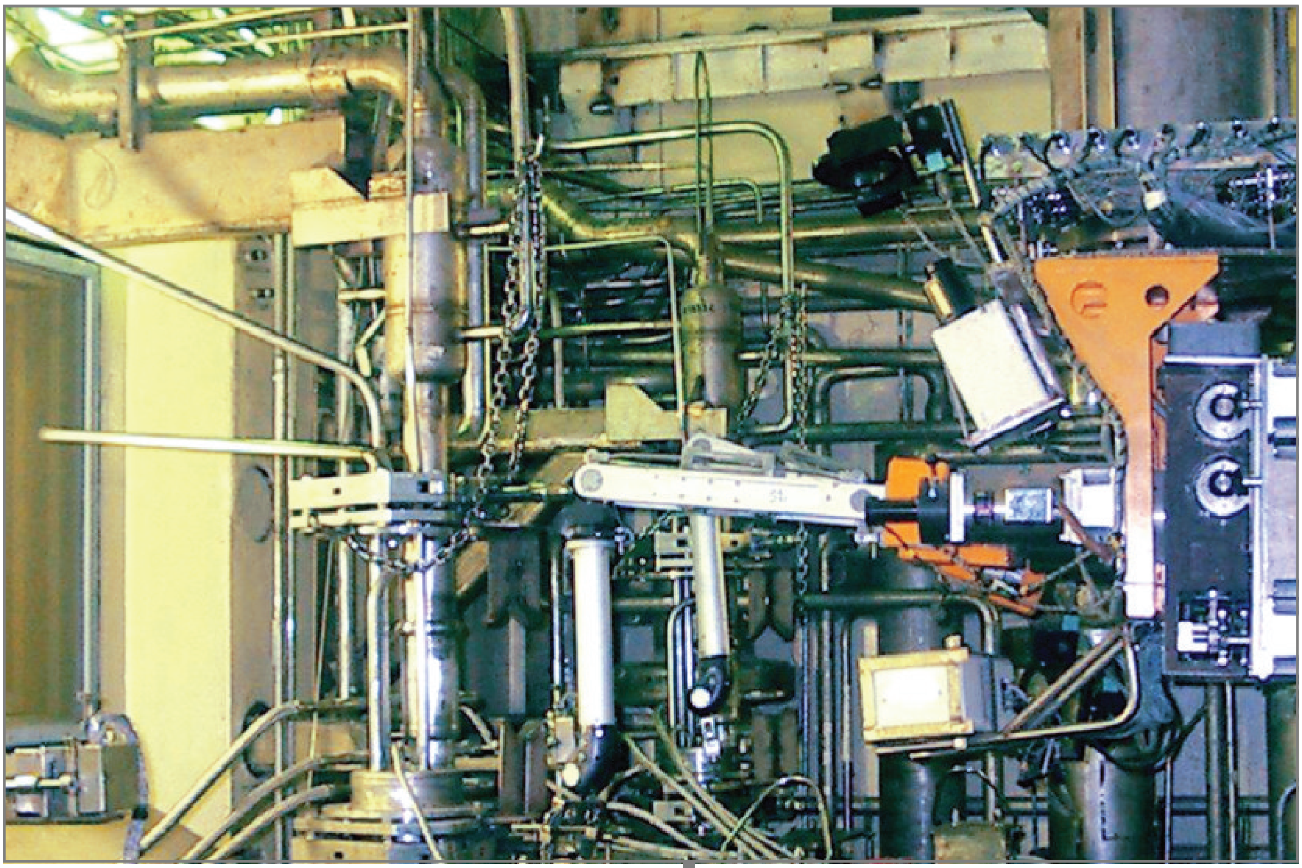




Progressive Reduction in Annual Discharges from TAPS, Tarapur

discharge/storage of radioactive waste generated from fuel fabrication, research/ power reactors, fuel reprocessing, nuclear laboratories, isotope production etc. The release of airborne activity to the environment is negligible and the radiation fields in the working areas are well within the limits.

Waste Immobilization Plant, Trombay inaugurated by the Prime Minister in Oct. 2002 has vitrified over 100 canisters of vitrified waste products. The Advanced Vitrification System involving Joule Heated Ceramic Melter is under advanced stage of commissioning at Tarapur. A scheme for separation of sulphate, residual uranium and recovery of radiocesium from HLW at Trombay is under development. Implementation of this scheme will not only lead to value recovery of radio cesium but will also result in higher waste loading in borosilicate glasses.



Vitrification at WIP, Trombay

C. WASTE MANAGEMENT

12. LOW & INTERMEDIATE LEVEL WASTES

INTRODUCTION

Low & Intermediate level waste streams from the entire fuel cycle have been well characterized and various processes for their treatment, conditioning and disposal are being practiced. Emphasis is on adoption of processes leading to high volume reduction and removal of major radionuclides like Cs-137, Sr-90 etc. Appropriate management techniques are also adopted for organic wastes emanating from the the fuel cycle.

12. LOW & INTERMEDIATE LEVEL WASTES

Low & Intermediate level liquid wastes are generally characterized by high volumes and relatively low levels of activity. These wastes are normally subjected to treatment so as to reduce their activity concentrations to a level at which they are allowed to be discharged as per national regulations. The concentrates emanating from the treatment processes are subjected to immobilization in suitable matrices. In view of their large volumes, attention is focused on the technology adoption that can result in downsizing of equipment, effective decontamination and minimization of secondary waste.

12.1 TREATMENT OF ALKALINE REPROCESSING WASTES BY SELECTIVE ION EXCHANGE

The intermediate level waste (ILW) streams from reprocessing operations are generally alkaline in nature and include the neutralized concentrates obtained from waste evaporation cycle and solutions resulting from chemical dejacketing of aluminium clad fuel.

Characteristics of alkaline reprocessing waste

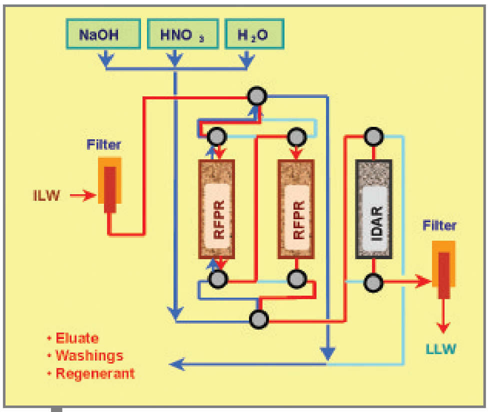
- **High concentration of Na-salts**
- **Radioactivity mainly due to ^{137}Cs**
- **Traces of ^{90}Sr, ^{106}Ru, Pu etc**

An innovative scheme based on separation of radionuclides by selective ion exchange has been developed and adopted for the management of this waste. When compared to direct fixation, this new approach leads to considerable reduction in the final waste volumes that require disposal.

The scheme utilizes indigenously developed cesium-selective Resorcinol Formaldehyde Polycondensate Resin (RFPR) to separate ^{137}Cs with very high efficiency. Phenolic -OH groups in the resin ionize under alkaline conditions and serve as cation exchange sites that have high selectivity for Cs^+ ions. An in-house facility has been established for its bulk production. The removal of ^{90}Sr is carried out using a commercially available macroporous Poly (styrene-DVB) Chelating Iminodiacetic Acid Resin (IDAR). Both these resins are used in repeated loading-elution-regeneration cycles. Suitable methods are used for the removal of other minor radionuclides also present in these waste streams, e.g., Zn-charcoal column for ^{106}Ru and chemical co-precipitation with sodium diuranate for Pu.

Resorcinol formaldehyde polycondensate resin (RFPR) showing Cs-selective phenoxide ion exchange sites

In a recent campaign at Trombay, nearly 700 M^3 of ILW was successfully decontaminated using this process. Using 50 and 100 L capacity ion exchange columns, ^{137}Cs activity was reduced from 40 mCi/L in the feed to 1-3x10^{-3} mCi/L in the treated effluent (DF>10,000). Elution of loaded activity could be carried out satisfactorily in 20 bed volumes of 0.5 N HNO_3 after every cycle.



Ion exchange process flow diagram for removal of ^{137}Cs and ^{90}Sr from ILW

About 28 KCi of ^{137}Cs was separated during the campaign. Adoption of this treatment scheme thus makes it possible to recover ^{137}Cs in large quantities for use as a radiation source.

S.K.Samanta, "Recent developments in the application of selective ion exchange process for the treatment of radioactive effluents and recovery of 137Cs", Nucl. & Radiochem. Symp., Amritsar (2005).

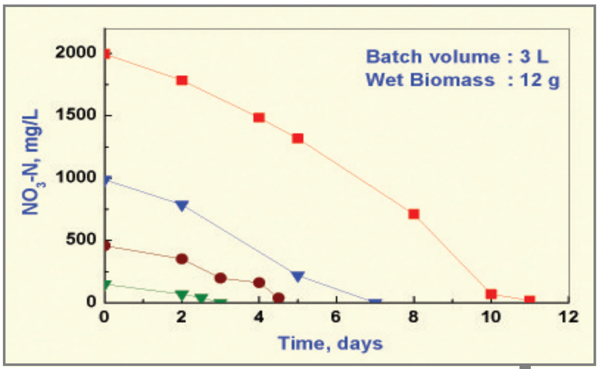
D.Banerjee and S.K.Samanta, Process chemistry and resin performance in the treatment of alkaline intermediate level waste by selective ion exchange", 14th Annual Conf. of Indian Nucl. Soc., Kalpakkam (2003).

12.2 BIODENITRIFICATION OF EFFLUENTS

Management of nitrates present in various liquid radioactive waste streams is a challenging task. The reprocessing of spent fuel results in low and intermediate level waste containing substantial quantity of sodium nitrate. After decontamination, it is essential to remove the nitrates prior to discharge of the treated effluents to the environment. Laboratory studies using a batch bioreactor have shown that biological denitrification under anoxic conditions in the presence of an added carbon source like methanol is an effective process for conversion of nitrates to nitrogen gas. A novel bench-scale flow-through bioreactor has been extensively tested for its denitrification efficiency using nitrate-bearing simulated waste. Effect of residence time, NO_3-N concentration, C/N ratio, micronutrients, etc. is being investigated. Complete destruction of 3500 ppm NO_3-N has been accomplished and efforts continue with higher concentrations.

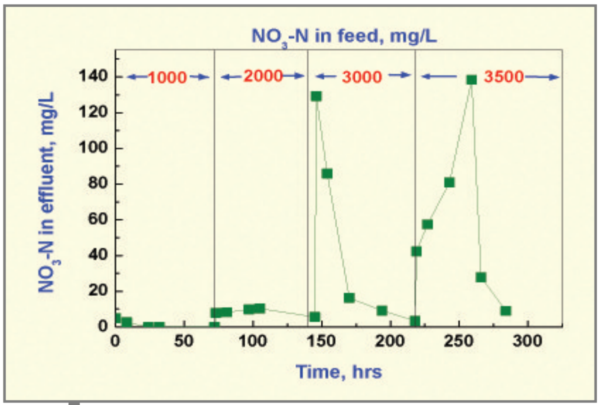
Waste containing sodium nitrate at the back end of nuclear fuel cycle

- Low level waste
- Intermediate level waste
    - ✓ Neutralized waste evaporation cycle concentrates
    - ✓ Decladding waste
    - ✓ Solvent wash waste



Denitrification in batch bioreactor

Upflow column bioreactor for denitrification (inset showing biomass attached to porous support within the column)



Denitrification in 4.8 L column bioreactor with increasing levels of NO_3-N in feed (Hydraulic residence time: 10 h for 1000 & 2000 mg/L; 36 h for 3000 & 3500 mg/L)

S.K. Samanta <sks@barc.gov.in>

12.3 MANAGEMENT OF SPENT ORGANIC SOLVENTS

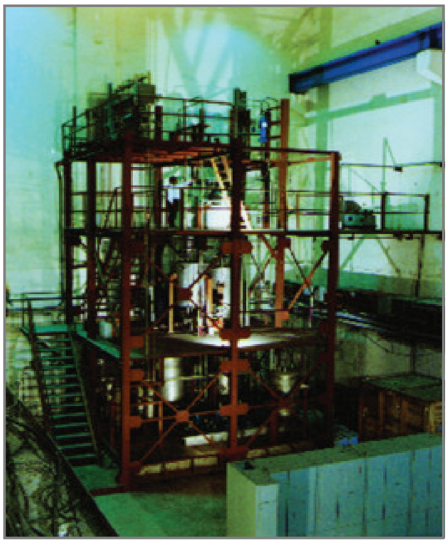
Repeated use of 30% TBP in n-dodecane during reprocessing operation leads to generation of spent solvent waste stream. Management options for this waste stream have to address their organic nature along with the associated radioactivity.

A total solution to the problem of such spent solvents has been achieved with the induction of the '*Spent Solvent Management Facility ETP, Trombay*'. Fresh wastes from reprocessing plants as well as backlogs are now being managed routinely in this facility.

