

**Editorial**

*Over the past decade, increased public pressure to provide more electricity, reduce air pollution, and slow the rate of global warming has led many to revisit the potential of nuclear power to meet anticipated demands for more energy.*

*However, global warming is real. It is counterproductive to continue to spat over whether it is a natural phenomenon or the consequence of industrialisation and deforestation. It is far too risky to do nothing, just in case the enviro-sceptics are right. Billions of people in Asia alone live under a smog cloud kilometres high. Yet there is no single solution; just a complicated array of possibilities.*

*Nuclear power can contribute significantly to reducing emissions of greenhouse gases. Annual Green House Gas (GHG) emissions (expressed as CO<sub>2</sub> equivalent) would reach some 6.3 Gigatonnes (Gt) in 2050, i.e. around one-third of the total GHG emissions from the energy sector. The factor of four greater reduction in GHG emissions from continued nuclear growth, relative to nuclear phase-out, highlights the significant role that an expanded use of nuclear energy could play in helping to alleviate the risk of global climate change. This illustrates clearly the importance of timely implementation. The immediate option includes taking a very long, hard and careful look at nuclear power.*

*In a longer-term perspective, non electrical applications of nuclear energy, such as heat, potable water and hydrogen production, could be developed, and these applications could enlarge significantly nuclear power's contribution to GHG emission reduction. The country takes pride in the conduct of the unique FBTR mixed carbide fuel that was fabricated in BARC and has surpassed all the expectations in performance. This was possible through strict adherence to specifications and characterization at every stage.*

*This bulletin on 'Nuclear Materials' Guest Edited by Dr.V.N.Vaidya, DAE-BRNS Dr. Raja Ramanna Fellow, Fuel Chemistry Division, brought out the salient features that are involved in the design, development, fabrication and characterization of nuclear fuels and I am sure readers would find the reading informative. IANCAS is indebted to Shri R. Kalidas for providing 'FOCUS' on the theme of the bulletin.*

**G.A. Rama Rao**

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## *From the Secretary's Desk*

*Dear Members,*

*Greetings from Mumbai.*

*As you are aware, the eligibility criteria for IANCAS awards have been modified to facilitate larger participation. The age limit of Dr Tarun Datta Memorial Award has been increased to 45 years from 35 years earlier. Similarly, the window period for Prof H.J. arnikar Best Thesis award has been increased to 2 years. The relevant details along with proforma has been published in this bulletin. The same can also be found in our web site ([www.iancas.org](http://www.iancas.org)). The last date for receiving application is 30<sup>th</sup> November 2005 and I urge you, especially members from universities, to bring this information to the notice of eligible candidates.*

*The process of electing the next executive committee (for 2006-2008) has already started. The relevant notification is carried in this bulletin as well as the web site. It has been scheduled to complete the entire process by first week of January 2006 and charge will be handed over to the elected EC during the annual general body meeting in February-March 2006.*

*We have already completed two National Workshops at Chandigarh & Guwahati, and the third one will be held at GITAM, Vishakhapatnam during 21-29<sup>th</sup> November 2005. We continue to get overwhelming response to our Workshops (both National & College level) and I thank you all especially the resource persons for this success.*

*The present issue deals with nuclear materials & characterisation. I put on record my sincere thanks to Dr V.N. Vaidya, former Head, Fuel Chemistry Division, BARC who is the guest editor for bringing out this bulletin. I am sure you will enjoy reading this issue.*

**P.K. Pujari**



## **Dr. Tarun Datta Memorial Award**

*Indian Association of Nuclear Chemists and Allied Scientists (IANCAS) invites nominations for the annual Tarun Datta Memorial Young Scientist Award from eligible scientists for their outstanding contributions to the field of Nuclear and Radiochemistry. The Award, carrying a cash prize of Rs.5000/-, a citation and a medal, will be presented to the selected candidate during the Annual General Body Meeting (AGM) of IANCAS.*

### **Eligibility**

*Citizens of Indian nationality below 45 years of age as on 31<sup>st</sup> December of the calendar year of the Award. The candidate must have made significant contributions in the field of Nuclear and Radiochemistry, or Applications of Radioisotopes for the basic research in any branch of sciences.*

*It may be noted that the award would be given for research work carried out in India.*

### **How to apply ?**

*The application should be as per the proforma given on the reverse side of this announcement. Photocopies of the proforma may also be used or downloaded from the web site ( [www.iancas.org](http://www.iancas.org)). Applicants should submit the proforma along with a summary (not exceeding 500 words) highlighting the significant research contributions & achievements especially during the last five years. In addition, they should enclose two passport size photographs, proof of age, and reprints of ten best published papers in support of the application and a declaration by the applicant ratified by the Head of the Department, Research Guide or Head of the Institution. The declaration should also bring out clearly the contributions of the co-workers. The application, complete in all respects should reach the General Secretary, IANCAS on or before 30<sup>th</sup> November of the calendar year.*

### **Selection**

*An expert panel will scrutinise the applications and judge the best research contribution for the award. The awardee has to present her/his work by giving a lecture during the AGM of IANCAS. The awardee will be provided with DA & first class/AC III tier return railway fare, if the awardee cannot get the same from any other source.*

*It may please be noted that the decision of the expert panel is FINAL and canvassing in any form is a disqualification.*

*Completed application may please be forwarded to*

*General Secretary, IANCAS  
C/o Radiochemistry Division  
BARC, Trombay, Mumbai 400 085*

# Dr. Tarun Datta Memorial Award

(PROFORMA FOR APPLICATION)

1.	Name in full	
2.	Present office address with telephone, e-mail and FAX	
3.	Date of Birth (attach proof)	
4.	Academic Qualifications (attach certificates)	
5.	Details of employment	
6.	Awards / Recognitions	
7.	Field of specialisation	
8.	Research experience	
9.	Number of publications (Journals only) Attach list	
10.	Invited talks / Session Chairperson in National / International Symposia / Conferences, if any	
11.	Reviews / Books / Chapter contributed to books / Technical Reports, if any	
12.	Popular Science articles, if any	
13.	Citation Index of 10 best papers published (if any)	
14.	Any other contribution(s), academic or otherwise, supporting your candidature	
15.	Signature of the Applicant	
16.	Signature, Name, Designation and full address of the proposer of the nomination with Telephone, e-mail and FAX	

(Please include (i) two passport size photographs, (ii) brief write-up not exceeding 500 words, clearly bringing out significant research contributions, (iii) reprints of ten best published papers, (iv) list of publications and (v) a declaration stating that the work was carried out in India)

### DECLARATION

(By Head of the Institute or Head of the Department or Research Guide)

I certify that the research work mentioned by Dr. / Mr. / Ms ..... of ..... (Name of the Institute) was carried out by him / her. The candidate is mainly responsible for the outcome of this work. I request the Committee to consider the nomination for Dr. Tarun Datta Memorial Award.

Signature and Seal



## IANCAS - Prof. H.J. Arnikar - Best Thesis Award

*The Indian Association of Nuclear Chemists and Allied Scientists invites applications for the Prof. H.J. Arnikar Best Thesis Award in the field of Radiochemistry and Allied Sciences. The award carries a medal, a citation and Rs.5,000/- in cash. The awardee will be provided return I class/AC III tier fare to attend the award function, which will be held during the Annual General Body meeting of IANCAS, the date and venue of which will be intimated to the selected candidate.*

### **Eligibility**

1. *Ph.D. Degree awarded by any of the Indian Universities preceding two years from June of the calendar year of the Award e.g. for the calendar year 2005, the Ph. D. degree should have been awarded to the candidate between July 2003 to June 2005.*
2. *The work reported in the thesis should be in any one of the following fields*
  - *Radiochemistry*
  - *Nuclear Chemistry*
  - *Nuclear Materials*
  - *Radioanalytical Chemistry*
  - *Isotope Production*
  - *Radiotracer Studies*
  - *Radioactivity Measurement or*
  - *Any Allied Fields wherein Radioisotopes are Used*
3. *Age limit : There is no age limit for this award*

### **How to Apply?**

*The nomination should be sent by the Ph.D. Guide along with*

- (a) 3 copies of the synopsis as submitted to the University,*
- (b) a write up not exceeding 500 words highlighting the significant achievements of the work carried out leading to the award of the degree,*
- (c) list of publications (journals only) & reprints/preprints of five best papers. It is essential that the list of publications & reprints cover only those papers that are included in the thesis,*
- (d) A copy of the Ph.D. Degree /provisional certificate from the University.*

### **Last Date : on or before November 30, of the calendar year**

*The application, complete in all respects, should reach the General Secretary, IANCAS, C/o Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai - 400 085.*

### **Selection**

*A panel of experts nominated by the Executive Committee of IANCAS comprising members from the Department of Atomic Energy and the Universities will select the best thesis. It may please be noted that the decision of the panel is FINAL and canvassing in any form will be a disqualification. The awardee will be given an opportunity to present his/her work during the Annual General Body Meeting of IANCAS.*

## Prof. H.J. Arnikar Best Thesis Award

(PROFORMA FOR APPLICATION)

1.	Name and address of the Candidate	
2.	Name and affiliation of the Guide(s)	
3.	Institute where the work was carried out	
4.	Name of the University awarding the degree	
5.	Title of the Thesis	
6.	Year and month of the award	

### CERTIFICATE

I hereby confirm that the work pertaining to the Ph.D. Thesis mentioned above of .....

..... was carried out under my supervision

(Signature of Guide)

# INDIAN ASSOCIATION OF NUCLEAR CHEMISTS AND ALLIED SCIENTISTS

(Reg. No. MAH/232/1984/GBBSD)  
C/o. Radiochemistry Division  
Bhabha Atomic Research Centre, Mumbai 400 085.

Ref: IANCAS/Elections/2005/1

September 5, 2005.

SUB: Triennial Elections to the Executive Committee 2006-2008

Dear Members,

The term of the seventh executive committee of IANCAS will be completed by December 31, 2005 and the elections are due to elect the eighth executive committee of IANCAS for the term 2006-2008. Schedule of the election programme is as follows:

## I. SCHEDULE OF ELECTION

1.	Closure of the list of Eligible Voters	31/08/2005
2.	Announcement of election	05/09/2005
3.	Last date for receipt of nominations	17/10/2005
4.	Announcement of the list of valid nominations	20/10/2005
5.	Last date for withdrawal (in writing)	11/11/2005
6.	Posting of ballot papers	02/12/2005
7.	Last date for receipt of ballot papers	06/01/2006
8.	Counting of votes	09/01/2006

## II. POSTS FOR WHICH ELECTIONS ARE TO BE HELD

Sl. No.	Name of the post	Number of posts	Remarks
1.	President	ONE	--
2.	Vice-President	TWO	One from H.Q.
3.	General Secretary	ONE	From H.Q.
4.	Joint Secretary	ONE	--
5.	Treasurer	ONE	From H.Q.
6.	Joint Secretary	ONE	--
7.	Editor	ONE	--
8.	Members	EIGHT	--

### **III. ELIGIBILITY FOR NOMINATION TO EXECUTIVE COMMITTEE**

Any member of the Association except the Associate Members, shall be eligible to contest the election for the Executive Committee provided

- (a) She/He is not in arrears of payment of membership subscription as on 31/08/2005 as per the Association's Register of membership
- (c) She/He has been a member of the association for a minimum period of TWO years continuously
- (c) President, Vice-Presidents, General Secretary, Joint Secretary, Treasurer, Joint Treasurer and Editor of the Out-Going Committee are not eligible to contest for the same post.

### **IV ELIGIBILITY FOR VOTING**

All members who are not in arrears of membership as on 31/08/2005 are eligible to vote in the election.

### **V PROCEDURE FOR NOMINATION**

All nominations have to be made in the prescribed proforma. One proforma is enclosed herewith. Photocopies of the nomination form may also be used if necessary. Each nomination shall be proposed and seconded by eligible members. The prospective nominee shall confirm his willingness by signing on the nomination form. Nomination forms completed in all respects should reach the undersigned before the due date i.e., up to 16.00 hrs. on 17/10/2005. The address for sending nominations is:

Dr.Y. Babu,  
Election Officer, IANCAS,  
Radiochemistry Division  
Bhabha Atomic Research Centre,  
MUMBAI 400 085

All the contestants whose nominations are found in order will receive a complete list of valid nominations to exercise their options for withdrawal before the last date of withdrawal.

Soliciting the co-operation of all IANCAS members.

Yours sincerely,

sd/-  
(Y. Babu)  
Election Officer, IANCAS

To all members of IANCAS

**INDIAN ASSOCIATION OF NUCLEAR  
CHEMISTS AND ALLIED SCIENTISTS  
(IANCAS)**

ELECTION TO THE EIGHTH EXECUTIVE COMMITTEE 2006-2008

**NOMINATION FORM**

I propose the name of Dr/Shri/Smt/Ms. \_\_\_\_\_  
of \_\_\_\_\_  
for the post of \_\_\_\_\_ in the eighth Executive committee.

PROPOSED BY: \_\_\_\_\_ Membership Number : \_\_\_\_\_

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

Address: \_\_\_\_\_

SECONDED BY: \_\_\_\_\_ Membership Number : \_\_\_\_\_

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

Address: \_\_\_\_\_

I hereby confirm my consent to my nomination for the post of \_\_\_\_\_

NAME: \_\_\_\_\_ Membership Number: \_\_\_\_\_

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

Address: \_\_\_\_\_

Email: \_\_\_\_\_

DULY FILLED NOMINATIONS SHOULD REACH THE FOLLOWING ADDRESS NOT LATER THAN 16.00 Hrs. ON OCTOBER 17, 2005.

Dr Y. Babu,  
Election Officer, IANCAS,  
Radiochemistry Division,  
Bhabha Atomic Research Centre,  
MUMBAI 400 085.

## **Nuclear Materials**

*Guest Editor*

**V.N. Vaidya**

DAE-BRNS Dr. Raja Ramanna Fellow  
Fuel Chemistry Division  
Bhabha Atomic Research Centre  
Mumbai 400 085



## FOCUS

**Shri R. Kalidas**

*The inevitability of the nuclear option has been well appreciated in the context of skyrocketing crude oil prices and of the increasing volumes of green house gases and continual and rapid depletion of finite fossil fuel resources. Countries, who previously felt constrained to moderate their nuclear power programmes, are now re-evaluating their options in the light of Kyoto protocol. India has long been a proponent of nuclear power. The contribution of nuclear power in India has so far been a small percent of the total power; ambitious plans have been drawn and are being vigorously executed to significantly increase the generation capacity to support the momentum of a fast developing economy.*

*Nuclear materials include fuel and clad materials, and also structural, control, moderator and shielding materials. Thanks to the vision and initiative of Bhabha, India occupies a place of pride among the few countries that have mastered the entire nuclear fuel cycle including processing of uranium, zirconium, thorium etc.*

*The Directorate of Atomic Minerals has been actively prospecting for mineral resources of uranium, thorium, etc, and Uranium Corporation of India is carrying out the task of mining and beneficiation of the available ores of uranium. Thorium is a byproduct of the Indian Rare Earths Ltd, which, along with zircon sand and several other materials, also supplies the burnable poison gadolinium.*

*India with meager resource of low cost uranium desires to develop the technology and utilize the vast and low cost thorium deposits embedded in the beach sands. The extraction processes employed for the beneficiation and refining of uranium and thorium are brought out in this issue to underline the fundamental studies. The process chemistry and metallurgy of uranium and thorium are well understood today. As a result of conscientious efforts over decades, we have built up a high-quality infrastructure of skilled manpower, technology and industrial support as demonstrated by the successful operations of Indian research and power reactors.*

*The thermal properties of nuclear fuels for fast and thermal reactors are significant to understand the fuel performance at operating temperatures. The database generated for some of the important fuels for our thermal and fast reactors have been highlighted in the bulletin.*

*India is the first country to have developed and used mixed carbide fuel for its fast reactor programme. The fabrication of carbide fuel is difficult as it requires handling in inert gas atmosphere and the number of process steps is more in comparison to oxide fuel. The salient features of the fabrication of plutonium based fuels for MOX as well as its mixed carbides for the fast reactors are elucidated. Chemical Quality Control is an integral and indispensable component in nuclear technology. A wide gamut of analytical methodologies required for the chemical quality control measurements on nuclear materials have been developed indigenously.*

*Fuel, Cladding, Structural, control rods, end shields, turbines, heat exchangers require for materials of exacting property requirements. The Nuclear Fuel Complex (NFC) at Hyderabad, established in early 1970s has been fully meeting all the requirements of oxide fuel and structural materials needed for all the Nuclear Power Reactors in the country. Both uranium and zirconium are being handled in large quantities in one single campus while fully addressing environmental concerns. In addition to zirconium alloy fuel tubes, end-plugs,*

*spacers, bearing pads and end-plates needed for the fuel assemblies, NFC also makes coolant tubes, calandria tubes, garter springs, reactivity mechanisms etc. in different zirconium alloys. Stainless steel tubes of various grades are also being made for application in fast breeder reactors. In addition, several special ( tantalum and niobium and their oxides) and high purity materials (antimony, bismuth, cadmium, gallium, gold, indium, lead, mercury, selenium, tellurium, tin, zinc and their compounds) are also made to order in the Complex.*

*Nuclear Fuel Complex caters to all the three stages of Nuclear Power Programme – to PHWRs in the first stage, FBRs in the second stage and AHWR in the third. With the increasing share of nuclear power in the total electricity generation capacity in the country, NFC is poised for steep growth to meet the enhanced requirements and looking ahead for challenging tasks and exciting times.*

*Shri R. Kalidas  
Chief Executive, Nuclear Fuel Complex  
Hyderabad*

## Guest Editorial

V.N. Vaidya



*IANCAS brings out thematic bulletins periodically. These bulletins deal with important topics related to nuclear science and technology and myriad of applications of radioisotopes in various fields. The present bulletin on 'Nuclear Materials' discusses the science and technology behind the development. Nuclear materials used in nuclear reactors are fuel materials, cladding, reactivity control materials, moderator, coolant, structural materials etc. These materials exposed to the hostile environment of a nuclear reactor have to withstand high temperatures, very high neutron and gamma dose as well as changing chemical environment inside the fuel tube as well as in the reactor. These conditions impose a great discipline on processes used for the fabrication of these materials. Some of these have already been discussed in earlier bulletins. This bulletin deals with exploration mining and refining of uranium and thorium, purification to obtain nuclear grade materials, conversion to pellet fuel, manufacturing of fuel bundles, physical and chemical quality control, properties and manufacture of plutonium based fuels. This issue also deals with structural and cladding materials like zirconium and zirconium alloys and boron technology for the control rod fabrication.*

*Significant contributions have been made by a very large number of scientists and technologists all over the years. Their endeavor has made it possible to get maximum output from these nuclear materials during their service in the Indian power and research reactor programme. One of the glaring examples is the development and deployment of Zr-Nb alloys for their use as pressure tubes and calandria tubes in pressurized heavy water reactors (PHWR) resulting in the extended life of such reactors. Similar strides have been made in the fuel fabrication technology with a very large improvement in plant throughputs bringing down the overall cost of fuel. There has been an unflinching effort by all the concerned agencies to minimize the cost of operations and showing a continuous improvement in the quality of the product which reflected in overall reduction in the cost of construction of nuclear power plants and the unit cost of power.*

*Exploration for atomic minerals in India is being carried out solely by the Atomic Minerals Directorate for Exploration and Research (AMD) since 1949, with its headquarters located at New Delhi and Hyderabad. There is a shortage of uranium supplies from indigenous sources and all efforts are focused for a massive exploration.*

*Nuclear Fuel Complex (NFC) is responsible for manufacturing natural  $UO_2$  fuel for the operating and forthcoming Pressurized Heavy Water Reactors (PHWRs) in India in addition to low enriched fuel for the two Boiling Water Reactors (BWRs). High density (96-98%TD), high purity  $UO_2$  fuel pellets in cylindrical form are produced in mass scale from  $UO_2$  powder through Powder Metallurgical steps like pressing, sintering followed by wet grinding of sintered pellets to produce uniform diameter finished pellets. As finished  $UO_2$  pellets need to meet stringent requirement with respect to purity, density and integrity; the powder production and pellet fabrication processes must follow close operational control at various stages of production.*

*Over the years a number of fast reactors have been built for experimental purposes and for power generation (Rapsodie, FBTR, KNK, JOYO, FFTF, EBRI & II, PFR, Phenix, Superphenix), in Europe, Japan, USA, Russia and India using plutonium bearing fuel. However, the numbers of fast reactors built and operated are very few.*

*Physical properties refer mostly to the fuel while mechanical properties refer to the cladding and structural material. Neutronic characteristic applies to the whole core material, i.e. fuel, cladding, moderator, coolant etc. The data on the thermophysical properties of Nuclear fuels are important to the reactor designer. Knowledge of these properties is essential for predicting fuel behavior in the reactor, designing the fuel pin and to generate a computer code for the in-reactor fuel performance and whole core accident analysis of the reactor system. Some of the important properties of concern are Solidus temperature, Specific heat, Thermal diffusivity / thermal conductivity, thermal Expansion and mechanical properties at ambient and high temperature.*

*The most commonly used fuel configuration all over the world is the pellet-pin type and the same is also being used in majority of our reactor system. The fuel is in the form of solid or annular cylindrical sintered ceramic pellets, which is encased in a cladding. The life of a fuel pin is dictated by the degradation of the fuel or loss of integrity of the cladding in the form of a breach of clad due to fuel-clad mechanical/chemical interaction. In order to avoid any early disposal of the fuel pin, it is essential to know the out-of-pile properties of the fuel and cladding material so that corrective action can be taken at the design stage.*

*Boron is one of the few elements to possess neutron absorbing properties. Boron and its compounds are extensively used in nuclear industry for application as control rod, human shielding against neutrons and as sensor elements.*

*I am very much thankful to all authors of the articles in this bulletin who have made it possible to bring out this special IANCAS bulletin on nuclear materials.*

# Exploration for Atomic Minerals in India- An Overview



*Shri R.M. Sinha joined the Atomic Minerals Directorate for Exploration and Research (AMD) as a Scientific Officer in October, 1966 after obtaining M.Sc. degree (Applied Geology) from the Indian School of Mines, Dhanbad. For the past 38 years Shri Sinha has executed exploration projects on uranium and other atomic minerals in different geological environments all over the country. His professional experience encompasses conceiving, planning, development and execution of exploration strategy for four (4) major types of Uranium deposits, viz., the Structurally-Controlled Vein-type deposits in Singhbhum, Bihar and Bodal, Madhya Pradesh; the Quartz-pebble-Conglomerate deposits at Walkunji and Arbail, Karnataka; the Sandstone-type deposit at Domiasiat, Meghalaya; and the unconformity-related deposit, on the fringes of the Srisaigham Sub-basin at, Lambapur in Andhra Pradesh. Shri Sinha has published more than 20 papers in National and International Journals of repute. In recognition of the significant discovery and proving the first unconformity-related deposit in Lambapur-Peddagattu outlier in Andhra Pradesh, the “National Mineral Award – 1996” was conferred upon Shri Sinha by the Ministry of Steel and Mines, Government of India. Shri R.M. Sinha is the Director of the Atomic Minerals Directorate for Exploration and Research since 31.7.2003.*

## Introduction

Exploration for atomic minerals in India is being carried out solely by the Atomic Minerals Directorate for Exploration and Research (AMD) since 1949, with its headquarters at New Delhi and Hyderabad.

Uranium occurs in a large variety of geological environments and in rocks of almost all geological ages, and therefore makes the task of discovering a rich deposit a very difficult one. The major uranium deposits, known around the world are classified into fourteen major groups. Majority of the large-tonnage and higher grade deposit types are confined to the early part of the earths geological history namely to the Early-Middle Proterozoic Era (2200 to 1400Ma time period). Younger deposits involving larger transport of uranium in low temperature environments have also produced large deposits, but these are of lower grade (0.1-0.3%  $U_3O_8$ ). Increase in the abundance of oxygen in the atmosphere since 2200 Ma has played an important role in dissolution, migration and precipitation of uranium, which has two valences of 4 (four) and 6

(six). The tetravalent uranium gets converted to hexavalent state, in oxidizing environment, which is soluble in water and thus becomes mobile.

Planning of exploration is largely based upon the knowledge of the geological and tectonic setting of the area and involves four stages viz., (i) Planning for different types of deposits and selection of geologically favorable target areas based on thorough knowledge of the geological setting and its comparison with the known uranium deposits in the world; (ii) Radiometric reconnaissance survey and prospecting for quick appraisal and delineation of important smaller areas for follow up investigations; (iii) Detailed exploration stage involving large scale geological mapping, geophysical surveys, geochemical investigations and reconnaissance drilling; and (iv) Exploratory and evaluation drilling followed by estimation of ore reserves. A clear-cut boundary is difficult to define between the different exploration stages, as the techniques and methodology of exploration more or less remain the same and are overlapping.

Shri R.M. Sinha, Atomic Minerals Directorate for Exploration and Research, Hyderabad  
E-mail: amdhyd@ap.nic.in

Depending on the field set-up, terrain conditions and logistics, integrated maps are prepared using various combination of airborne and car borne gamma-ray spectrometry, ground radiometric, radon emanometry, hydrogeochemical, pedo-geochemical and geophysical data.

Normally, reconnaissance drilling on large grid spacing, say 400m x 400m, is done in the initial exploration stage for specific type of uranium deposit expected in the area – say the sedimentary (Sandstone) or the unconformity-types. The geological data accrued in this stage is very important in guiding further progress of exploration in the successive stages.

In the case of these sandstone and unconformity-related uranium deposits, which have more lateral spread but occur within limited vertical depths, advantage of gamma-ray logging technique is used by drilling non-coring boreholes. This involves significantly less time and money compared to core drilling, to define the approximate geometry of the ore deposit. For steeply dipping uranium ore bodies, such as veins, however, core drilling is inevitable, as the delineation of correct ore body geometry require drilling of inclined boreholes also.

After defining the geometry of the uranium ore body, the next objective is to establish the economics of the deposit. The exploration of atomic minerals, like any other metal deposits, is carried out in three main stages comprising preliminary, detailed and mine exploration. As the exploration progresses the cost of exploration steeply increases and the relative risk of defining the deposit decrease.

In the Preliminary Exploration stage, the objective is to establish a general size, approximate geometry and quality of mineralised body. At this stage a detailed topographic survey is completed and accurate geological maps on 1:10,000 to 1:5,000 scale are prepared. Various aspects of exploration, comprising isograd mapping, trenching, pitting, channel sampling, shielded probe logging, exploratory drilling, petrography and ore mineralogical studies are also carried out. These studies help in defining the approximate geometry, grade, thickness and mineralogy of the ore body and finally an approximate ore tonnage contained in the

deposits. The reserves estimated with the help of data obtained at this stage are classified as inferred reserves. The uranium mineralogy, ore textures and rock compositional data are very useful in deciding the method of uranium leaching to be adopted in future.

Detailed Exploration is undertaken in areas where a deposit is to be developed in the near future. At this stage the contour and attitude of each mineralised body are outlined with great accuracy and results plotted on 1:2,000 to 1:1,000 scale. To obtain reliable information at this stage, new exploratory boreholes are drilled for thickening the exploration grid. For estimation of accurate grades, the parts of ore body with higher and more fluctuating grades require more close space sampling than areas with low and uniform grades.

This stage also involves drilling of evaluation boreholes. For estimation of ore reserves, initially, ore body geometries are defined by considering different cut-off grade and thickness criteria. Finally, after taking into consideration the uranium leaching characteristics, most probable mining methods and economics related to recovery, an acceptable ore reserve figure, with selected cut-off criteria, is arrived at. The detailed exploration data provide ore reserve data, categorized into indicated category that is closer to the true value of a deposit compared to the inferred category reserve.

Mine Exploration begins with the commencement of exploratory mining operations and continues until the deposit is almost worked out. At this stage accurate information on grade and thickness of the ore body is obtained by sampling the network of underground development like levels, crosscuts, raises and winzes developed and ore bodies are very precisely outlined. The geological and the ore body maps are prepared on a very large scale (1:500 to 1:100) to give all possible details. Reserve, estimated at this exploration stage, is classified as proved/measured reserves.

The sequence of operations in any mineral exploration programme, indicating the risk element at various stages and hypothetical costs are presented in Table 1 [1].

**TABLE 1. Sequence of operations in Exploration and Development of an Ore Deposit**

Stage	Type of work	Possible methods  employed	Hypothetical costs (millions of \$)	Apprx period	Risk
Exploration	Reconnaissance	Geological mapping, geochemistry, geophysics, airborne surveys	0.5	1-2 Years	Extremely high
Prospecting	Initial follow-up	Geological mapping, geochemistry, geophysics, limited drilling	1.0	1-2 Years	Very high
Exploration	Detailed follow-up	Drilling, limited metallurgical testing	4.0	3-5 Years	High
Development	Feasibility study	Drilling, metallurgical testing, mine design, trial mining	10.0	3 Years	Moderate
	Mine development	Drilling, mining	100.0	-	Low
Mining	Extraction and Beneficiation of ore	Mining and mineral processing applications	Operating cost	-	Low

### World Uranium Scenario

The total uranium reserve of the world, falling under cost category of US\$80/kg U is 2.49 million tonnes. Uranium deposits worldwide can be grouped into 14 major categories, based on their geological setting. Among these the major uranium resources (Fig.1a) are contributed by the Unconformity-related (33%), Sandstone type (18%), Breccia complex (17%), Quartz-pebble conglomerates (13%) and Vein type (10%). Rest (9%) of the uranium resources are contributed by Surficial, Volcanic, Phosphorite, Collapse breccia and pipe, Intrusive, Metasomatite, Metamorphic, lignite and black shale deposits. In India, the uranium deposits so far identified, are mainly of five types viz., the Quartz-pebble conglomerate, Shear-controlled vein/disseminated type, Unconformity related, Stratabound type and Sandstone type. The total identified insitu uranium reserve of the country is 94,200t U<sub>3</sub>O<sub>8</sub> (Fig. 1b).

### Uranium Exploration – Case Studies in India

A brief account of the investigations carried out, highlighting the application of various

exploration techniques to suit the specific geological environment and priorities assigned for establishing some of the deposits, is presented. A brief note on the classical deposits of the world is also made.

### Quartz Pebble Conglomerate (QPC)

Quartz-pebble conglomerate type uranium deposits make up approximately 13% of the world's uranium resources and the main deposits are the Elliot Lake in Canada and the Witwatersrand gold-uranium deposits in South Africa. These are usually of a lower grade (0.01%-0.15% U<sub>3</sub>O<sub>8</sub>), however mining of lower grades as low as 0.010% U<sub>3</sub>O<sub>8</sub> has been possible as a byproduct in areas having Au mineralisation. Individual deposits contain from 6000-170 000t U<sub>3</sub>O<sub>8</sub>.

In India, the gold-uranium bearing QPCs represent oldest synsedimentary deposits located at the base of, the Bababudan and Chitradurga Groups in Karnataka (Fig. 2), the Dhanjori Group in Singhbhum, the Iron Ore Group of Jharkhand and Orissa and the Aravalli Group in Rajasthan.

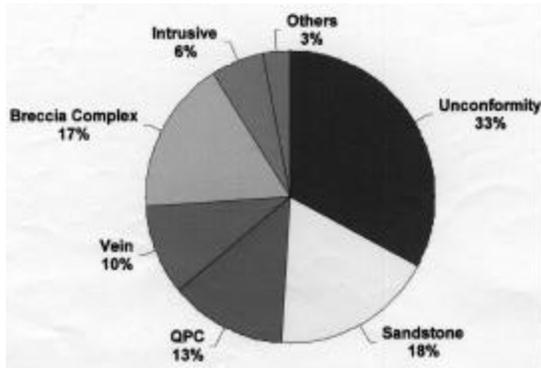


Fig. 1a Types of World Uranium deposits and their distribution (Total reserves : 2.49 million tonnes[~US\$80/kg U).