The process adopted by this facility involves a treatment step developed in-house based on '*alkaline hydrolysis of TBP*', which renders the diluent practically free of TBP and activity. The recovered diluent after hydrolysis is incinerated or could be recycled. The aqueous bottom from the alkaline hydrolysis step is immobilized in cement matrix.

■ Engineering Scale alkaline Hydrolysis Demonstration Facility

Alkaline hydrolysis of TBP using NaOH leads to the formation of sodium salt of di-butyl phosphate and butanol which are both aqueous-soluble. The diluent, n-dodecane remains unchanged during the reaction and separates out as the top phase. Nearly all the activity associated with the spent solvents gets transferred into the aqueous phase resulting in the top dodecane, free of TBP as well as activity.



Repeated operations have established that the temperatures during the reaction did not exceed 110°C and pressure was maintained below -400 mm WC. The conversion of TBP to the reaction products was >99.6% in nearly 5 hours.

Quantitative recovery of diluent virtually free of activity and TBP content is being carried out routinely by this facility. The activity associated with the diluent is normally in the range of 0.4 to 4.0 Bq/ml for alpha and 0.04 to 10.0 Bq/ml with respect to gross beta. The Plutonium retention of this recovered diluent was 6.23 x 10^{-3} mg/L as compared to 2.8 x 10^{-3} mg/L for fresh dodecane thereby qualifying it for recycle. Non-recyclable diluents are incinerated in a specially designed excess air incinerator.

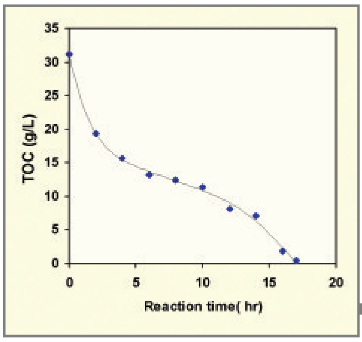
Organic Waste Incinerator

Smitha Manohar <smanohar@barc.gov.in>

12.4 PHOTOCHEMICAL OXIDATION PROCESS FOR ORGANIC WASTE TREATMENT

Photochemical oxidation process is under development for treatment of organic radioactive wastes. Among the organic wastes being currently addressed are spent ion-exchange resins, oxalate supernatant of reprocessing origin. Detailed laboratory investigations using immersion type photoreactor showed that photo-Fenton oxidation reaction can be used to decompose spent resins and oxalate. A tubular flow photochemical reactor was developed in-house for pilot scale photochemical oxidation studies.

A two-step process was developed for resin decomposition. In the first step, the resin is chemically converted into water-soluble product form using Fentontype reaction at 55-75°C with hydrogen peroxide in the presence of Cu^{2+}/Fe^{3+} catalyst. In the second step, the aqueous degraded resin solution is subjected to photo- Fenton reaction for complete oxidation of the organic matter under ambient conditions. The experiments were conducted upto about 7-litre scale. Kinetic



Kinetics of Resin Photooxidative Decomposition

results showed that photo-Fenton reaction requires 500 wh of uv energy per litre of resin solution.The organic-free solution resulting from the mineralisation reaction can be decontaminated by conventional methods to obtain high volume reduction. Similar studies on oxalate supernatant showed that nearly 250 units of uv energy/litre is required for its mineralisation.

C.Srinivas, G.Sugilal and P.K.Wattal, 'Management of spent organic ion exchange resins by photochemical oxidation', Waste Management Symposium WM'03, Tucson, Arizona (USA), Feb. 23-27, 2003.

12.5 PYROLYSIS STUDIES FOR SPENT ORGANIC IX RESIN

Pyrolysis of spent IX resins followed by immobilization of residues in cement matrix is being considered as an alternative to direct fixation in polymer matrices. Feasibility studies carried out at laboratory scale and pilot scale have established operating parameters for pyrolysis and the cementation step. Pyrolysis of IX resins at $> 350^{\circ}$C leads to generation of aromatic hydrocarbons, amines, SOx, H_2S off-gases. The use of Transition metal oxide catalysts are being studied for thermal destruction of these organics to meet discharge criterion. This process would eventually lead to a volume reduction factor of 3.

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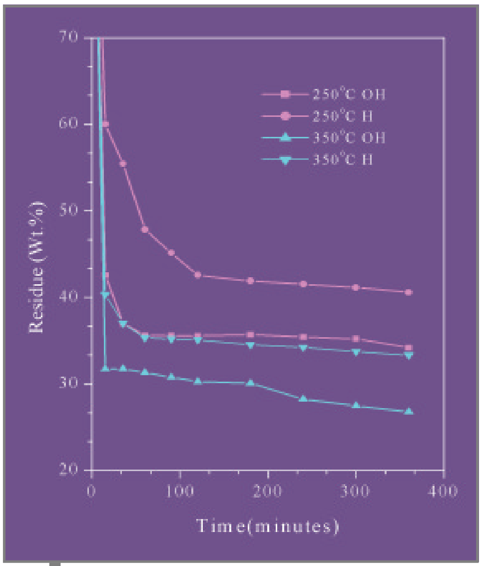
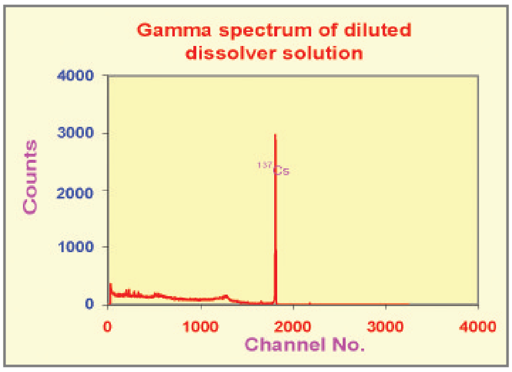


Carbonisation of IX resins at various Temperatures

12.6 DEVELOPMENT, TESTING AND APPLICATIONS OF COMPOSITE INORGANIC EXCHANGERS

Inorganic ion exchangers offer many advantages like high selectivity, good radiation stability and compatibility with matrices used for immobilization but are unsuitable for direct use in column due to microcrystalline nature and poor mechanical properties. Composite exchangers represent a group of inorganic exchangers, modified by using a small amount of binder to get larger particle size and granular strength. A universal binder has been developed to convert eight different inorganic exchangers in to composites form, which are being tested and evaluated as potential partitioning agents for

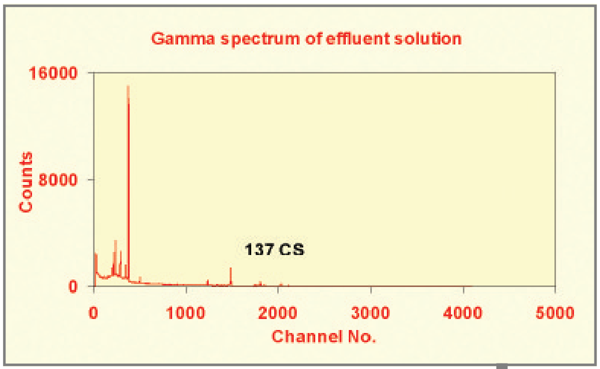


treatment of liquid waste streams generated at different sources of nuclear fuel cycle. Very high loading (75-90% w/w) of active component has been achieved in these materials.

Two varieties of composite AMP ion exchanger have been synthesized which were tested in three successful column runs with actual dissolver solution, simulated HLW solution and actual HLW. Results of dissolver solution column run as shown below indicate quantitative separation of radiocesium from these solutions.

Future work planned includes increasing the scale of the ion exchange columns over those used in the Laboratory and evaluate the associated effects on cesium removal from simulated/actual HLW.

A novel composite *polyantimonoic acid (PAA)* has been developed, which is being tested for removal of radio-strontium from acidic HLW.

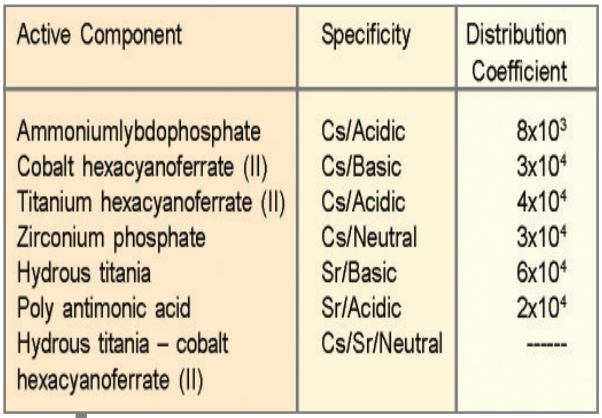


Gamma spectrum of effluent solution

A composite resin production facility has been setup for preparation of ion exchanger beads from the powder exchanger with organic polymer.

A resin extruder has been developed in-house for production of large samples of uniform beads of different mesh sizes.

A list of few composite ion exchangers already prepared in our laboratory is shown in the following table which have been tested for selective uptake of radionuclides.



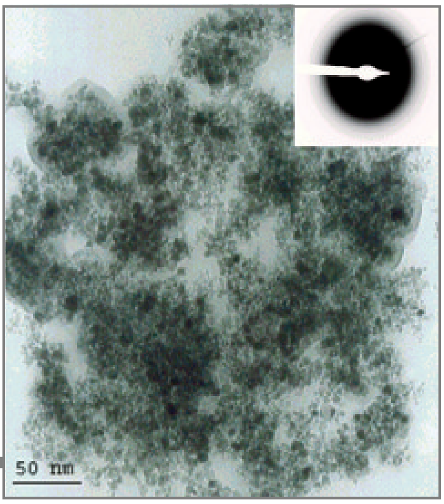
Active Component	Specificity	Distribution Coefficient
Ammoniumlybdophosphate	Cs/Acidic	8×10^{3}
Cobalt hexacyanoferrate (II)	Cs/Basic	3×10^{4}
Titanium hexacyanoferrate (II)	Cs/Acidic	4×10^{4}
Zirconium phosphate	Cs/Neutral	3×10^{4}
Hydrous titania	Sr/Basic	6×10^{4}
Poly antimonic acid	Sr/Acidic	2×10^{4}
Hydrous titania – cobalt hexacyanoferrate (II)	Cs/Sr/Neutral	------

Some of the composite exchanger successfully prepared

I.J.Singh, P.V. Achutan & P.K.Wattal, Proc. NUCAR-2001, Pune, 416(2001).

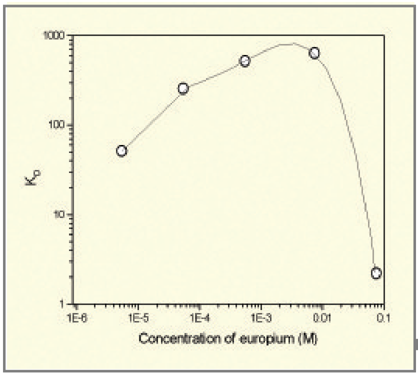
12.7 SYNTHESIS AND INVESTIGATION OF PROPERTIES OF MAGNETIC NANOPARTICLES IN RADIONUCLIDE REMOVAL FROM AQUEOUS WASTES

Magnetically-assisted chemical separation, emerging as a promising technology for decontamination of radioactive effluents, has the advantage of low inventory utilisation and

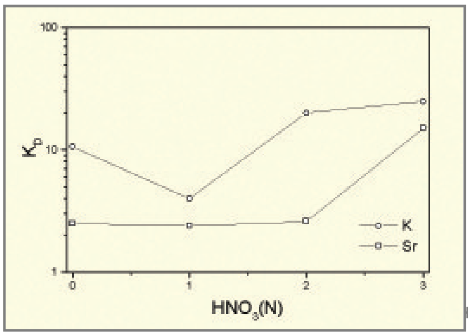


TEM image of clustered nanoscale magnetite particles within polymer matrix (Scale measures 50 nm) faster kinetics of separation. Nanoaggregates of magnetite potassium nickel hexacyanoferrate and magnetite calcium hydroxide phosphate composites, synthesised in-house have given a distribution coefficient (K_D) of 10^4mL/g for Cs and ~10^3mL/g for Sr from 3M $NaNO_3$ at pH~12. Different solvent extractants, such as dibenzo-18-crown-6, dicyclohexano-18-crown-6 and octyl (phenyl) diisiobutyl carbamoyl methyl phosphine oxide (CMPO), have also been studied by impregnating them on nanoaggregates of magnetite polymer composites. A K_D of ~10^3 has been observed for Eu in 2N HNO_3 with CMPO. TEM studies confirm the formation of nanoscale composites.

Bulk synthesis upto kilogram quantities of magnetite sorbents have been taken up for magnetic filter separation on a batch reactor with simulated wastes.



Distribution coefficient of europium between CMPO loaded magnetic particles and 2N HNO_3 versus concentration of europium (M)



Comparison of distribution coefficient of strontium and potassium between dibenzo-18-crown-6 loaded magnetic particles and 2N HNO_3 with variation in concentration of nitric acid

Ritu D Ambashta, Seikh Muhammed Yusuf, Mayuresh D Mukadam, Sher Singh, Piaray Kishan Wattal, D. Bahadur, Physical and chemical properties of nanoscale magnetite-based solvent extraction, Journal of Magnetism and Magnetic Materials, 293(1), 2005, 8-14.

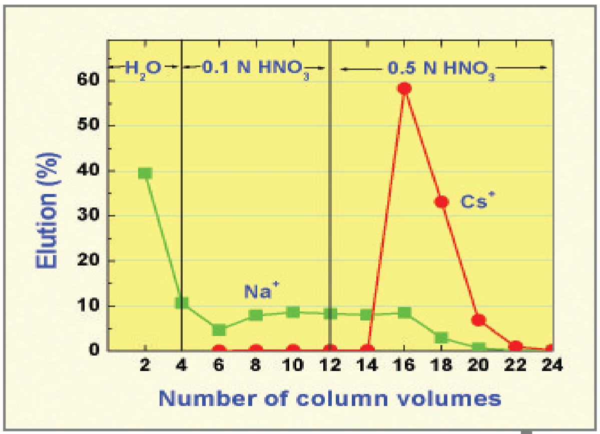
12.8 RECOVERY OF ^{137}Cs FROM RADIOACTIVE WASTE AND ITS UTILIZATION AS A RADIATION SOURCE

The importance of ^{137}Cs as a radiation source for use in industry and healthcare is well known. It has favourable decay characteristics ($T_{½}$: 30 y, E_y: 662 Kev) and its fission yield is high. When compared to the more commonly used ^{60}Co ($T_{½}$: 5 y), the use of ^{137}Cs as a radiation source is advantageous because of reduced frequency of source replenishment. Recovery of ^{137}Cs present in liquid waste streams from reprocessing plants is thus an attractive proposition. As noted already, the treatment of alkaline intermediate level waste by selective ion exchange process in India is associated with the separation of multi kilocurie quantities of this fission product. There are also plans to treat acidic high level waste at Trombay to separate sulphate which limits the loading of waste in the vitrified matrix. This treatment results in an alkaline ^{137}Cs-rich stream which can be processed by selective ion exchange to recover hundreds of kilocuries of this useful isotope. The separated ^{137}Cs, after immobilization in a vitreous matrix, can be utilized as radiation source for a variety of applications.

Applications of ^{137}Cs as radiation source

- **Brachytherapy**
- **Blood irradiation**
- **Hygienisation of sewage sludge**
- **Food irradiation**

The acidic eluate from ion exchange columns contains ^{137}Cs and high concentrations of Na^+ ions. The excess Na^+ ions have to be removed before ^{137}Cs can be immobilized to produce a radiation source of high specific activity. An innovative post-elution ion exchange processing step has been devised for this purpose. In this process, the primary



Separation of Na and Cs during sequential elution from loaded column

eluate is neutralized and then subjected to one more loading-elution cycle on RFPR. The higher ^{137}Cs activity and lower Na/Cs ratio in the eluate, as compared to the waste feed, results in higher loading of ^{137}Cs on RFPR. Only a small (2-3 L) RFPR column is required for this post-elution processing step because the volume of primary eluate is not large. Sequential elution of the loaded column finally results in a solution that has much higher concentration of ^{137}Cs and very low Na/Cs ratio as desired.

For immobilization of the purified ^{137}Cs concentrate, a borosilicate glass matrix has been developed. The matrix has low formation temperature (900 °C), low volatilization loss of Cs during vitrification and high leach resistance. A technique has also been developed for converting Cs-glass into small spherical beads of 3-5 mm diameter suitable for filling in source pencils. Efforts also continue to develop the technique for direct casting of molten Cs-glass in source pencils.

Cs-glass beads

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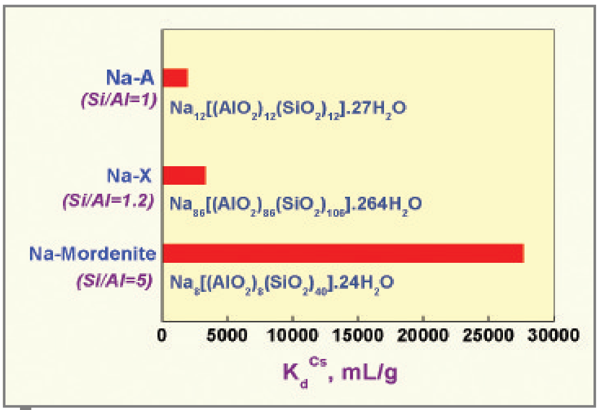
12.9 SYNTHETIC ZEOLITE FOR REDUCTION OF ACTIVITY IN SPENT FUEL STORAGE POOL

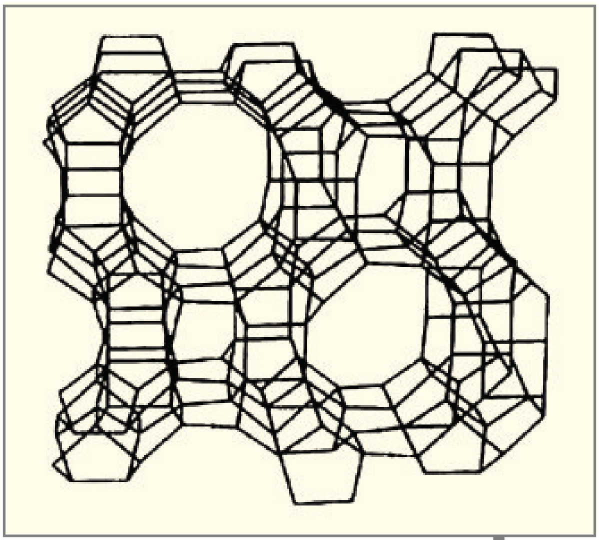
Synthetic aluminosilicate zeolites are attractive candidates for use as ion exchangers for efficient trapping of radionuclides present in nuclear waste because of their high thermal/radiation stability, ready commercial availability in column-usable granular form and compatibility with common immobilization matrices like cement or glass.



Uptake of Cs by different zeolites from a test solution containing 0.01 M $NaNO_3$ + $7.5x10^{-5}$ M $CsNO_3$

Zeolites 4A (Na-A), 13X (Na-X) and AR1 (Na-mordenite) are amongst the synthetic zeolites that are produced in India. The Cs selectivity of mordenite is well known. It is attributed to the high Si/Al ratio leading to low framework charge density. The uptake of Cs^+ ions by these zeolites from a test solution containing low concentration of Na^+ ions is as shown in the figure.

Mordenite has a two-dimensional channel system containing water and exchangeable cations. The main channels have



Structure of mordenite showing its two dimensional channel system

Initial ^{137}Cs activity	5x10^{-2} μCi/mL
Volume of zeolite	120 L
Volume processed	6900 M^3
Run duration	300 days
Total ^{137}Cs removed	96 Ci
Final ^{137}Cs activity	2.9x10^{-3} μCi/mL

Zeolite column performance summary

a cross-sectional diameter of 6.7x7.0 A. Smaller channels (2.9x5.7 A) branch out from the main channels. The uptake of Cs^+ ions by mordenite decreases significantly with increase in the concentration of competing Na^+ ions. Hence this zeolite is suitable for removal of ^{137}Cs from relatively clean effluents containing very low concentrations of dissolved salts, e.g., contaminated demineralized water in spent fuel storage pools. In a successful industrial scale application described below, synthetic Na-mordenite was used for reduction of activity in spent fuel storage pool at AFR (Away from Reactor) Facility, Tarapur Atomic Power Station.

The pool contains 1400 M^3 of demineralized water that was contaminated with 5x10^{-2} μCi/mL of ^{137}Cs activity. The water was passed in a recirculating arrangement at 1200 L/hour through a cartridge filter, a shielded column containing 120 L of Na-mordenite and finally a column containing 100 L of mixed-bed resin for control of pH, conductivity and silicate. The zeolite column very effectively removed ^{137}Cs from pool water.

The effluent from the zeolite column was always in the range of 10^{-4}-10^{-5} mCi/mL. The mixed-bed column downstream helped to control the pH, conductivity and silica content.

C. WASTE MANAGEMENT

13. HIGH LEVEL WASTE MANAGEMENT

INTRODUCTION

Management of HL waste has to take into account the need for their isolation and surveillance for extended periods of time. To meet this objective in the long term perspective, waste isolation system comprising multiple barriers are employed. The vitreous matrix in which these waste are immobilized constitute the primary barrier. This along with its packaging, engineered barriers in the repository and the surrounding geology (secondary barriers) together are expected to prevent the recycling of radionuclides back into human environment so as to pose no hazard. The long term strategy for management of High Level Waste would involve partitioning of long lived radionuclides that would result in reduction of radioactivity. Ceramic matrices are also being pursued to address specific waste streams.

13. HIGH LEVEL WASTE MANAGEMENT

Reprocessing of spent fuel leads to generation of High Level Liquid Waste. In line with internationally endorsed practices, a three stage programme for HLW management is adopted by India.

Stage 1: Immobilisation of HLW by converting it into inert and stable vitreous matrices.

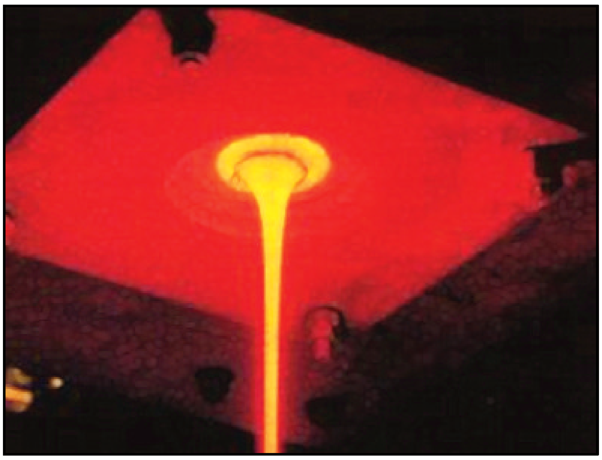
Stage 2: Interim Storage under surveillance and cooling

Stage 3: Ultimate Disposal of Solidified HLW.

India has a unique distinction of having operating vitrification plant at Tarapur & Trombay and another vitrification plant under advanced stage of construction at Kalpakkam. A solid storage and surveillance facility (SSSF) has been set up at Tarapur for interim storage of vitrified high level waste. An elaborate programme on deep geological disposal is also being pursued to realize the third stage of the programme.

The long term strategy for High Level Waste would involve its partitioning that would not only result in the reduction of radioactivity but could also have resource advantage. The final utilization / transmutation of the partitioned long lived radionuclides would be evolved based on the available technological options involving Fast Breeder Reactors and Accelerator Driven Systems.

Development of ceramic waste forms like synroc, NZP etc. are also being pursued to address specific waste streams on account of partitioning leading to waste volume reduction and enhanced long term safety.



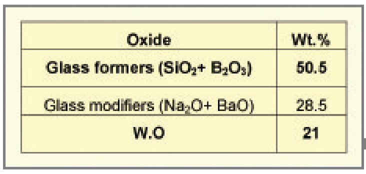
13.1 HIGH LEVEL WASTE FORMS

■ Vitreous Matrices for Sulphate Bearing HLW

The presently stored HLW at Trombay is characterized by significant concentrations of uranium, sodium and sulphate in addition to fission products, corrosion products and small amount of other actinides. Sulphate in the waste is derived from ferrous sulphamate used as a reducing agent for conversion of Pu^{+4} to Pu^{+3} during partitioning stage of reprocessing and is one of the troublesome constituents with respect to vitrification. Sulphate in the form of sodium sulphate can be accommodated in borosilicate matrix only to a limited extent i.e. 1 wt% maximum. At higher sulphate concentrations, a separate phase of alkali sulphate known as "gall" is formed. Its presence in the glass is not desirable as this phase is enriched with Cs and has high solubility in water. It was also experienced that the presence of this soluble separated yellow phase adversely affects homogeneous distribution of radionuclides and also causes problems during pouring of vitreous products into storage canisters. Barium-based borosilicate glass matrix (SB-44,) has been developed to accommodate sulphate homogeneously in the glass matrix. Lead Borosilicate showed phase separation on plant scale and was replaced by barium borosilicate. Barium borosilicate glass matrix is able to contain sulphate upto 3.5% wt without impairing the properties of the conditioned product. Phase separation of sulphates is shown in the figure.

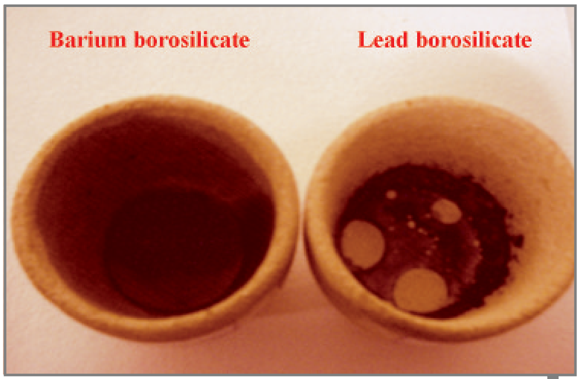
Vitrified Waste Product (VWP) made from simulated waste based on this matrix was evaluated for chemical durability, homogeneity, phase separation, thermal conductivity, viscosity, glass transition temperature, thermal stability etc. Experimental investigations indicated that conditioned product is homogeneous and has adequate leach resistance, meeting product acceptance criterion as per international norms. The developed composition of glass was tried in plant with chemically equivalent simulated waste. Based on the satisfactory performance, the newly developed matrix has been adopted in the plant for vitrification of HLW, after passing through critical review by safety / regulatory processes applicable to BARC facilities. More than 100 canisters

(9090 Kg) have been made so far immobilizing about 1,45,000 Curies of radioactivity safely and successfully.