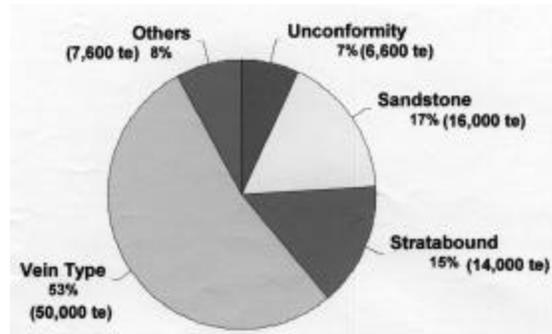


Fig. 1b Types of Uranium deposits and their distribution in India

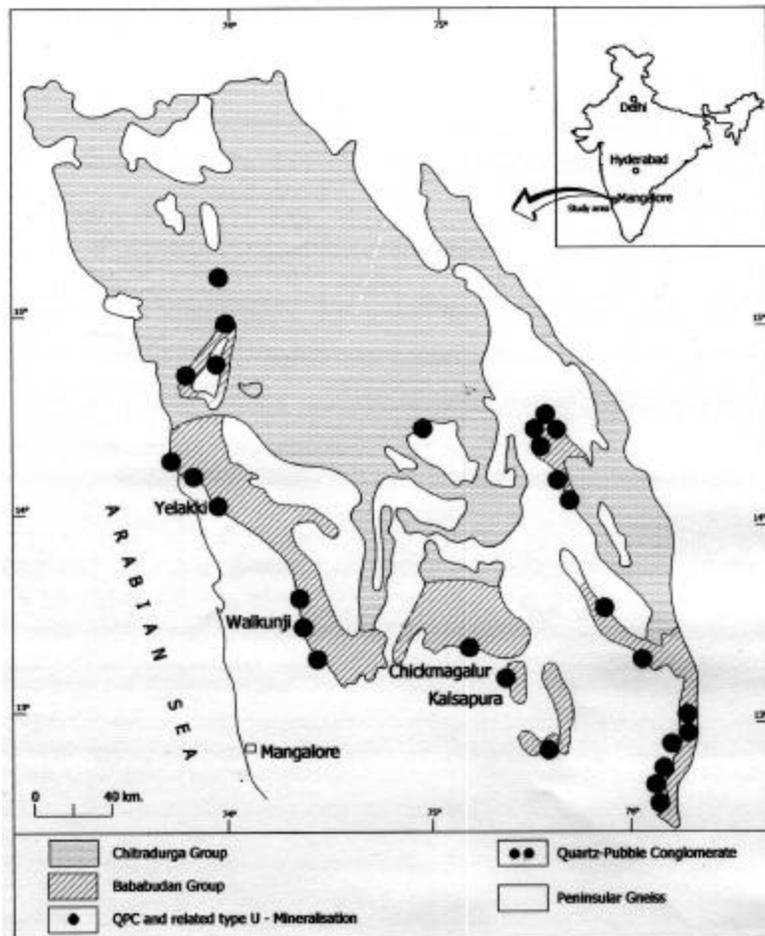


Fig. 2 Geological map of Western part of Karnataka showing location of Uraniferous Quartz Pebble Conglomerates

In Karnataka the occurrence of pyritiferous QPC in the neighbourhood of Chikmagalur (Karnataka) at the base of the Dharwar Group rocks, with traces of gold (up to 1.5ppm) was well known. Due to its geological similarity with the Witwatersrand formation of South Africa, the Chikmagalur conglomerates were re-examined and found to contain leachable uranium. Subsequently, the presence of uraninite was also confirmed in the core samples of Kalsapura area. Some of the samples analysed upto 0.21%  $U_3O_8$  [2]. The QPC occurring in the Sarara inlier in the Aravalli belt (Rajasthan) indicated uranium values upto 2.3%. The heavy minerals assemblage of QPC includes the presence of redox sensitive minerals such as pyrite, pyrrhotite, chalcopyrite, uraninite and pitchblende. Other minerals observed in the matrix are brannerite, platinoides, rutile, zircon, thucolite and gold. Similar occurrences were located at Walkunji, south Kanara district and in Arbail-Dabguli, north Kanara district (Karnataka). Geochronological studies revealed that these conglomerates were deposited 3,000 to 2,500 million years ago.

The uranium mineralisation in the Dabguli-Arbail area, located about 60 km east of Karwar In Karnataka, is associated with the upper nonconglomeratic horizons of QPC in the northern parts of the Shimoga basin. At Arbail, uranium mineralisation is confined to psammopelitic sediments lying below the limestone and Mn-Fe formation of the Chitradurga Group. The Arbail uranium occurrence suggests younger uraniferous horizon, besides the QPC in the Dharwar succession of Karnataka. Similar horizon has also been established in South Africa.

In the Singhbhum craton uranium mineralisation occurs in QPC and pebbly quartzites of the Iron Ore Group in intracratonic Badampahar basin, in the Mayurbhanj district of Orissa. Uraninite occurs as fine grains and veinlets in the sulphide-rich matrix. Minor amounts of gold (0.2-0.7 g/tonne), along with monazite and zircon, are also present.

Similar QPC occurrences have developed all along the basal parts of the Dhanjori basin, overlying the Singhbhum Granite in Singhbhum district, Jharkhand. In the Dhanjori basin, Singhbhum district, the most notable occurrences are at Butgora and Phuljhari.

The QPC deposits constitute a marker horizon between the Archaean and Proterozoic eras (2800-2200Ma). Like Africa and Canada, India has vast expanse of Archaean shield area (>2500Ma) covered with lower Proterozoic rocks, which hold enormous potential for QPC type uranium deposits. However, we have to overcome the severe constrain in the exploration of QPC type uranium deposit caused by the presence of thick pile of younger volcanic rocks and Iron Ore Formation in most of such basins.

#### *Vein/Disseminated Type Deposits*

Vein deposits constitute about 10% of world uranium resources. Major deposits of structurally controlled deposits are in the lower Proterozoic Tazin Group in Beaverlodge area (1780 Ma), Canada, Jachymov in Czech Republic and Shinkolobwe in Zaire. All the major vein deposits of the world fall in Early-Middle Proterozoic Eras (2200Ma -1400Ma).

In India, the occurrences of vein type uranium mineralisation occurs in the mobile belts of the Chotanagpur-Singhbhum region (Jharkhand and Orissa), Dongargarh Supergroup (Chattisgarh), Aravallis Supergroup (Rajasthan), Bhima basin (Karnataka) and the lesser Himalayas. The mineralisation in all these geological settings include both disseminated and vein type and constitute the major proportion (53%) of the known uranium reserves in India.

#### *Singhbhum Shear Zone*

The Singhbhum shear zone in the state of Jharkhand, is traceable for about 200km, marking the tectonic boundary between southern Iron Ore Group and Singhbhum granite and northern Chaibasa Formation. All the uranium producing mines of the country lies in this zone. Discovery of important uranium occurrences in this belt such as Jaduguda in 1951, Narwapahar in 1953, Keruadungri in 1954 and Bhatin in 1957 were largely attributed to ground radiometric surveys using Geiger Muller Counters coupled with geological mapping. During 1951 to 1954, nineteen (19) boreholes were drilled by outside agencies for AMD in these areas. Drilling by AMD commenced in 1955 with 4 drilling units, which was increased to

20 rigs by 1966. Underground development in the form of three adits in Jaduguda commenced during 1955-56. Ground magnetic surveys during 1955-56 and airborne radiometric surveys (total count) during 1956-57, were followed later by ground resistivity surveys and radon emanometry to delineate more potential areas. Exploratory underground mines were opened at Narwapahar and Bhatin in 1962. By 1975 more than 25 prospecting areas were identified in this belt (Fig. 3).

On the basis of geological and mineralogical considerations, the shear zone has been broadly divided into two sectors. In the southeastern sector, it cuts across the Dhanjori metavolcanics, conglomerate and quartzite and also the soda-granite body and encloses copper and uranium deposits with minor quantities of Ni, Mo, Co, Se, Te, Au, Ag and Bi. The western sector comprises chlorite-sericite schist, quartzite and highly sheared soda granites.

Uranium ore bodies are relatively thicker in this part. Uranium occurs as en-echelon lenses, both along the strike as well as along the dip, mainly on the hangwall side of copper lodes, except in the Roam-Rakha-Badia sector, where uranium and copper occur together [3,4]. The extent of individual ore bodies varies from a few meters to as much as 300m with a maximum width of about 30m.

The richest uranium deposit has been encountered in the central part of the thrust belt, at Jaduguda, which persists beyond 900m depth with an average grade of 0.067%  $U_3O_8$ . The mineralisation extends further westward, after dislocation by the Tirukoccha fault, with additional reserves at Bhatin and Nimdih. The mineralised host rocks are biotite-chlorite-quartz-granular rocks, brecciated quartzites, shaled conglomerates and biotite-chlorite schists. The uranium ore body of this area is rich in Nickel (402 ppm) and Molybdenum

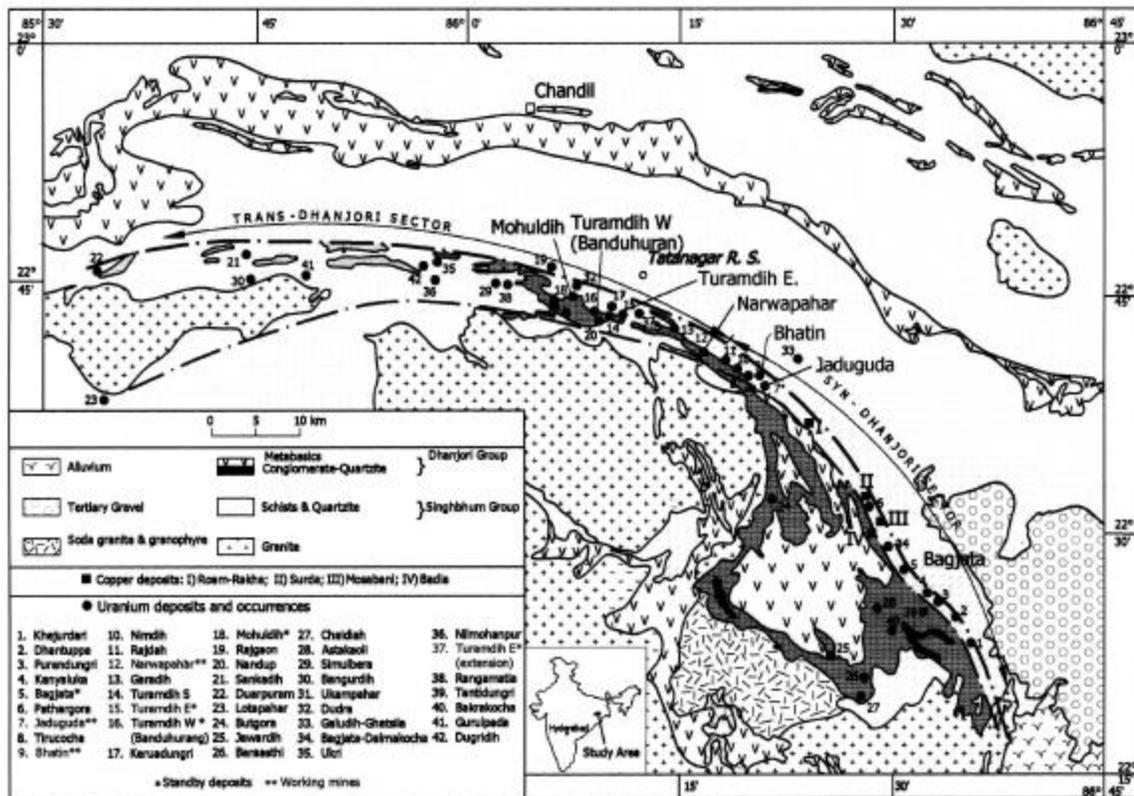


Fig. 3 Geological map of Singhbhum Shear zone showing Uranium and Copper deposits / occurrences

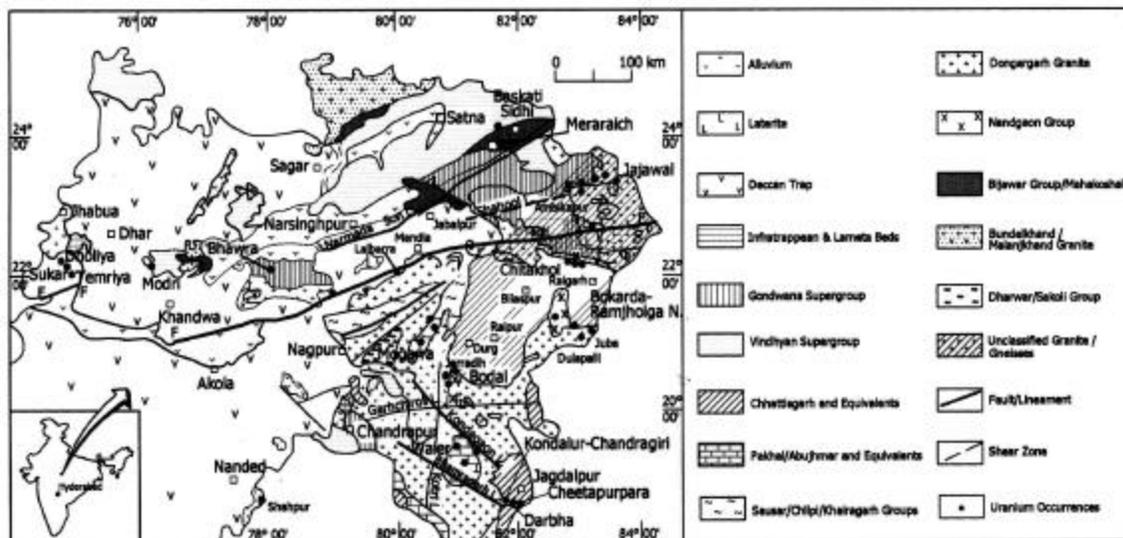


Fig. 4 Geological map of parts of Bodal - Jajwal area showing Uranium occurrences

(47 ppm) along with yttrium (up to 290 ppm). Molybdenite occurs as disseminations along shear fractures within the uranium rich zone. Various phases of mineralisation caused polycyclic mobilisation of uranium and other metals from multiple sources by combination of geologic process, active over a considerable span of time (1,478 Ma to 1,580 Ma) bridged by events of magmatic and hydrothermal activity in the deep but narrow tectonised zones.

#### Bodal Deposit, Chattisgarh

In the early sixties a favourable area of about 38,000 sq km consisting Early-Middle Proterozoic Sakoli and Dongargarh Group of rocks in Madhya Pradesh was examined by air borne radiometric survey followed by ground checking which resulted in location of several uranium occurrences in Durg district hosted by conglomerates, sandstones, rhyolites and gneisses. Test pitting, trenching and some exploratory drilling was undertaken. Because of limited extent of uranium mineralisation the exploration programme was discontinued in late sixties.

Study of U-Th distribution and their ratios in samples from the above area, were however indicative of uranium province in the region and on

this basis detailed ground radiometric studies were again undertaken in 1973. This resulted in discovery of a unique type of uranium mineralisation at Bodal, that is associated with an uncommon rock viz., amphibolite facies hybrid basaltic-andesite of tholeiitic affinity (Fig. 4). The metarhyolites also host uranium mineralisation although ore grade mineralisation is confined to the amphibolite, which occur close to the contact with the ferruginous shale [5]. As the area around this anomaly is soil covered, detailed investigations in 1974 comprised isorad mapping which resulted in defining anomalous NW-SE trending high gamma count zone. Shallow test pitting and trenching in the anomalous zone were of limited help and therefore exploratory drilling was resorted within six months of the discovery of this anomaly. Ground geophysical surveys during 1975-76 were of use in delineation of contact zone between the amphibolite host rock and ferruginous shale/banded hematite quartzite. Exploratory drilling was continued till mid-eighties and persistence of ore bodies was established upto 300m depth. Exploratory mining was taken up in 1976 and over 1000m of mine development was completed.

#### Jajawal Uranium Deposit, Madhya Pradesh

At Jajawal, quartzo-feldspathic cataclasite, syenite, brecciated schist/metabasic schist and

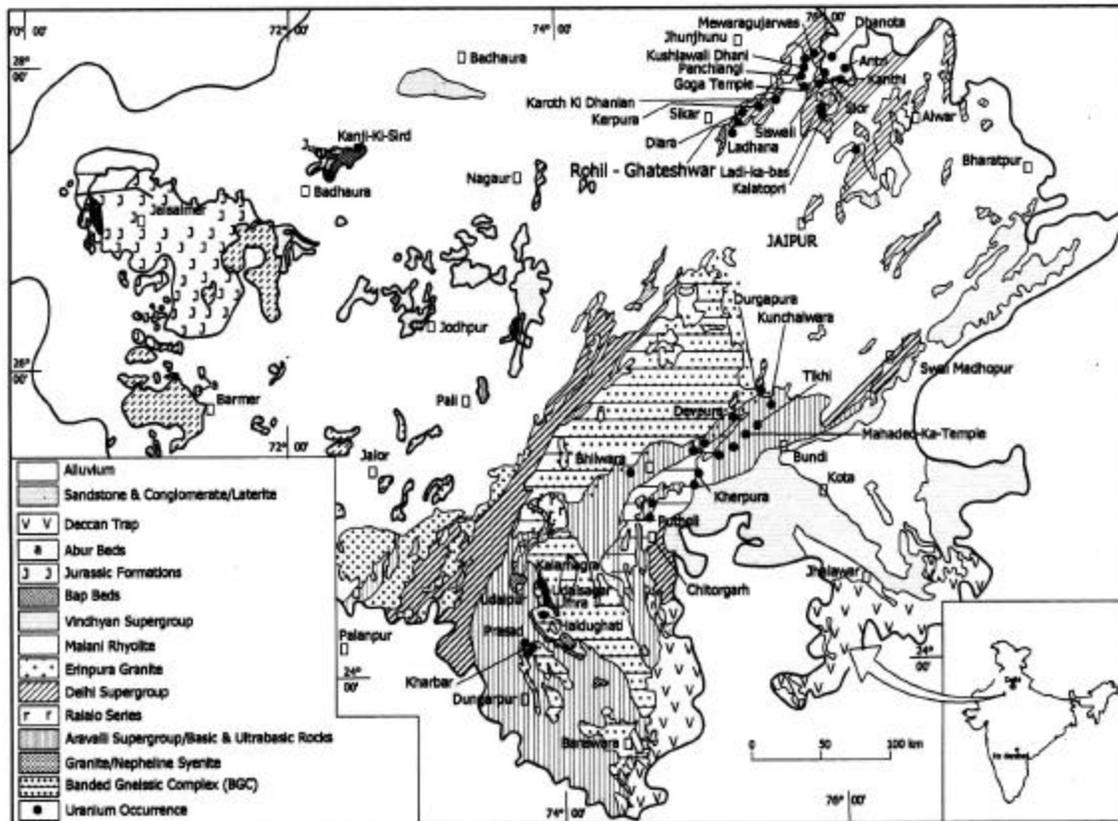


Fig. 5 Geological map of part of Rajasthan showing Uranium occurrences

sheared granite gneiss/pink granite host the uranium mineralisation (Fig. 4). Ore mineralisation occurs as discontinuous lenses and shoots of variable size and shape, are confined to the sheared portions of the host rock. In the mineralised zones, the rocks show various degrees of hydrothermal alterations.

#### Aravalli Sector (Rajasthan)

In Rajasthan uranium mineralisation occurs in the lower Proterozoic Aravalli Super Group, associated with the carbon phyllites of the Umra-Kalamagra belt underlying the dolomitic horizons (Fig. 5). The carbon phyllites are highly tectonised, hosting both uranium and copper mineralisation. It is a shear controlled mineralisation extending over a strike length of 20 Km. Four main phases of deformation have affected the Proterozoic Aravalli Supergroup rocks of Umra area. Uranium mineralisation (uraninite and secondary uranium

minerals) occurs in the form of thin veins, stringers, and streaks in carbonaceous phyllites/calcareous-arenaceous-argillaceous phyllites.

Albitic intrusives within rocks of the Aravalli Super Group (Lower Proterozoic) and the Delhi Super Group (Middle Proterozoic) are wide spread within the northern and central parts of Rajasthan. They are invariably uraniumiferous and form an albitite-line for a length of 270 Km. along a NNE-SSW trend. In one of the area presently under active exploration, at Rohil-Ghateshwar, ore reserve of approximately 2000te  $U_3O_8$  has already been established.

#### Bhima Basin, Karnataka

Integrated exploration approach was adopted in Bhima basin and the first success was met by gamma ray logging of available borewells near

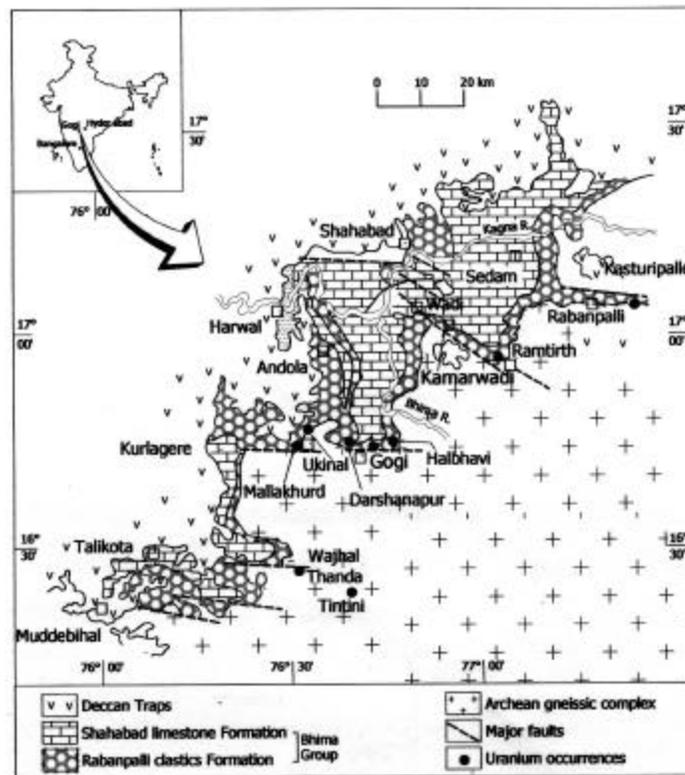


Fig. 6 Geological map of Bhima basin showing Uranium occurrences

Gogi, Gulbarga district, Karnataka (Fig. 6). Exploratory drilling in the area indicated promising uranium mineralisation hosted by brecciated limestone along major fault proximal to the unconformity contact of sediments with the basement granites [6]. During 1998-99 extensive drilling and further exploration including airborne radiometric and magnetic surveys continued through out the Bhima Basin. The ore grade mineralisation in the area also follow weak structural plane in the basement granite, in addition to the limestone. At Gogi, ore reserve of approximately 2096te  $U_3O_8$  has been established.

#### The Himalayas

The vein-type uranium occurrences of the Himalayas are hosted in highly tectonised and sheared Central gneissic complex and the under-thrusted sequence of metasedimentary and metavolcanic rocks. Disseminated, shear controlled mineralisation has also been noted along the Main

Central Thrust with distinct Stratabound characteristics. Mineralisation occurs in the form of veinlets and disseminations forming lenticular bodies, and generally occupies the sites of intersections of major fractures. The ore minerals include uraninite, sooty pitchblende, brannerite, davidite, U-Ti oxide complex, xenotime, cyrtolite and a variety of secondary uranium minerals such as uranophane, boltwoodite, becquerelite, masuyite, etc. Associated minerals include iron oxide, chlorite, and quartz with occasional fluorite and fluorapatite [7,8]. The uranium occurrences, however, are localised in nature due to post mineralisation tectonism. The host rocks suffered polyphase deformation, metamorphism and granitisation during the Precambrian era and later subjected to shearing, crushing and mylonitisation during the Himalayan orogeny.

Other examples of vein-type occurrences are the basement fractures in granitoids near the SW

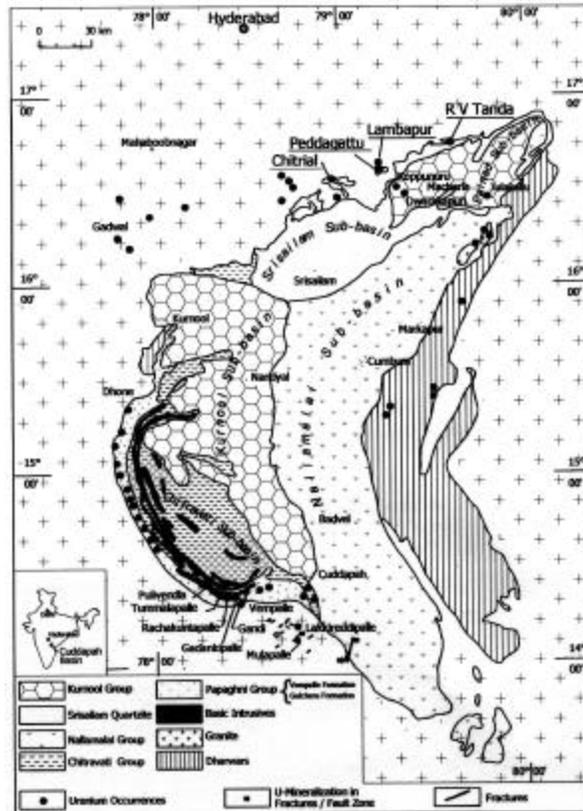


Fig. 7 Geological map of Cuddapah basin

margin of the Cuddpah Basin of Andhra Pradesh, the Chattisgarh Basin in the Raigarh district of Madhya Pradesh and in the Bargarh district of Orissa. Geological indications suggest continuation of fractures beneath the cover rocks and these areas are suitable in search of Unconformity type deposits.

#### **Stratabound Uranium Deposits (Tummalapalle)**

Until the early 1980's, all the mineralisation in Gulcheru quartzite and conglomerate within the Cuddapah Basin were found to be thoriferous. Preliminary work by the Geological Survey of India (1985-86) and subsequent detailed radiometric survey by AMD brought to light promising uranium mineralisation in the dolostone of Vempalle Formation in the lower part of Cuddapah Supergroup. The mineralised rocks, with a maximum thickness of 20m, are intercalated with shale and mudstone. Mineralisation occurs as fine granular pitchblende, in association with organic

matter and phosphate, and rarely as U-Ti complex. Organic material produced by the decomposition of algal microflora seems to have played a critical role in the fixation of uranium and subsequent precipitation of pitchblende as well as pyrite, by creating a reducing environment [9,10]. The explored blocks at Tummalapalle, Rachakuntapalle and Gadankipalle contain over 15,000 tonnes  $U_3O_8$  with an average grade of 0.042%  $U_3O_8$ . In these deposits, ultrafine vanadium-bearing pitchblende and U-Si-Ti complexes are associated with pyrite (As and Ag bearing), molybdenite, chalcopyrite, bornite, digenite and covellite. Exploratory mining confirmed the nature of the ore body as established by drilling.

Airborne spectrometric surveys (1987-88) were helpful in tracing the strike extensions. This stratabound mineralisation extends for more than 60 km with uraniferous occurrences exposed all along the SW margins of the Cuddapah basin (Fig. 7).

### *Unconformity Related Uranium Deposits*

Unconformity-related deposits forms due to geological changes occurring close to major unconformities. They constitute approximately 33% of the world's uranium resources, and include some of the largest and richest deposits. The main deposits occur in the Athabasca Basin, Saskatchewan, Canada and Alligator Rivers Basin in the Pine Creek Geosyncline, Northern Territory, Australia. Some of these deposits contain exceptionally high uranium grades: the examples being the Cigar Lake (averaging 14%  $U_3O_8$ , some zones over 50%  $U_3O_8$ ) and Mc Arthur River deposit (Average 21% U).

In search for similar deposits in India, ground radiometric surveys were undertaken in northern parts of the Cuddapah Basin. This led to the discovery of uranium anomalies occurring near to the unconformity between the basement granite (Archaean-Lower Proterozoic) and the overlying Srisailam Quartzite (Middle Proterozoic) in a number of dissected outliers on the northern fringe of the Srisailam sub-basin in the Nalgonda district of Andhra Pradesh in 1990 [11-13]. Exploratory drilling in Lambapur outlier commenced in March 1992 and the follow-up evaluation drilling recorded very high success rate. On understanding the geological and mineralisation model at Lambapur, exploratory drilling programme was extended simultaneously in adjoining outlier, namely Yellapur and Peddagattu (Fig. 7). Substantial uranium reserves have been established in these deposits and they are ready for exploitation.

In Koppunuru area, lying at about 25 km southeast of Lambapur deposit, the Kurnool Group sediments unconformably overlie the basement granite and host uranium deposit at the unconformity [14,15]. Besides, in this area, uranium ore bodies also occur in the Kurnool sediments. This deposit contains substantial uranium reserves.

At present, typical unconformity-type deposits, like in Canada and Australia, are not known in India but many Proterozoic basins, possess geological settings appropriate for hosting them. The target area comprises the Ampani, Abujhmar, Bhima, Chattisgarh, Cuddapah, Delhi-Aravalli Belt, Indravati, Kaladgi-Badami, Khairagarh, Kunjar, Pakhal, Sukma, Shillong, Vindhyan-Gwalior and

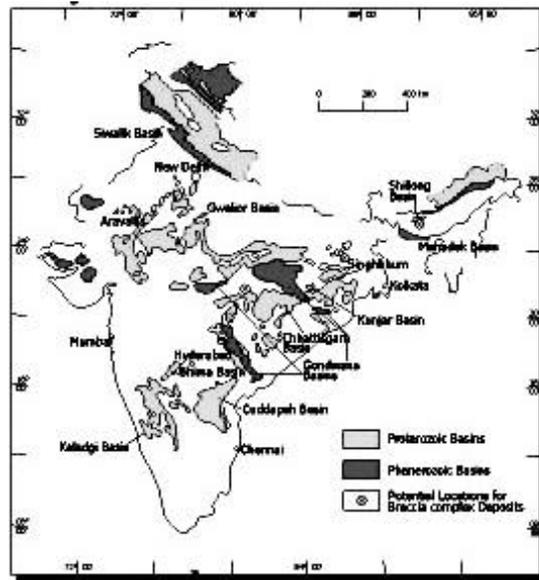


Fig. 8 Proterozoic and Phanerozoic basins of India

Vindhyan-Mahakoshal basins (Fig. 8). In many of these basins, many favourability factors such as presence of carbonaceous pelitic sediments of lower Proterozoic age in the basement rocks, evidences of major tectonic features in the form of basement faults and fractures, and younger igneous intrusives have been established. Parts of these basins are geologically modelled, and airborne magnetic, electromagnetic and other geophysical surveys are planned to identify conducting horizons. Some areas are also being explored by reconnaissance drilling.

### *Sandstone Deposits*

Sandstone deposits constitute about 18% of world uranium resources. Ore bodies of this type are commonly low to medium grade (0.05 - 0.4%  $U_3O_8$ ) and are small to medium in size (containing upto a maximum of 50,000 te  $U_3O_8$ ). The main primary uranium minerals are uraninite and coffinite. Sandstone uranium deposits occur in medium- to coarse-grained sandstones deposited in continental fluvial or marginal marine sedimentary environments.

The United States has large resources in sandstone deposits in the Western Cordillera region, and most of its uranium production has been from

these deposits, recently by in-situ leach (ISL) mining method. The Powder River Basin in Wyoming, the Colorado Plateau and the Gulf Coast Plain in south Texas are major sandstone uranium provinces. Other large sandstone deposits occur in Niger, Kazakhstan, Uzbekistan, Gabon (Franceville Basin), and South Africa (Karoo Basin). Kazakhstan has reported substantial reserves in sandstone deposits with average grades ranging from 0.02 to 0.07% U. The Frome Embayment area in Australia comprises Beverley, Honeymoon, East Kalkaroo and Billaroo West-Gould Dam deposits, which are amenable to ISL mining methods.

In India, the major uranium concentrations of sandstone-type are located in the (i) Cretaceous Mahadek Formation of Meghalaya, (ii) Siwalik sediments of Tertiary age occurring along the sub-Himalayan foothills and (iii) Gondwana basins.