Oxide	Wt.%
Glass formers (SiO_2+ B_2O_3)	50.5
Glass modifiers (Na_2O+ BaO)	28.5
W.O	21

Composition of Barium Borosilicate



A view of vitrified waste product based on barium borosilicate and lead borosilicate glass

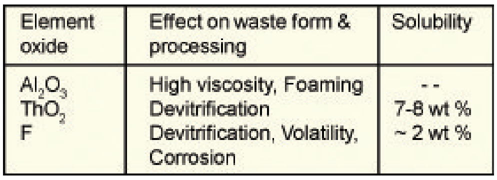
Kaushik C. P., et. Al., "Studies on Barium and Lead borosilicate systems for immobilization of sulphate bearing high level waste," in 14th Conference of INS "Nuclear Fuel Cycle Technologies: Closing the Fuel Cycle" IGCAR Kalpakkam December 17-19, 2003.

Vitreous Matrix for Futuristic Waste

Characteristics of high level waste from reprocessing of spent AHWR fuel are different from that of PHWR. It contains substantial amounts of problematic waste constituents like Al, Th and F. Their limited solubility in glass not only results in low waste loading but also has an impact on processing on account of viscosity, conductivity of molten glass and corrosion behavior.

Studies are being undertaken to optimize waste loading on different vitreous formulations. Borosilicate as well as iron phosphate based glasses have been considered.

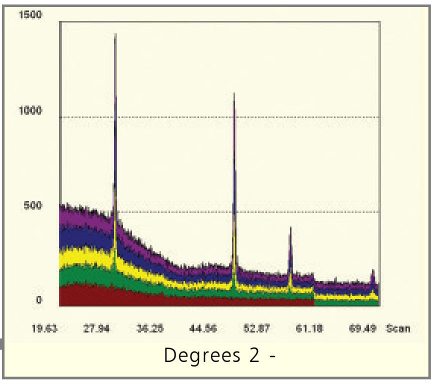
Borosilicate glasses containing fluoride beyond its solubility limit crystallize into their corresponding alkaline earth fluorides.



Element oxide	Effect on waste form & processing	Solubility
Al_2O_3 ThO_2 F	High viscosity, Foaming Devitrification Devitrification, Volatility, Corrosion	- - 7-8 wt % ~ 2 wt %

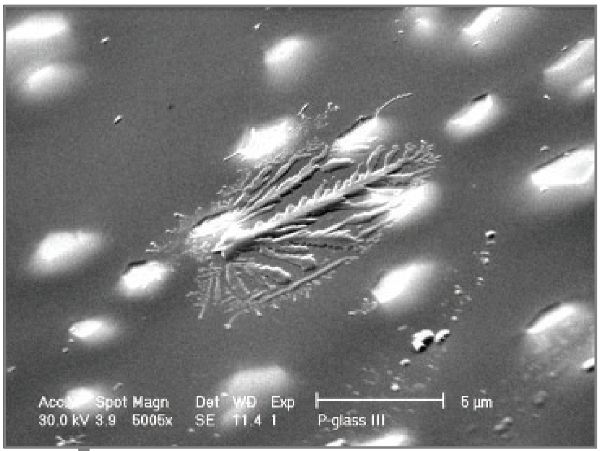
Glasses containing Na_2O & Al_2O_3 indicate crystallization of Nephline phase. Solubility of Platinum Group Metals (PGMs) & rare earths is also limited and they remain insoluble in glass matrix.

To accommodate higher Al_2O_3, Iron Phosphate glasses were studied. They are associated with crystallization of Fe, Ni are spinels.

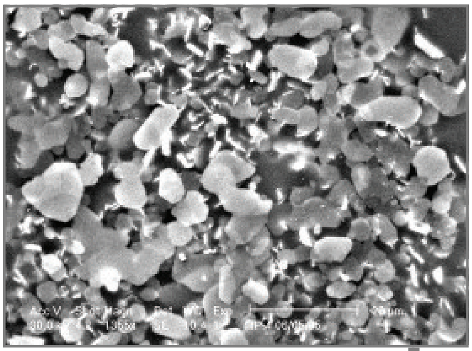


Crystallization of Fluoride in Borosilicate Glass

Alternatively, to increase waste loading, laboratory scale study related to removal of Al & F from HL waste by



CeO_2 crystals in Borosilicate glass



Fe, Ni Spinels in Iron Phosphate Glass

co- precipitating Fluoride along with Aluminum Hydroxide have been initiated. Preliminary results indicate that fluorides can be removed quantitatively as $Al(OH)_{3-x}F_x$ if resultant p_H is maintained between 5 to 6.5.

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Synthesis and characterisation of SYNROC

SYNROC is an assemblage of titanium, zirconium, aluminium, barium and calcium oxides blended with constituents of high level waste forming phases of zirconolite, perovskite, rutile, hollandite and intermetallics. Reprocessed waste of spent fuel of fast breeder reactor origin was chosen for immobilization into SYNROC (titanate based ceramics) due to the presence of higher concentration of devitrification causing elements such as noble metals and actinides. A four-stage preparation route for 100 gram batch synthesis was adopted. This was

1. Alkoxide hydrolysis under nitrogen atmosphere of precursor (Ti, Zr, Al).
2. Waste blending at isoelectric point of hydrolysed product with hydroxide of Ba and Ca.
3. Calcination of mixture at 700^{0}C under hydrogen/ nitrogen in quartz reactor.
4. Compaction of calcined product at 1250^{0}C under 50 M Pa.

Wavelength dispersion analyses of the phases show that Phase 1 is possibly a mixture of zirconolite, perovskite and hollandite phases. Phase 2 is identified as zircon phase. Phase 3 is possibly a rutile type TiO_2 phase with additions of Ca, Al, Ba and Zr. Phase 4 comprises of two types of phases I) rich in Ru (Te) and II) rich in Mo (Fe, Ni, Nd, Ag).

Bulk synthesis upto kilogram quantities of SYNROC with simulated waste are planned.

This work is being pursued in collaboration between BARC, IGCAR and NCL, Pune.

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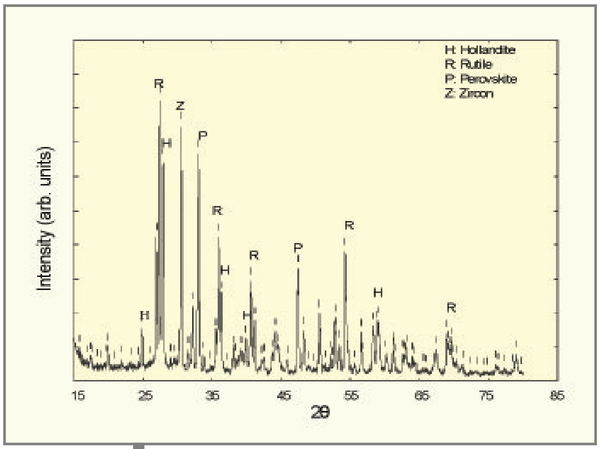
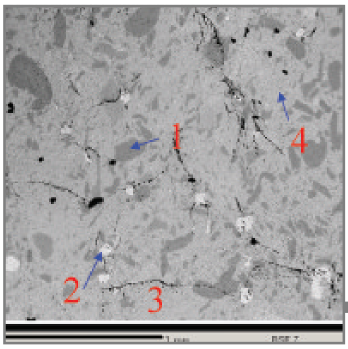
Calcined and Compacted Product



XRD of Compacted Product



Back Scattered Electron Image Showing Different Phases

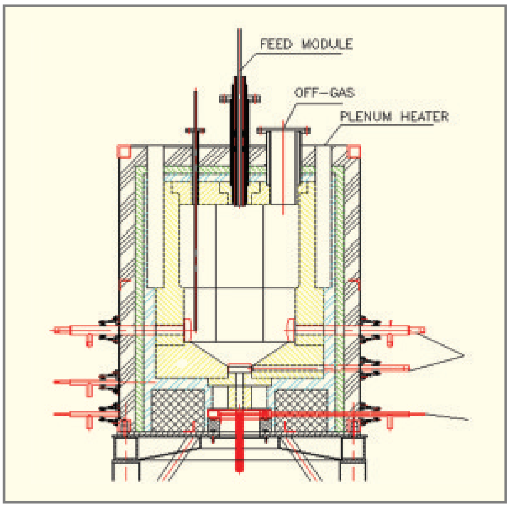
13.2 MELTER TECHNOLOGIES FOR VITRIFICATION

Melters for vitrification have to address not only the required throughputs but also material performance at elevated temperature(1000-1200 °C) and in contact with highly corrosive molten glass environment. Vitrification plants in India have been using the liquid fed metallic pot induction heated melters. The inherent limitations with these melters have been limited throughput and short melter life. Joule heated ceramic melters are being inducted in view of their higher throughput, better operational flexibility & prolonged life. Based on their performance, Joule heated ceramic melters could replace existing metallic melters in a phased manner. Advanced melters adopting cold crucible technology are also under study as a viable alternative to attain high temperature availability, compactness and ease out decommissioning problems associated with ceramic melters.

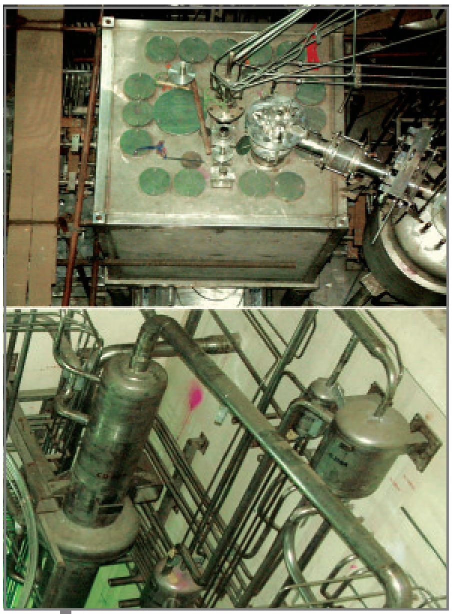
■ Advanced Vitrification System – Joule Heated Ceramic Melter

One of the achievements made in technology upgradation was the setting up of a Joule-heated Ceramic Melter-based Advanced Vitirification System (AVS) in the existing process cells of SSSF, Tarapur.

The Joule Melter Technology is essentially a single step process of direct resistance heating where immobilisation of HLW in a borosilicate glass matrix is achieved in a refractory-lined melter. The Joule Heated Ceramic Melter (JHCM) process exploits the high temperature behaviour of glass whereby it becomes an electrical conductor at elevated temperatures and favourable changes in its viscosity near the pour point helps in product withdrawal and shut off. The distinct features of the AVS are increased throughput, availability of higher furnace temperature and minimum dependence on operator skills.



Retrofitting of JHCM in the existing cell blocks was a challenge to associated systems without affecting the regular operation and maintenance of the plant. An additional limitation was suitably locating melter cell equipment like off-gas scrubber, condenser, condensate collection feed tanks and piping inside the melter cell in such a way that the remote operations envisaged could be carried out smoothly.



Top view of JHCM inside the Cell

A well-planned strategy for final decontamination, decommissioning and dismantling of JHCM was also to be addressed. Keeping in view the free space required for the reach of the remote handling gadgets during operation, layout for remote handling was carried out very carefully with lot of innovations.

JHCM has a throughput of 25 LPH with its external dimensions 1.5 x 1.5 x 1.8 meters. The main refractory is high corrosion-resistant Alumina-Zirconia-Silica refractory backed up with layers of insulating materials encased in a stainless steel box on suitable structural supports. The melter cavity has a hold up volume of 125 liters which is sufficient to provide a mean residence time of around 25 hours at the normal glass production rate of 1.5 Kg/hour. The plant is now complete in all respects. Initial trials have shown the system to be robust and promising. Full-scale operation is expected to be taken up soon.

■ Development of Cold crucible Induction Melter

Cold crucible induction melting (CCIM) is emerging as an attractive technology for the vitrification of high level liquid waste. The cold crucible induction melting technology offers flexibility in treating various wastes, susceptibility to various wasteforms with better waste loading and enhanced melter life. Its compact design is advantageous as in-cell equipment. Developmental efforts are in progress at the Back-End Technology Development Division for establishing this technology.

Laboratory and Bench Scale Studies

The cold crucible is manufactured from contiguous segments forming a cylindrical volume, but separated by a thin layer of electrically insulating material. The number and the shape of the segments and the insulating gap between them must be optimized to minimize the power dissipation by the induced currents in the crucible while ensuring sufficient cooling of the crucible.

Detailed study has been carried out to decide the geometry and configuration of the segmented crucible. A laboratory scale segmented crucible of 500 mm diameter was employed to test the selected geometry and configuration. Subsequent to the successful demonstration of the laboratory scale unit, a bench scale cold crucible induction melter of 200 mm diameter was designed and tested to establish bottom glass pouring.