#### *Domiasiat Deposit, Mahadek basin, Meghalaya*

Uranium exploration in the Mahadek basin of Meghalaya was initiated as early as 1958 and the first find of mixed uranium and thorium anomaly was near Dawki during 1962-63 by jeep-borne survey. The first fascinating find, of a sample of coalified wood, occurring in the Lower Mahadek sandstone, containing 10%  $U_3O_8$  was from the Umrynga river section at Tarangblang, Jaintia Hills district by ground radiometric survey in 1974. In the same year other uranium occurrences were also located in Alukwadi and Gomaghat in the West Khasi Hills district.

The uranium anomaly discovery in the Killung stream section (Domiasiat) in West Khasi Hills district in 1983-84 and follow-up work, finally resulted in establishing the first sandstone-type deposit in India. The Domiasiat uranium deposit is confined to the Lower Mahadek Formation comprising poorly- to moderately-sorted quartz arenite with organic matter (OM). The OM has been derived from the decay of the plants. Uranium occurs as pitchblende, coffinite and urano-organic compound. The ore body is essentially tabular to lensoid (5-10° dips) with thickness varying from 1 m to over 15 m. The overburden varies from a few meters to over 20 m, thus making it a near surface, medium tonnage, and low-cost uranium deposit amenable to open-cast mining.

After its discovery, exploratory and evaluation drilling not only resulted in establishing the Domiasiat deposit, with reserves of 10,000 t  $U_3O_8$ , but also resulted in establishing other important deposits, such as Wahkyn with so far identified reserves of 5,266 t  $U_3O_8$ , exploration of which was also largely based on a model based programme. The present exploration programme of AMD is aimed at locating more deposits of the type in the Mahadek Basin, which has an area of about 1100 sq km (Fig. 9). They are under intensive investigations, but access is hampered by difficult logistics and heavy rainfall.

#### *Uranium Mineralisation in the Siwaliks (~25Ma)*

The Siwalik belt comprises a thick (6,000m) sequence of fresh water sediments laid down in the fore-deep stretching along the southern fringe of the rising Himalayas over a linear stretch of about 2,500 Km (Fig 9). Uranium exploration in the Siwaliks was initiated with the identification of high uranium values (0.011% to 0.34%  $U_3O_8$  chemical) in the vertebrate fossils from the Pinjore area of Ambala district in Haryana.

Uranium mineralisation occurs at different stratigraphic levels, encompassing the upper parts of the Lower and Middle Siwaliks and the lower part of the Upper Siwalik. Numerous uranium occurrences, over a stretch of nearly 700 km between Poonch in Jammu and Kashmir and Tanakpur in Uttar Pradesh, have been located and investigated. In each horizon, uranium mineralisation is confined to a stratigraphic thickness of 100m to 250m and occurs as small peneconcordant lensoid bodies with the longer dimension of individual lenses traceable from a few tens of metres to 700m. The average thickness of mineralisation in different occurrences varies from less than a metre to 4m and with low grades (0.06%  $U_3O_8$ ).

#### *Uranium in Gondwana Basins*

Major uranium deposits formed during 300-100Ma period are in the Karoo basin (South Africa), Grants belt (USA), Lodeve sandstone (France), Arlit sandstone (Niger), Permian sandstone of Argentina and Italy, and Mussorie phosphorite of Krol-Tal belt, Uttaranchal, India. Exploration for uranium in some of the Gondwana

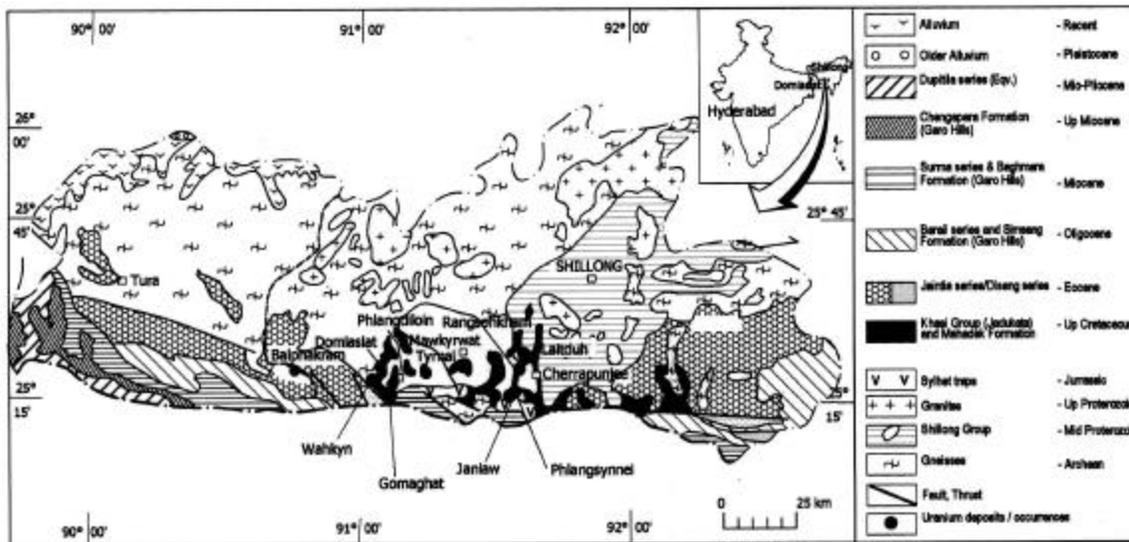


Fig. 10 Geological map of Meghalaya Plateau showing Uranium deposits / occurrences

rocks of India commenced in the early 1960's with radiometric surveys in the Satpura Basin and a large number of uranium and thorium anomalies were located in Motur sandstones. Significant anomalies were located in the Wardha-Pranhita valley (Maharashtra), Hutar-Auranga Basin (Bihar) and Hasdo-Arand Basin (Madhya Pradesh). Other favourable basins are the Damodar valley-Mahanadi and Son valley. The Gondwana rocks of Siang district in Arunachal Himalayas have also indicated appreciable uranium values.

The Gondwana Basins in India, spread over an area of over 0.1 million-km<sup>2</sup> (Fig 9), with thickness of 6,000 to 7,000 m, have high uranium potential for hosting the sandstone-type deposits as these intracratonic basins are located adjacent to uplifted granitic and/or volcanic suite of rocks and contain immature sediments, organic matter and pyrite (essential criteria).

#### Breccia Complex Deposits

Giant uranium (17% of the world resources) and REE deposits of the world, hosted by Early to middle Proterozoic (1.1-1.8 Ga) rocks, in intracratonic rifts in cratonic or continental margin environments, and associated with magnetite and hematite belong to this category. The Olympic Dam

uranium deposit (U+Cu+REE+Au+Ag) accounts for about 66% of Australia's reserves plus resources.

The possibility of locating such deposits in India is very bright as the geological settings such as the existence of failed-rift and the mantle plume-type of environment exists. The North Singhbhum Mobile Belt in West Bengal and the areas of large magnetic anomaly close to Anek uranium occurrence, in Garo Hills, Meghalaya are being targeted presently (Fig 9).

#### Surficial Deposits

Surficial deposits comprise about 4% of world uranium resources. They formed where uranium-rich granites were deeply weathered in a semi-arid to arid climate. The Yeelirrie deposit in Western Australia (WA) is by far the world's largest surficial deposit. In WA, the calcrete uranium deposits occur in valley-fill sediments along Tertiary drainage channels, and in playa lake sediments. These deposits overlie Archaean granite and greenstone basement of the northern parts of the Yilgarn Craton. The associated uranium mineral is carnotite (hydrated potassium uranium vanadium oxide). Other significant deposits in WA include Lake Way, Centipede, Thatcher Soak, and Lake

Maitland. Calcrete uranium deposits also occur in the Central Namib Desert of Namibia.

In India, no deposit of this class is established. High hydrouanium values in the Thar deserts in parts of Rajasthan and Gujarat are however indicative of possibilities of such deposits. Such geological and geomorphic set-ups are currently under investigation.

#### Beach and Heavy Mineral Sand

The occurrence of placer minerals along SW coast of India is known since the beginning of the 19th century when monozite was first reported in 1911 by schomberg. The earliest report on the black sands of Andhra coast is by Tipper [16]. Occurrence of monazite in Visakhapatnam coast was reported [3].

Scientists of AMD systematically explored, evaluated and established large reserves and resources of heavy minerals along the Indian coast over the last half-century. The earliest work of the Directorate on the Andhra coast dates back to 1954, when parts of Visakhapatnam and Srikakulam districts, were explored. Since then numerous workers have carried out preliminary and detailed exploration and evaluation for mineral sand deposits. The exploration strategy of AMD has been designed to cater to the immediate and long-term needs of mineral sand industry and national mineral policy for development and exploration of these strategic minerals. The present heavy mineral reserves of the country are presented in Table 2.

New economic policy and liberalization of the sector in the 1998 have opened-up all activity to Indian and foreign private participation. Investments up to 74% by Multi National Companies (MNCs) have been permitted with an invitation to establish downstream industries.

#### Rare Metal and Rare Earth Minerals

These comprise minerals of Nb, Ta, Be, Li, Zr, Ti and REEs. AMD has standardised the techniques for exploration of these elements and uses satellite imagery data, airborne surveys, regional geochemical sampling of soil, stream sediments, rocks and minerals in their search.

**TABLE 2. Heavy minerals Reserves of coast of India**

Mineral	Reserves (In million tonnes)
Ilmenite	375
Leucoxene	14
Rutile	21
Zircon	24
Monazite <sup>@</sup>	8
Garnet	118
Sillimanite	139
Magnetite	N.A.
Others	N. A.

<sup>@</sup> Includes reserves from inland placers

The major occurrences of Nb, Ta, Be and Li minerals in India are in mica pegmatite belt of Bihar, Orissa, Rajasthan, Andhra Pradesh and Tamilnadu; pegmatites in schist belt of Karnataka; pegmatites in tin belt of Bastar, Madhya Pradesh and Koraput, Orissa; granite of Kanigiri and Darsi, Andhra Pradesh; Carbonatites of Sung valley, Meghalaya and Sevatur, Tamilnadu. Besides these, other less important sources are the pegmatites in Purulia district, West Bengal and at Kadaval in Ratnagiri district of Maharashtra. Slags produced after recovery of tin (Sn), from Bastar in M.P. and Koraput in Orissa area also used for recovery of Nb-Ta.

Mica pegmatites of Bihar, Andhra Pradesh and Rajasthan enclose significant quantities of beryl, columbite-tantalite, samarskite and fergusonite, besides mica. In Andhra Pradesh pegmatites, intrusives into the Nellore schist belt, and Kanigiri granite, intrusives into the gneissic rocks, host potential rare metals mineralisation [17].

#### Discussion

With the systematic application of carefully selected geological and radiometric tools, important uranium deposits have been established in the Singhbhum Shear Zone, Jharkhand, Lambapur-Peddagattu and Tumallapalle in Andhra Pradesh; Rohil-Ghateshwar in Rajasthan, Gogi in Karnataka and Domiasiat-Wahkyn in Meghalaya.

Besides these, smaller deposits of significance are established at Bodal and Jajawal in Chattisgarh and in the Siwalik sandstones in the Himalayas. Only small areas of these basins / belts have been covered and a very large part remains unexplored. Quicker solution to various socio-political, environmental, infrastructural and accessibility problems would result in significantly augmenting the uranium reserves of the country. All the initial discovery of radioactive anomalies, which resulted in these deposits, except at Gogi, was located by ground radiometric surveys. In Gogi, initial location of the mineralisation was due to gamma-ray logging of a borewell in the area.

To fulfill the increasing need for larger and high-grade uranium deposits, particularly of the unconformity-type and the iron-oxide breccia type deposits, which are known to exist at deeper levels in the known deposits in Canada and Australia, indirect exploration methods acquires tremendous importance. In many geologically potential areas, that are soil covered, hydro and lithogeochemical investigations are given high priorities to understand their signatures and for delineation of mineralisation-related alterations haloes to identify promising area for detailed exploration. These methods allow quicker and direct studies and evaluation of larger areas in relatively shorter time. Geophysical and remote sensing tools are applied in select areas for studying the signatures of known mineralisation and guiding in exploring extension areas.

With the application of the multidisciplinary approach, we expect to add substantially to our uranium resources in a short time.

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## Benefaction and refining of U/Th



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### Introduction

The basic requirement for an atomic energy programme is the element uranium. Uranium, as found in nature, consists of two important varieties, the isotopes  $^{235}\text{U}$  and  $^{238}\text{U}$ , which are chemically identical but differ in their atomic weights, with the further difference that  $^{235}\text{U}$  is fissionable or can burn, whereas for practical purposes  $^{238}\text{U}$  will not. However, another isotope of uranium,  $^{233}\text{U}$ , is fissionable and can be produced artificially by irradiating thorium in a reactor. As India has the largest known deposits of thorium, the atomic energy programme has been planned to exploit the large reserve of thorium for future generation of power using advanced reactors. The programme in brief, will be implemented in three stages, using three types of reactors which, in addition to producing electricity, also produce fuel for other reactors. In the first stage, natural uranium after appropriate purification is fed as fuel to a reactor; when the nuclear reactor converts some of  $^{238}\text{U}$  to plutonium, an element which, does not exist in nature and can be used as a fuel like  $^{235}\text{U}$ . In the second stage when sufficient plutonium is produced, it is used in another type of reactor with thorium where during nuclear reaction some of the thorium is converted to  $^{233}\text{U}$ , it is used in thoriated reactor where thorium is again converted to  $^{233}\text{U}$  and production of fissile material is more than actually consumed. This type of reactor is known as a 'breeder' reactor and all that is required to feed it is

additional thorium – of which India has a super abundant reserves.

With this long term vision, at the initial stage of atomic energy programme, for achieving self-sufficiency in the nuclear field, the Atomic Energy Commission assigned top priority to the production of uranium and thorium compounds and its fabrication into fuel elements.

### Beneficiation and Refining of Uranium

The most important uranium deposits in India are located in South Bihar in the Singhbhum Thrust belt, which is well known for its copper, apatite, magnetite and kyanite deposits. From 1950 onwards radiometric surveys undertaken by the Rare Minerals Group along the 60 to 80 miles long belt, revealed 34 additional locations. Preliminary test drilling established Jaduguda as a project of promise and thereafter departmental borehole drilling was commenced at this site and underground exploratory developments by means of adits started in the years 1954-55. Uranium apart from secondary sources, is made available largely through excavation of rock containing uranium mineralization. Uranium mining shares all the concerns of conventional mining besides issues related to its radioactive aspects. A number of financial and social issues have made pronounced impact on metal mining industry, the methods and technology employed in uranium mining closely resembles the rest of the mining sectors, engaged in hard rock excavation. Presently all uranium is mined from underground mines in

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India, though open cast mining of a few deposits are on the anvil. Processing of ore can be basically divided in two parts, mining of ore from underground mines and processing of ore to produce uranium concentrate, the yellow cake. Uranium Corporation of India Ltd. (UCIL), a public sector undertaking was set up to process and recover uranium from ore deposits at Jaduguda, assaying 0.07-0.04%  $U_3O_8$ . For production of yellow cake from the minerals mined at Jaduguda, the ore processing plant, capable of processing 1000 tons of ore per day was set up at Jaduguda in 1967 based on laboratory and plant trials conducted at Trombay. The primary responsibility of meeting the demand of uranium rests on Uranium Corporation of India Ltd. (UCIL). At present UCIL is mining ore from three underground mines, viz. Jaduguda, Bhatin and Narwapahar. A typical Jaduguda ore analysis is given in Table 1.

New exploitable deposits have been located at

- Turamdih in East Singhbhum district of Jharkhand State
- Lambapur and Peddogatla in Nalgonda district of Andhra Pradesh
- Gogi in Gulbarga district of Karnataka
- Domiasiat in West Khasi Hills district of Meghalaya

Feasibility studies for exploiting these new deposits are in hand.

## Uranium Ore Processing

### Uranium Ore Types

Uranium ores can be classified into five categories based on the chemical nature of the uranium minerals and their response to leaching, they are:

#### i. Ores containing tetravalent uranium

Most of the world's important deposits contain a significant proportion of their uranium in the tetravalent form. The important examples in this category are primary minerals like uraninite, pitchblende, coffinite and uranothorite.

#### ii. Ores containing hexavalent uranium

Among these minerals are the hydrated oxides like gummite, phosphates like autonite and torbernite and vanadates like carnotite and some silicates.

#### iii. Refractory uranium minerals

These ores are characterized by their resistance to chemical attack. Davidite occurring in Radium Hill deposits of South Australia and brannerite, a common constituent of ores of Elliott Lake district, Canada, are two well known examples.

#### iv. Associations of uranium and carbon

Lignites of north and south Dakota and the uranium deposits of Utah district where uranium occurs as an organo complex are the main examples.

**TABLE 1. Typical Uranium Ore Analysis**

Mineralogical		Chemical	
Constituent	% by weight	Constituent	% by weight
Quartz	60.0	$U_3O_8$	0.07 - 0.04
Chlorite	20.0	$SiO_2$	67.2
Magnetite	9.0	FeO	6.37
Tourmaline	3.5	$Fe_2O_3$	7.87
Apatite	3.0	$Al_2O_3$	5.5
Sulphides	2.0	$TiO_2$	0.66
Ilmenite	1.0	MnO	0.13
Others	1.5	CaO	5.4

v. *Phosphates*

Uranium is a common constituent of the phosphate rock deposits of Florida and Idaho as well as some other places in the world.

**General Scheme for Uranium Concentrates**

**Production**

It has already been mentioned that high grade uranium deposits are scarce. Uranium content of a very large proportion of the ores, at present exploited in the world is in the range 0.2 - 2 kg. U<sub>3</sub>O<sub>8</sub> per ton. The process of uranium concentrate production from ore consists of three main operations: dressing of the ore by physical methods, attack of the ore with dilute acid or alkali carbonate to dissolve the uranium and recovery of uranium as concentrate (70–80 % U<sub>3</sub>O<sub>8</sub>) from the leach solutions. The operations are discussed in more detail in the following pages.

*Physical Dressing of Ores*

Ore dressing methods include a wide variety of operations intended either simply to reduce the ore particles to such a size that the subsequent operations can proceed conveniently or going further than this to upgrade the concentration of uranium by selective segregation of uranium bearing minerals. While the size reduction is achieved by various techniques of crushing and grinding, the upgrading methods employ electronic sorting, gravity separation, froth flotation, heavy media separation etc. Sometimes ore dressing is needed to separate out acid consuming gangue minerals such as calcite or sulphides from the ore.

It may, however, be mentioned that a majority of the known uranium deposits in the world are not amenable to economical physical upgrading and for this reason are treated by direct leaching. Thus the only dressing that all ores undergo is size reduction.

*Roasting and Fusion*

Oxidative roasting is followed for ores where uranium is bound up as an organo complex, to facilitate subsequent leaching process. In the case of ores containing large amount of clay minerals roasting is found to improve settling and filtering characteristics of leached pulps. In the case of carnotite ores salt roasting helps recovery of

vanadium. Fusion is a more drastic method used only for refractory ores and these cases are very rare.

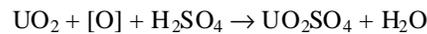
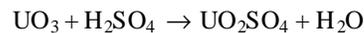
*Leaching*

Uranium is solubilised in almost every case (on record) by leaching the ground ore with either dilute sulphuric acid or sodium carbonate bicarbonate mixture. The choice between acid and alkaline leaching is made on the basis of the overall composition of the ore and its effect on reagent cost. However, the world's supply of uranium is almost entirely derived employing dilute sulphuric acid for the attack.

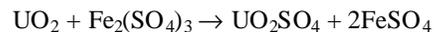
**Chemistry of Uranium Leaching**

*Sulphuric Acid Leaching*

In acid leaching uranium is taken into solution as uranyl-ion. In the case of ores where uranium is present as trioxide (UO<sub>3</sub>) or as other non refractory hexavalent compounds, the dissolution in dilute sulphuric acid takes place readily. On the other hand, when a part or whole of the uranium is present in quadrivalent form as in Uraninite, Pitchblende, Coffinite etc. the dissolution is brought about by the presence of an oxidizing agent.



While a number of oxidizing agents like atmospheric oxygen, manganese dioxide, sodium chlorate and ferric iron have been employed, ferric iron has been found to be the most effective. Manganese dioxide, for example, works according to the following equations.



Hence for effective dissolution of quadrivalent uranium an excess of ferric iron in the leach pulp is essential and this is indirectly measured by the emf of the pulp with a platinum and saturated calomel electrode system.

In the case of ores containing refractory minerals like brannerite and davidite a relatively

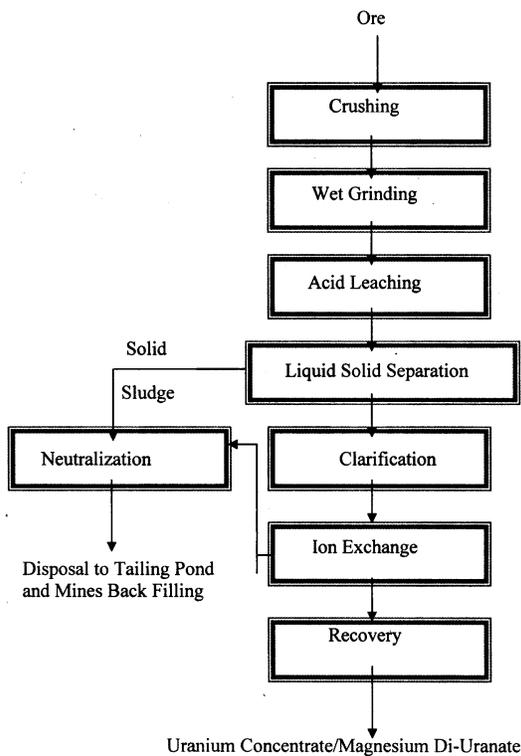


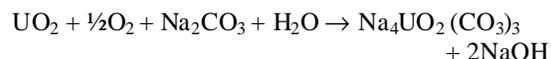
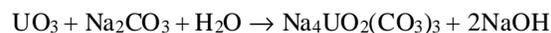
Fig. 1 General Flow Sheet of Jaduguda Uranium Mill

high concentration of free acid (50-60g per liter of solution) in the leach pulp is necessary. In such cases the reaction is facilitated by employing higher temperature. On the other hand, in the case of uraninite and pitchblend type of minerals satisfactory leaching rates are obtained by maintaining a low acidity in the pulp, corresponding to a pH 1.5 – 2.0. By such leaching at controlled pH it is possible to prevent the dissolution of acid consuming minerals like apatite. This practice is followed for leaching Jaduguda ore. Process flow diagram of Jaduguda ore processing is given in Fig. 1.

#### Alkaline Leaching

Many minerals containing hexavalent uranium react with sodium carbonate solution to produce a soluble uranyl carbonate complex. In the case of minerals carrying quadrivalent uranium, an oxidizing agent is needed. Oxygen under pressure,

especially in presence of a catalyst like cuproammonium complex, and permanganate are normally employed for this purpose.



Sodium bicarbonate is also added to the leach solution to react with the hydroxide formed in the reaction and prevents reprecipitation of uranium.

Carbonate leaching has been particularly useful for ores with high content of acid consuming minerals. Other advantages are the relatively non-corrosive nature of the medium and the more or less specific solvent ability of the medium for uranium. Some of the important limitations are:

- (i) Many uranium minerals are not attacked by carbonate solutions;
- (ii) Since the gangue material is virtually not attacked by the reagent, usually a fine grind of ore is necessary to expose uranium minerals to attack;
- (iii) For obtaining satisfactory rates of dissolution needs higher temperature.

#### Liquid-solid Separation

The next step after leaching is liquid-solid separation. Depending on the characteristics of the leach pulp the choice of the most effective flow-sheet is made to give maximum economic recovery of soluble uranium. The main factors considered are: (i) the settling characteristics and filterability of the pulp, (ii) the grade of the ore and (iii) final dilution of uranium tolerated. The flow-sheet is chosen in such a way that loaded solution has uranium content suitable for the subsequent ion exchange or solvent extraction operation (0.5 – 1.0 g.  $\text{U}_3\text{O}_8$  per liter).

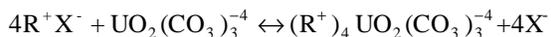
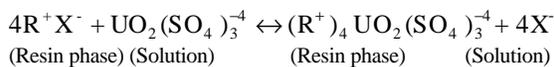
#### Recovery and Concentration of Uranium from Leach Liquors

Direct precipitation methods were used in the earlier stages of technology when high grade and medium grade (over 0.5%  $\text{U}_3\text{O}_8$ ) uranium ores were processed. Difficulties, technical and economical, were encountered in applying these methods to leach

liquors obtained from low grade ores due to the low concentration of uranium and relatively high content of impurities. The discovery of ion exchange and solvent extraction methods was a significant step in the field of hydrometallurgy of uranium and offered a satisfactory solution to this problem by providing almost quantitative recovery of uranium from solution, reducing the volume of solution treated for uranium precipitation and leading to a final product of higher purity than could be obtained by direct precipitations.

#### *Application of Ion Exchange Resins*

During the period 1948-1950 researchers at the Battelle Memorial Institute, Dow chemical Company, Massachusetts Institute of Technology and Rohm and Hass Company working in a co-ordinated effort succeeded in developing an anion exchange resin process to recover and concentrate uranium from sulphate liquors. It has been found that in these solutions uranium occurs as an anionic complex. A similar process for carbonate solutions was known for some time earlier. The basic reactions involved in the uptake of uranium by a strong base anion exchange resin can be



(X<sup>-</sup> is an exchangeable anion like chloride or nitrate)

The elution of uranium from the loaded resin is carried out by following the reverse reaction indicated above.

Quaternary ammonium type polystyrene base resins are the most widely used ones while other type have been studied with varying degree of success.

The uranium uptake by the resin at saturation is governed by the composition of the solution, particularly pH, sulphate and uranium content. A pH 1.6- 1.8 is about the optimum.

One of the special problems encountered in ion exchange operation is "Resin Poisoning". Accumulated experience has shown that colloidal silica, polythionates (from sulphides present in the ore), small concentration of titanium, zirconium,

thorium and molybdenum cause this trouble. Periodic regeneration of the resin with caustic soda and acid solutions is practiced to overcome this effect to more or less extent.

From the equipment point of view, static bed columns are the most widely used. While this type of operation leads to very low uranium loss in the barren solutions, there are some drawbacks which need to be noted before use. The drawbacks are (i) very clear liquors needed for operation, (ii) cleaning of resin by backwashing in the same column, (iii) fouling due to fungus growth, heavy accumulation of silica and (iv) relatively large number and size of equipment required.

#### *Solvent Extraction*

In the solvent extraction process by contacting the acid leach liquors with an organic solvent uranium is transferred to it and the loaded solvent is, in turn, brought into contact with a suitable aqueous solution when the extracted uranium is transferred back into the aqueous phase in a more concentrated and purified form. Thus the extraction and stripping processes are similar to the adsorption and elution steps in ion exchange operation. The chemical mechanism of extraction is also similar to the ion exchange.. Two types of solvents are in use for uranium extraction: organo phosphoric acid esters and long-chain alkyl amines.

#### *Comparison of Ion Exchange and Solvent Extraction*

By and large ion exchange is a batch or semi-continuous process while solvent extraction is a continuous process with the added advantages. For effective adsorption of uranium on the resin, the liquors are to be slightly acidic (pH 1.5-1.8) while a fairly high acid concentration can be tolerated (10-15 g. free H<sub>2</sub>SO<sub>4</sub> per liter) in the case of solvent extraction. While there are many constituents in leach liquors which "poison" the resins temporarily or permanently the solvents are by far free from these troubles and regeneration is relatively simpler. The final uranium product is usually of a better grade in the case of solvent extraction, especially when amines are employed, than in the case of ion exchange.

### Uranium Refining

Historically the initial needs of uranium metal required for nuclear energy development during world war II and immediately afterwards were met by processing high grade uranium concentrates (for example the diuranate from Belgium Congo and Great Bear Lake area of Canada) which accumulated over a long period. Refineries to obtain pure uranium in the form of metal were established in U.S.A., and later in other countries like U.K., France and Canada at convenient locations to be fed with such concentrates from wherever they are available. The uranium plants which were subsequently set up to extract uranium from moderate to low grade ores were geared to produce suitable concentrate (sodium, magnesium or ammonium diuranates) to be transported to the refineries for further refining. It thus became an established practice to bifurcate the working of an ore processing mill and a uranium refinery. In India, leached liquor obtained after ion exchange is treated with magnesia to precipitate crude magnesium diuranate. Composition of the diuranate cake is given in Table 2. Product of uranium mill is magnesium diuranate which is bright yellow and is termed as yellow cake. Further refining to nuclear reactor grade uranium oxide and uranium metal is being done in two different refineries located at Nuclear Fuel Complex (NFC), Hyderabad and Uranium Metal Plant (UMP) at Trombay. Typical impurity analysis in nuclear grade uranium is given in Table 3.

**TABLE 2. Typical assay of uranium concentrate (yellow cake) on dry basis**

Constituent (major)	% by weight
U <sub>3</sub> O <sub>8</sub>	74.8
SiO <sub>2</sub>	3.4
Cl <sup>-</sup>	0.27
SO <sub>4</sub> <sup>2-</sup>	0.52
P <sub>2</sub> O <sub>5</sub>	0.11
Fe (total)	0.38
Ca+Mg (as MgO)	6.31
Th	0.03
Rare earths	0.13

**TABLE 3. Specification for Nuclear Grade Uranium Metal**

Impurity	Maximum limit value in ppm
Aluminium	100
Boron	0.12
Cadmium	0.12
Carbon	800
Cerium	0.2
Chromium	65
Cobalt	1.2
Dysprosium	0.1
Erbium	0.1
Europium	0.04
Gadolinium	0.04
Iron	150
Magnesium	25
Manganese	25
Nickel	100
Nitrogen	100
Samarium	0.1
Thorium	10
Ytterbium	0.1
Yttrium	0.1

The Indian process for conversion of crude U-concentrate to uranium dioxide, tetrafluoride or uranium metal of nuclear purity is given in Fig. 2.

Presently it is being realized that an integrated scheme can be worked to get refined uranium from mill which can eliminate the necessity of separating out an intermediate solid concentrate like the present day diuranates.

### Secondary Sources of Uranium

None of the presently known ores has a potential for recovering economically attractive byproducts in a major way which can offset the high cost of uranium production. However, limited possibilities exist for byproduct uranium from secondary sources. Some of them are discussed here.

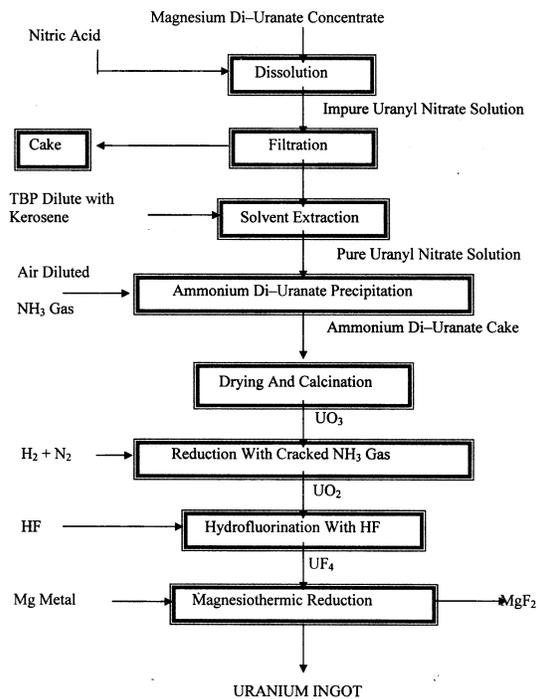


Fig. 2 Process flow sheet for the production of Uranium Metal Ingots

### Monazite

Though monazite is relatively rich in uranium (0.30–0.34%) the total quantity of mineral available from beach sand operations is limited (likely to increase in the near future). Taking into account the limited demand for thorium and the problems associated with the chemical processing of monazite only about 5 to 10 tons U per year at present and about 10 to 20 tons in future can be expected from this source.

### Copper Tailings

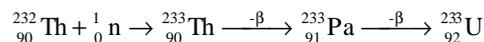
An attractive source for byproduct uranium, though a poor one, is the tailings from the copper concentration plants in Singhbhum area (Bihar). They carry 80-100ppm of  $U_3O_8$ . At present a part of this uranium is recovered as gravity concentrates and processed in the Jaduguda uranium mill along with the ore from the mine.

### Phosphate rock

As mentioned earlier wet-process phosphoric acid is considered all over the world as a promising source of byproduct uranium. A major part of the country's requirement (about 3 million tons) of rock phosphate is met by imports. The phosphoric acid produced in the country from this raw material offers the possibility of recovering uranium. The know-how for the solvent extraction process is already available based on the R&D work carried out in BARC. During sulphuric acid digestion of such rocks, uranium dissolves into wet process phosphoric acid at a concentration of 0.1 – 0.2 g/l  $U_3O_8$ . In addition to phosphatic rocks, many Indian Fertilizer Companies also import large quantities of Merchant Grade Acid (MGA) which is a concentrated form of WPA analysing 50-55%  $P_2O_5$  and 0.2-0.3 g/l  $U_3O_8$ . IREL has been entrusted with the responsibility of setting up of a series of suitable plants adjacent to the host fertilizer companies to produce hundreds of tons of yellow cake at a cost much less than that produced by UCIL by its operation on primary uranium resources.

### Beneficiation and Refining of Thorium in India

Thorium is important in the nuclear energy programme due to its ability to get converted into fissionable uranium-233 on exposure to neutrons :



Thorium is about three times as abundant as uranium. However, the geographical distributions of uranium and thorium do not follow the same pattern. The resource ratio of low cost uranium and thorium in some countries are shown in Table 4. It is understood that most of the countries that are advanced in nuclear technology have relatively large deposits of low cost uranium which would last for many decades even if thermal converter reactors alone are employed to burn the uranium, and would last much longer if fast breeder reactors are introduced. Such nations can wait very long to develop the technology for thorium utilization. But in case of India, low cost uranium resource is very small, while the low cost thorium deposit is the largest in the world.

Although Indian monazite with analysis in Table 4 considered as an important primary resource

**TABLE 4. Monazite composition and ratio of low cost thorium and uranium resources in India and some other countries**

Constituent	Indian	Brazilian	U.S.	South African (Monazite rock)	Madagascar
ThO <sub>2</sub>	8.88	6.5	3.1	5.9	8.75
U <sub>3</sub> O <sub>8</sub>	0.35	0.17	0.47	0.12	0.41
(RE) <sub>2</sub> O <sub>3</sub>	59.37**	59.2**	40.7**	46.41**	46.2**
Ce <sub>2</sub> O <sub>8</sub>	28.46	26.8	—	24.9	23.2
P <sub>2</sub> O <sub>5</sub>	27.03	26.0	19.3	27.0	20.0
Fe <sub>2</sub> O <sub>3</sub>	0.32	0.51	4.7	4.5	—
TiO <sub>2</sub>	0.36	1.75	—	0.42	2.2
SiO <sub>2</sub>	1.00	2.2	8.3	3.3	6.7
Ratio of Th/U resources	76.19	8.65	0.38	N.K.	N.K.

\*\* Includes Ce<sub>2</sub>O<sub>3</sub>

of thorium (8-10% ThO<sub>2</sub>) and rare earths (58-60% REO), it contains significant concentration of U<sub>3</sub>O<sub>8</sub> (0.35%) to warrant its recovery along with other constituents. In India recovery and refining of rare earths, thorium and uranium from monazite are being carried out by M/s Indian Rare Earths, Kerala.

#### ***Recovery of Thorium and Rare Earths***

The conventional process for recovering rare earths and thorium from monazite consisted of digestion of the sand with concentrated sulphuric acid followed by the dissolution of the digested products in aqueous. Aqueous solution contains all the phosphates thereby seriously complicates the subsequent separation and purification of thorium and rare earths.

Presently the mineral is digested with sodium hydroxide to recover all phosphate value in the form of trisodium phosphate and all rare earths, thorium and uranium are converted to their respective hydroxides. This process is followed in IRE, Kerala.

The hydroxide-trisodium phosphate mixture is diluted and heated at 90°C. Resultant slurry after over night settling, decanted to separate out hydroxide cake from phosphate solution. This sodium phosphate solution is further treated to separate the sodium phosphate crystal which is sold in commercial market.

Leaching of residual hydroxide cake with dilute hydrochloric acid at pH 3.5 leads to dissolution of rare earth value leaving behind a thorium concentrate containing uranium and any residual rare earths. Since there was not much demand for thorium earlier, this hydroxide concentrate has been stored in seven silos build up at the premises of RED, Alwaye. So far 33,000 tons of thorium hydroxide has been stock-piled which contains 0.6% U<sub>3</sub>O<sub>8</sub>. This is being considered as the important secondary source of uranium and primary source of thorium. With this assured source of raw material, we have the advantage that mining, beneficiation and ore-break down process are already carried out.

#### ***Thorium Refining***

The crude hydroxide cake is dissolved in conc. HCl to solubilize all hydroxides to form a feed solution composed of chlorides of rare earths, thorium and uranium. Separation of these three components are done by two cycle solvent extraction. To start with uranium value present is extracted with basic extractant called ALAMINE-336 leaving thorium and rare earths in the raffinate.

The uranium loaded extractant is stripped with dilute hydrochloric acid and made free of iron by precipitation at pH 3.5 before recovering uranium as

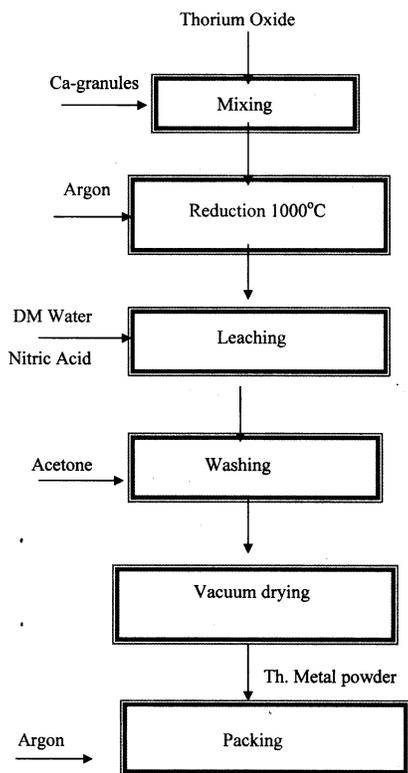


Fig. 3 Process flow diagram for the production of Thorium Metal Powder

wet diuranate cake containing about 32%  $U_3O_8$ . The raffinate from uranium circuit next enters another set of extractors where thorium is preferentially extracted with acidic extractant called PC 88A leaving all rare earths in the raffinate to join the rare earths recovery stream. The thorium loaded solvent is stripped with sulphuric acid before precipitating it as thorium oxalate for its storage. Reactor grade thorium metal powder production flowsheet is given in Fig. 3. Typical analysis of thorium metal is given in Table 5.

### Conclusion

The process chemistry and metallurgy of uranium and thorium is well understood today. As a result of diligent efforts over four decades, we have built up a good infrastructure of skilled manpower, technology and industrial support as demonstrated by the successful operations of Indian research and power reactors.

The safety experience in various nuclear fuel cycle installations in the country has enabled us a good scientific understanding of radiation protection problems involved and to devise proper methods and procedure to reduce radiation exposure to workers as well as population to ALARA. Close involvement of scientific and research workers in the safety

TABLE 5. Typical impurity analysis of thorium metal powder (in ppm)

Element	Content	Element	Content
Aluminum	10	Manganese	5
Antimony	1	Molybdenum	10
Boron	0.1	Nickel	1.5
Beryllium	0.1	Nitrogen	40
Calcium	100	Oxygen	1200
Cadmium	0.1	Silicon	35
Carbon	200	Silver	2
Chromium	20	Sodium	5
Copper	10	Uranium	2.5
Cobalt	1	Vanadium	1
Iron	100	Zinc	20
Lithium	1		
Lead	1		
Magnesium	30		

surveillance and production facilities has ensured maintaining a high standards in safety and product quality.

However, the present emphasis is on the economic aspects. The present economic rate accepted by the leading uranium producing countries in the world is lower than that prevails in India. One of the important reasons of higher cost is the poor grade of uranium ore available in India. Thus the major challenge today remains in cost optimization in processing low grade uranium or thorium sources, without compromising the quality of product and safety standards.

#### **Acknowledgement**

The author wishes to acknowledge the staff of Uranium Extraction Division, Atomic Fuel Division, Indian Rare Earths Limited, Uranium Corporation of India Ltd. and Nuclear Fuels Complex for the indigenous developments carried out over the years in the field of uranium and thorium processing and refining. Author also wishes to express her gratitude to Shri R.K. Garg, Shri T.K.S. Murthy, Shri S. Sen, former Directors of Chemical Engg. Group, BARC, Dr. T.K. Mukherjee, former Chairman and Managing Director, IRE and Shri R. Gupta, Chairman and Managing Director, UCIL for

providing excellent publications on the respective subjects for future references.

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## Processing of Uranium from MDU to UO<sub>2</sub> Pellets



*Shri R.N. Jayaraj obtained BE (Mech.) in 1973 from Osmania University and joined the Atomic Fuels Division, BARC through 17<sup>th</sup> batch of Training School. He contributed in the production of metallic uranium fuel assemblies for CIRUS and development of production processes for the manufacture of fuel assemblies for DHRUVA reactor. After his transfer to Nuclear Fuel Complex, Hyderabad in the year 1978, he played a key role in establishing the assembly plant for the production of core sub-assemblies for Fast Breeder Test Reactor. He was instrumental in successfully fabricating and supplying all the core sub-assemblies for FBTR for the first time in India. In mid-80's, he successfully executed the responsibility of production of natural uranium dioxide fuel bundles for all the Pressurized Heavy Water Reactors adhering to the fuel requirements of Nuclear Power Corporation of India Ltd. While carrying out regular production of fuel bundles for PHWRs, Shri Jayaraj immensely contributed in the indigenous development of various critical process equipment involving welding, machining centres and assembly stations. He also contemplated several process improvements in the UO<sub>2</sub> pellet production and fuel bundle fabrication resulting in substantial increase in the production recoveries. As Dy Chief Executive (Fuel Fabrication), Shri Jayaraj is presently responsible for the production of Natural Uranium fuel bundles for PHWRs, enriched uranium fuel assemblies for Boiling Water Reactors and activities related to fabrication of core sub-assemblies for the forthcoming Prototype Fast Breeder Reactor.*

### Introduction

Nuclear Fuel Complex (NFC) is responsible for manufacturing natural UO<sub>2</sub> fuel for the operating and forthcoming Pressurized Heavy Water Reactors (PHWRs) in India in addition to low enriched fuel for the two Boiling Water Reactors (BWRs).

UO<sub>2</sub> powder is produced through Ammonium-Di-Uranate (ADU) precipitate route through various wet and dry thermo-chemical processes. The process uses Magnesium Di-Uranate (MDU) as starting raw material, which contains about 55-60% Uranium.

High density (96-98%TD), high purity UO<sub>2</sub> fuel pellets in cylindrical form are produced in mass scale from UO<sub>2</sub> powder through Powder Metallurgical steps like pressing, sintering followed by wet grinding of sintered pellets to produce uniform diameter finished pellets. These pellets are visually inspected for physical defects before they

are encapsulated in zircaloy tubes followed by various stringent welding, machining and assembly operations during manufacturing of PHWR fuel bundles.

As finished UO<sub>2</sub> pellets need to meet stringent requirement with respect to purity, density and integrity; the powder production and pellet fabrication processes must follow close operational control at various stages of production.

The scrap generated at various stages of pellet-fabrication is recycled to the initial process step in powder production.

The following sections brief on process descriptions, quality control steps and discuss the important aspects of process-evolution.

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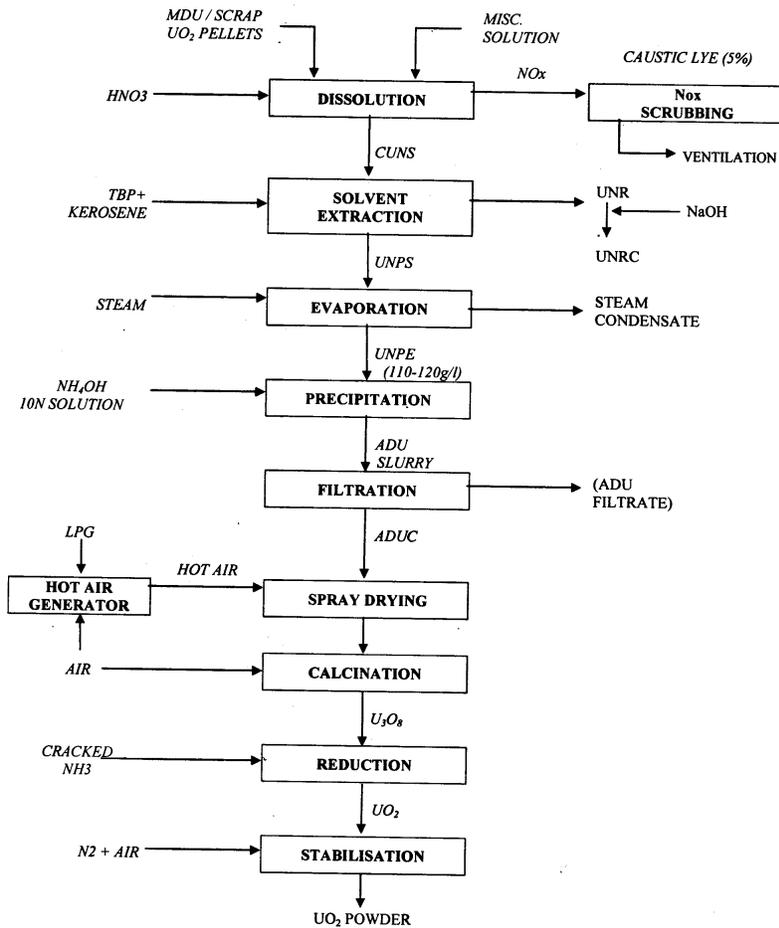


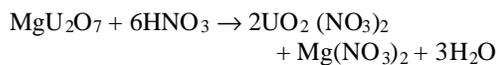
Fig. 1 Process flow sheet MDU to UO<sub>2</sub> powder

### Process Description for Powder Production

The process steps followed in powder production are shown in Flow-sheet (Fig. 1). The individual process steps are briefed below:

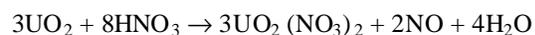
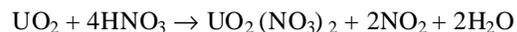
#### Dissolution

In this step, MDU is dissolved in commercial Nitric acid (12 N) under steam heating & agitation at a temperature of 80 – 85°C, to yield Crude Uranyl Nitrate Slurry (CUNS) as per the following reaction:-



The dissolver tank is maintained at a negative pressure of 5 to 10 mm WC to prevent leakages of fine dust & nitric acid fumes. The off gases containing nitric acid vapours & 'U' dust are scrubbed in packed columns by contacting with caustic lye / water.

Reject materials (scrap) like UO<sub>2</sub> pellets & UO<sub>2</sub> powders & sludge as obtained from the pelletising plants are also dissolved in commercial Nitric acid to yield Uranyl Nitrate Solution, as per the following reactions :



The dissolution of scrap material is highly exothermic and hence does not require external heating. To control the rate of generation of NO<sub>x</sub>, the acid is added in a controlled manner under mild air agitation. The dissolver is maintained at a positive pressure of 2000 mmWC and the NO<sub>x</sub> fumes are scrubbed in water by passing through bubble columns.

### ***Solvent Extraction***

The CUNS is adjusted for Uranium concentration and free acidity before transferring to the Solvent Extraction Section. The Solvent Extraction section consists of two major operations namely Extraction & Stripping. Tri-Butyl Phosphate diluted in kerosene (33% TBP, 67% kerosene) is used as Solvent.

The CUNS obtained from MDU dissolution contain a maximum 6% solids (mostly silica). Conventional mixer-settler units like box-type mixer settler, pulsed columns cannot handle slurries due to choking. The CUNS had to be filtered and the cake repulped a number of times to make it suitable for pulsed columns which were previously used. Repetitive filtration & repulping resulted in generation of large volumes of lean Uranium solution, besides being labour intensive. A new mixer settler unit, slurry extractor was indigenously developed at NFC which is designed to handle slurries. The mixing & inter-stage transfer of aqueous is done using compressed air involving airlift principle, while the organic flows counter currently due to gravity. The aqueous is kept as dispersed phase throughout the unit, excepting in the last stage settler, where it is allowed to form a continuous phase. This prevents the settling of the solids, which are carried by the aqueous and hence choking of pipelines are avoided.

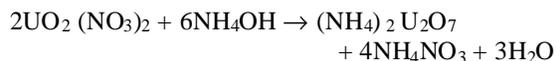
In the Extraction operation, the organic is admitted counter currently to the aqueous feed, in a ratio of 2:1. Solvent loading to the extent of 85% with uranium is maintained to achieve nuclear grade pure extract and keeping uranium losses in the raffinate to a minimum. The Uranyl Nitrate Raffinate (UNR) generated in the process, containing all the undissolved solids, is neutralized with caustic lye at pH of 8.0. The resultant slurry is

filtered and the cake (Uranyl Nitrate Raffinate Cake) is packed in 200ltr. polythene lined MS drums, sealed and transported back to UCIL, Jaduguda for recovery of Uranium. The Sodium Nitrate Filtrate is sold to approved private parties.

In the stripping operation the nuclear grade pure extract is counter currently treated with demineralised water in conventional box type mixer settler unit. The Uranium is transferred from the organic phase to the aqueous phase. Nuclear grade Uranyl Nitrate Pure Solution (UNPS) is taken out from the unit at one end and the lean solvent, taken out from the other end, is recycled back to Extraction process.

### ***Precipitation***

The UNPS is precipitated with 10 N Ammonium hydroxide solution, at a temperature of 60°C and pH of 8.0 to obtain Ammonium-Di-Uranate, as per the following reaction:



The Precipitation process is carried out in batch mode, wherein required quantity of UNPS is taken. The UNPS is heated to 60°C, by steam in coil heating. Ammonium hydroxide (10N) is added slowly under gentle agitation ensuring uniform distribution and the reaction is allowed to proceed till a pH of 8.0 is achieved. Sedimentation or settling tests of the ADU slurry is carried out and 500 ml of the slurry should settle to 55 – 70 ml in 5 minutes.

Some times Ethylene Diamine Tetra acetic Acid (EDTA) is added to the UNPS before Precipitation process, so as to prevent co-precipitation of rare earth impurities present in the UNPS.

### ***Filtration***

The ADU slurry is filtered in a horizontal pan filter under a vacuum of about 450mmHg. The Ammonium Nitrate filtrate obtained is treated with Tri-Sodium Phosphate to precipitate out rare earth materials such as Thorium and coagulated with ferric chloride and allowed for settling. The supernatant ammonium nitrate is sold to approved private parties.

Sl. No.	Parameter	Value	Unit	Min - Max
1	Ag	< 1.0	ppm	<1.0
2	Al	< 25.0	ppm	<25.0
3	B	0.12	ppm	<0.3
4	Ca	13.0	ppm	<50.0
5	Cd	< 0.1	ppm	<0.2
6	Ce	< 0.5	ppm	
7	Co	< 2.0	ppm	
8	Cr	< 10.0	ppm	<15.0
9	Cu	< 6.0	ppm	<10.0
10	Dy	< 0.1	ppm	<0.15
11	EBC	~ 0.71	ppm	<1.1
12	Er	< 0.1	ppm	
13	Eu	< 0.1	ppm	
14	Fe	47.0	ppm	<50.0
15	Gd	~ 0.08	ppm	<0.1
16	Mg	9.0	ppm	<50.0
17	Mn	2.0	ppm	<5.0
18	Mo	5.0	ppm	<100.0
19	Na	35.0	ppm	
20	Ni	1.0	ppm	<20.0
21	O/U	2.032	ratio	<2.15
22	SSA	2.55	m <sup>2</sup> /gm	2.0-4.5
23	Si	< 30.0	ppm	<30.0
24	Sm	< 0.1	ppm	
25	U	87.98	%	<88.1
26	Zn	< 1.0	ppm	

Fig. 2 Typical powder purity data

### Drying

The ADU cake, from the filter unit is dried in turbo drier. Alternatively it is also repulped and spray dried. The hot off gases, containing Uranium bearing dust are filtered in bag filter, pre-filter & HEPA filter before being let out through high rise stack.

### Calcination

The dried ADU is thermally cracked in a multi-zone rotary kiln at 675- 700°C in air atmosphere. ADU dissociates into U<sub>3</sub>O<sub>8</sub> and NH<sub>3</sub>

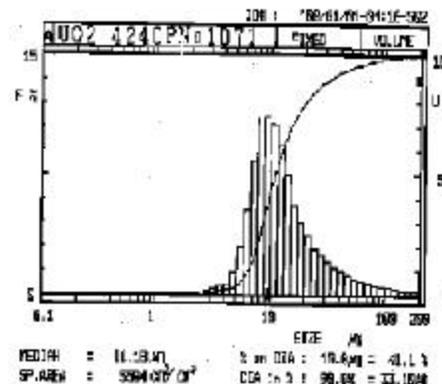


Fig. 3 Typical particle size distribution of powder

gas. The exhaust air from calcinator is passed through a wet scrubber to remove NH<sub>3</sub> & Uranium dust. The U<sub>3</sub>O<sub>8</sub> powder is collected in a bunker. The furnace is maintained at a negative pressure of -10mm WC to prevent leakages of uranium powder into the atmosphere.

### Reduction

In this step, U<sub>3</sub>O<sub>8</sub> powder is reduced to UO<sub>2</sub> at about 600°C in a similar rotary furnace using cracked ammonia as reducing agent. The furnace is maintained at positive pressure of about 100mmWC to prevent ingress of air in to the furnace to avoid explosion condition. N<sub>2</sub> sealing is used to avoid any leakages. The exit gases are passed through a wet scrubber to recover the UO<sub>2</sub> powder.

### Stabilization

UO<sub>2</sub> having CaF<sub>2</sub> structure is pyrophoric in nature. So, a controlled oxidation step is carried out using air in a stabilizer furnace to form a thin film of U<sub>3</sub>O<sub>8</sub> over UO<sub>2</sub> particle. This is carried out at room temperature in a rotary kiln by adopting counter current contact between air & N<sub>2</sub> and UO<sub>2</sub> powder.

The powder thus produced through various steps is identified by assigning a Lot number which is maintained from precipitation stage itself. Powder characteristics have remarkable effect on sintering kinetics and microstructure development. Powder is characterized for morphology, phase homogeneity, purity, particle size distribution, specific surface area,. Typical purity data (Fig. 2), Particle size distribution (Fig. 3), SEM Micro graph (Fig. 4),

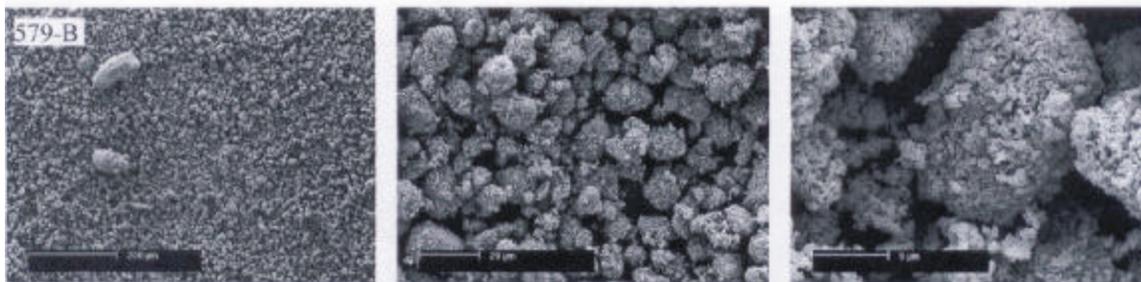


Fig. 4 SEM micrograph of  $UO_2$  powder.

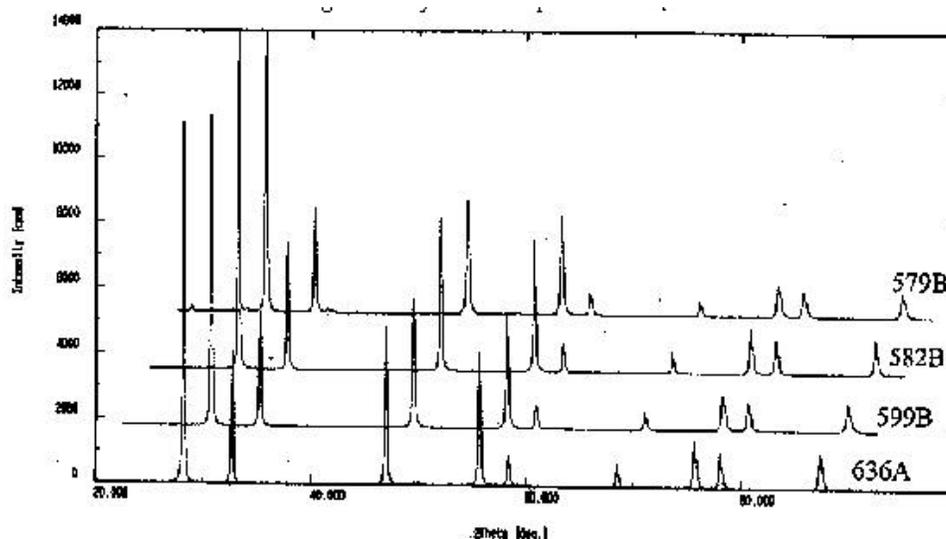


Fig. 5 X-ray diffraction pattern of  $UO_2$

X-ray diffraction pattern for different lots (Fig. 5) are enclosed.

Pellet fabrication is carried out lot-wise and the lot identity is maintained from Pre-compaction till loading of finished pellets in zircaloy tubes.

#### Process Description for Pellet Fabrication

The steps in pellet fabrication are shown in the flow sheet (Fig. 6). The individual process steps are briefed below:

##### *Pre-compaction & Granulation*

In this step, the fine powder is compacted at a lesser pressure and the compact is granulated and sieved on line to increase the bulk density and flowability of the powder. The bulk density of

granulated powder is maintained in the range of 24 to 27%TD (Theoretical Density of  $UO_2$  is 10.96g/cc). The process step is essential for uniform die-fill in the final compaction press which is required for production of consistent quality green pellets.

##### *Blending*

In order to prepare the press feed in the final compaction, the granules are admixed with solid powder lubricant (Zinc-stearate or organic fatty acids) by blending in batches. This process enhances the flowability of the granules further and lubricate them in order to minimize the ill-effects of friction on the quality of the green pellet in die-compaction of the press-feed.

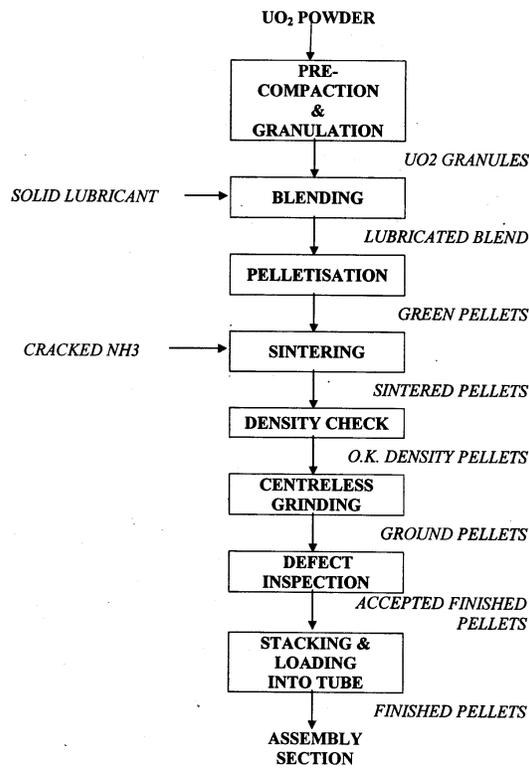


Fig. 6 Process flow sheet for pellet fabrication

### Final Compaction

In this step, the lubricated granules are compacted in a double acting multi-die hydraulic press at about  $3 \text{ ton/cm}^2$  pressure to produce green pellets. The pressure is equalized to all the top punches to produce constant density pellets. Green density of about 52 to 54%TD is maintained in the pellets so as to facilitate uniform densification in sintering. The pellets are cylindrical in shape with dish at either end. The pellet edges are chamfered to avoid formation of chip during handling at green stage and grinding after sintering. The punches are designed accordingly. The dish is provided to accommodate thermal expansion of  $\text{UO}_2$  in reactor condition. Typical Green Pellet is shown in photograph (Fig. 7).

### Sintering

Sintering of green pellets is carried out in a continuous multi-zone, sintering furnace at high



Fig. 7 Typical green pellet



Fig. 8 Sintering furnace

temperature ( $1700^\circ\text{C}$ ) in reducing atmosphere. The temperature profile is so maintained that the charge is gradually heated to sintering temperature, soaked for a desired period at  $1700^\circ\text{C}$  and then cooled gradually to almost ambient temperature before the charge is discharged from the furnace. Cracked ammonia is continuously passed to the furnace for maintaining reducing atmosphere. The reducing atmosphere is required for minimising oxygen content of non-stoichiometric  $\text{UO}_2$  pellet. Excess oxygen in  $\text{UO}_2$  lattice acts as neutron absorber in the reactor, hence not desirable. Typical Sintering Furnace is shown in Photograph (Fig. 8).

Due to density gradient in green pellet in axial and radial direction (minimum density at the center), radial shrinkage is maximum near the middle of the pellet. Hence, after sintering the pellet no longer remains cylindrical and takes an hour-glass shape.

### ***Centreless Grinding***

Centreless grinding of sintered pellet is done to remove the hour-glass defect and to obtain perfect cylindrical shape of the pellet.

The ground pellets are visually inspected for defects like chip, end cap, pit, crack, etc. before they are washed, dried, stacked to a specified length and loaded into zircaloy tubes. Such defects are not acceptable for the intended performance of the fuel assembly in the reactor operation.

# Zirconium Technology for Cladding and Calandria Tubes



*Shri Tapas Sanyal is Deputy Chief Executive, Nuclear Fuel Complex (NFC), Hyderabad responsible for Zirconium Sponge Plant, Special Materials Plant and Melt shop. Sri Sanyal did his B.Tech. (Hons.) in Metallurgical Engineering in 1968 from IIT, Kharagpur. He completed his training from the 12<sup>th</sup> batch of BARC Training School in 1969 and joined NFC. He is a specialist in the production of reactor grade zirconium sponge and melting of zirconium alloy ingots, fabrication of ingot into mill products such as tube, plate, strip, rod, wire etc. He also looks after production of niobium, tantalum and high purity metals and characterization of advanced materials. He is a member of Institute of Metals, Indian Vacuum society, Indian Nuclear Society and Powder Metallurgical Association of India.*

## Introduction

The metal zirconium, identified by the famous Swedish Chemist Berzelius, was produced for the first time in 1824. Zirconium was first used as a nuclear fuel cladding material in 1951 in the first nuclear submarine 'the Nautilus' in USA. Today zirconium alloys are extensively used as a material for cladding nuclear fuels and for making core structurals of water-cooled nuclear power reactors all over the world for generation of nearly 16% of the world's electricity. Only four countries in the world, namely France, USA, Russia and India, have a large zirconium industry and capability to manufacture reactor grade zirconium sponge, a number of zirconium alloys and a wide variety of structural components for water cooled nuclear power reactor. Zirconium occurs in nature mostly in the form of silicate mineral known as zircon which is extensively used in glass and ceramic industries and in foundries. Zirconium oxide is prepared from zircon and used all over the world as traditional and advanced ceramics and as a refractory material. Only a limited quantity of zircon is used for making nuclear grade zirconium metal.