Laboratory scale cold crucible melter

Engineering scale facility

An engineering scale facility is being set-up to establish the cold crucible technology employing a liquid-fed melter with a throughput of 15 LPH. The industrial scale melter is under construction and will be used to establish melter start-up procedure and melter operational stability. The crucible has an inside diameter of 500 mm with a glass holding capacity of 65 L. An induction heating power supply of 350 kW, 200 kHz will be employed to meet the total energy requirements.

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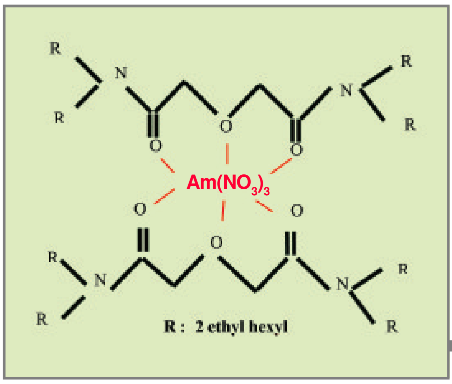
Glass pouring from bench scale cold crucible melter

13.3 PARTITIONING STUDIES FOR HIGH LEVEL WASTES

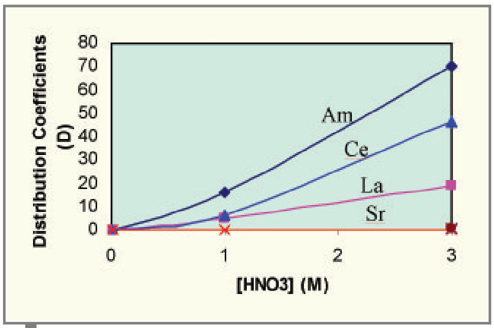
The long term strategy for the management of high level liquid waste in Indian context includes partitioning of minor actinides and useful fission products. Partitioning of HLW is presently being addressed through hydrometallurgical routes involving multi-step extraction employing different solvent systems.

In-house R&D studies have resulted in the development & synthesis of novel solvent like organophosphorous based CMPO (Octyl (phenyl)N N di-isobutyl carbomyl methyl phosphine oxide) and diglycol amide based TEHDGA (Tetra (2- ethyl hexyl diglycolamide) solvent systems. Bulk synthesis of both these solvents at the required purity has been carried out and suitable process for their use in actual application has been developed.



Diglycol Amide based Tridendate TEHDGA

The synthesized CMPO was used as a TRUEX solvent for all further studies. The TEHDGA solvent entailed systematic studies leading to a solvent system of 0.2 M TEHDGA along with isodecyl alcohol as a phase modifier in n-dodecane as the diluent. It has been observed that D_{Am} :26 was obtained using 0.25 M CMPO +1.2 M TBP in n-dodecane and D_{Am} : 70 for 0.2 M TEHDGA + 30% isodecyl alcohol in n-dodecane at 3 M HNO_3. Near total stripping was observed for the TRUEX system by the use of DTPA containing tailor-made strippants and 0.01 M HNO3 for the TEHDGA solvent. Further studies are underway to establish these systems for adoption in actual applications.



Distribution Coeff (D) for 0.2 M TEHDGA +30% iso-decyl alcohol in n-dodecane

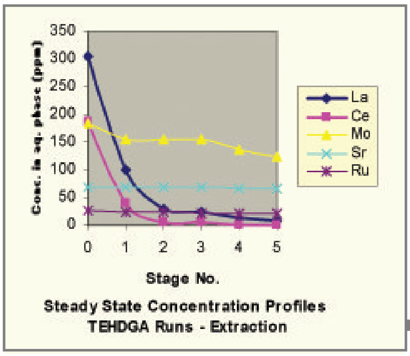
Both these solvent systems are being used on inactive engineering scale to establish the process of bulk separation of trivalent actinides from HLW. Lanthanides like cerium and lanthanum were used in realistic concentrations in the simulated HLW to simulate trivalent actinides for the bulk removal step. The engineering runs comprised of simultaneous extraction and stripping operations to establish reuse of the solvent system. In-house developed mixer settlers using passive system of mixing were used for these runs.

The results of such trials carried out over 8-10 hrs period have repeatedly shown near-total removal of cerium. It could therefore be concluded that separation of minor actinides from HLW along with lanthanides is feasible on engineering scale. Based on these studies an active engineering scale Actinide Separation Demonstration Facility is being set up at SSSF, Tarapur.

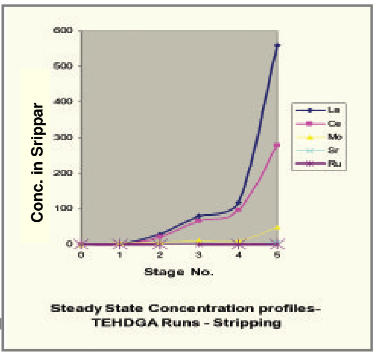
Summary of Engg. Scale Studies : TEHDGA Process
Solvent (O) : 0.2 M TEHDGA +30% iso-decyl alcohol in n-dodecane
Strippant (S): 0.01 M HNO_3
Flow Rates (W/O/S) : 30/12/15 LPH
Method of analysis : ICP

Separation of minor actinides from high acidity HLW is invariably accompanied by co-extraction of lanthanides which are present

Process Stream	La (ppm)	Ce (ppm)	Mo (ppm)	Sr (ppm)	Ru (ppm)
Sim. HLW (H^+ : 3.8 M)	304	186	185	68	26
HLW raffinate	7	0.5	123	66	25
Stripped Product	596	305	47	5	1



Steady State Concentration Profiles
TEHDGA Runs - Extraction

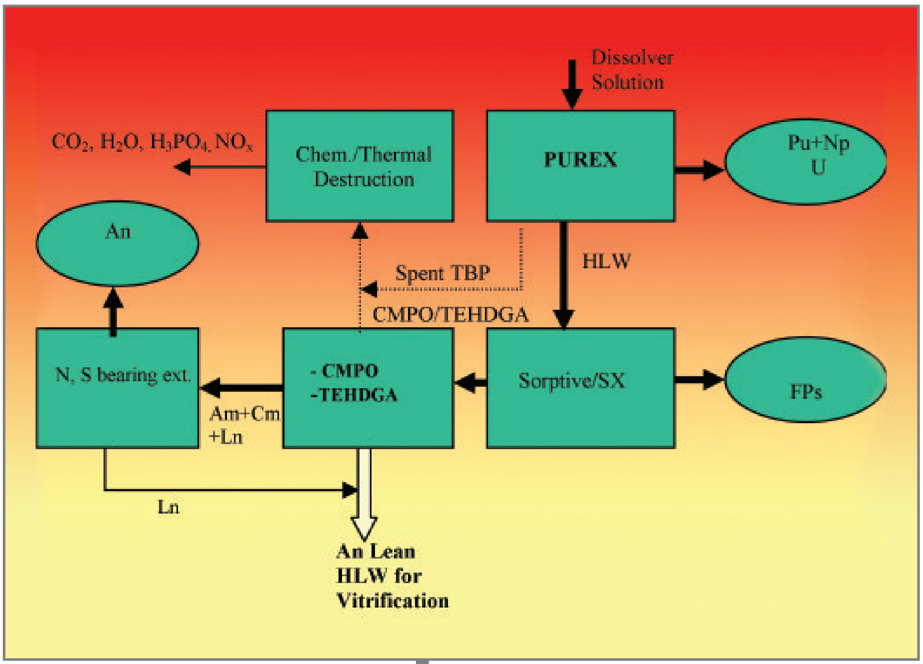


Steady State Concentration Profiles
TEHDGA Runs - Stripping

in much higher concentrations in the waste stream. Engineering scale separation of chemically similar trivalent actinides from trivalent lanthanides poses a challenge on account of non-availability of suitable extractants which work in acidic range. Nitrogen/Sulphur bearing 'soft donor' extractants are being synthesized and tested for separation of trivalent actinides from low acidity stripped product from the previous cycle.

While inorganic ion-exchangers like AMP and PAA are being developed for the separation of cesium and strontium from HLW, work on development of specific solvents like crown ethers is also being attempted.

Based on these R&D efforts a reference diagram for partitioning of HLW is shown below.



Partitioning of HLW – Reference Diagram

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C. WASTE MANAGEMENT

14. REMOTE HANDLING & TRANSPORTATION

INTRODUCTION

Indigenous development of remote handling equipment is pursued to address the concerns of radioactivity and other hostile environments encountered in the back end of the fuel cycle. Three Piece Manipulator developed in-house is being used in many of the facilities. Remote Inspection Devices, Servo-Robot, power manipulators etc. have also been developed for use in radioactive areas. Indigenization of Radiation Shielding Windows has lead to attaining self reliance in the production of RSW glasses.

14. REMOTE HANDLING & TRANSPORTATION

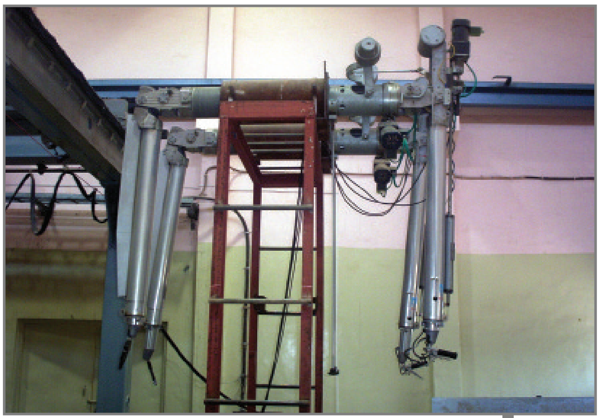
Back end of nuclear fuel cycle involving reprocessing and waste management has to reckon with hostile environment of high radioactivity, toxicity, high temperatures and corrosion concerns. Indigenous development of remote handling equipments is pursued to address these concerns. Remote handling equipments developed indigenously in active collaboration with industry includes Three piece manipulator, Remote Inspection/ surveillance Device, Power Manipulator, Custom designed Robots, Remote welding Units, Radiation Shielding Windows. Brief account of the systems developed is given below.

14.1 THREE PIECE MANIPULATOR (TPM)

TPMs are finding day-to-day use in radiochemical cells for the purpose of general remote handling. Out of the various designs developed internationally, three-piece modular manipulators are extensively employed in reprocessing and waste management plants. NRG has successfully carried out development of three piece manipulator for in-house use. The specifications of this TPM are as follows.

- Modular design
- Non gas tight type
- Fully shielded wall tube
- Payload capacity of 25 Kg
- Full extension of 3000 mm.

First pair of these TPMs have been successfully designed, manufactured, tested and put to use. Further units are currently under production. All components for the TPMs are of Indigenous origin.



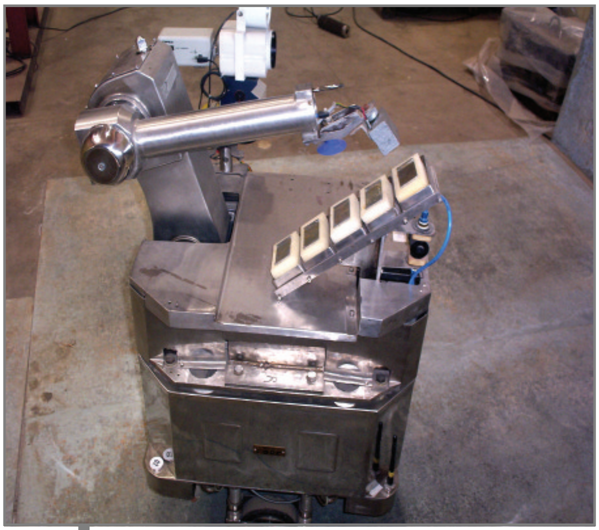
Three Piece Manipulator

14.2 REMOTE INSPECTION DEVICE (RID)

RID is an equipment developed by NRG for in-service surveillance / inspection of underground waste tank farms. RID consists of a radio-controlled mobile vehicle which carries the surveillance equipment / instruments and a remote station for control of the vehicle and display of the data collected by the vehicle.

Basic mission of the vehicle is to carry out videography of the tank farm, air sampling, radiation monitoring and swab collection of tank surface.

The radio-controlled mobile vehicle of RID consists of Power/ Steering Module, Payload module comprising of instruments, articulated arm and camera module as per mission requirements. The battery pack is designed for one-hour mission.



Remote Inspection Device

The RID has been developed in collaboration with M/s CDAC, Thiruvananthapuram. RID is a compact unit having overall size of 600 mm x 500 mm dimensions and about 800 mm height.This equipment could also find extensive use in radiochemical cells and other nuclear facilities for In-service Inspection (ISI).

14.3 POWER MANIPULATOR (PM)

Power Manipulator (PM) is an electrical manipulator employed for remote handling and maintenance work in radioactive areas.

The indigenous development of the Power Manipulator was carried out by BETDD, NRG for use in Revamping Of Power Reactor fuel reprocessing (ROP) project.

The PM developed is a seven axes bridge mounted manipulator with 100 Kg payload capacity at all positions of articulated arm with 0-100 Kg-f adjustable clamping force and 1000 Kg lifting capacity of the hook at bottom of telescopic boom. Out of these seven axes, three are in Cartesian framework i.e. bridge travel (X), cross travel of trolley (Y), and telescopic boom on the trolley (Z). Spatial positioning of the end of the boom is achieved by actuation of the X, Y and Z movements. At the end of the Z boom an articulated arm is fixed with four degrees of freedom - rotation of shoulder (main roll), primary & secondary pitching (main & second pitch) and a tool rotation (second roll). End-effector is a two-fingered gripper.


Power Manipulator

Ease of remote maintenance is facilitated by modular construction of the equipment.

Safety features such as overload protection in all axes, self-locking gearboxes and protection against external jacking have been incorporated in the PM. The PM has been operational at CDCFT for testing.

14.4 SERVO ROBOT FOR DECOMMISSIONING (SRD)

Servo Robot for Decommissioning (SRD) is a six axes servo controlled gantry robot with 25 Kg Payload capacity of the arm. SRD is intended for volume reduction of the components/ equipments declared as metallic waste in the Nuclear facilities.

SRD has three axes Cartesian Positioner with an operating speed of 0-1000 mm/sec and a servo arm with three rotary axes. SRD is an equipment, which incorporates features such as programmable pick up of tools from a designated tool station and returning to the same station after use in a fail safe manner.


Servo Robot for Decommissioning

A commercially available quick tool holding shunk has been employed for holding different tools such as plasma torch, gripper and a grinder, which connects tools electrically or pneumatically as per requirement.

SRD could be operated in programmed mode through a PC or in supervisory/teach mode. The SRD has been equipped with a vision system, which consists of CCTV cameras and monitors for obtaining visual feedback from the work area.

14.5 REMOTE WELDING UNIT (RWU)

The RWU is a special purpose-welding machine to be deployed in a hot cell facility of WIP plant. This unit has been developed for welding of vitrified high-level waste canisters/ overpacks with its lids remotely. The pulsed TIG welding process in the presence of

Ar gas is being used for the RWU. The lips of canisters/ overpacks are welded autogenously without using any filler metal.

Remote Welding Unit

The unit comprises of an inverter-based power supply, control panel and a welding head.

The self-positioning remote welding head has the welding torch positioned on a radial arm with remote adjustment provisions for welding of different diameters. A heat pipe design of heat sink provided for the electrode holder makes it very compact and can be easily replaceable remotely. The welding head has the provision of endless rotation of the welding electrode.

Additional features of RWU are remotely removable drive motor and quick electrical connectors.

First indigenously developed RWU is under successful operation at WIP, Trombay for the last three years. It has welded 100 canisters and around 33 overpacks successfully.

Remotely operated Forklift

14.6 REMOTELY-OPERATED FORKLIFT

A radio-frequency controlled, battery-operated forklift has been indigenously designed and developed for remote handling of low active drums. All the operations such as lifting, moving, tilting, steering, braking, grappling of drum are carried out remotely with the help of radio-frequency signals from a control panel located at a distance of 300 meters. Forklift is provided with a drum-grabbing unit with all motions to pick and place standard 200 liter drum at desired locations.

This forklift can be remotely operated through GUI (Graphic user interface) from a computerized control panel, mounted on a portable cabin and can be located conveniently. All the operations of forklift can be seen on a control panel through cordless broadcasting cameras installed on the front and rear side of the forklift. The system has been fitted with anti-collision sensors to avoid accidental striking of forklift with the object. Extensive testing of the forklift has been carried out at Trombay.

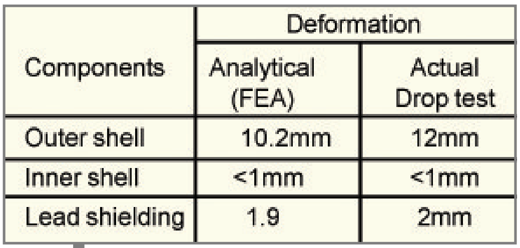
This remotely operated forklift is extremely useful for reducing radiation exposure during handling of low-active waste drums in near surface disposal facilities and also in waste assaying areas.

14.7 VITRIFIED WASTE PRODUCT SHIPPING CASK

Vitrified high level waste product overpacks are to be stored over a period of nearly thirty years prior to their deep geological disposal.

Presently vitrified waste product overpack produced at WIP, Trombay will be located at Solid storage and surveillance facility (SSSF) Tarapur which is nearly 150 km away from Trombay.

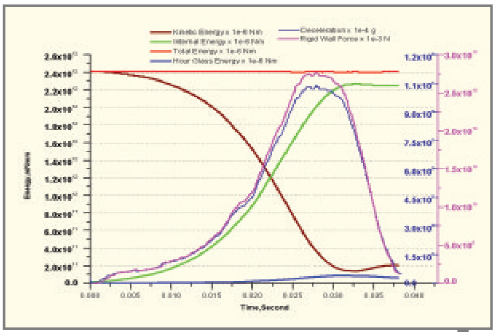
A shipping cask weighing approximately 26 tons has been designed to transport these vitrified waste product overpacks satisfying



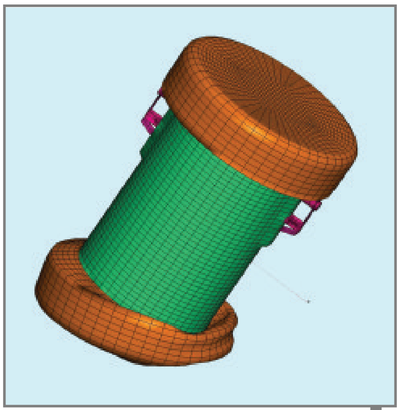
Components	Deformation	
	Analytical (FEA)	Actual Drop test
Outer shell	10.2mm	12mm
Inner shell	<1mm	<1mm
Lead shielding	1.9	2mm

Validation of deformations by FEA

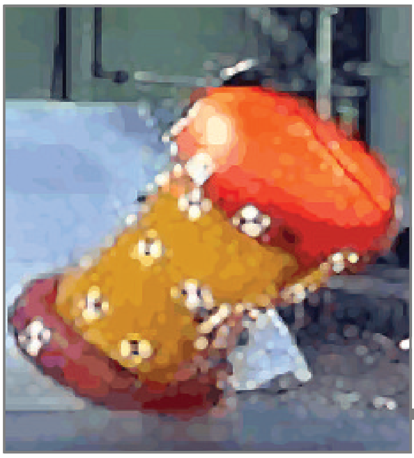
all the regulatory requirements of Type B (M) packages for transportation of high level radioactive material through public domain.



Simulation curves for 9 m Corner Drop



FEA Model after 9m Corner drop



Actual 9m-corner drop test on a scale down model of shipping cask

As a regulatory requirement, 9m drop tests at different orientations on an unyielding target surface and 1m drop on a rigid punch have been carried out. FEA model has proved that the deformations and stresses, energy absorbed, deceleration, rigid wall forces in various components are within acceptable limits. Validation of analytical models has been carried out by actual drop testing of scale down models up to a limit of 1:4 using high-speed photography, strain gauges and accelerometers.

14.8 ENMASSE COOLANT CHANNELS - HANDLING AND DISPOSAL

Pressurized Heavy Water Reactors (PHWR) used in India have demonstrated high reliability during several decades of reactor years of operation. One of the life-limiting components of the reactor is the coolant channel assembly, which is designed to be replaced periodically. In India to date, three reactors have undergone the Enmasse Coolant Channel Replacement Campaign (ECCR). In earlier two campaigns the pressure tubes were cut and disposed into tile hole in a non-retrievable manner. Strategy for management of pressure tubes from MAPS-1 has been considered with the objective to retrieve the pressure tubes for the following two alternatives:

(a) Compaction for achieving volume reduction prior to disposal

OR

(b) Chemical treatment and recovery of Zirconium for recycling.

In order to meet this requirement an underground pool was designed and constructed along with suitable facilities of handling and storage of pressure tubes. As Cobalt-60 is the major radionuclide present in the irradiated tubes, it is planned to store these tubes for a period of five years.

Handling of 300 pressure tubes of contact dose of about 3000R/hr each was carried out by using remotely-operated tools, pneumatically-operated tube grabbing devices for stacking the tubes in storage racks and shielded cask specially designed for underwater operations. Total campaign was successfully completed in record time of 45 days with reduced manrem expenditure of 1.3 manrem as against 65 manrem in earlier campaign paving the way for management strategy for future campaigns.

Under water storage of Coolant tubes from MAPS-1, Kalpakkam

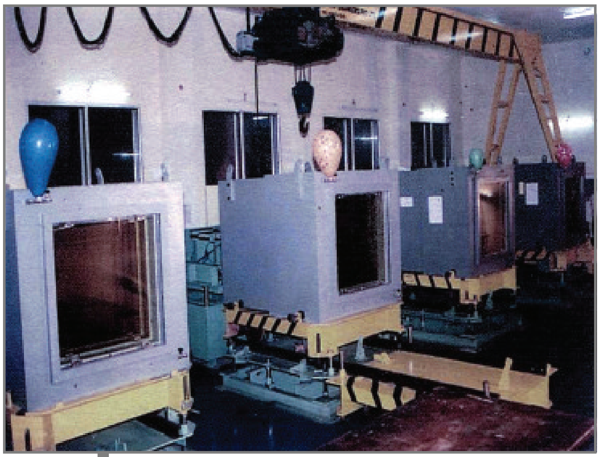
14.9 RADIATION SHIELDING WINDOWS

Development efforts towards indigenisation of Radiation Shielding Windows (RSW) has lead to attaining self reliance in the production of RSW glasses. Over the years, continuous development in this field has resulted in locating indigeneous sources for the supply of most RSW components such as high and medium density glass blocks, lead wool, mineral oil, gaskets etc. Extensive in-house tests and trials have been carried out to qualify such components for use in the manufacture of RSW.

A typical RSW comprises of a combination of various types of radiation-resistant glass blocks. This combination is based on the radiation-shielding requirement and for achieving optimum optical characteristics. Glass blocks are then assembled in a custom designed carbon steel/steel-concrete composite housing employing carefully selected components and special glass handling techniques in a clean room area. There are two basic design concepts in the construction of a shielding window; Dry and Oil Filled. has many performance advantages such as reduction of reflection losses and enhancement of viewing angles within a given liner size. In both designs, the sizes could range from large hot side viewing area (typical - 1100 mm x 1100 mm) for concrete cells to hot side viewing area of 150 mm x 150 mm for lead and steel cubicles. While the RSWs for concrete cells are a combination of glasses ranging in densities from 2.5 gm/cc to 5.2 gm/cc, the ones used in lead/steel cubicles are essentially built up of medium and high-density glasses. Completed Window assemblies are usually inserted into a steel or cast iron wall liner, embedded into the wall.

In a notable achievement 54 large-sized dry-type RSWs of 8 different designs for concrete cells have already been manufactured in the heavy press unit of M/s Hindustan Machine Tools Limited located at Hyderabad . BARC engineers created a clean room facility at HMT for this purpose. HMT personnel were also trained on glass assembly techniques. Plans are afoot to take up manufacture of oil-filled RSW required for other projects and smaller RSWs for lead and steel-walled cubicles and laboratories.

With a view to achieving total self reliance this department has also entered into an agreement with CGCRI Kolkata for the manufacture of high-density lead glass blocks. These glasses in combination with available borosilicate glass slabs can be used to manufacture oil-filled RSWs required by users in BARC and other DAE units. As per our requirements CGCRI has installed a plant-scale facility for producing large-sized lead glasses of densities varying from 3.6 gm/cc to 5.2 gm/cc and complete supply of approx. 20 tones of glasses within the next few years. Work on this project is proceeding well at CGCRI. On successful completion of this endeavor we would achieve full indigenisation in the case of RSWs.



Radiation Shielding Window

C. WASTE MANAGEMENT

15. WASTE VOLUME REDUCTION - SOLID WASTE

INTRODUCTION

Solid waste management plants in India are equipped with facilities for segregation, repacking, compaction, incineration and embedment of radiation sources. Compaction provides economic benefit in terms of lower volumes for disposal of non-incinerable waste. The present emphasis is on design of super compactors (> 1000 te) with a view to achieve higher volume reduction factors and minimize exposure to personnel.

15. WASTE VOLUME REDUCTION – SOLID WASTES

Radioactive solid waste is generated during various processes and operations. These compactable solid wastes include air filters and other materials like mops, clothing, papers, plastics etc. The compactable waste and air filters contribute to nearly 50% of the total solid waste. Except filters, other wastes are placed in a standard 200 litre drum. Compaction technique leads to safe disposal of lower volumes of waste.

Drum / Filter Pelletizor – Trombay

15.1 PELLETISATION FOR COMPACTABLE SOLID WASTE

A hydraulic compactor of 200 tonne capacity has been developed and deployed along with the requisite material handling and PLC-based control system. The waste is compacted along with the metallic drum and reduction in volume of 4-5 times is achieved.