The unique features of zirconium and its alloys are as follows:

- Low neutron absorption cross section
- Transformation temperature :  
862°C  $\alpha$  (HCP)  $\rightarrow$   $\beta$  (BCC)

- c/a of  $\alpha$  < ideal axial ratio making prismatic slip on (10.0) plane most predominant.
- Anisotropic properties causing unequal thermal expansion along different crystallographic directions, the development of strong crystallographic textures during fabrication and the irradiation induced growth of textured alloys.
- High reactivity with O, N & C and high solubility of these interstitial elements in the  $\alpha$ -phase.
- Low solubility of 'H' in the  $\alpha$ -phase, excess 'H' causes hydride precipitation which could lead to serious embrittlement problem.
- Alloying behaviour

$\alpha$  -  $\beta$  isomorphous systems (Zr-Ti, Zr-Hf)

$\beta$  monotectoid systems (Zr-Nb, Zr-Ta)

$\beta$  eutectoid systems (Zr-Fe, Zr-Ni, Zr-Cu, Zr-Cr, Zr-H)

$\alpha$  stabilizing systems (Zr-Al, Zr-Sn, Zr-O, Zr-N)

The production of hafnium-free zirconium oxide powder and reactor grade zirconium sponge have increased significantly and several components like seamless zircaloy-4 square channels for Boiling water Reactors and calandria tubes for the new Pressurized Heavy Water Reactors (PHWR 540) have been manufactured for the first time in the world.

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### Production of Reactor Grade Zirconium

The principal economic source of zirconium is zircon, which is the zirconium silicate ( $ZrSiO_4$ ). The mineral baddeleyite, a natural form of zirconium oxide, is a distant second to zircon in its economic significance. In India, zirconium occurs only as zircon in the coastal beach sands of Kerala, Tamil Nadu and Orissa along with many other valuable minerals. Fig. 1. gives reserves of zircon sand in India.

State	Zircon (million MT)
Kerala	1.993
Tamilnadu	7.785
Andhra Pradesh	1.302
Orissa	1.077
West Bengal	0.386
Bihar	0.085

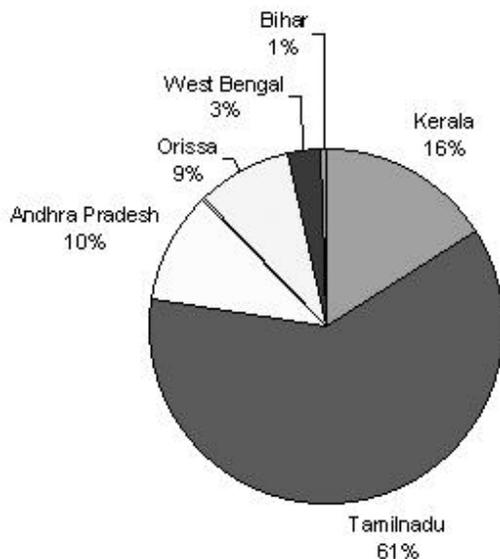


Fig. 1 Reserves of Zircon sand in India

The production of zirconium from raw material involves the following three major steps:

- removal of silica
- removal of hafnium
- production of zirconium metal / sponge

Fig. 2. Flow sheet for production of nuclear grade zirconium oxide, zirconium sponge and zirconium alloy ingots

### Removal of Silica

Mineral zircon, the raw material for the production of zirconium, is always associated with hafnium, which is a neutron poison. Hence, the separation of hafnium from zirconium is essential in the production of zirconium. Prior to the separation of hafnium, the mineral zircon has to be opened up and a suitable intermediate compound of zirconium / hafnium produced to facilitate separation.

### Fusion with NaOH

Zircon sand is fused with sodium hydroxide in steel pots at around 600 to 650°C to convert to sodium zirconate and silica gets eliminated as water soluble sodium silicate. The residue containing sodium zirconate and un-reacted zircon is filtered, washed, dried under controlled conditions to render the residual silica insoluble and then dissolved in nitric acid or sulphuric acid to bring the zirconium into solution to facilitate Zr-Hf separation by Solvent Extraction process.

### Removal of Hafnium

#### TBP- Nitrate Process

The zirconium nitrate solution obtained in the fusion with NaOH route is subjected to multi-stage solvent extraction using 'Tributyl Phosphate (TBP)' dissolved in kerosene as solvent. Zirconium gets preferentially extracted into the organic phase, leaving the hafnium and other impurities in the aqueous phase. Thus, this process is best suited for the production of high purity zirconium, while the aqueous phase requires further purification steps for recovering the hafnium in a pure form. This process has been adopted for the production of hafnium-free zirconium oxide thus meeting the nuclear grade specifications. The quantity of production during 2004-05 was 270 tons. Table 1 gives the typical analysis of Hf-free zirconium oxide and reactor grade zirconium sponge.

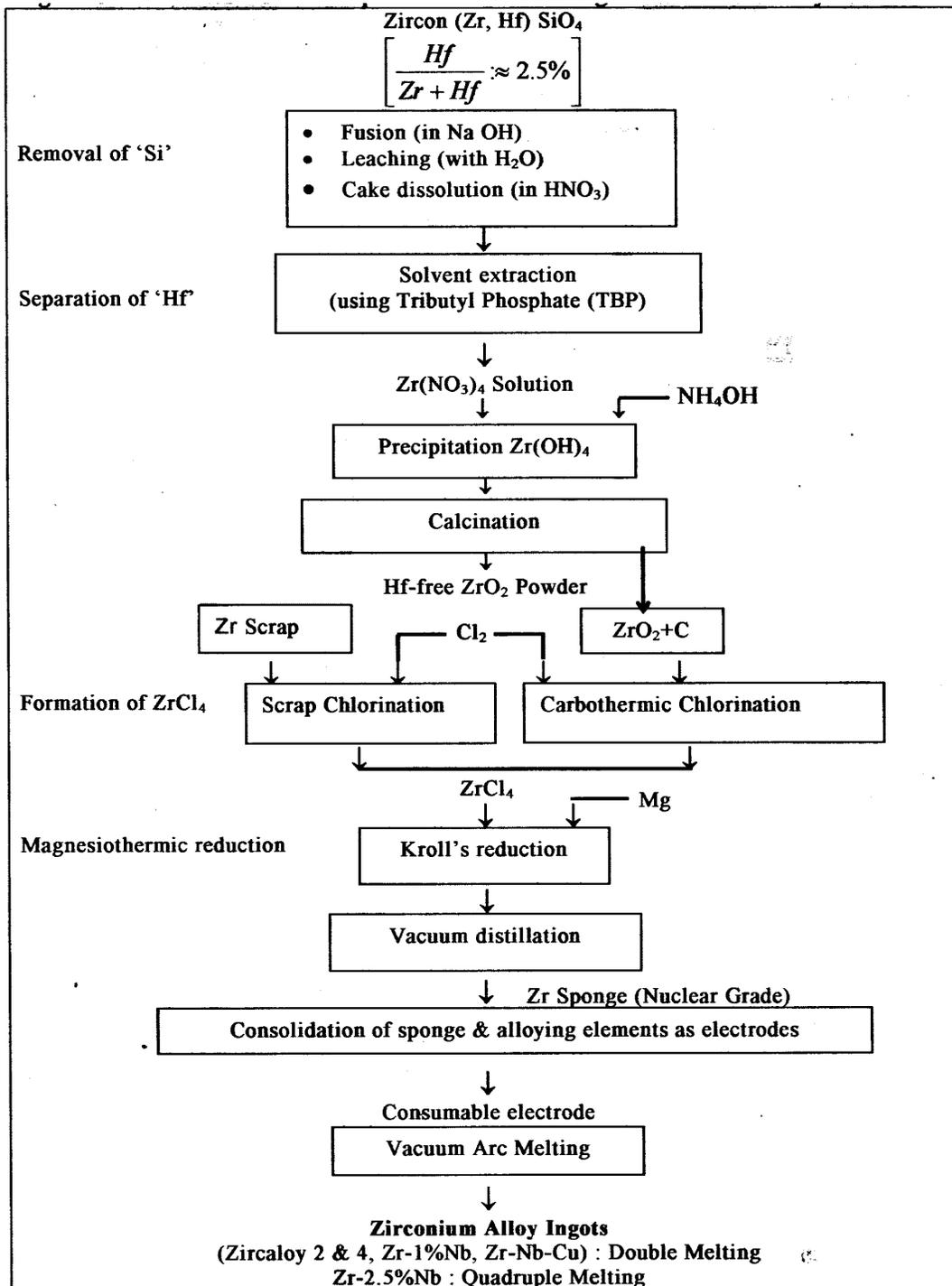


Fig. 2 Flow sheet for production of nuclear grade zirconium oxide, zirconium sponge and zirconium alloy ingots

**TABLE 1. Typical analysis of ZrO<sub>2</sub> & Zr sponge manufactured at NFC, Hyderabad**

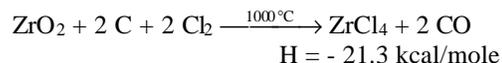
Element	Hafnium free Zirconium Oxide	RG Zirconium Sponge	
	NFC	ASTM	NFC
Al	50	75	75
B	1	0.5	0.5
C	-	250	125
Cd	0.5	0.5	0.5
Cl	-	1300	200
Cr	100	200	150
Cu	25	30	25
Fe	600	1500	800
Hf	25	100	25
Mg	25	600	150
Mn	25	50	50
Mo	25	50	25
N	-	50	25
Ni	25	70	50
O	-	1400	1000
Si	-	120	50
Sn	25	50	50
Ti	150	50	25
U	10	3	3
W	25	50	50
LOI	1.2 – 1.8 %	-	-
Sulphate	0.8 – 1.2 %	-	-
Sieve Analysis	-325 mesh 85 – 95 %	-	-

**Production of Zirconium Tetrachloride**

**Chlorination of Zirconium Oxide**

A mixture of ZrO<sub>2</sub> and carbon in the form of briquettes are chlorinated in a self resistively heated static-bed reactor. The reactor is essentially a low alumina, high purity silica brick-lined mild steel vessel with a provision of three graphite electrodes for feeding power to the bed. Chlorine is admitted into the reactor through a pipe distributor at the bottom. The zirconium tetrachloride vapours are condensed in condensers made out of Inconel-600

and solid zirconium tetrachloride is discharged into cans.



Rate of chlorination reaction is governed by the bed temperature and increases with increase in temperature.

**Scrap Chlorination**

Zircaloy scrap in the form of briquettes is chlorinated in a water cooled static-bed reactor.

Chlorine is admitted into the reactor through a distributor at the bottom. Zirconium tetrachloride vapours are condensed and discharged into cans. The reactor is made up of Inconel-600 lined inside with graphite.



The reaction being highly exothermic, the reactor is water cooled externally to keep the reaction temperature under control.

### Production of Zirconium

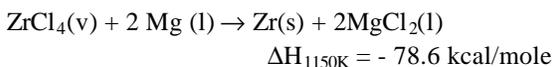
Conversion of zirconium tetrachloride intermediate to zirconium, meeting stringent nuclear specifications once again involves complex technologies and currently only two processes are being followed for commercial scale production. These are (a) The Kroll's Process and (b) The molten-salt electrolysis. The other process which is mainly used for refining to get high pure zirconium is Van Arkel Iodide Process. NFC follows Kroll's process for production of zirconium metal in the form of sponge.

### Kroll's Process

In this process, zirconium sponge is produced by the magnesio-thermic reduction of pure zirconium tetrachloride followed by pyro-vacuum treatment of the reduced mass to separate excess magnesium and byproduct magnesium chloride from zirconium. This process, invented by Dr. W. J. Kroll at the Albany Research Center of the US Bureau of Mines in the late 40's, continues to be employed by all countries barring Russia for the production of zirconium. Over the years many technological and engineering improvements have, however, been incorporated and there has also been a significant increase in the batch size from a mere 50 kg to 750 kg today.

### Magnesiothermic Reduction

The magnesiothermic reduction reaction involves vapour (v), liquid(l) and solid (s) phases as shown below:



The reduction reaction is carried out at 900°C in a closed retort heated in a pit-type electrical resistance furnace. Zirconium tetrachloride and magnesium are loaded in separate containers inside the retort separated by a baffle with holes at the sides for passage of chloride vapours. The magnesium container is a combination of crucible and a liner placed in the retort. Reaction takes place in the liner. The retort is made of AISI 310S, crucible and baffle are made of AISI 316, the liner is made of AISI 430 (nickel free) and chloride can is made of Inconel-600. Pressure inside the retort due to the subliming chloride vapours is monitored by measuring the backpressure of argon gas purged into the retort and controlled by means of an air-cooling coil and two pressure relief valves one of which is a stand-by. The chloride bled through the relief valve is condensed and recycled in the reduction process. The retort is given a low temperature soak at 150°C for removal of moisture and a high temperature soak at 250°C for removal of low boiling chloride impurities of titanium, aluminum, silicon and boron from the zirconium tetrachloride.

### Pyro-vacuum Distillation

Pyro-vacuum distillation of reduced mass of zirconium sponge is carried out in a closed retort at 980°C under very low pressure of <100 μ Hg to distill off the magnesium chloride and magnesium impurities. Vapour pressure of magnesium and magnesium chloride at 900°C are 100 and 8mm Hg respectively. The vacuum distillation assembly consists of a top retort in which reduced mass is loaded and a bottom retort, externally cooled with water to condense the distilled out magnesium and magnesium chloride vapours. The top retort is made of AISI 310S and is heated by means of a bell type electrical resistance furnace. The bottom retort and all the inner components like can, shrouds and tables are made of AISI 316. Vacuum is generated by a combination of rotary piston pump and roots pump connected in series. The furnace is also maintained under vacuum by means of a rotary piston pump to avoid buckling of retort. 152 tons of Zr-sponge was produced during 2004-05.

### Ingot Production by Vacuum arc Melting

The various alloys of zirconium such as Zircaloy-2 (Zr-2), Zircaloy-4 (Zr-4),

**TABLE 2. Composition of various grades of Zirconium alloy ingots produced at NFC**

Elements	Zircaloy-2	Zircaloy-4	Zirconium-2.5% Niobium alloy	Zirconium-2.5% Niobium-0.5% Copper alloy
Tin	1.20 - 1.70	1.20 - 1.70	--	
Iron	0.07 - 0.20	0.18 - 0.24	--	
Chromium	0.05 - 0.15	0.07 - 0.13	--	
Nickel	0.03 - 0.08	--	--	
Niobium	--	--	2.40 - 2.80	2.4 - 2.8
Total Fe+Cu+Ni	0.18 - 0.38	--	--	
Total Fe+Cr	--	0.28 - 0.37	--	
Carbon (ppm)	150 - 400	150 - 400	--	
Oxygen (ppm)	900 - 1400	900 - 1400	900 - 1300	900 - 1300
Copper	--	--	--	0.3 - 0.7
Zr + permitted impurities	Balance	Balance	Balance	Balance
Impurities (ppm) :				
Aluminum	75	75	75	75
Boron	0.5	0.5	0.5	0.5
Cadmium	0.5	0.5	0.5	0.5
Carbon	—	—	125	270
Chlorine	—	—	< 0.5	—
Cobalt	20	20	20	20
Copper	50	50	50	—
Chromium	—	—	200	200
Hafnium	100	100	50	150
Hydrogen	25	25	5	25
Iron	—	—	650	1500
Lead	130	130	130	130
Magnesium	20	20	20	20
Manganese	50	50	50	50
Molybdenum	50	50	50	50
Nickel	—	70	70	70
Niobium	100	100	—	—
Nitrogen	80	80	65	65
Phosphorus	—	—	< 10	—
Silicon	120	120	120	120
Tantalum	200	200	200	200
Tin	—	—	50	100
Titanium	50	50	50	50
Tungsten	100	100	100	100
Uranium	3.5	3.5	3.5	3.5
Vanadium	50	50	50	50

Zirconium-2.5% Niobium and Zirconium-2.5% Niobium-0.5% Copper etc. are produced for several applications and their composition is given in Table 2.

### **Melting of Zirconium Alloy Ingot**

50mm X 100mm X 500mm compacts of zirconium sponge mixed with alloying elements are pressed in 1000 tons hydraulic press. 15 such compacts are assembled together and welded in electron beam welding equipment under vacuum. The power of electron beam gun is 30 KW. Electrode after welding is melted in 240mm dia. vacuum arc melting furnace to obtain a 240mm dia. X 650mm long 1<sup>st</sup> melted ingot. The 1<sup>st</sup> melting ingots are machined on OD and both ends are faced. Two / three such ingots are re-welded in Electron Beam Welding equipment to yield 240mm dia. X 2.0 meters long consumable electrode. The electrode is melted in 300mm dia. vacuum arc melting furnace to obtain 300mm dia. X 800mm long ingot. The ingot is machined and sampled for chemical analysis.

Different equipment and their design features in brief is as below :

#### **1000 ton press**

The press is used for making compacts of Zr-sponge with alloying elements. It is a hydraulic press with maximum load of 1000 tons on main plunger used for making compacts of size 50mm X 100mm X 500mm mixed with other alloying elements.

#### **Electron Beam Welding Units**

High voltage rectifiers and power supply to produce 22 KV for input to the electron gun with current rating upto 1.5 amps whereas operation parameter is 20 KV at 1.5 A. Pumping system to attain vacuum better than 1 micron.

#### **240mm dia. arc furnace**

The equipment consists of two systems i.e. furnace chamber and pumping system. The melting power is supplied through transformer and DC rectifier and it is located adjacent to the furnace. The furnace body is a four columns steel structure. The furnace chamber is made of MS shell and its movement is guided on supporting columns and is

done through an integrated hydraulic system. The electrode drive system is mounted on a platform on top of the steel structure. The electrode ram (stinger rod) is inserted into the furnace chamber via. a sliding seal, it contains scrappers to keep clean the electrode ram and several Wilson seals in order to ensure vacuum tightness. The water jackets are provided for copper mould in which the melting is carried out and can be moved manually from charging position to melting position on rails which makes it possible to melt in one assembly while the other assembly is kept ready with the charge in it. The vacuum pumping system consists of two mechanical booster pumps (roots blower) backed by one rotary mechanical pump. The pumping system is capable of giving an ultimate vacuum of 10 micron in the chamber. Operating current during melting is 4500 AMPS at 35 Volts.

#### **300mm dia. Melting Furnace**

Used for double melting of zircaloy ingots (initially melted in 200 dia. furnace and subsequently welded in EBW). The power supply for this furnace is designed for 10000 A whereas operating current during melting is 8500 A at 35 volts. The pumping system of the furnace is designed to attain adequate vacuum. Other features of this furnace are same as in 240mm dia. furnace.

#### **Plasma Beam Melting Furnace**

This furnace is used for consolidation of various types of re-meltable zircaloy scrap into consumable electrodes for re-melting in vacuum arc melting furnaces. Hence zircaloy scraps of relatively large mass are charged in a water-cooled copper hearth having a U-groove for initial melting and smaller sizes of scrap are added as and when required during melting.

Initially selected sponge compacts / reverts are charged into the water-cooled copper hearth after the reverts are thoroughly cleaned. The chamber is closed and pumping down of the system is started. The pumping system designed for evacuating the chamber is having a rotary pump; mechanical booster pump and an oil booster pump and gives an ultimate vacuum of mechanical  $3 \times 10^{-4}$  torr in the chamber. Once the ultimate vacuum is reached, hot Argon gas with a pressure of  $0.5 \text{ kg/cm}^2$  is fed to the

chamber after it is purified in the purifier. The flow rate of Argon is maintained in the range of 2 to 4 NI/min. Argon gas is admitted through the Tantalum-cathode in the gun assembly.

The argon flow is maintained to operate the system at a vacuum 0.01 torr to 0.08 torr. The power is supplied to the Plasma Gun through a starter system having a high frequency system (Initially the voltage across the Ta-cathode is 200V and current is 200V and current is gradually increased from 0 to 40 A. Once the plasma is stabilized (which is observed through decrease of voltage from 200V to 50V) the main power supply is fed to the Gun and the current is increased to 1800 A (Furnace-I) and 2800A (Furnace-II). The melting is carried out by moving the copper hearth below the gun with adjustable speed varying from 0 – 200mm / min.

### Zirconium Alloy Components

#### *Fuel and components for the fuel assembly*

The flow sheet for fabrication of fuel clad and their dimension and mechanical properties is given in Fig. 3. The Zircaloy-4 fuel clad for the PHWR is made by extrusion of the double melted 300 dia ingots to 150 dia rounds. These rounds are cut and

beta quenched. This beta quenching is an important step as it gives a) random texture before extrusion and b) leads to uniform distribution of the segregated impurities. The rounds are heated to single phase beta region in induction furnace followed by soaking in resistance furnace, and water quenched. Deep hole drilling and copper jacketing are then carried out to prepare the hollow billet for extrusion. Copper jacket prevents oxidation during the heating and soaking, it also acts as a lubricant during the extrusion. Extrusion is carried out in two-phase region, at a temperature and speed to allow the dynamic recrystallisation during the hot working. The extruded blanks are de-jacketed and further annealed. For the further processing the tubes are made using the seamless tube pilgering in 3 stages with intermediate anneal. The final tubes are stress relieved, straightened and ground. The tubes are subjected to ultrasonic testing and the accepted tubes are cut to final size. The fuel-clad material is tested for various destructive and non-destructive tests as per the specification.

List of components for fuel bundle assembly for both 235 MWe and 540 MWe reactor is given in Table 3. For all the other components of fuel bundles, ingots are extruded to rectangular billet /

**TABLE 3. Requirement of fuel tube and components for 235 MWe and 540 MWe PHWR fuel bundle**

Requirement per bundle			235 (19 . bundle)	500 (37 . bundle)
1.	Hardware			
	Fuel tube	Nos.	19	37
	End plug	Nos.	38	74
	Bearing pad	: 1.6mm Nos.	24	-
		: 1.3mm Nos.	12	18
		: 1.01mm Nos.	-	36
	Spacer pad	: 0.8mm Nos.	72	-
		: 0.92mm Nos.	-	144
		: 3.27mm Nos.	-	12
	End plate	Nos.	2	2
2.	1 ton of fuel needs			
	Tubes	Nos.	1355	1860
	Bar	kg	33	33.5
	Sheet	kg	15.5	17.7
3.	Initial charge / reactor		21.3 Te of Zr (55 T fuel)	54.5 Te of Zr (125 T fuel)
4.	Running charge / year		13.5 Te of Zr	37 Te of Zr

<b>Fabrication Route</b>	<b>Critical dimensions</b>
Cast & machined ingot, 294mm dia. x 740mm length ↓	Outside dia. : 19 element 15.2151mm ± 0.063mm
Hot extrusion at 800°C to billet, 150mm dia. (with copper jacket) ↓	: 37 element 13.08mm + 0.076mm
Dejacketing, cutting into pieces, machining & hole drilling ↓	Wall : 0.381mm ± 0.076mm
Beta – quenching @ 1040°C ↓	Length : 485.80mm ±0.051mm
Machined hollow billet, 142mm OD x 45mm ID x 550mm length ↓	Straightness : 1 in 1200
Extrusion at 800°C to shell, 52mm OD x 9mm wall (with copper jacket) ↓	Surface finish : 0.8 microns or better
Dejacketing & annealing ↓	End squareness : 0.05mm (max.)
1 <sup>st</sup> , 2 <sup>nd</sup> , pass cold pilgering ↓	<b>Mechanical &amp; Corrosion properties</b>
Annealing ↓	Ultimate tensile strength : 483 MPa
Straightening / grinding ↓	Yield strength ( $\bar{x} - 3\sigma$ ) : 393 MPa
Final pass cold pilgering ↓	% Elongation : 20.0
Stress relieving ↓	% Total circumferential ( $\bar{x} - 2\sigma$ ) : 10.0 elongation
Straightening / grinding ↓	Hoop stress : 621 Mpa
Ultrasonic testing ↓	Corrosion test : 22 mg / dm <sup>2</sup> at 400°C / 100 kg/cm <sup>2</sup> / 72 hours.
Cutting ↓	Fn value : 0.35 maximum
<b>Final inspection</b>	Microstructure : Grain size 10μ average 25μ maximum

Fig. 3 Flow sheet for fabrication of zircaloy-4 cladding tubes for PHWR fuel bundle at NFC, Hyderabad, their dimensions and mechanical properties

<b>Fabrication Route</b>	<b>Critical dimensions</b>	
Extrusion to shell ↓	Outside dia.	: 12.522mm ± 0.038mm
Annealing ↓	Wall	: 0.889mm ± 0.076mm
1 <sup>st</sup> & 2 <sup>nd</sup> , pass cold pilgering in cold pilger mill ↓	Length	: 3878.58mm ± 0.051mm
Annealing ↓	Straightness	: 1 in 1200
Straightening / grinding ↓	Surface finish	: 0.8 microns or better
Final pass cold pilgering ↓	End squareness	: 0.38mm (max.)
Annealing ↓	<b>Mechanical properties</b>	
Straightening / grinding ↓	RT	HT(343°C)
Ultrasonic testing ↓	UTS	: 434 Mpa      200 MPa
Autoclaving ↓	YS ( $\bar{x} - 2\sigma$ )	: 393 Mpa      103 MPa
<b>Final inspection</b>	% El	: 20.0      --
	Hardness (RB) (cold worked)	: 98 Max.      --
	Burst test ( $\bar{x} - 2\sigma$ )	: % TCE 18%

Fig. 4 Flow sheet for fabrication of clad tube for BWR

slab. These slabs are hot rolled followed by a number of cold rolling steps with intermediate annealing to finished size strip. The components are punched from strip. For end plugs, 150mm dia. round billet are extruded to rod, which are cold swaged to final size rod that are cut and finally machined to plugs.

A comparison of the requirement of fuel bundle for the PHWR 235 MWe and PHWR 540 MWe nuclear power reactor is given in Table 3. The number of components and the total inventory required in the 540 MWe PHWR is large as compared to 235 MWe PHWR.

The flow sheet of Zircaloy-2 clad for BWR is shown in Fig. 4. The Zircaloy-2 fuel clad for the BWR tubes (12.5mm ID X 8.9mm WT X 3878 mm length) has similar route as for PHWR clad tube with extrusion, 3 pilgering stages and final autoclaving. A large number of Zircaloy-2 components are required

for assembly of the BWR fuel bundle, which are made from the sheet and rods.

#### Seamless calandria Tube and Square Channel

Calandria tubes are thin-walled large diameter zirconium alloy (zircaloy-4) tubes – an important structural component in pressurized heavy water nuclear reactor (PHWR). Similarly square channels are large size square tubes used as coolant channel in boiling water type nuclear reactor (BWR). Sizes of these tubes are :

- Calandria tube for 235 MWe reactor: 110mm OD x 1.25mm ± 0.05mm Wall thickness x 5100mm length.
- Calandria tube for 540 MWe reactor: 132.5mm OD x 1.4mm ± 0.05mm Wall thickness x 6060mm length.

- TAPS square channel: 113.5mm A/F x 1.524 ± 0.076mm Wall thickness x 4030mm length, with a corner radius of 0.53mm ± 0.254mm.

Because of its high diameter to wall thickness ratio, these tubes were earlier manufactured by hot / cold rolling of slab into strip, brake forming into tubular / square section and seam welding by TIG process. A novel fabrication route, through hot extrusion and cold-pilgering of seamless tubes, has been successfully established at NFC.

The Zircaloy-4 seamless calandria tube is made by pilgering of the mother blank in 2 stages with intermediate annealing and final stress relieving. Similarly the Zircaloy-4 square channels for the BWR are made from seamless tube blanks by 2 stage pilgering followed by two stage drawing, firstly through turks head and then followed by the fixed die. Finally the channels are stress relieved and autoclaved.

#### **Non-Destructive Evaluation**

NDT examination is carried out to detect the defects originating during the processing from the ingot to the final stage. At ingot stage the contact ultrasonic testing is carried out using the pulse-echo technique. Flat bottom holes are used as standard reference to detect any deep defects in ingots. The fuel tubes, calandria tubes and square channels at final stage are subjected to 100% immersion ultrasonic testing using angle beam pulse echo technique. A notch with depth 2% of thickness is used as a reference standard to detect defects in the longitudinal and transverse direction. Additionally the 100% dimensional measurement of the wall thickness, outside and inside diameter is carried out using the straight beam pulse-echo technique. In case of the calandria tubes, additionally ultrasonic normal beam testing is done to detect lamination type defects.

The calandria tubes are subjected to eddy current testing on the inside surface to detect very shallow defects, which are possible to miss in the ultrasonic test. For eddy current test a differential ID bobbin coil is used with a buttress transverse notch of depth 2% of the wall thickness as a standard. The rods for end plugs are also subjected to 100% eddy

current testing using the bobbin encircling differential coil.

Presently calandria tubes are subjected to X-ray residual stress measurement at the final stage on sample basis to ensure the final stress relieved condition. This shall avoid in-reactor distortion, failures like stress corrosion cracking and stress reorientation of hydrides.

The welds in the fuel bundle for PHWR and BWR are thoroughly examined using the NDT techniques. The resistance welded end caps of the PHWR are examined using immersion angle beam ultrasonic testing for defects like lack of fusion. These elements are also subjected to 100% helium leak testing at the element stage and after assembly. Similarly the BWR elements are subjected to radiography of the welded end plugs and helium leak testing.

#### **Mechanical and Corrosion Property Evaluation**

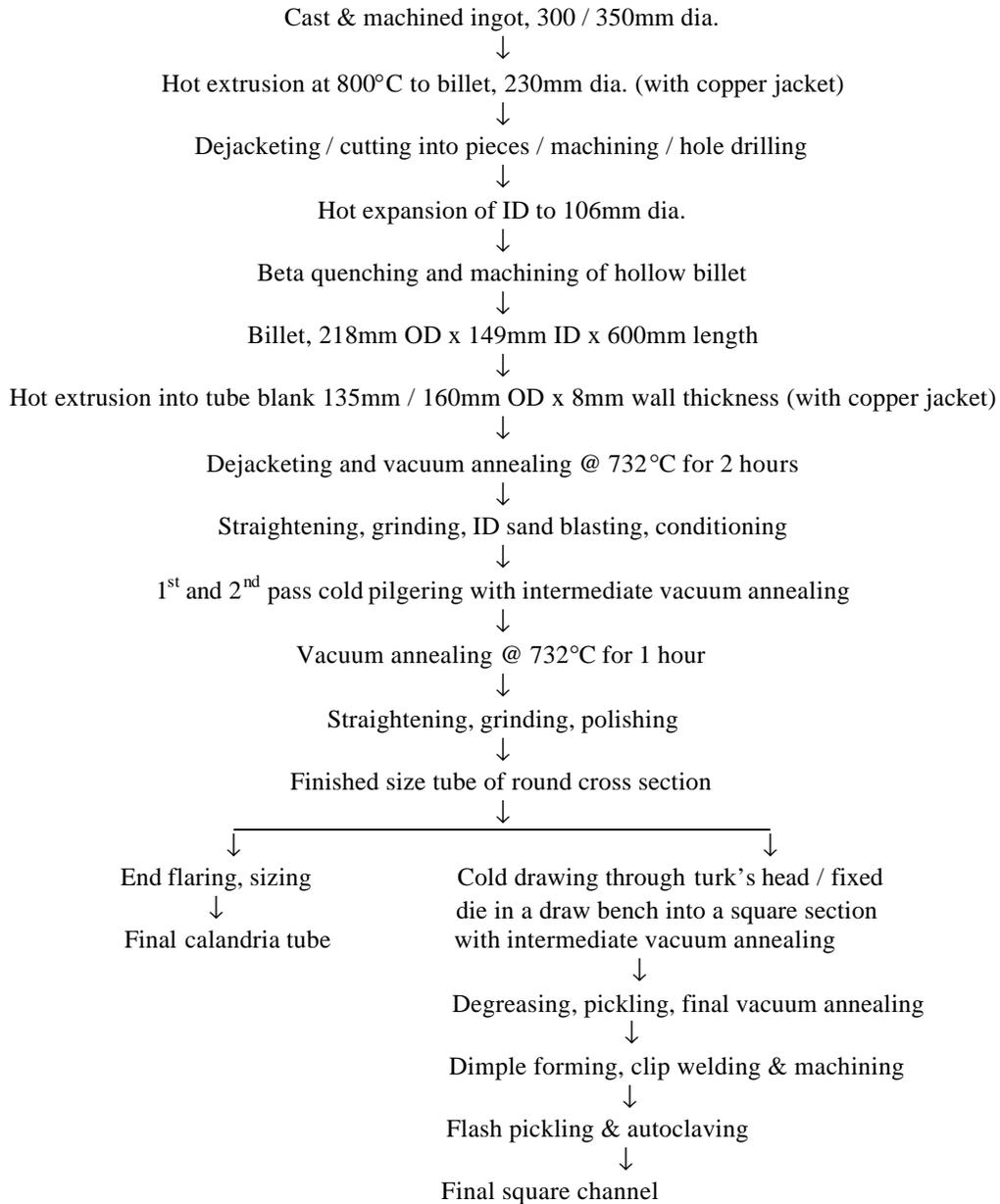
The mechanical properties are monitored for all the products like fuel tubes, calandria tubes, strip and rod for fuel bundle components, such as spacers and end caps. In case of fuel tube material, the statistical sampling plan is followed while in case of the structural materials like square channel and calandria tubes 100% sampling is done. The calandria tubes are tested for the property in the longitudinal and transverse direction. The fuel tubes are tested as a tube directly. In case of the fuel tubes, bi-axial mechanical test is carried out using the closed end-burst test. The circumferential elongation measured gives the ductility of the material under bi-axial stress condition.