The final pelletized product is achieved employing three-stage compaction. This ensures safe and control release of contaminated entrapped air & water. Pelletisation of filters and other waste have not only resulted in the saving of disposal modules, but also major reduction of release of dust associated with otherwise uncompacted filter.

On an average 1500 drums and 1200 filters are compacted annually.

15.2 METALLIC WASTE COMPACTOR

A metallic waste compactor of 1000-ton capacity capable of pelletization of radioactive metallic waste drums has been developed indigenously. This remotely-operated compactor is for handling Cat III & IV solid metallic wastes in shielded facility. The charging of feed drums with subsequent handling of the product pellets is done remotely ensuring adequate containment and ventilation. Safety interlocks have been provided for protection against overpressure, over travel and collision during operations. Remote operations ensure total containment of displaced air / liquids during pelletization. The system includes built-in product ejection systems with PLC-based controls and diagnostic features.

Based on the operational experience of this compactor, a supercompactor of 2000 ton capacity is being engineered addressing compaction of highly irradiated components like zircaloy hulls, coolant tubes, glove boxes and other solid wastes (metallic) generated during decommissioning of various nuclear facilities.

Metallic Waste Compactor

C. WASTE MANAGEMENT

16. ALPHA BEARING WASTES

INTRODUCTION

Stringent regulations with regard to the disposal of alpha bearing wastes call for special handling and management techniques. Low active solid/solidified waste with specific activity less than 4,000 Bq/ml is disposed of in near surface disposal facilities. Higher active solid waste is presently stored retrievably in alpha tight containers or in tile-holes. A number of alpha assaying, treatment and conditioning methods are at different stages of development or demonstration.

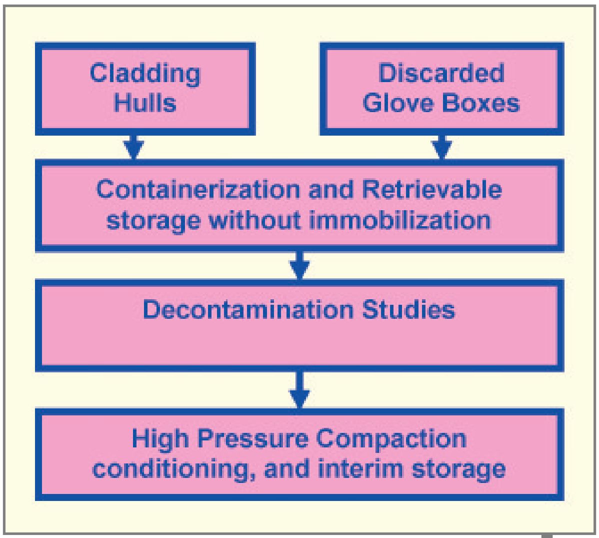
16. ALPHA BEARING WASTES

Alpha active wastes are generated in different nuclear facilities of DAE. Stringent regulations with regard to their disposal call for setting up of centralized interim storage facilities for the higher active packages, pending their final treatment, conditioning and/or ultimate disposal in deep geological formations. Further, safety and economic considerations emphasize a need for development of processes suitable for their volume reduction and solidification. Constant improvement in safe management of alpha waste is in progress in Nuclear Recycle Group covering aspects from design, operations to long term R&D.

16.1 PRACTICES & DEVELOPMENT ACTIVITIES FOR ACCUMULATED ALPHA WASTES

Practices: Aqueous alpha active wastes are subjected to direct cementation or treated by precipitation techniques with provision for recycle of sludge with potential of recovery of U and Pu. Aqueous wastes with low alpha contamination, generated during alkaline hydrolysis treatment of organic wastes, is also similarly dealt with.

Low active solid/solidified waste with specific activity less than 4,000 Bq/gm is disposed of in Near Surface Disposal Facility (NSDF), while the higher active solid waste is presently stored retrievably with the generators in alpha tight containers or in tile-holes in NSDF. Setting up of dedicated interim storage facility at each site is on hand. Alpha Waste Management Facility (AWMF), at Kalpakkam will provide waste-assaying/sorting/segregation to be followed by compaction or acid digestion. The facility also incorporates systems for cementation/packaging of solid waste and treatment of TBP waste by alkaline hydrolysis.



Management Approach for Special Alpha Waste

Alpha waste interim storage facility, Trombay

Developmental Activities: A number of alpha assaying, treatment and conditioning methods are at different stages of development or demonstration. Special wastes such as cladding hulls and discarded glove boxes are being studied for volume reduction involving final stage of compaction. Towards this, initial studies with high pressure metal waste compactor are successfully completed and engineering scale facilities are being set up. Remotized dismantling and feasibility of prior decontamination will also be studied. Incineration of ash-less paper, alkali dissolution of cellulosic waste, acid leaching from PVC items, decontamination of glove boxes are some of the methods tried by operating plants for Pu recovery. As a long term plan, establishing these methods on a plant scale and also process development for recovery and recycle of Pu from chemical sludges and acid digestion-residues will be attempted.

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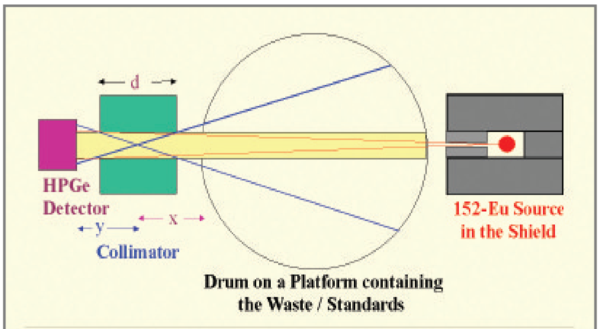
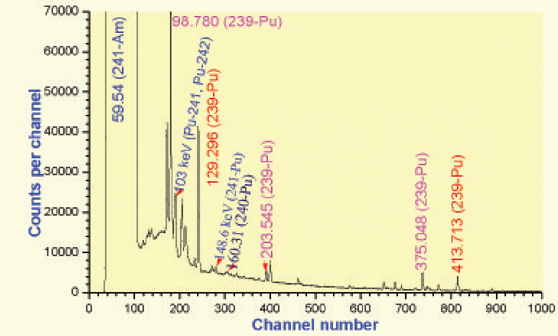
16.2 SEGMENTED GAMMA RAY SCANNING FOR ALPHA WASTE PACKAGES

A segmented gamma ray scanner using a 10% HPGe detector system has been developed for detection/analysis of special nuclear materials and other radionuclides in waste packages. The waste drum is positioned on a platform, where the drum can be scanned radially as well as axially by the collimated HPGe detector system.

The gamma rays spectrum analysis is carried out using computer program based on digital signal processing developed in-house. The ^{239}Pu activity above 25 mg can be detected in a 200-litre drum. The detection limits will go up in the presence of gamma ray background or high-density materials. A safe estimate can be above 50 mg of ^{239}Pu.



Block diagram for the waste drum monitor



Gamma ray spectrum of Plutonium (239-Pu) on HPGe detector

The detection efficiency of the HPGe detector system was determined using standard sources of plutonium, distributed uniformly in the drum along with inactive waste. The attenuation correction factor for the 129.3, 203.5, and 375.0 and 413.7 keV gamma rays of ^{239}Pu has been evaluated using the gamma rays of ^{152}Eu. The attenuation corrected C.P.S. of the standard drum and unknown drum are used to determine the amount of ^{239}Pu present in the waste drum.

Using the present system, the ^{239}Pu up to gram level can be estimated with an accuracy of 20% depending upon the distribution of the activity in the drum. The accuracy improves as the amount of ^{239}Pu increases.

In order to improve the accuracy and reduce the time of counting for each drum, a passive gamma ray scanning system using a set of HPGe Detectors for the assay of special nuclear materials and nuclear waste is being planned in future. Active and passive computed tomography will be incorporated in this system. Detection limits will also get lowered and identification of the physical form of the material will be possible.

Sarbjit Singh and V.K. Madan; Automatic processing of gamma ray spectra employing classical and modified Fourier transform approach; Report BARC/1994/E/038.

C. WASTE MANAGEMENT

17. DISPOSAL OF RADIOACTIVE WASTES

INTRODUCTION

A multi barrier approach is followed in the disposal of radioactive solid wastes. The overall safety against migration of radionuclide is achieved by proper selection of waste form, suitable engineered barriers, backfill materials and the characteristics of the geo-environment of the repository site. Based on the nature and type of the radionuclide present in the solid waste and its concentration the repository could be near-surface or in deep geological formations. Operation of various Near Surface Disposal Facilities (NSDF) has led to considerable expertise in this field. Our programme on site selection & host rock characterization is under evaluation for deep geological disposal.

17. DISPOSAL OF RADIOACTIVE WASTES

Disposal as a final step in the management of radioactive waste involves confinement or isolation of these wastes from biosphere in the repositories. Based on the longevity and concentration of the radionuclide present in the waste, the repository could be either near-surface or in deep geological formation.

India has extensive & varied experience in the operation of near surface disposal facilities (NSDFs) in widely different geohydrological and climatological conditions. Over the years, considerable expertise has gone in refining and improving the design and construction of these NSDFs. A system of multiple barriers employed in these NSDFs ensures isolation and release of radionuclides below permissible limits to the environment. This is ensured by regular monitoring and periodic performance assessment of these NSDFs.

Disposal of long-lived and high level waste in deep underground geological formation is one option which has received world-wide attention. In India, the most promising formation is granitic rocks. In this context, our programme of site selection and host rock characterization for an Underground Research Laboratory is under evaluation.

17. 1 NEAR SURFACE DISPOSAL

As a national policy, each nuclear facility in India has its own Near Surface Disposal Facility (NSDF). There are seven NSDFs currently operational within the country. These NSDFs in India have to address widely varied geological and climatological conditions.

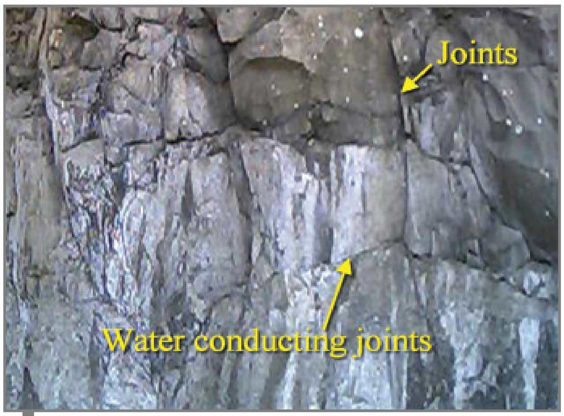
The performance of these NSDFs is continuously evaluated to enhance the understanding of migration, if any and to adopt measures for upgrading the predictability over a long period of time.

■ Performance assessment and service life prediction of Reinforced Concrete Trenches:

Performance assessment of Reinforced Concrete Trench (RCT) is systematically undertaken through field investigations and predictive modeling. NDT investigations on operating RCTs and laboratory studies on NSDF materials have demonstrated that RCTs are in sound condition even after an operational period of three to four decades. Mathematical models have been developed to predict the probability of failure as a function of target lives for various safety indices such as concrete cover thicknesses, climatic factors, maintenance period for the structure, water to cement ratio, water proofing etc. Modeling studies for a typical RC trench under limiting conditions have predicted a minimum service life of nearly 240 years. This study was completed in collaboration with CBRI, Roorkee.

■ Geohydrological studies – A tool to identify the groundwater pathways for migration

Sub-surface evaluation of these NSDFs is carried out systematically by geological and geohydrological investigations to identify potential groundwater pathways defined by top soil, weathered rock, fracture networks, interflow porous layers, contact planes etc. in different lithological units as depicted in fig. below.

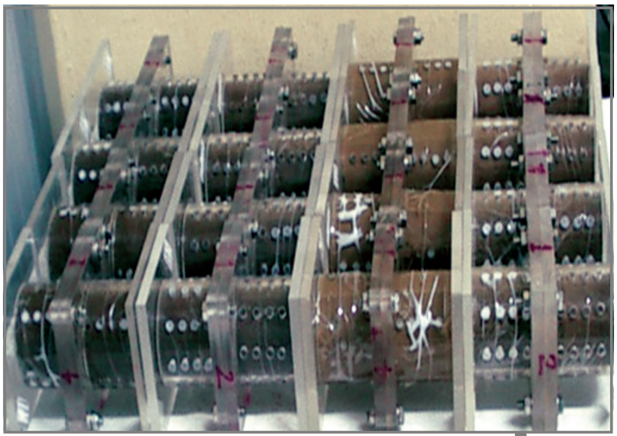


Typical Groundwater Pathways due to Intersecting Joints in Basaltic Formations – Trombay

Fig. typically depicts groundwater pathways due to intersecting joints in basaltic formation at RSMS Trombay. This sub-surface information has been obtained by means of drilling and lithological studies, i.e. heterogeneity and multi-well tracer experiments. For precise determination of subsurface pathways, state-of-art geophysical surveys using Ground Penetration Radar (GPR) are planned up to a depth of 30m.

Radionuclide migration through unsaturated soil – Laboratory and Field studies

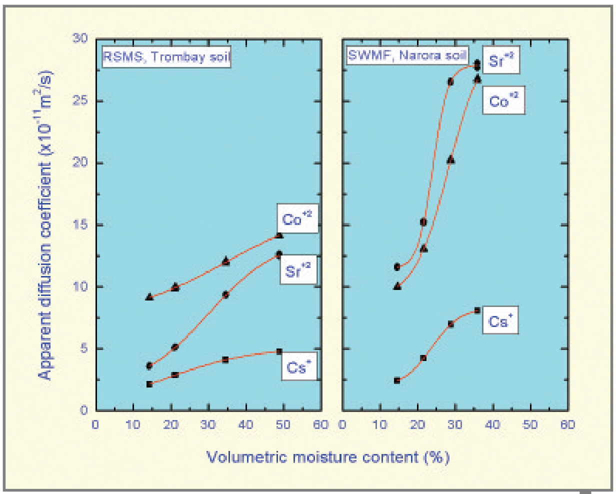
The top soil in NSDFs is generally unsaturated and provides a retarding barrier against contamination of groundwater. Understanding of migrational behaviour of contaminant through this zone, is carried out both at laboratory and field.



Diffusion cells with spiked and virgin soils

In laboratory experiment apparent diffusion coefficients have been determined using soil samples from Trombay and Narora for radioisotopes ^{137}Cs, ^{90}Sr and ^{60}Co in the dedicated lab scale diffusion cells.

The study reveals that apparent diffusion coefficient is a function of moisture content and it can't be linearly extrapolated over the range of moisture content.



The variation of apparent diffusion coefficient with volumetric moisture content for different soil samples

The apparent diffusion coefficient for Trombay soil, ranges from (2.12-14.20) E-11 m^2/s and for Narora soil from (2.41-28.06) E-11 m^2/s depending upon compaction states of the soil samples and radionuclides.

Lysimeter experiments include Time Domain Reflectometer (TDR) along with pore solution samplers

Field tracer experiments (Lysimeter experiment) have been initiated to evaluate *in-situ* hydraulic conductivity and radionuclide migration through unsaturated soil.

These experiments provide valuable information on the travel time of different radionuclides.

Monitoring and validation of mathematical models of migration

Mathematical models are developed to predict the migration of radionuclides in near and far field as a part of safety assessment of NSDFs. Continuous monitoring is undertaken to validate the assessments and to enhance confidence.

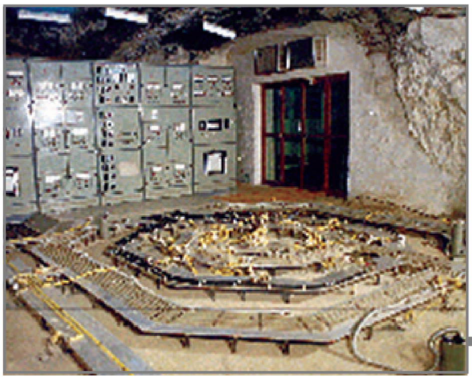
Based upon these studies the average migration rate of radionuclide is calculated, which corroborates well with the prediction of mathematical modeling.

17. 2 DEEP GEOLOGICAL REPOSITORY

A programme for development of a geological repository for vitrified high level long lived wastes is being pursued actively, involving *Insitu* experiments, site selection, characterization and laboratory investigations.

A. *Insitu* underground experiments

For assessment of the rock mass response to thermal load from disposed waste overpack, an experiment of 8-years duration was carried out at a depth of 1000 m in an abandoned section of Kolar Gold mine. The thermal processes were also modeled by developing suitable codes. Good agreement between predicted and measured parameters was obtained.

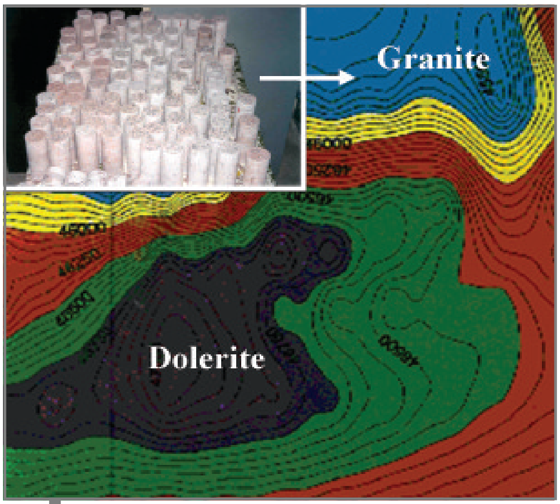


Underground experiment in Kolar Gold Field, Mysore

Some more *in situ* experiments pertaining to testing of full-scale engineered barriers i.e. simulated waste overpack, bentonite clay buffers and clays sand admixture, are planned to study the behavior of thermal, chemical, mechanical and hydraulic processes around overpack. Also for development of methodology and technology for charecterization of field scale fractures as pathways for radionuclide and gas migration, experiments are planned in abandoned underground mines in future.

B. Site selection and characterization

Geologically, India is endowed with a number of suitable rocks to serve as host rocks for geological repository viz. granites, basalts, shales etc. The current investigations focus on granites due to availability of vast regions occupied by these massive granitic rock with very good mechanical, geochemical and geohydrological properties.



Magnetic Intensity map of a site with granitic rocks retrieved from 450m (inset)

A few promising areas lying in NW and Central India, occupied by good quality granites were systematically investigated using satellite data, geological and structural mapping on different scales, geophysical surveys viz. electro-magnetic, resistivity and magnetic to generate three dimensional structural and lithological models. These models were validated and refined with shallow and deep drilling amounting to about 5000 m in 25 boreholes.

After characterizing the host rock for its geochemical, hydraulic and rock mechanical properties, about 22 zones, 100 sq km each have been demarcated as potential regions for further investigations. One on these zones has been investigated in detail to narrow down an area of about 4 sq km as suitable candidate site.

Such investigations are being pursued with the involvement of national agencies like Geological Survey of India, Mineral Exploration Corporation Ltd. and National Geophysical Research Institute, Central Mining Research Institute, National Institute of Rock Mechanics, IISc, IIT etc.

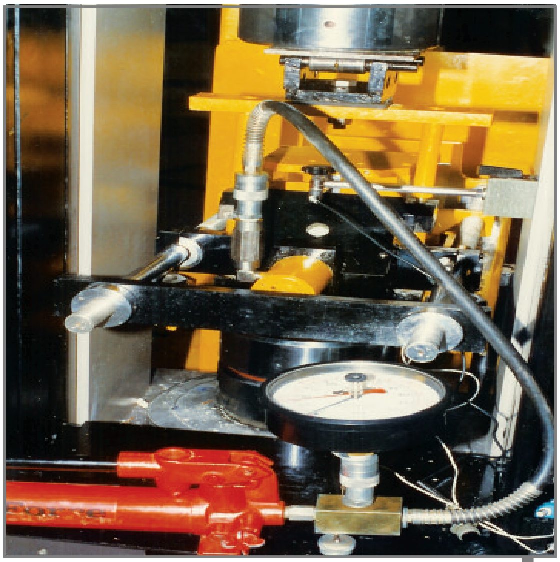
C. Laboratory Investigations

Geochemical Characterization

The host rock from potential sites has been subjected to detail petro-mineralogical and geochemical investigation to evaluate the their impact on rock mechanical and hydraulic properties. Diffusion coefficient for a number of radionuclides like Cs, Sr etc have been determined.

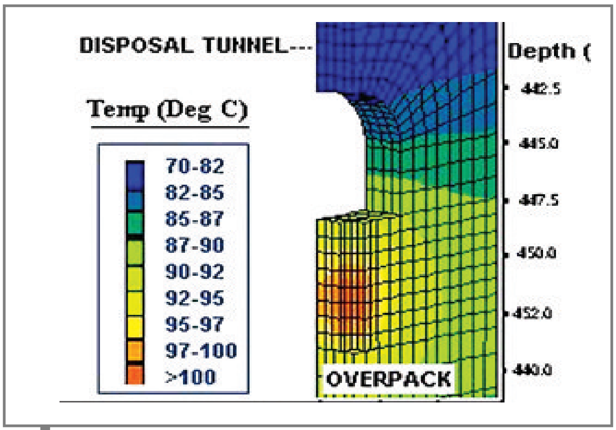
Rock mechanical Characterization

As a part of host rock characterization, study on the pre and post failure behavior of granitic rocks under varying loading and permeability test at different temperatures (30° -160°C) including three-dimensional micro-crack development at aforesaid temperatures using SEM, acoustic emission and ultrasonic techniques. Rock mechanical properties like Joint roughness, basic friction angle, joint wall compressive strength, peak shear strength, normal stiffness, shear stiffness in heat treated rocks from deeper level have also been measured with the help of instruments specifically designed for such purpose.



Shear apparatus developed at NIRM for rock mechanical studies of jointed rock

Finite Element Modelling of thermo-mechanical response in granites



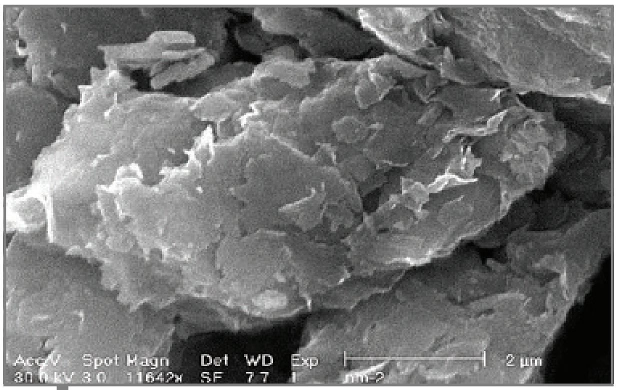
Numerically simulated temperature fields around a disposed over in a disposal tunnel of 5m diameter

Numerical analysis for the rock mass has been performed using three-dimensional finite difference code to model the inelastic behavior of the rock mass, simulate the excavation sequence and ground support installations and thermal–mechanical coupled behaviour. The thermal impact on host media has been modeled for 1000 overpacks.

A typical case of disposal of single overpack with a heat out put of 500 W in a 5 m diameter disposal tunnel in granitic rock is shown in figure.

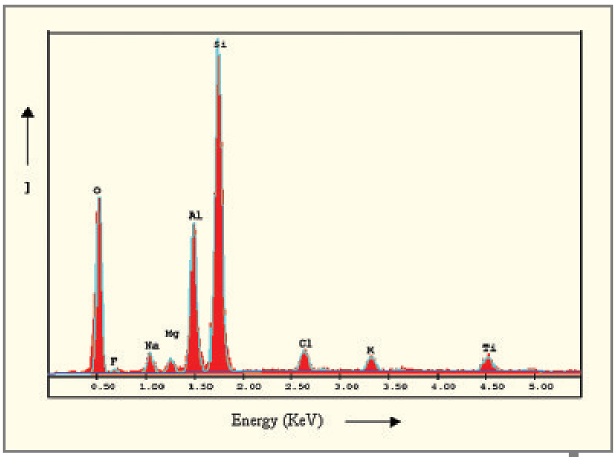
17.3 BACKFILLS AND BUFFERS FOR GEOLOGICAL DISPOSAL

Backfills and buffers constitute the most important components of multibarrier scheme adopted in a geological disposal system in hard rocks. These layers are placed between



SEM Micrograph indicating Flake Morphology the waste overpack and the host rock mainly to restrict the groundwater flow towards the waste form and to retard the migration of radionuclides in the event of their release from the overpack. Swelling bentonitic clays predominantly composed of smectite mineral have emerged as preferable choice for such use due to their very low hydraulic conductivity and high retardation for radionuclides. Besides, their swelling property adds in sealing the fractures in the host rock.

Indian swelling clay deposits are being evaluated for their suitability. Studies are underway to characterize their mineralogical compositions, geochemical characteristics viz. pore water compositions, hydration, cation effect, diffusion and adsorption for various radionuclides, engineering properties viz. Atterberg limit, plasticity index, swelling potential etc both under normal and elevated temperatures. Suitable admixtures of these clays with sand and crushed rocks are also being optimized for future testing *insitu* environment.



EDX spectra of swelling clay-2 from western India

Studies suggest that Bentonite deposits of Barmer Basin in Rajasthan with reserves of about 20 million tonnes are suitable. Mineralogicaly, they mainly contain mineral smectite (50-60 %) with quartz, felspar, kaolinite etc.

XRD pattern of heat treated (400 & 600°C) clay samples show a change in d-value corresponding to Montmorillonite phase indicating temperature dependent transformations of the mineral, This is also supported with thermogravimetry analysis. Smectite content, free swelling volume (20 – 30 mL/g) and also Cation Exchange Capacity (50 – 65 meq/100 g) of these clays have been found to decrease with temperature.

A mixture of 50% Barmer clays and 50% sand, with maximum dry density of 1.61 g/cc and optimum moisture content 21% with good compaction characteristics has been found suitable for fabrication of highly compacted bentonite clay bricks for use as buffer around disposed waste overpacks. Future investigations will involve laboratory and *insitu* testing of these compacted buffers under varying temperatures for evaluation of change in key functions like swelling, dehydration, illite conversion, thermal conductivity and evolution of near-field geochemistry.

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