All the materials are subjected to high pressure (105 Kg/cm<sup>2</sup>)– high temperature (400°C) steam autoclave corrosion test (72 Hrs) to determine the corrosion oxide weight gain. The tested samples are examined for the black lustrous adherent oxide surface layer for best corrosion property.

#### **Compositional Analysis**

The oxide and sponge is analyzed to meet the requirements for reactor grade before further processing. The composition analysis is carried out at the ingot stage for all alloy elements, impurities

## Fabrication Route



and gases. The final product is analyzed for alloy elements, gases and other key trace impurities.

The composition of the materials are analyzed using secondary methods (instrumental) calibrated by primary (wet) methods. Various instrumental methods are used for alloying element, trace impurities and gas analysis. These include X-ray fluorescence (XRF), Atomic absorption spectrometry (AAS), emission spectrometry, inert gas fusion, etc.

Following methods are used for determination of elements / compounds in zirconium process streams.

#### ***Analysis of zircon sand***

- Zirconium oxide / hafnium oxide by gravimetric methods either through mandelate precipitation or through phthalate precipitation.
- Hafnium by optical emission spectro-graphic method.
- Silicon dioxide by gravimetric method.
- Iron oxide by 1,10-orthophenanthroline (photometric) method.
- Titanium dioxide by hydrogen peroxide (photometric) method.
- Aluminum oxide by atomic absorption spectrophotometric method.
- Loss on ignition by gravimetric method.

#### ***Analysis of dry powder (zirconium + hafnium oxide) obtained from zircon sand through caustic fusion and leaching***

- Soluble silica by gravimetric method zirconium
- Hafnium oxide by X-ray fluorescence spectrometric method.
- Moisture by gravimetric method.

#### ***Analysis of zirconium oxide (hafnium-free)***

- Sulphur by gravimetric method.
- Iron by 1, 10-orthophenanthroline (photometric) method.
- Silicon by molybdenum blue (photometric) method.
- Purity analysis by optical atomic emission spectrographic method.

- Particle size by sieve analysis method.
- Loss on ignition by gravimetric method.
- Tap density and bulk density by tapping method.
- Particle size distribution by laser diffraction particle size distribution analyzer
- Sulphate by combustion method.
- Uranium by laser fluorimetric method.

#### ***Analysis of reactor grade zirconium sponge***

- Chlorine by turbidimetric method.
- Nitrogen by photometric method.
- Iron and magnesium by atomic absorption spectro-photometric method.
- Purity analysis by optical atomic emission spectrographic method.
- Hafnium by optical atomic emission spectrographic method.
- Uranium by laser fluorimetric method.
- Oxygen by inert gas fusion method.
- Uranium by fluorimetric method.

Following methods are used for determination of carbon, chlorine, nitrogen, oxygen, uranium and impurities in zirconium alloy samples.

- Carbon by combustion method.
- Chlorine by turbidimetric method / pyro-hydrolysis and ion chromatographic method.
- Nitrogen by micro-kjedahl method or inert gas fusion "LECO" analyzer (thermal conductivity method).
- Oxygen by inert gas fusion method.
- Purity analysis by atomic absorption spectrophotometric / optical atomic emission spectrographic method.
- Uranium by laser fluorimetric method.
- Iron by 1, 10orthophenanthroline (photometric) method.
- Tin by lodate (titration) method.
- Hydrogen by inert gas fusion thermal conductivity method.

## **Conclusion**

Production of zirconium alloy clad tubes and components for fuel bundles for meeting fuel requirement of Indian nuclear power reactors has been accomplished at NFC for more than three decades. NFC has also fabricated and supplied all the zirconium alloy structural materials for Indian PHWR nuclear reactor core such as calandria tube, coolant tube, reactivity and control mechanism etc. and also fuel bundle and square channel for Tarapur Atomic Power Station (BWR)

NFC is an unique organization in the world, where all the processes of zirconium technology starting from zircon sand such as production of reactor grade zirconium oxide, extraction of high purity zirconium sponge metal, melting of zirconium alloy ingots and its fabrication into fuel tubes and components for fuel bundles and also

structural materials for nuclear reactor core is being carried out in a single location. The caption “Ore to Core” aptly describes the activities at NFC in the field of zirconium technology.

## **Acknowledgement**

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# Chemical Quality Control of Nuclear Materials



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## Introduction

Chemical quality control provides a means to ensure that the quality of the fabricated fuel conforms to the chemical specifications for the fuel laid down by the fuel designer. These specifications are worked out for the major and minor constituents which affect the fuel properties and hence its performance under conditions prevailing in an operating reactor. Nuclear reactor design incorporates detailed specifications of different systems, which must be satisfied for smooth and efficient functioning of the reactor. Fuel being the heart of the reactor, its chemical characterisation is an important component of this design. Both the fuel materials and finished fuel products are to be characterised for this purpose. Each fuel batch has to be subjected to comprehensive chemical quality control for trace constituents, stoichiometry and isotopic composition.

## Effect of Trace Constituents

It should be realized that nuclear fission occurs only in the fissile atoms (U-235 or Pu-239) and during nuclear fission a number of fission products

starting from Se to Gd are produced making the nuclear fuel a highly heterogeneous system. But to start with the nuclear fuel should be as pure as possible except for the matrix elements (U, Pu O or C). But invariably a number of trace impurities are always present in the fuel. There are a number of factors which need to be considered for realizing the designed performance of the nuclear fuel in side the reactor. Some of them are indicated below:

- (a) As neutrons are the primary particles causing nuclear fission, their economy is of utmost importance. They should not be absorbed by any other impurity element thus causing the loss of neutrons and curtailing the fission rate. Boron, cadmium and some rare earth elements (Sm, Eu, Gd, Dy) have very large neutron absorption cross sections. Hence control of these elements is required.
- (b) Fluorine, chlorine and moisture cause corrosion of the clad. Further, moisture can modify the O/M of the fuel and also release hydrogen which can cause pressure build-up
- (c) Carbon can react with oxygen forming gaseous carbon monoxide which facilitates transfer of

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carbon from fuel to the clad causing damage to it.

- (d) Nuclear fuel under irradiation conditions is a very complex system. As a result of nuclear fission, high temperatures are reached and the behaviour of many trace elements present in the fuel their reactions among themselves and with the fuel particularly in the presence of liberated oxygen is very complex and these should not cause any detrimental effect on the performance of the fuel. For example low melting elements such as zinc, if present will cause liquid metal embrittlement (LME) altering the fuel structure and failure. On the other hand, refractory elements such as tungsten may cause “creep resistance” resulting in clad damage.
- (e) Control of uranium and plutonium contents and their isotopic compositions is also essential in order to ensure the required fissile content
- (f) Variations in O/M can affect many properties such as thermal conductivity, melting point, number of phases, chemical reactivity and mechanical strength. O/M has to be maintained in the specified limits of hypostoichiometry since the oxygen potential significantly increases with irradiation which may lead to clad corrosion.

Hence control of trace constituents in the fuel is necessary to obtain the designed burn-up. Certain upper concentration limits have been specified for a number of trace elements in nuclear fuel materials. These are called specification limits. It is interesting to note that during the time of first nuclear reactor construction in USA in 1940's, designers, with whatever knowledge and expertise available at that time with them and in consultation with nuclear physicists, technologists and chemists laid down these specifications. It is remarkable that these specifications are accepted even today.

Fabrication of fuel pellets starting from sinterable  $UO_2$  and  $PuO_2$  involves steps which are shown in Fig. 1.

The specifications for  $UO_2$  and  $PuO_2$  powders and final sintered pellets for a typical thermal and fast reactor fuel are shown in Table 1. Some impurities may be picked up during grinding,

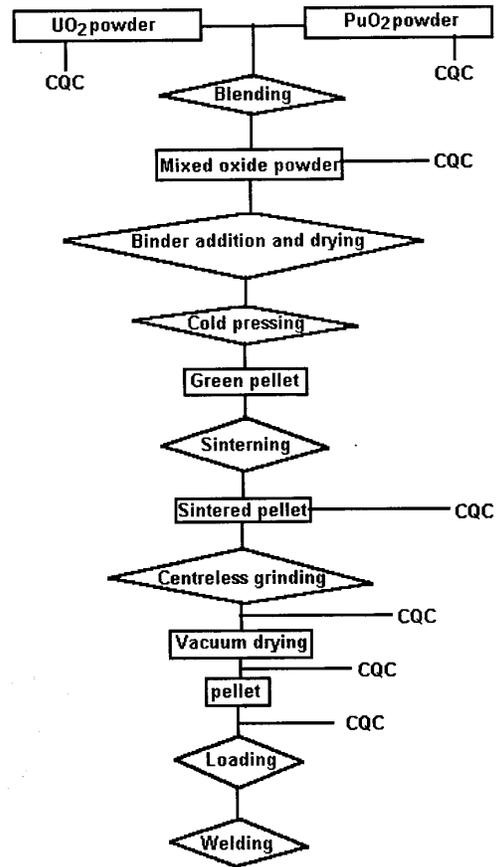


Fig. 1 Flow shet of nuclear fuel fabrication

blending, pressing and sintering operations and from the atmosphere with which the powders and the pellets come into contact. Hence, it is necessary to carry out the chemical quality control at different stages of fabrication, namely blended powder, sintered pellet and the finished pellet. These CQC stages are also shown in Fig.1.

**Differences between the chemical quality control of plutonium bearing fuels and that of uranium fuels**

1. All operations have to be carried out in glove boxes to avoid personnel exposure and radioactive contamination.
2. The quantities of material available are limited and hence sensitive methods have to be developed.

3. Additional analyses have to be carried out in order to ascertain the homogeneity of U and Pu.
4. Analytical efforts become more involved since the number of fabrication batches becomes large due to the higher neutron and gamma doses associated with plutonium produced in power reactors. Each batch handles only small quantity of material to eliminate criticality problems. Hence number of batches increases.
5. Non-availability of adequate standards poses some problems.
6. Plutonium has to be recovered and accounted for after analyses.

#### ***Experience of Plutonium utilization in Indian Nuclear Reactors***

Plutonium as plutonium oxide was first used as fuel for PURNIMA reactor at BARC. Characterisation of this fuel was the first experience in chemical quality control (CQC) in BARC. This experience was valuable for the next phase in which full-fledged facilities for chemical quality control of plutonium bearing oxide fuel (MOX) to be used in TAPS, were set up. A lot of development work was carried out to standardize methodologies for characterization of a large number of chemical parameters specified by the designer. In the late seventies, a decision was taken to use (U,Pu)C fuel, having 70% Pu, as fuel for FBTR. Standardization of procedures for CQC of this fuel were also required. These include chemical specifications included O/M (oxygen / metal) ratio of starting oxides, U and Pu concentration, isotopic composition of Pu, C/M ratio, metallic and nonmetallic impurities and total gas content. For the prototype fast breeder reactor, India has decided to use  $(U_{0.72}, Pu_{0.28})O_2$  fuel. Some CQC aspects of these are briefly described below. India has embarked on an ambitious programme of developing Advanced Heavy Water Reactor concept, which envisages utilization of our vast thorium resources to meet our ever increasing energy needs. CQC measurements are also required to be carried out for thorium based nuclear fuels.

#### **Analytical Methods for Chemical Quality Control**

Analytical methodology for chemical quality control measurements is described below under

different sections depending on the nature of measurements. These are:

1. Dissolution of samples
2. Thorium, uranium and plutonium content
3. Isotopic composition (for fissile and fertile content)
4. Americium content
5. Oxygen to metal ratio
6. Trace metals determination
7. Trace non-metals determination

#### **Dissolution of Refractory Oxides and Carbides**

The dissolution of (U,Pu) oxide is normally carried out by treatment with conc.  $HNO_3$ -0.05 M HF followed by evaporation of the fluoride. In the case of mixed carbide, conventionally carbide was being converted to oxide which can be dissolved using the above mentioned procedure. A direct dissolution method by refluxing the sample in 1:1  $HNO_3$ - $H_2SO_4$  mixture eliminated the oxide conversion step reducing the overall time required for dissolution.

#### **Thorium, Uranium and Plutonium Determination**

Thorium is analysed by the classical EDTA complexometric titration method. Pu interference could be eliminated by preferentially oxidizing it Pu (VI) by  $AgO$  prior to titration. Another interesting development in the EDTA titration of thorium has been employing potentiometric end point detection using Fe(III)/Fe(II) couple for end point detection. This eliminated the personal bias in the volumetric titration using xylenol orange as indicator for end point detection.

Classically a volumetric method based on titrating U(IV) with standard ammonium vanadate using sodium diphenylamine indicator is available for uranium analysis. But now a days electroanalytical methods like voltammetry, amperometry, conductometry and coulometry are widely used and are extremely useful in the determining the concentration of Pu and U. In all sample analyses more than one technique is used to ensure reliability of measurements. Broadly the electroanalytical methods are based on REDOX reactions involving different oxidation states of U and Pu. Uranium is analysed by reducing it to U(IV)

**TABLE 1. Specifications for Typical Thermal and Fast reactor fuels**

Impurity	Thermal re ac tors (ppmw)			Fast re ac tors (ppmw)		
	UO <sub>2</sub>	PuO <sub>2</sub>	(U,Pu)O <sub>2</sub>	UO <sub>2</sub>	PuO <sub>2</sub>	(U,Pu)O <sub>2</sub>
Li						
Be						10
B	0.3	2	1	0.3	2	2
C	200	200	200	200		
N		100	100		100	100
F	10	25	10	10	25	
Na			400			100
Mg	50	200	200	10	200	50
Al	25	250	400	25	250	500
S	3	250	300	30	250	800
Cl		25	15			
Ca	50	500	250	50	500	100
V			400			100
Cr	25	200	400	15	200	300
Mn	10	100	400	10	100	200
Fe	100	500	400	100	500	1000
Co		25	75		25	200
Ni	20	200	400	20	200	500
Cu	20	50	400	10	50	100
Zn		200	400		200	100
Zr						100
Mo	4	200	400	2	200	200
Ag	1	10	25	1	10	20
Cd	0.2	6	1	0.2	6	1
Sn						10
Sm						
Eu			0.2			
Gd	0.1	1	1	0.1	1	
Dy						
Ta			100			
W					200	200
Pb		200	400		200	200
Th			10	200		
<sup>241</sup> Am		2500			2500	

in conc.  $\text{H}_3\text{PO}_4$  acid with Fe(II) ion. The excess Fe(II) ion is oxidized and U(IV) is titrated with standard dichromate using potentiometric or amperometric end point detection. Reducing uranium to U(IV) by Ti(III) in  $\text{HNO}_3$  acid and titrating U(IV) with standard dichromate is also followed. It has definite advantage over phosphoric acid medium in terms of ease of precious actinides from analytical waste so generated. Another common method is the controlled potential coulometry involving the reduction of U(VI) at  $-0.325$  V at a mercury electrode. Coulometry is an absolute method and does not need any reference material for validating the analytical results. But it is very sensitive to the purity of mercury and also presence of other elements, which can get oxidized or reduced at the potential. In another method, determination of uranium has been carried out by a successive addition technique using the activated platinum gauze electrode and carrying out the reduction of U(VI) to U(IV) at a controlled potential of  $-0.150$  V vs. SCE. Precision and accuracy of better than 0.2% could be achieved.

The existence of plutonium in different oxidation states simultaneously in solution offers many possibilities for its determination. Methods are available based on Pu(III)-Pu(IV) or Pu(IV)-Pu(VI) couple. In one method Pu is oxidized to Pu(VI) by the addition of  $\text{AgO}$ . Then excess Fe(II) is added to reduce Pu(VI) to Pu(IV). The excess unreacted Fe(II) is titrated with standard dichromate to potentiometric or amperometric end point. It is possible to achieve a precision and accuracy of better than 0.2%. In constant potential coulometry, Pu is reduced to Pu(III) at 0.3 V vs. SCE and then quantitative oxidation to Pu(IV) at 0.7 V vs. SEC. Oxidation of plutonium to Pu(VI) with  $\text{HClO}_4$  in presence of Fe(III) ions and determination of Pu(VI) by coulometry can also be carried out.

For some applications measurement of very small quantities of plutonium (100  $\mu\text{g}$  range) is required. For this biamperometric method was developed in the Division for determination in the microgram range (5  $\mu\text{g}$  to 300  $\mu\text{g}$ ) by direct titration as well as by standard addition method. The method is found to be satisfactory with precision of 0.2% at 300  $\mu\text{g}$ , 1% at 50  $\mu\text{g}$  and 5% at 10  $\mu\text{g}$  levels.

Methods are also available for direct and rapid determination of Pu in (U, Pu)C pellets by XRF. The XRF method can also be extended for the determination of Th in total (U + Th) in sintered  $\text{UO}_2$ - $\text{ThO}_2$ , having  $\text{UO}_2\%$  from 1-3% in powder samples

### Isotopic Composition

Isotopic composition of uranium and plutonium in (U, Pu) $\text{O}_2$  is carried out by thermal ionisation mass spectrometry following their ion exchange separation. The method is highly reliable over the abundance range of 0.01 to 100% extendable to still lower levels, provided mass interference is absent and chemical separations are carefully carried out without cross-contamination. Present generation mass spectrometers are capable of analysing nanogram amounts of these materials with a precision and accuracy which is ten times superior to that of earlier instruments. This is achieved by close control of the ionisation conditions and sequential peak jumping with complete automation.

Gamma spectrometric method can also be used for the determination of isotopic composition of uranium and plutonium. Though it cannot compete with the mass spectrometric method for precision and accuracy, it is useful as a non-destructive method. Measurements made on a typical MOX fuel gave a precision of 0.5% with a measurement time of 2 hours.

Alpha spectrometry is an alternative to the mass spectrometric determination of isotopic ratios of plutonium and is especially useful for determination of Pu in samples in which the uranium contamination interferes with the mass spectrometric determination. The alpha activity of  $^{238}\text{Pu}$  is measured with silicon surface barrier detector and multichannel analyser. The  $^{238}\text{Pu}$  abundance is calculated from the alpha spectrum and from mass spectrometric measurements for major plutonium isotopes on a separate portion of the sample. The relative standard deviation is 1% at a  $^{238}\text{Pu}$  abundance of 0.01 wt %.

### Americium-241 Content

The  $^{241}\text{Am}$  content in (U, Pu) $\text{O}_2$  is best determined by alpha spectrometry. Am-241 is an

alpha emitter and emit an alpha particle with 5.50 MeV the same as that of Pu-238. The method involves measuring the peak intensity at 5.5 MeV in unpurified (Pu + Am) and in purified (only Pu) sample. The difference in the two peak intensities is a measure of  $^{241}\text{Am}$  content. The determination of  $^{241}\text{Am}$  in different plutonium samples with varying isotopic composition of plutonium and having  $^{241}\text{Am}$  content ranging from 0.001 to 2.5% by weight of plutonium gives a precision and accuracy of 1%.

### **Oxygen to Metal Ratio**

Thermogravimetric, gas equilibration and EMF methods are used for the determination of O/M ratio. Of the three, the thermogravimetric method is the most widely employed. It involves measurement of weight change that occurs when an oxide sample is converted to a stoichiometric reference state of O/M of 2.000 by heating it at  $800^{\circ}\text{C}$  for 6 hours in an atmosphere in which the oxygen potential is maintained at approximately -100 Kcal/mole. The precision is 0.001 unit of O/M. In predictive thermogravimetric technique, initial weight change data are used to predict overall weight change. It is expected that the analysis time can be greatly reduced to 6 minutes by this technique.

In the  $\text{CO}/\text{CO}_2$  equilibration method, the sample is converted to hyper-stoichiometric state by adding a known amount of oxygen and then reduced to the reference state of O/M of 2.000 by equilibrating the sample with a mixture of CO and  $\text{CO}_2$  in the ratio 10: 1 at  $850^{\circ}\text{C}$ . The amount of  $\text{CO}_2$  produced is measured. From the amounts of oxygen added and the  $\text{CO}_2$  produced, the O/M is calculated. The precision is 0.0005 unit of O/M.

The EMF method can also be applied to measure O/M ratio in mixed oxide fuels. The difference of the electrochemical potential between the fuel pellet and one of the two standard electrodes (Ni/NiO, Fe/FeO) is measured. A precision of 0.0005 unit of O/M is reported.

### **Determination of Trace Metallic Impurities**

Spectroscopic methods are extensively used for trace element characterization in nuclear industry. The spectrochemical analysis of trace elements in uranium in the early 60s was based on

chemical separation of trace elements followed by copper spark atomic emission spectroscopy. The trace metal assay of plutonium samples was based on the ion exchange separation of plutonium from analytes followed by their determination using dc arc emission spectroscopy. In the early 70s, the dc arc - carrier distillation technique was adapted for the determination of a large number of trace elements in U/Pu samples without employing chemical separation. Carriers such as silver chloride and gallium oxide have unique ability to sweep the impurities from the matrix into the excitation zone without vapourising the matrix thereby avoiding the spectral interference. Only rare earth elements being refractive are not vapourised by the carrier. The conventional chemical separation technique is therefore valuable for their analysis.

With the advent in early 1980's, of a direct reading emission spectrometer with Inductively Coupled Plasma (ICP) source and electronic detection system, the detection limits and precision were improved. With ICP source, direct analysis of solution samples is possible. Another interesting feature with ICP AES is to combine it with carrier distillation for the direct solid sample insertion into running plasma. Alternatively sample can be introduced into the plasma using carbon rod vapourization for the analytes from nuclear materials.

Recently American Society for Testing and Materials (ASTM) has recommended the application of inductively coupled plasma mass spectrometry (ICP-MS) for the specification analysis of  $\text{UO}_2$ .

Efforts are underway in DAE to exploit ion chromatography and HPLC for the chemical quality control measurements.

### **Determination of Nonmetallic impurities**

Determination of trace constituents like carbon, halogens, nitrogen and total gas involves gas- solid reactions and optimum experimental conditions have to be employed to ensure their quantitative recovery. Nitrogen is determined by wet method also.

Carbon is converted to  $\text{CO}_2$  by combustion of the sample in oxygen atmosphere. In order to affect

quantitative and rapid combustion to  $\text{CO}_2$ , various accelerators such as copper, tin and tungsten are employed. Manometric, conductometric, gas chromatographic, and infrared absorption methods are employed for the measurement of carbon dioxide. In the manometric method  $\text{CO}_2$  is quantitatively condensed in a capillary tube and its pressure is measured after allowing it to expand at laboratory temperature. The precision of this method is 5% and the time taken is about 1 hour. In the conductometric method,  $\text{CO}_2$  is absorbed in barium hydroxide and the decrease in conductivity gives a measure of carbon content. A precision of 10% is attainable with an analysis time of 1 hour. In the gas chromatographic method,  $\text{CO}_2$  is separated using a silica gel column and its thermal conductivity is measured. A recent improvement in this method is the introduction of rapid heating and measuring devices in commercial instruments which leads to a precision of 2% and an analysis time of 5 minutes. In the infra-red absorption method,  $\text{CO}_2$  is separated and measured. Now a days, commercial analysers are available for measuring the infra-red absorption of  $\text{CO}_2$  and  $\text{SO}_2$  for the simultaneous determination of carbon and sulphur.

Halogens (chlorine and fluorine) in the sample are liberated by pyrohydrolysis as  $\text{HCl}$  and  $\text{HF}$  respectively and measured by spectrophotometry, ion selective Electrodes, titrimetry or ion chromatography (IC). The sample is heated at  $900\text{-}1000^\circ\text{C}$  in a stream of air or argon saturated with water vapour. The separated fluoride and chloride are collected in an acetate buffer solution. Fluoride is measured using a fluoride ion selective electrode or by spectrophotometry using Zr-alizarin complex. Chloride is measured by spectrophotometry using ferric thiocyanate complex. Measurement by chloride ion selective electrode is applicable to solutions containing 2 ppm and higher concentrations of chloride. A precision of 5 to 15% is obtained with 5-20 micrograms of chlorine and fluorine. Time taken for analysis is between 1 and 3 hours. Using ion chromatography, using carbonate/bicarbonate buffer or  $\text{NaOH}$  as mobile phase, it is possible to carry out simultaneous determination of ultra trace amounts of fluorine and chlorine in different nuclear fuel systems after their separation by pyrohydrolysis with in a few minutes.

For determining nitrogen, the most widely employed method is the classical Kjeldahl's distillation. It consists of conversion of nitride nitrogen to ammonium salt by refluxing the sample with sulphuric acid and steam distillation of ammonia in alkaline medium into boric acid followed by spectrophotometric measurement using Nessler's reagent or indophenol blue. Time taken for analysis is about 5 hours. In the past two decades inert gas fusion techniques have been developed for fast and accurate determination of nitrogen. The inert gas fusion method consists of fusing the oxide sample rapidly in a graphite crucible using an impulse heating furnace at  $2300^\circ\text{C}$  in a flowing helium atmosphere with a flux of Pt or Ni. The carbon monoxide released is converted to  $\text{CO}$  by passing through hot  $\text{CuO}$  and then trapped at liquid nitrogen temperature. Nitrogen and hydrogen are absorbed on a silica gel column at liquid nitrogen temperature. The column is then warmed to  $50^\circ\text{C}$  and the nitrogen liberated is measured by thermal conductivity. A precision of 5% is obtained and the analysis time is about 1 hour. A temperature of  $3000^\circ\text{C}$  is used in the inert gas fusion method with commercial determinators. In these instruments, removal of  $\text{CO}$  and  $\text{H}_2$  is achieved by converting them to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively and absorbing them in ascarite and anhydron respectively. An improved precision of about 2% is achieved in a short analysis time of 15 minutes. An ion chromatographic method of measuring nitrogen as ammonium ion can also be used. This is more sensitive and fast.

Phosphorus is determined by a wet method. The sample is dissolved in  $\text{HNO}_3\text{-HF}$ . After fuming with sulphuric acid the phosphate is converted to ammonium phosphomolybdate which is extracted into n-butanol. After reduction with  $\text{SnCl}_2$ , the optical density of molybdenum blue is measured. A precision of 3% is obtained with 10 micrograms of phosphorus.

Sulphur is measured by both wet and dry methods. In one of the wet methods, sulphur is converted into  $\text{SO}_3$  and oxidation to sulphate is completed by  $\text{H}_2\text{O}_2$  in alkaline solution. The sulphate is converted into barium sulphate which is measured turbidimetrically. A precision of 20% is obtained with 40 to 100 micrograms of sulphur. In

the dry method, the sulphur is converted to  $\text{SO}_2$  by burning the sample in oxygen at  $1600^\circ\text{C}$  with tungsten as flux. A mass spectrometer can also be employed to measure the intensity of  $\text{SO}_2$  and sulphur content can then be estimated. As mentioned earlier, now a days commercial instruments are available for determination of carbon and sulphur simultaneously using IR detection.

Total Gas is determined by heating the sample in vacuum and measuring the pressure r the released gas. The recommended procedure consists of heating the sample at  $1600^\circ\text{C}$  in a tungsten crucible, removal of water in a cold trap and measurement of the gases evolved at  $1600^\circ\text{C}$  using a manometer. A precision of 10% is obtained at  $0.025 \text{ cm}^3/\text{gram}$  of gas. Rugged commercial instruments employing ultra-high vacuum sample lock are now available.

Recently, Spectroscopy section was involved in organizing inter comparison experiments for the analysis of uranium oxide samples involving 12 DAE laboratories. Based on these experiments five well characterized DAE reference samples were obtained for their use in DAE. Analytical support for trace metal characterization of Pu bearing fuel materials has been provided throughout the fuel development programme of NFG. The major campaigns successfully executed include development of methodologies for the analysis of

MOX (Tarapur), U-Al alloy (KAMINI),  $\text{U}_3\text{Si}_2$  and (U-Pu)C (FBTR) fuels.

#### **Availability of Reference Materials**

Standard reference materials are required to (1) calibrate analytical methods (2) evaluate the capabilities of analysts and (3) assure the reliability of routine measurements. They are commercially available only for uranium and plutonium contents (chemical) and their isotopic composition (isotopic). Even these are subject to special regulations. In BARC efforts have been going on to prepare and characterise reference materials for thorium, uranium and plutonium. BARC has prepared rubidium uranium Sulphate and potassium plutonium Sulphate reference materials for U and Pu contents respectively. These have been demonstrated to have all the qualities of chemical assay standard materials. Recently two series of reference materials of  $\text{U}_3\text{O}_8$  and  $\text{ThO}_2$  have been prepared for trace elements and these have been evaluated by inter laboratory intercomparison experiments.

#### **Conclusions**

CQC is an integral and indispensable component in nuclear technology. A wide gamut of analytical methodologies is required for the chemical quality control measurements on nuclear materials.

# Development of Plutonium fuel for Thermal and Fast Reactors



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## Introduction

There are three fissile nuclides, which are generally used as fuel in a nuclear reactor. These are  $^{235}\text{U}$ ,  $^{239}\text{Pu}$  and  $^{233}\text{U}$ . Uranium is the only naturally occurring element, which contains only 0.7% of the fissile nuclide  $^{235}\text{U}$ , the rest being the fertile nuclide  $^{238}\text{U}$ . The other two fissile nuclides,  $^{239}\text{Pu}$  and  $^{233}\text{U}$ , are produced in a nuclear reactor by the irradiation of the  $^{238}\text{U}$  and  $^{232}\text{Th}$  respectively. Plutonium produced by irradiation in the nuclear reactor contains the fissile isotopes  $^{239}\text{Pu}$  and  $^{241}\text{Pu}$  along with the fertile isotopes,  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{242}\text{Pu}$ . The best use of plutonium as a fuel is in fast breeder reactors because

of its nuclear characteristics. In a breeder, there is more production of fissile material than that consumed and hence increases the potential of utilization of  $^{238}\text{U}$  and  $^{232}\text{Th}$ . Over the years a number of fast reactors have been built for experimental purposes and for power generation (Rapsodie, FBTR, KNK, JOYO, FFTF, EBRI & II, PFR, Phenix, Superphenix), in Europe, Japan, USA, Russia and India using plutonium bearing fuel. However, the numbers of fast reactors built and operated are in no way near the number of uranium fuelled thermal reactors. The delay in the commercial deployment of fast reactors in the world in a big way is due to a variety of reasons, the most

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**TABLE 1. Isotopic composition of Plutonium produced in UO<sub>2</sub> fueled thermal reactors**

Reactr type	Fuel Burnup (MWD/TeU)	Plu to nium iso topes at dis charge a%				
		<sup>238</sup> Pu	<sup>239</sup> Pu	<sup>240</sup> Pu	<sup>241</sup> Pu	<sup>242</sup> Pu
(MAGNOX)	3000	0,1	80.0	16.9	2.7	0.3
	5000	Not avail able	68.5	25.0	5.3	1.2
CANDU	7500	Not avail able	66.6	26.6	5.3	1.5
BWR	27500	2.6	59.8	23.7	10.6	3.3
	30400	Not avail able	56.8	23.8	14.3	5.1
PWR	33000	1.3	56.6	23.2	13.9	4.7
	43000	2.0	52.5	24.1	14.7	6.2
	53000	2.7	50.4	24.1	15.2	7.1

Source: Nucl. Tech. vol.106, April' 1994, p62.

burn up plutonium there is also the existence of isotope <sup>236</sup>Pu. From a practical perspective isotopic production terminates at <sup>242</sup>Pu as half life of <sup>243</sup>Pu is only 5 hrs.

The isotopic content of plutonium depends on the type of reactor and burn up to which uranium fuel is exposed. Typical values are given in Table 1.

Plutonium is extracted from spent (irradiated) fuel mainly by PUREX process. In this process the spent fuel is first dissolved in hot nitric acid. Fission products and Uranium nitrate are separated from Plutonium nitrate by Solvent Extraction / Ion Exchange processes. Plutonium from plutonium nitrate is precipitated as an oxalate and then the oxalate is calcined to get PuO<sub>2</sub> powder. Conversion of PuO<sub>2</sub> to Pu metal is done by flourination to PuF<sub>4</sub> followed by metallothermic reduction.

#### **Nuclear Properties and Handling of Plutonium**

Plutonium is a highly radiotoxic material and primarily decays by alpha emission. It has high specific activity and high biological half life. Inhalation of plutonium particulates is the main hazard in plutonium handling. Hence, plutonium & plutonium bearing materials have to be handled in leak tight glove boxes and the operating area of the laboratory/plant requires to be well ventilated with sufficient number of air changes to control Derived Air Concentration (DAC) level. Table 2 gives a few nuclear properties of plutonium isotopes which affect plutonium handling.

<sup>241</sup>Pu with a half life of 14.4 years decays primarily by β-emission to the non-fissile isotope <sup>241</sup>Am. <sup>241</sup>Am is alpha active and decays to <sup>237</sup>Np with γ emission of 60 keV energy. This aspect is important in plutonium handling. If plutonium is stored after separation for long periods, the radiation level increases due to the buildup of <sup>241</sup>Am and hence provision of shielding becomes essential to limit personnel exposure. Therefore it is prudent to have a minimum time gap between reprocessing, fabrication of fuel and its use in the reactor.

Neutrons are emitted by all the even mass numbered isotopes <sup>238</sup>Pu, <sup>240</sup>Pu, <sup>242</sup>Pu which undergo spontaneous fission. Neutrons are also produced by (α,n) reactions with light elements which are present either as impurities or as constituent of Pu compounds viz. oxygen in PuO<sub>2</sub>. Hence depending on the isotopic composition of plutonium, shielding for reducing neutron exposure to personnel involved in fabrication activities also becomes a requirement. Besides the emission of radiation, <sup>238</sup>Pu and <sup>241</sup>Am due to their high specific alpha-activity generate about 560w/Kg and 114w/Kg heat respectively, and the heat (specific power) increases progressively with the aging of plutonium. Hence storage and fuel fabrication facility should consider these aspects as well and the system design should be capable of heat evacuation. Daughter products of isotope <sup>236</sup>Pu (Tl & Bi) may also be present inppm level in high burn up plutonium. These are hard gamma emitters and

**TABLE 2. Nuclear properties of isotopes of plutonium**

Isotope	Half life (yrs)	Decay mode	Alpha energy in MeV	Specific Activity (10 <sup>9</sup> Bq/g)	Spontaneous fission neutron rate (n/g.s)	Heat Generation (W/Kg)	Product Isotope
<sup>236</sup> Pu	2.85	α	5.763	1.96 X 10 <sup>4</sup>	-	-	U <sup>232</sup>
<sup>238</sup> Pu	87.7	α	5.49	6 X 10 <sup>2</sup>	2.6 X 10 <sup>3</sup>	560	U <sup>234</sup>
<sup>239</sup> Pu	2.41 X 10 <sup>4</sup>	α	5.096	2	0.03	1.9	<sup>235</sup> U
<sup>240</sup> Pu	6.6 X 10 <sup>3</sup>	α	5.162	8	1.02 X 10 <sup>3</sup>	6.8	U <sup>236</sup>
<sup>241</sup> Pu	14.4	β	-	3.7 X 10 <sup>3</sup>	-	4.2	<sup>241</sup> Am
		α(0.002%)	4.893	-	-	-	<sup>237</sup> U
<sup>242</sup> Pu	3.8 X 10 <sup>5</sup>	α	4.898	0.1	1.7 X 10 <sup>3</sup>	0.1	U <sup>238</sup>
<sup>241</sup> Am	4.3 X 10 <sup>2</sup>	α	5.48	1.2 X 10 <sup>2</sup>	1.1	114	Np <sup>237</sup>

**TABLE 3. Fission parameters in fast and thermal spectrums**

Parameter	<sup>235</sup> U		<sup>239</sup> Pu		<sup>241</sup> Pu		<sup>233</sup> U	
	fast	thermal	fast	thermal	fast	thermal	fast	thermal
n-spectrum	fast	thermal	fast	thermal	fast	thermal	fast	thermal
σ <sub>f</sub> barns	1.78	580	1.91	740	2.54	1000	2.69	530
σ <sub>c</sub> barns	0.435	100	0.438	270	0.29	400	0.29	50
α=(σ <sub>c</sub> /σ <sub>f</sub> )	0.244	0.172	0.231	0.365	0.114	0.400	0.108	0.094
η-1	1.01	1.06	1.40	1.12	1.73	1.13	1.32	1.28

(Source:Fast reactor technology:Plant Design by John G. Yevich(ed))

Legend: σ<sub>f</sub> - Fission cross-section, σ<sub>c</sub> - Neutron capture cross section, η – number of neutrons produced per neutron absorbed. η-1 gives the extra number of neutrons available after fulfilling the fission chain reaction requirement. A higher value of η-1 means a higher availability of neutrons for conversion of fertile nuclides to fissile nuclides apart from taking care of leakage losses and capture in structural materials

should be considered in plant design and during material handling.

**Nuclear Properties of Plutonium as a Nuclear Fuel**

Table 3 gives the fission parameters of plutonium along with that of other fissile nuclides, <sup>235</sup>U and <sup>233</sup>U. It can be inferred from the table that <sup>239</sup>Pu is a better fuel for fast reactors because of the higher number of neutrons emitted per fission. However it is not an efficient thermal reactor fuel because of higher capture cross section (σ<sub>c</sub>) and higher σ<sub>c</sub>/σ<sub>f</sub> value.

Figure 2 shows fission to absorption cross section ratio for plutonium isotopes in a LWR & FBR spectrum This shows that although only <sup>239</sup>Pu & <sup>241</sup>Pu are fissile isotopes of plutonium, in a fast neutron spectrum all the isotopes of plutonium are fissionable.

Additionally, <sup>239</sup>Pu & <sup>241</sup>Pu have smaller delayed neutron fraction than <sup>235</sup>U which affects the reactor core kinetics/transient behaviour. Also, since <sup>239</sup>Pu has a particularly low delayed neutron fraction compared to <sup>241</sup>Pu, use of research reactor (<sup>239</sup>Pu around 90% to 95%)Pu as reactor fuel requires special consideration.. Table 4 gives the delayed neutron fraction of the fissile nuclides.

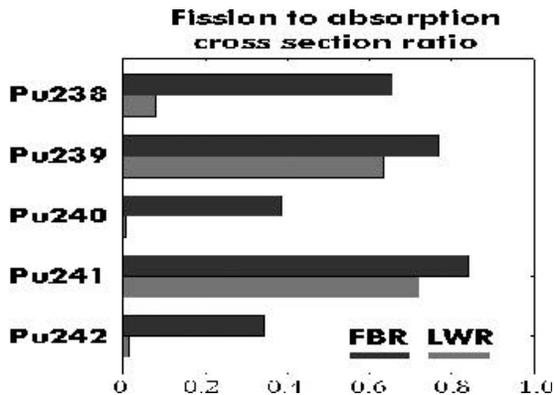


Fig. 2 Fission to absorption cross section ratio for plutonium isotopes in a LWR spectrum and a FBR spectrum. Even number neutron isotopes have a very small probability for direct fission in thermal spectra. (source: [www.neutron.kth.se/courses/transmutation/neutronEconomy/NeutronEconomy.html](http://www.neutron.kth.se/courses/transmutation/neutronEconomy/NeutronEconomy.html))

**TABLE 4. Delayed neutron fractions of fissile nuclides**

Fissile nuclide	<sup>235</sup> U	<sup>239</sup> Pu	<sup>241</sup> Pu	<sup>233</sup> U
Delayed neutron fraction	0.0065	0.0020	0.0053	0.0026

### Criticality considerations during handling of Plutonium

In order to avoid setting off an accidental chain reaction from triggering during the handling/fabrication of plutonium bearing material, criticality safety measures are required to be followed. Some of these measures are:

1. Mass control to keep plutonium bearing material within the specified level
2. Shape/dimension control to keep the containers/process vessels in specified shape and dimensions
3. Avoiding/minimizing use of moderating materials like water

4. Neutron absorbent control: to remove neutrons by use of neutron absorbing material e.g. Boron
5. Administrative control

Due to criticality safety considerations, the through-put of a fast reactor fuel fabrication line is considerably lower than that of a thermal reactor fuel fabrication line, as the quantity of fissile material to be handled, is higher

### Multiple Recycling of Plutonium in Thermal and Fast Reactors

Isotopic content of plutonium obtained from spent MOX fuel from thermal reactors gets degraded as effective fissile content (<sup>239</sup>Pu and <sup>241</sup>Pu) gets lowered and content of non-fissile even mass number isotopes viz. <sup>238</sup>Pu, <sup>240</sup>Pu & <sup>242</sup>Pu go up. This besides creating additional problems in Pu handling, leads to a higher plutonium requirement in the next cycle. According to an OECD/NEA Working Party on the Physics of Innovative Power Reactors (WPPR) study plutonium content of MOX fuel has to be kept below 12 w% for safety reasons, since otherwise the moderator void coefficient of reactivity may become positive. These requirements of keeping plutonium content below 12 w% limits the number of recycles to 2 in commercial LWRS, unless fresh plutonium/enriched uranium /novel fuel management schemes are incorporated.

However, since all the isotopes of plutonium are fissionable in fast spectrum there is no limitation in the number of recycles in fast reactors. Further, the plutonium discharged from MOX fuels used in thermal reactors can be used in fast reactors without any significant technical penalty. The plutonium discharged from fast reactors does not show significant degradation because all the isotopes are fissionable and also high quality Pu (rich in <sup>239</sup>Pu) gets generated in the Uranium blanket.

### Plutonium Fuel Development for Fast Reactors

The primary purpose of a fast reactor is to breed more fissile material than it consumes while generating power. For a country like India which has limited uranium resources, the FBR technology is of great relevance as it can increase the potential of the limited U reserve manifold by converting fertile U <sup>238</sup>

to fissile  $^{239}\text{Pu}$ . India has also a large reserve of Thorium and large scale deployment of fast reactors will help in adding to the fissile resources by converting  $\text{Th}^{232}$  to  $^{233}\text{U}$  by placing Thorium in the blanket region of the fast reactor.

As breeding requires a fast neutron spectrum, normally the fissile enrichment required in a fast reactor fuel is high and a typical fast power reactor fuel contains 15-25% plutonium with depleted or natural Uranium. Some experimental fast reactors (Rapsodie in France, FBTR in India) have been designed with much higher enriched fuel in order to reduce the core size.

The core volume of a fast reactor is much smaller than a thermal reactor because of absence of moderator and high fissile enrichment in the fuel, hence coolant having a high heat removal capacity e.g. sodium is used. Use of liquid metal makes it possible to operate the reactor at higher coolant temperature ( $\approx 550^\circ\text{C}$ ) and thus increase the cycle efficiency. Higher coolant temperature requires cladding and other structural materials having high temperature performance capability. In order to reduce the fuel cycle cost, fast reactor fuel should have burn up capability of around 10% ha (heavy atom) to 20% ha. This in turn requires that cladding and wrapper material of fuel element/assembly should be resistant to irradiation induced void swelling, creep and embrittlement. Austenitic stainless steels (SS-316, SS-316-Ti, 15-15Ti SS, D-9 SS etc), high nickel alloys (PE-16, INC-706) and ferritic/martensitic SS (HT9 & EM10) have been evaluated and used in different fast reactors the world over. Though, until now the most used material is austenitic SS.

The initial fast breeder reactor development in the world was based on metallic fuels, later followed by emphasis on ceramic fuels and most recently includes renewed interest in development of metallic fuel forms.

### **Metallic Fuel**

The first prototype fast reactors were designed and constructed with metallic fuel (1945-1960), as they offered highest breeding ratios and the shortest doubling time (operating time of fast reactor to produce excess fissile material equal to the initial

quantity in the fuel cycle). Cast delta stabilized plutonium alloy clad in mild steel was used as fuel in the first fast reactor Clementine (mercury cooled) of LASL in the late 1940s. However there was an incidence of clad-breach due to low temperature eutectic formation with the clad and operation of the reactor was discontinued. Subsequently breeding was demonstrated using Mark IV fuel, (Pu-1.25%Al alloy), in the EBR-I of ANL. Molten eutectic Pu-2.3%Fe alloy in Tantalum capsule was used in early 1960s in LAMPRE-I & LAMPRE-II reactors. The operating experience gained in these reactors and in other reactor development programmes throughout the world showed that metal/alloy fuel element designs available at that time could not reliably operate at required temperatures to the high burn ups required in FBRs. Hence ceramic fuel development, specially oxides, was started for the fast reactors.

Work, however, on metallic alloy fuels continued, to take advantage of their higher breeding ratios and short doubling times. Based on experience gained in metal/alloy fuel development (U-Fs alloy, U-10 wt% Zr alloy) between mid 1960 to 1984 at ANL, development of U-20%Pu-10%Zr alloy fuel for the Integrated Fast Reactor (IFR) was initiated. Recently, this fuel has been chosen by India for further development & intensive investigation. The advantage of U-Pu-Zr alloy is its adequate solidus temperature and good compatibility with SS cladding alloys. Since metallic fuels have high thermal conductivity, fuel temperatures are low. Thus, during loss of flow of coolant event the Doppler reactivity feedback is small and readily compensated by negative reactivity insertion from thermal expansion of core materials thereby giving inherent safety feature in metallic fuelled cores. This reactor concept like the original EBR-II, is integrated with an onsite fuel cycle of pyrometallurgical reprocessing and re-fabrication and thus renders proliferation resistance features. Since 1985, hundreds of experimental U-Pu-Zr fuel elements have been successfully irradiated in EBR-II and FFTF with burn ups of 19 ha% or more. The U-Pu-Zr fuel elements are manufactured by injection casting and then encapsulated in cladding along with sodium. Sodium works as high conductivity bond material between fuel and clad during reactor operation. The smeared fuel density is

kept around 70% and sufficient plenum space is provided to accommodate swelling and fission gases released from the fuel at high burn ups.

### **Oxide Ceramic Fuel**

The slow progress in the 1950s and 1960s towards achievement of desired burn up levels using metallic fuels led to selection of ceramic fuels as an alternative. Mixed (U,Pu)O<sub>2</sub> became the most preferred alternative. The reason being excellent performance of UO<sub>2</sub> fuel in power reactors including potential for high burn up, established fuel fabrication industry and proven safety response of oxide system to power transients.

As fuel for fast reactors should have a capability to withstand high burn ups, it should have a smear density (defined as the mass of the fuel inside a fuel element divided by the total internal available volume in the fuel element) of about 80% TD to accommodate swelling due to fission products. This low smear density is obtained either by going in for low density pellets, use of high density pellets with high pellet clad gap or by going for annular pellets of high matrix density (95%TD). Annular pellets are considered the better option because of their better transient behaviour and low central temperature. RAPSODIE & PHENIX in France, JOYO & MONJU in Japan have used solid Mixed oxide pellets as their driver fuel, where as PFR in UK & Super PHENIX have used annular MOX fuel pellets.

Mixed oxide fuel pellets for reactors are fabricated by traditional ceramic processes starting from UO<sub>2</sub> & PuO<sub>2</sub> powder. The flow sheet contains a mixing/milling step for homogenization of UO<sub>2</sub> and PuO<sub>2</sub>, binder/lubricant addition, a granulation step followed by compaction, dewaxing if required and sintering in slightly reducing atmosphere (argon+hydrogen / nitrogen+hydrogen) at around 1650°C. Centerless grinding is generally avoided for safety reasons and to minimize scrap / waste by specifying higher tolerances on pellet diameter. A small number of pellets from a sintered batch however may require centre-less grinding. Figure 3 gives the fuel fabrication flow-sheet developed for PFBR (Prototype Fast Breeder Reactor)Kalpakkam, India.

Some of the important mixed oxide pellet specifications are U/Pu content, isotopic content, O/M ratio, solubility in HNO<sub>3</sub>, homogeneity, total impurities, off gas content etc. Homogeneity of Pu distribution in fuel affects reactor performance (Pu rich agglomerate leads to hot spots) and dissolution behaviour of fuel during reprocessing. O/M ratio affects fuel/clad & fuel/coolant compatibility, thermal conductivity and fuel plasticity (i.e. creep) U/Pu redistribution & fission product state and their migration. Hence all the processes & equipments are selected with great care to achieve the desired specification.

Use of (U, Pu) co-precipitated powder gives a high degree of homogeneity as U & Pu are mixed in liquid state. However, this route has not been generally followed because the product from the reprocessing plant is the form of PuO<sub>2</sub> powder. Further, even if a decision were taken to prepare the co-precipitated powder at the reprocessing plant itself, the issue of bulk material transport of Pu bearing co-precipitated material to the fuel fabrication plant has to be addressed. Another technique which has been investigated is Sol-Gel Microsphere Pelletization (SGMP) route. This process raises less dust during fuel fabrication and hence lowers the radiation exposure to operators. Process steps like mixing/milling & pre-compaction/granulation that are followed in conventional route are not required when SGMP technique is used as microspheres have good U/Pu homogeneity and are free flowing. This process is more amenable to automation and remotization. However this process has not matured till now to a commercial state.

In some reactors viz. PFR vibro-compacted (VIPAC) fuel of 78-83% smear density has been test irradiated but their performance was not satisfactory. The reason was segregation of fine particles, higher central temperature and chances of fuel washout in case of cladding breach.

Mixed oxide fuel performance in fast reactors with pellet fuel so far has been quite satisfactory. PFR programme in UK has demonstrated achievement of 21ha% burn up in PE-16 clad fuel pins, 10.5 ha% burn up has been achieved in PHENIX & 21 ha% in RAPSODIE with SS 316

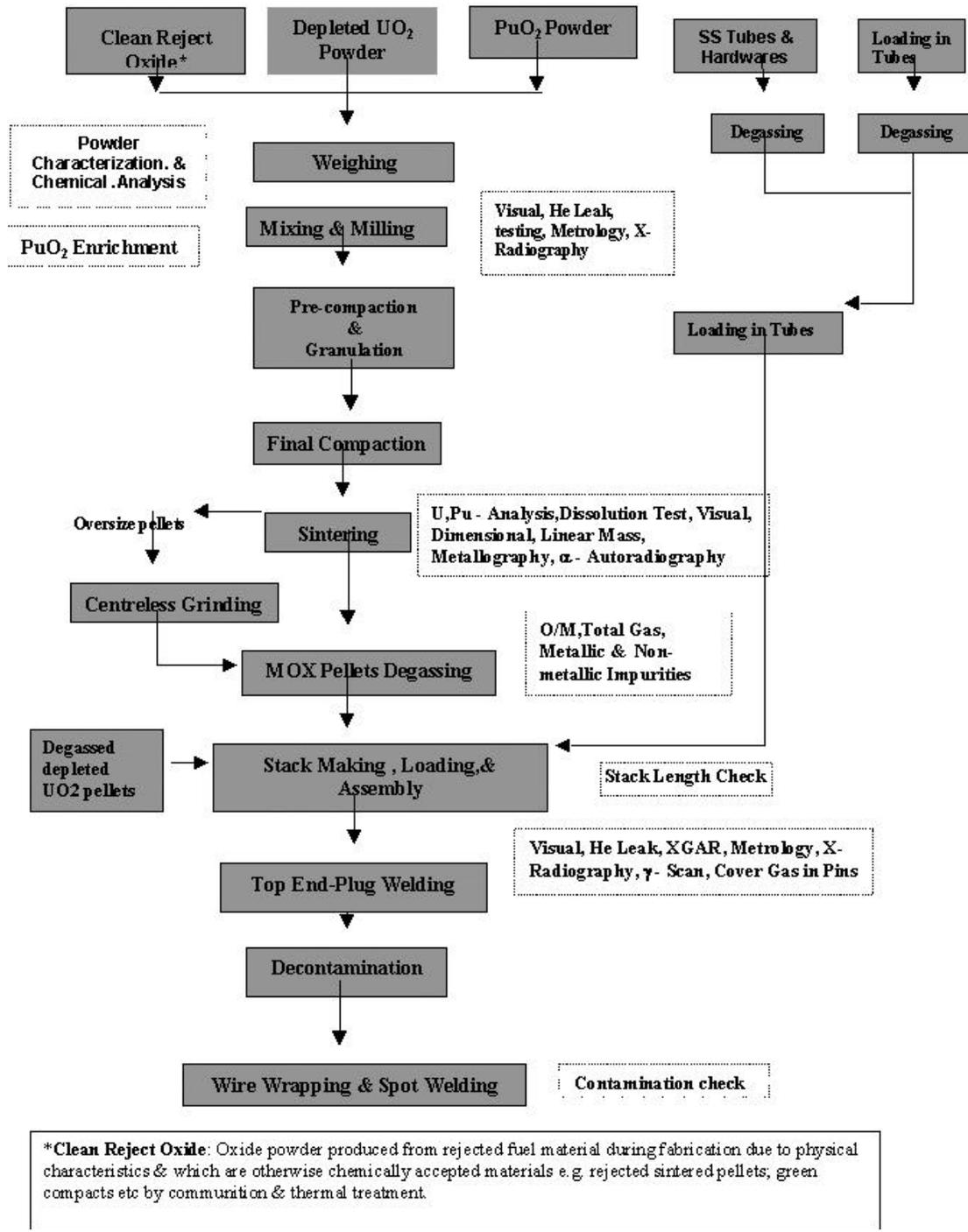


Fig. 3 PFBR Fuel Pin Fabrication Flowsheet with QC STEPS

cladding. In U.S. burn up of 21 ha% has also been demonstrated in FFTF.

### Non Oxide Ceramic Fuels

A fast breeder reactor should have the potential to give a high breeding ratio & high specific power in order to achieve shorter doubling time. High breeding ratio is possible with fuel having a high heavy atom density and hard neutron spectrum (light elements like C, O moderate the neutrons) while a high specific power rating is achievable with fuel having high heavy atom density and high thermal conductivity.

Metallic (U-Pu-Zr) alloy fuel gives a high breeding ratio of around 1.4, while for (U,Pu)O<sub>2</sub> it is about 1.1 to 1.2. The lower breeding ratio in oxide fuel is due to the low heavy atom density. Mixed carbide (U, Pu) C fuel and mixed nitride (U,Pu)N fuel are considered advanced fast reactor fuels because of their high thermal conductivity, high heavy atom density and an excellent compatibility with the liquid sodium coolant. The high thermal conductivity of MC & MN fuel makes it possible to operate them with a high linear heat rating (1000W/cm with sodium bonded carbide fuel compared to 450W/cm for oxide fuels). MC fuel can give a breeding ratio of 1.25 where as MN fuel can give a breeding ratio of 1.23. A still higher breeding ratio using MN fuel is possible with enrichment of nitrogen in N<sup>15</sup> (as parasitic absorption of neutron in N<sup>14</sup> is reduced). The enrichment of nitrogen in N<sup>15</sup> also reduces generation of C<sup>14</sup> (product of neutron absorption in N<sup>14</sup>) which is an environmental hazard.

The fabrication of MC and MN fuel is difficult since they are susceptible to oxidation and hydrolysis. Hence they need to be handled in an inert atmosphere of Nitrogen or Argon. Additionally, MC is highly pyrophoric, requiring an inert atmosphere of high purity where in comparison commercial grade nitrogen atmosphere can be used for MN fuel. Large scale spent MC & MN fuel reprocessing by PUREX process is yet to be established.

MC and MN fuel pins with different cladding materials and bonding material (He or Na) in pellet clad gap has been satisfactorily tested to at least 10 %ha burn up. Fission gas release is around 30% for this burn up but at higher burn ups (>15%ha) the

release probably exceeds 50% but remains always lower than that in oxide. The fuel shows high swelling rate and high mechanical interaction with cladding because of close packed NaCl type crystal structure. Oxide fuel has more open calcium fluorite type crystal structure which can accommodate fission products to a certain extent without swelling. Plasticity of the fuel is also lower than oxide at the same Linear Heat Generation Rate (LHGR) because of high thermal conductivity and low volumetric temperature. Hence these fuels should be designed with enough porosities/ pellet clad gap to accommodate swelling. However this leads to reduction in thermal conductivity and hence sodium bonded fuel element is a better choice to exploit the full potential of MC & MN fuel.

MC fuel is prepared from MC powder by powder metallurgy processes. MC powder is prepared by carbothermic reduction of oxide powder in vacuum or flowing inert gas (Argon). The process involves co-milling of UO<sub>2</sub> and PuO<sub>2</sub> powder with graphite, followed by compaction of the milled powder at low pressure. This is done to increase the contact of oxide with graphite leaving enough porosity for expulsion of gaseous reaction product CO: these pre-compacts are heated in a vacuum furnace at around 1500<sup>0</sup>C. The MC clinkers so formed are crushed and milled to getsinterable grade MC powder. The MC powder is mixed with suitable binder/lubricant and then pre-compacted, granulated, compacted to green pellets and sintered in Ar+H<sub>2</sub> gas mixture. Pellets are then stacked and loaded in fuel cladding tube and welded by TIG under Helium atmosphere to manufacture helium bonded fuel elements. Sodium bonded fuel elements are made by putting fuel pellets in a metallic shroud and loading them in the clad tube with required quantity of sodium. Elements are encapsulated again by TIG welding in Helium. All the manufacturing operations from carbothermic reduction onwards is done in glove boxes under Nitrogen environment.

MN fuel is also prepared almost in the same way as that of MC fuel except that carbothermic reduction is done in Nitrogen atmosphere (instead of vacuum or Argon). All other processes remain the same.

### **Plutonium Fuel Development for Thermal Reactors:**

As discussed earlier, though plutonium is not as efficient a fuel as  $^{235}\text{U}$  in thermal reactors, the use of plutonium as MOX fuel in light water reactors began in a significant way in the late eighties in Europe due to i) reduced pace of deployment of FBRs & ii) ageing characteristics of plutonium produced from LWRs which leads to increased radiation level and loss of fissile value ( $^{241}\text{Pu}$  decay). The first use of MOX as fuel in a LWR was done in the PWR reactor BR-3 in Belgium in 1963. VAK, Kahl in Germany, a BWR, was loaded with MOX fuel in 1966.

Belgium and Germany, started investigation and evaluation of MOX fuel for LWR in 60's and continued to do so right through 1970's. These two countries had established industrial fabrication capacity and had qualified their MOX fuel with sufficient database by 1970's. In France EDF decided to embark on a massive commercial utilization of MOX fuel in their LWR, because of the slow down of its fast reactor programme. In the intervening period Germany discontinued its MOX activities because of its national policy.

Recycling of plutonium in the existing LWRs is presently being done with partial MOX cores (around 30%) from safety considerations. This limitation arises because introduction of Pu in existing  $\text{UO}_2$  fuelled LWR hardens the neutron spectrum and thus reduces control rod worth. However, new LWRs with 100% MOX core are being designed in countries like Japan and Finland.

The  $\text{PuO}_2$  content in first cycle MOX fuel assembly for LWR is around 4-5%. Two types of fuel assembly design have been used in LWRs i.e. "Island design" and "All plutonium design". In the "Island design" the peripheral fuel rods of the assembly contain  $\text{UO}_2$  fuel with remaining inner ones having 2-3 enrichments of Pu to keep power-peaking under control. In the "All plutonium design" all the rods in the assembly contain MOX pellets. Power peaking in this assembly is also controlled by selecting proper concentration of Pu in different rods of the assembly. Around 3-4 enrichments are used. The Indian MOX fuel assemblies used in TAPS reactor were of "All plutonium design".

MOX pellets for thermal reactors are also normally manufactured using the powder pellet route as discussed in the fabrication of fast reactor fuels. A number of methods for the fabrication of MOX fuels, with minor modifications to the flow-sheet of the conventional powder pellet route, have been developed by different countries to suit their needs. UK and India use co-milling, using an attritor, to get U & Pu homogeneity in the fuel, whereas in the Belgian process termed MIMAS, first a master blend of 30w%  $\text{PuO}_2\text{-UO}_2$  is prepared by co-milling followed by blending the master blend with free flowing ex-Ammonium Uranyl Carbonate (AUC)- $\text{UO}_2$  powder to obtain the required composition. The MIMAS process does not require the additional step of granulation as ex-AUC- $\text{UO}_2$  powder is free flowing. In India free flowing granules are prepared by pre-compaction granulation route. In BNFL, UK free flowing granules are prepared by short binder-less route wherein 0.2% to 0.3% stearate binder is added to the powder during co-milling in an attritor and then tumbled in a vessel to form granules. From the granule stage onwards the processes remain the same. The diametric tolerance specified for thermal reactor MOX pellets is around  $\pm 0.02\text{mm}$  and to achieve this, a centre-less grinding operation on the sintered pellets is required. Another important specification on MOX pellets for thermal reactors is the hydrogen content of less than 1ppm. This is achieved by vacuum out-gassing. This specification on hydrogen is important due to the phenomenon of hydrogen embrittlement of the zircaloy-clad used in thermal reactors.

Recycling of plutonium in the Indian PHWR has been initiated recently. A number of MOX fuel bundles of a design, called MOX-7, have been loaded in the Kakrapar Atomic Power Station (KAPS) reactor. The advantage of loading MOX bundles is to increase the average burn-up from the present 6700 MWD/Te of the reactor fuel to 10700 MWD/Te, thereby improving the uranium utilization and reducing the load on back-end fuel cycle processes of reprocessing & waste management. The MOX-7 fuel bundle is similar to the existing 19 element natural  $\text{UO}_2$  fuel bundle being currently used in Indian PHWRs, with the difference that the inner seven elements of the

bundle contain MOX pellets with a composition of 0.4w%PuO<sub>2</sub>-UO<sub>2</sub>.

### **Plutonium Disposition**

A large amount of plutonium obtained from the operating reactors and disarmament of nuclear arsenal is getting stockpiled. Disposition of plutonium to reduce the stockpile is an important contemporary issue, especially in the western countries. Various schemes are under study to reduce the plutonium inventory by using it in thermal and fast reactors. Some of these are:

#### ***Plutonium Disposition in Thermal Reactors***

A PWR can be a net consumer or net producer of plutonium depending on the MOX core fraction. For a MOX core of about 30% (depending on the type of fuel management scheme adopted and the isotopic quality of plutonium), there is a net balance between production of plutonium in UO<sub>2</sub> assemblies and consumption of plutonium in MOX assemblies. At higher MOX core fractions the core becomes a net consumer of plutonium. Similarly a BWR or a PHWR can also be used as a net consumer of plutonium. Some schemes using inert matrix fuels could also be used in these reactors to consume more plutonium.

#### ***Plutonium Disposition in Fast Reactors***

Use of fast reactor as burner by operating the reactor at conversion ratio below 1

- (a) This can be achieved by replacing the fertile (depleted UO<sub>2</sub>) radial and axial blanket material by inert material (like S.S. /Ni etc.)
- (b) Use of inert matrix fuel where in Uranium oxide in MOX fuel is replaced by inert materials SiC, MgO, spinel, stabilized ZrO<sub>2</sub>. Thus it eliminates production of plutonium.
- (c) The CAPRA (Consommation Accrue de Plutonium dans les reacteurs Rapides) project in Europe envisages the use a dilute core having MOX fuel compositions of 45%PuO<sub>2</sub>. The reduced fuel content in the dilute core is achieved by the following
  - Fuel pellets having a large central hole to reduce fuel smear density.

- Each fuel sub-assembly contains a large number of small diameter pins of which about two-thirds contain fuel and the remaining one-third an inert material. The latter pins allow the reactor to be converted into a breeder if required.
- About 15% of the core sub-assemblies are diluents using no fuel at all. By interchanging diluent sub-assemblies containing neutron absorber or transparent materials, flexibility in controlling reactivity is provided.

All the plutonium disposition schemes discussed above are still in the development phase.

### **Highlights of Plutonium Fuel Development in India**

Efforts have been in progress since the late sixties, to develop and fabricate fuel required for the second stage of our nuclear program viz. Plutonium based fuels. A facility was set-up at Trombay to develop, fabricate & characterize plutonium based ceramic and alloy fuels. This facility produced SS clad plutonium oxide fuel elements for the first time in 1972 for the fast critical facility PURNIMA-I (Plutonium Reactor for Neutron Investigations of Multiple Assemblies).

The facility at Trombay has the capability to develop plutonium bearing fuels both with a low content of plutonium as well as those with a high content required for thermal and fast reactors respectively. MOX fuel, as an alternative to the use of LEU (Low Enriched Uranium) fuel for our BWR reactor at Tarapur was developed in the early part of eighties when 3MOX bundles were test irradiated in the research reactor CIRUS. In the early nineties this experience was used to fabricate MOX assemblies with an all plutonium design at the Advanced Fuel Fabrication Facility (AFFF), Tarapur. The first MOX assembly was introduced in the BWR at the Tarapur Atomic Power Station (TAPS) in 1994 and several MOX assemblies have since been irradiated successfully to the designed burn up. A number of MOX -7 design fuel bundles for PHWR were fabricated at AFFF and have been introduced in KAPS in a phased manner. The first set of bundles was introduced in year 2003. A few (Th, Pu)O<sub>2</sub> MOX fuel pins have also been test irradiated in the

CIRUS reactor to study their in-reactor performance for use in PHWRs in the early eighties and nineties.

In the seventies development of MOX fuel for the FBTR (Fast Breeder Test Reactor), was also initiated. The initial composition for the FBTR was MOX fuel containing 30%PuO<sub>2</sub> with UO<sub>2</sub> having 85% enrichment. The fabrication flow-sheet for this fuel was developed using PuO<sub>2</sub> and natural UO<sub>2</sub>. However, due to unavailability of enriched UO<sub>2</sub> this fuel composition was abandoned. To overcome this shortcoming, a new fuel composition of 76%PuO<sub>2</sub> with natural UO<sub>2</sub> was taken up for development and evaluation. However, this fuel composition was also not pursued intensely because initial results in France showed incompatibility with the liquid coolant sodium and low thermal conductivity (as O/M specified was also very low.)

This set the stage in the eighties for development of plutonium-uranium mixed carbide fuel for FBTR. The fabrication of this fuel is difficult as it requires handling of carbide material in inert gas atmosphere and the number of process steps are more in comparison to oxide fuel fabrication. This fuel was successfully fabricated for the FBTR, which was made critical in 1985. Initially the core was fuelled with a fuel composition of (70%Pu, 30%U)C and later with a composition of (55%Pu, 45%U)C. The FBTR carbide fuel has successfully reached a burn up of over 125000 MWD/Te. A hybrid core using both MC and MOX assemblies for the FBTR is being considered to raise the power of the FBTR. Towards this a few MOX bundles are being fabricated at AFFF. The composition of this MOX fuel is 44w%PuO<sub>2</sub>-UO<sub>2</sub>. Extensive evaluation of this fuel composition has been made for its dissolution behaviour (important for reprocessing of spent fuel) and its compatibility with sodium coolant.

India has designed and is currently constructing a 500MWe Prototype Fast Breeder Reactor (PFBR) at Kalpakkam. The fuel composition for this reactor is 21w%PuO<sub>2</sub>-UO<sub>2</sub> (for the inner core region) and 28w%PuO<sub>2</sub>-UO<sub>2</sub> (for the outer core region). The pellets are annular with a matrix density of around 94%TD and are encapsulated in D-9 SS cladding tube. Extensive work has been done at AFFF to develop the fabrication flow-sheet for this fuel. Irradiation

testing of this fuel is currently in progress in FBTR on a short length 37 element fuel sub-assembly fabricated at AFFF. This sub-assembly is under irradiation with a LHGR of 450W/cm. About 10Te of MOX fuel is required for the core of the PFBR. The initial fuel requirements for first few cores will be met by AFFF. Further reload fuel requirements of PFBR will be met by a co-located fuel fabrication plant being setup at Kalpakkam.

To facilitate the Nuclear Power programme towards the third phase of utilization of thorium as fuel, the design of the Advanced Heavy Water Reactor (AHWR) incorporates (Th, Pu)O<sub>2</sub> fuel for its initial core. Extensive development work has been taken up at Trombay to fabricate and characterize (Th, Pu) O<sub>2</sub> fuel pellets. The PuO<sub>2</sub> content of the AHWR fuel is around 3 to 4w% with remaining being ThO<sub>2</sub>. The flow-sheet for fabrication of these pellets are also similar to (U, Pu)O<sub>2</sub> fuel except for the fact that sintering can be carried out in air atmosphere as well, because ThO<sub>2</sub> has only one oxidation state.

U-Pu-Zr fuel development for fast reactors is currently in progress to take advantage of the higher breeding potential of this fuel. The current Indian programme on FBRs envisages that after setting up a few MOX fuelled FBRs, India may switch over to alloy fuels to enhance the growth of fast reactors.

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# Thermo Physical and Thermo Mechanical Properties of Nuclear fuel for Thermal and Fast Reactor



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## Introduction

Nuclear reactor producing power or research/test reactors could be of different types and configuration depending upon the specific requirement. The design of the fuel element could be pellet-pin type, plate type, vibro-compacted fuel micro spheres or fuel kernels in cladding material. The selection of fuel and cladding materials for any reactor type is based on the following:

- Physical Properties
- Mechanical Properties
- Neutronic characteristics

Physical properties refer mostly to the fuel while mechanical properties refer to the cladding and structural material. Neutronic characteristic applies to the whole core material, i.e. fuel, cladding, moderator, coolant etc. The present paper discusses the different techniques used to estimate these

properties and highlights some of the data for different type of fuels for thermal and fast reactors e.g.  $\text{UO}_2$ ,  $(\text{Th,U})\text{O}_2$ ,  $(\text{Th, Pu})\text{O}_2$ ,  $(\text{U, Pu})\text{O}_2$  and  $(\text{U,Pu})\text{C}$  and  $(\text{U, Pu})\text{N}$ , which are being used in our existing reactors or are under consideration for use in future reactors.

Thermo physical and thermo mechanical Properties of Nuclear fuels are of great technical importance to the Nuclear reactor designer. In nuclear reactor, fission energy in the form of heat is produced within a clad fuel element consisting of fissile material in metallic or ceramic form. This results in a temperature gradient across the fuel center and surface. Many of the properties of the fuel, particularly thermal properties, are to a great extent affected by this temperature gradient. Compositional changes across the temperature gradient are also set up by diffusion of the constituent fuel elements and transmutation products arising out of fission. Knowledge of some of the important thermo physical and thermo

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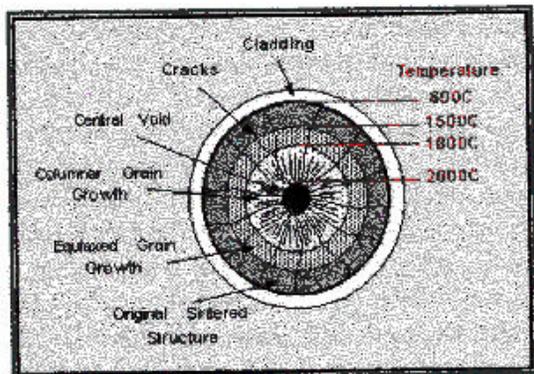


Fig. 1 Cross-section of irradiated fuel demonstrating restructuring and crack development

mechanical properties of the fuel which are affected by both temperature gradient and composition are essential for predicting fuel behavior in the reactor, designing the fuel pin and to generate a computer code for the in-reactor fuel performance and whole core accident analysis of the reactor system. Some of the important properties of concern are Solidus temperature, Specific heat, Thermal diffusivity / thermal conductivity, thermal Expansion and mechanical properties at ambient and high temperature (hot hardness).

The most commonly used fuel configuration all over the world is the pellet-pin type and the same is also being used in majority of our reactor system. In the pellet-pin type of fuel element, the fuel (fissile material) is in the form of solid or annular cylindrical sintered ceramic pellets, which is encased in a tube known as cladding. The purpose of the cladding material is to contain the fuel pellets and to isolate the fuel from the coolant used for extraction of heat generated by fission. The life of a fuel pin is dictated by the degradation of the fuel or loss of integrity of the cladding in the form of a breach of clad due to fuel-clad mechanical/chemical interaction. In order to avoid any early disposal of the fuel pin, it is essential to know the out-of-pile properties of the fuel and cladding material so that corrective action can be taken at the design stage.

When a virgin fuel pin is put inside a reactor, it undergoes fission and generates heat energy inside the fuel pellet resulting in a temperature gradient

from the fuel center to the periphery. The temperature gradient is dependent on the thermal conductivity of the fuel. The fuel also undergoes a lot of changes with burn up. A section of the fuel pin indicating changes in the structure of the fuel after it is put inside the reactor is shown in Fig. 1. The temperature gradient across the fuel pin results in changes in the physical and chemical properties of the fuel as there is migration of different species down the temperature gradient.

The parameters, which are of importance for fuel pin design, performance and Modeling, are:

- Fuel centre temperature,
- Fuel-clad gap conductance,
- Linear heat rating (W/m),
- Fuel plasticity,
- Fuel cracking,
- Plutonium redistribution / migration,
- In-pile densification,
- Fission product behavior,
- Dimensional and Microstructural stability

The above parameters could be defined or understood from knowledge of the following properties.

- Melting point / solidus temperature
- Co-efficient of thermal expansion,
- Thermal diffusivity / conductivity,
- Specific heat / heat capacity,
- Thermal toughness / creep

Different fuel systems are evaluated on the basis of their thermo physical and thermo mechanical properties during the stage of development.

#### Melting Point / Solidus Temperature

Melting/solidus temperature could be estimated by any of the following methods: Direct method, indirect method, Theoretical Estimation by Classical Molecular Dynamic Simulation method. In the direct method, the sample is heated in a covered crucible with a pinhole at the top through which the temperature of the sample is monitored by a pyrometer. The sample is heated by induction

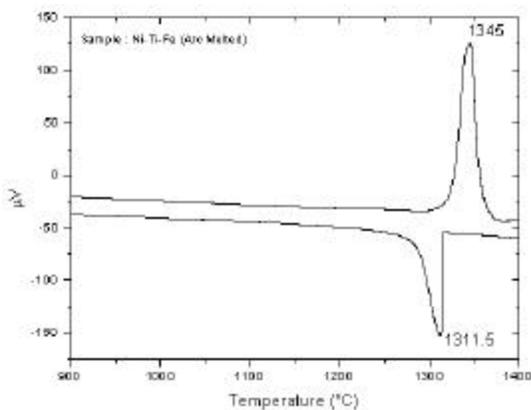


Fig. 2 DTA curve of melting of Ni-Ti-Fe alloy

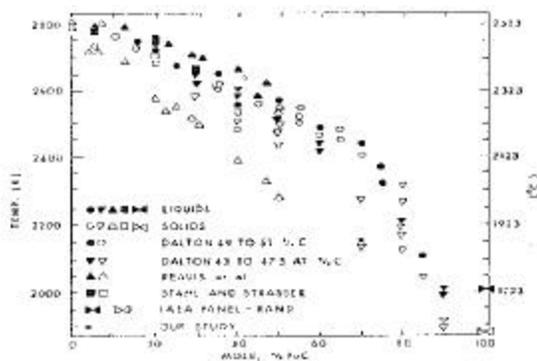


Fig. 3 Solidus/Liquidus temperature of (U-Pu) monocarbide [1]

heating to different temperatures near or above the melting point, equilibrated, cooled and observed metallographically to estimate the melting temperature. Alternately, high temperature differential thermal analyzers (DTA) could also be used to estimate the melting temperature. The sample is heated against an inert reference standard (Thoria or Blank) and an endothermic peak in the DTA curve at a particular temperature indicates the melting of the sample. A typical DTA curve on melting is shown in Fig. 2. Solidus temperature has been estimated indirectly by dilatometer in our laboratory.. In this method, the sample is heated continuously at a low heating rate under an inert atmosphere cover gas and the change in length ( $\Delta L$ )

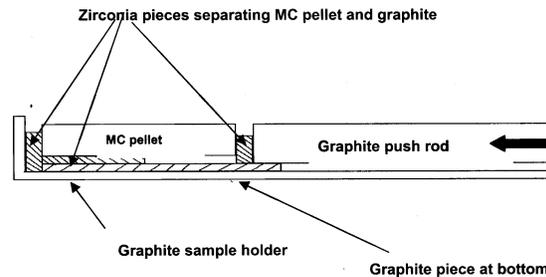


Fig. 4 Schematic diagram of loading of MC pellet (Mark II) inside dilatometer

is monitored as a function of temperature. The onset of melting in any part of a solid cylindrical pellet sample could be observed by a sharp change in slope of  $\Delta L/L$  vs. temperature plot. The dilatometric method needs to be supported by metallographic examination of the sample, which will reveal onset of melting at the grain boundaries.

Hyperstoichiometric mixed Uranium – plutonium carbide fuel containing 70% (Mark I) and 55% Pu (Mark II) are the driver fuel for the Fast Breeder Test Reactor at Kalpakkam, Tamil Nadu. The fuel containing ‘O’, ‘N’ as impurities and about 10-15 % sesquicarbide ( $M_2C_3$ ; M stands for U+Pu) is not a pure compound and hence has a range of melting temperature. The solidus/liquidus temperature is available in literature [1] and is shown in Fig. 3. These data are subject to changes depending upon the (C/M) ratio, (O+N) impurities and the sesquicarbide content.

For hyperstoichiometric mixed carbide fuel containing 70% PuC (Mark I), 10-15% sesquicarbide and (O+N) impurity 7000 ppm, the solidus temperature was estimated by heating a solid sintered pellet in a Tantalum crucible (covered with a lid with a pin hole for monitoring the temperature by a pyrometer). The sample was heated to different temperatures, cooled and observed by metallography to detect any incipient melting. The melting temperature of Mark I fuel was estimated to be 1875C [2].

For hyperstoichiometric fuel containing 55% PuC (Mark II), the melting temperature was estimated using a high temperature horizontal dilatometer (Fig. 4). The sintered pellet was heated

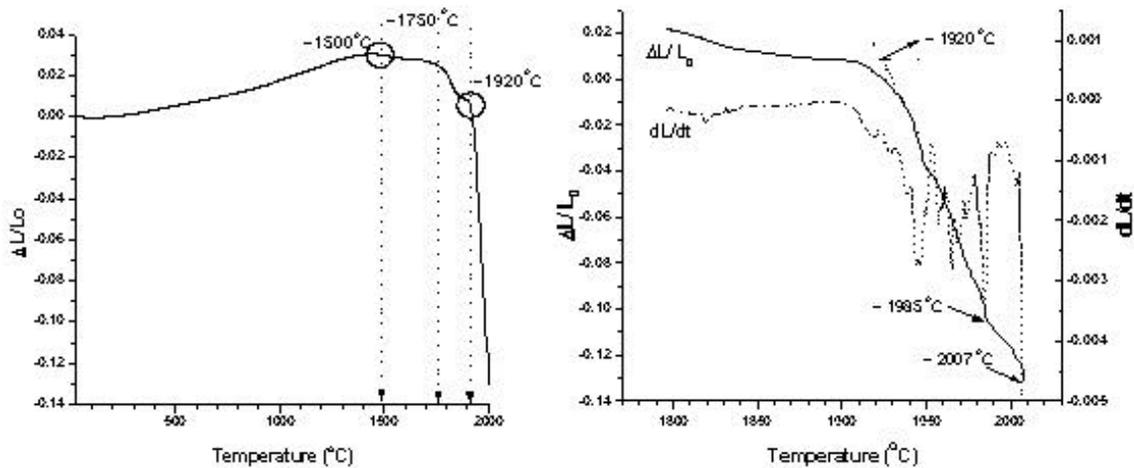


Fig. 5 Softening behavior of the fuel when continuously heating up to 2010°C in a dilatometer.

in high purity flowing Argon cover gas and the change in length was monitored as a function of temperature. Any melting is indicated by sudden change in  $\Delta L/L$  vs. temperature plot (Fig. 5). The sample was subjected to metallographic examination to detect any incipient melting. The estimated solidus temperature was 1920C for Mark II fuel.

#### Coefficient of Thermal Expansion

The coefficient of linear thermal expansion could be measured using a push rod type dilatometer or high temperature X-ray diffractometry. In the high temperature X-ray, lattice parameter ( $a_0$ ) is measured as a function of temperatures and the absolute expansion data is estimated from the increase in lattice parameter. However, dilatometry is the most commonly used method for measurement of expansion data of ceramic fuels where the increase in length of a sample is measured as a function of temperature.. The data is represented in terms of % increase in length ( $\Delta L/L \times 100$ ) as a function of temperature (T). The average coefficient of thermal expansion over a range of temperature i.e. technical expansion coefficient is also reported. It may be mentioned that the microscopic expansion data (by dilatometry) will always be higher than that measured by the X-ray lattice parameter. The

percent expansion data for different type of fuels are given below in the form of polynomials.

#### PFBR Fuel ( $UO_2$ with 28% $PuO_2$ )

$$[\Delta L/L_0 \times 100]_T = -0.3577 + 0.0012T - 2.7178E-8T^2 + 7.5387E-11T^3 \quad (1)$$

#### FBTR fuel (MARK II)

$$[\Delta L/L_0 \times 100]_T = -0.3333 + 7.1528T \times 10^{-4} T + 7.6889 \times 10^{-7} T^2 - 2.2249 \times 10^{-10} T^3 \quad (2)$$

#### AHWR fuels

- $ThO_2$ -2%  $UO_2$  :

$$[\Delta L/L_0 \times 100]_T = -0.2741 + 6.8563 \times 10^{-4} \cdot T + 1.0431 \times 10^{-7} \cdot T^2 - 5.3996 \times 10^{-11} \cdot T^3 \quad (3)$$

- $ThO_2$ -4%  $PuO_2$ :

$$[\Delta L/L_0 \times 100]_T = -0.3795 + 11.4000 \times 10^{-4} \cdot T + 1.8725 \times 10^{-8} \cdot T^2 - 8.4562 \times 10^{-11} \cdot T^3 \quad (4)$$

#### Thermal Conductivity

Thermal conductivity (k) is the most important property of a nuclear fuel. The total amount of heat that could be extracted from a fuel pin depends

primarily on the thermal conductivity of the fuel. This can also be expressed by the heat integral given by

$$\phi = 4\pi \int_{T_c}^{T_s} k \cdot dT \quad (5)$$

where  $T_c$  and  $T_s$  are the fuel center and surface temperature respectively. Thermal conductivity of the fuel limits the fuel surface temperature so that there is no center melting.

Thermal conductivity depends upon the type of fuel i.e. whether it is metallic or ceramic. For metallic fuel thermal conductivity is very high compared to ceramic fuel. Further, among the ceramic fuels, conductivity varies widely depending upon the crystal structure e.g. thermal conductivity of mixed Uranium Plutonium carbide (FCC, NaCl type) carbide fuel is 2-3 orders of magnitude higher than that of oxide (FCC, CaF<sub>2</sub> type) [3]. Presence of second phase, porosity, grain size, composition (Pu content, O/M ratio, transmutation products etc.) greatly affect the thermal conductivity.

Thermal conductivity could be measured by steady state method or transient method. For nuclear fuels, thermal conductivity has been most widely estimated by transient method from the measured thermal diffusivity data by transient laser flash technique of Parker et. al. [4], specific heat and density using the relation given below:

$$k = \alpha \times \rho \times C_p \quad (6)$$

The main advantages of Laser flash method are: small sample size, sample homogeneity, short time for measurement and number of data points could be generated from the same sample in a single measurement step. In this method, the sample, in the form of a small coin or disc, maintained under adiabatic condition, is irradiated on one surface with a pulse of laser and the temperature rise on the rear surface of the sample is measured as a function of time (Fig. 6). Thermal diffusivity is calculated using Clerk and Taylor's method [5] following:

$$\alpha = K_x \cdot L^2 / t_x \quad (7)$$

where 'L' is the sample thickness 'K'<sub>x</sub> is a constant corresponding to 'x' fraction rise in temperature for a time lapse of  $t_x$ .

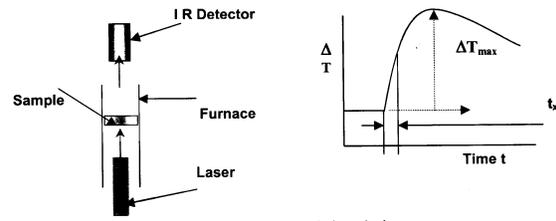


Fig. 6 Principle of Laser Flash method

The specific heat could either be measured experimentally or could be obtained from literature. For a multicomponent system the specific heat of the mixture is the sum of the weight fraction of the individual components' specific heat; density of the material also needs corrections utilizing measured coefficient of thermal expansion data.

Ceramic fuels are normally fabricated by powder metallurgy route and hence contain porosities in the final sintered product. The shape, size and distribution of pores vary depending upon fabrication techniques followed. Porosity plays a very important role as it lowers thermal conductivity. It can act as sink for fission gas and can accommodate creep deformation and swelling. However, from theoretical consideration thermal conductivity 'k<sub>p</sub>' of porous compact can be corrected for porosity using different empirical relations where k<sub>0</sub> is the conductivity corresponding to zero porosity.

$$k_p = k_o (1 - \alpha \cdot P), \quad \alpha = 206 - 0.5 t \quad (8)$$

$t = T(K)/1000$ , [6]

$$f = (1 - P)^{1.5} \quad 0 < P < 1. \quad (9)$$

'f' is the fractional conductivity [7]

$$k_p = k_o \frac{(1 - \alpha \cdot p)}{1 + \beta \cdot P} \quad \text{for } 0.1 < P < 0.2, \quad [8] \quad (10)$$

The above relations are mostly used to compare the data of different workers for any specific system. In our studies relation (10) has been used for mixed carbide/nitride fuels, and (8) and (9) for oxide fuel.

Thermal conductivity has been estimated for different fuel systems for thermal and fast reactors such as UO<sub>2</sub>, UO<sub>2</sub> with fission product addition (SIMFUEL), UO<sub>2</sub> with TiO<sub>2</sub>, dopant MOX

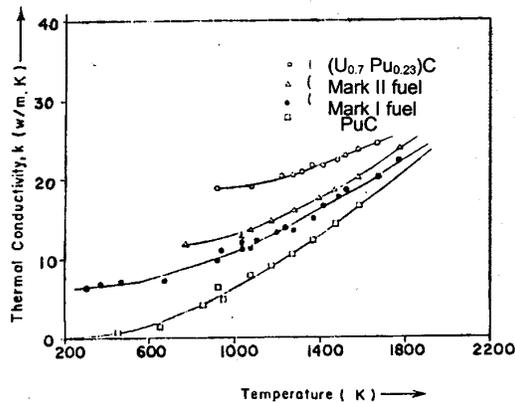


Fig. 7 Thermal conductivity of mixed carbide fuels (including Mark I & II) corrected to 100% TD

( $\text{UO}_2+4\%\text{PuO}_2$ ), MOX with  $\text{Gd}_2\text{O}_3$ , ( $\text{ThO}_2\text{-UO}_2$ ) [ $\text{UO}_2$ : 2-20%],  $\text{ThO}_2+\text{PuO}_2$  [ $\text{PuO}_2$ : 2-10%], ( $\text{U,Pu})\text{O}_2$  [ $\text{PuO}_2$ : 21, 28, 45%], ( $\text{U,Pu})\text{C}$  [ $\text{PuC}$ : 20, 30, 45, 70%] and ( $\text{U,Pu})\text{N}$ . In this paper thermal conductivity of some of the most important fuel e.g. Mixed ( $\text{U,Pu}$ ) carbide fuel for FBTR, mixed oxide fuels for PFBR, PHWR and ( $\text{Th,U}$ )  $\text{O}_2$  and ( $\text{Th,Pu}$ )  $\text{O}_2$  fuels for AHWR have been highlighted.

Apart from the higher thermal conductivity of mixed carbide / nitride fuels compared to mixed oxide, the variation of thermal conductivity of these fuels with temperature are also quite different. Oxides of Urania, Thoria and Plutonia having  $\text{CaF}_2$  type of structures are dielectric material, for which mode of heat conduction is predominantly phononic at low temperatures. As a result, thermal conductivity first decreases with increase in temperature, attains a minima and then increases with increase in temperature. This increase at high temperature could be attributed to the contribution to thermal conductivity by the electrons and radiative heat transfer. Mixed carbide and nitride fuels are metallic in nature and phonon conduction prevails at lower temperatures; however, at higher temperature, electronic heat conduction predominates which increases the conductivity considerably. Thermal conductivity decreases when any one of the component in a binary system is replaced by the other having lower thermal conductivity. This could be attributed to the different atomic sizes between the host and the parent atom, interaction parameter

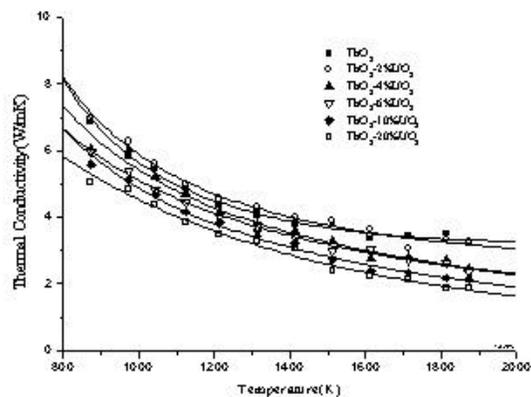
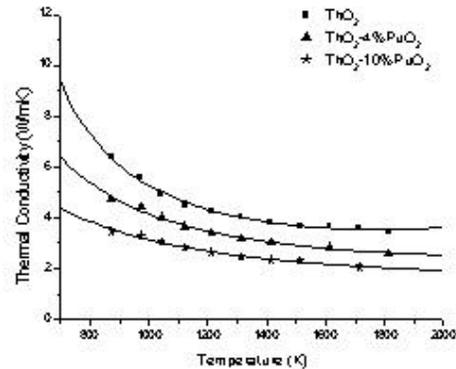


Fig. 8 Thermal conductivity of ( $\text{Th,U}$ ) $\text{O}_2$  and ( $\text{Th,Pu}$ ) $\text{O}_2$  fuels for AHWR

between the different type of atoms, mass difference etc. The details of these studies are shown in Figures 7, 8, 9 and 10.

## Mechanical Properties

### Elastic Constants

The longitudinal and shear sound velocities of  $\text{UO}_2$  and SIMFUEL were measured at room temperature by ultrasonic pulse echo measurement. Elastic modulus, bulk modulus, shear modulus and Poisson's ratio was determined from the measured longitudinal and shear sound velocities of  $\text{UO}_2$  and SIMFUEL and their densities. Vickers micro hardness was measured for  $\text{UO}_2$  and SIMFUEL. Yield stress and yield strain for  $\text{UO}_2$  and SIMFUEL was calculated from the calculated values of elastic modulus, Poisson's ratio and micro hardness.

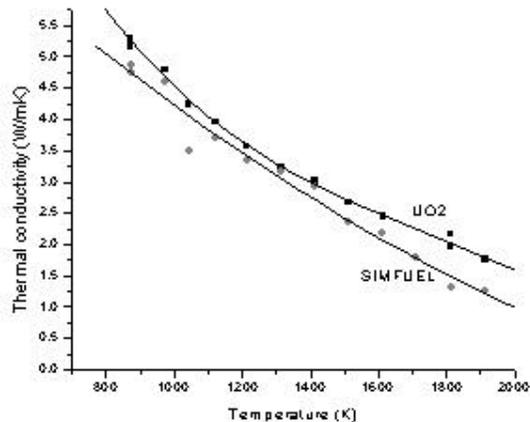


Fig. 9 Thermal conductivity of  $UO_2$  and SIM Fuel for PHWR

The longitudinal and shear sound velocities of  $UO_2$  and SIMFUEL were measured at room temperature. For isotropic media, the shear modulus  $G$ , Young's modulus  $E$ , Poisson's ratio  $\gamma$  and bulk modulus  $K$  are expressed in terms of the longitudinal sound velocities  $V_L$  and shear sound velocities  $V_S$  as,

$$G = \rho * V_S^2, \quad (11)$$

$$E = G * [(3V_L^2 - 4V_S^2) / (V_L^2 - V_S^2)] \quad (12)$$

$$\gamma = (V_L^2 - 2V_S^2) / 2 (V_L^2 - V_S^2) \text{ and} \quad (13)$$

$$K = \rho * (3V_L^2 - 4V_S^2) / 3 \quad (14)$$

where  $\rho$  is density

Elastic constants calculated by above relations for  $UO_2$  and SIMFUEL using measured longitudinal and shear wave velocities are as given in Table 1

Calculated values of Shear modulus ( $G$ ), Elastic modulus ( $E$ ), Bulk modulus ( $K$ ) and Poisson's ratio ( $\gamma$ ) are listed along with literature data for  $UO_2$  in Table 2. Calculated values agrees reasonably well with the literature data.

Elastic modulus, Bulk modulus, Shear modulus and Poisson's ratio of SIMFUEL are found to be less than  $UO_2$ ; this is analogous to the result obtained by Yamada [11] where Elastic modulus and shear modulus and Poisson's ratio of  $UO_2$  decreases with  $CeO_2$  addition, and with the results obtained by

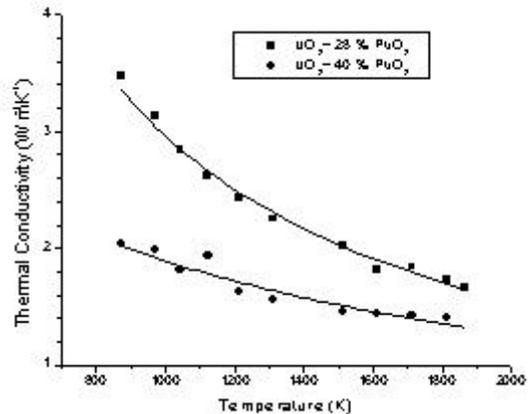


Fig. 10 Thermal conductivity of  $(U,Pu) O_2$  for PFBR

Yamanaka [21] where elastic modulus and shear modulus of  $(U,Ce)O_2$  decreases with  $Nd$  or  $Zr$  addition simulating fission product in MOX fuel.

Poisson's ratio of SIMFUEL is found to be less than  $UO_2$ . When Poisson's ratio increases, deformation can occur more easily and the brittleness of materials decreases. Thus the reduction in Poisson's ratio of simfuel compared to  $UO_2$  means SIMFUEL is more brittle than  $UO_2$ .

#### Micro Hardness

The Vicker's hardness measurement was performed to calculate yield stress and fracture toughness of  $UO_2$  and simfuel. Micro hardness,  $H_V$  measurement at room temperature for  $UO_2$ , was performed by using micro-Vicker's hardness tester. The Vicker's hardness  $H_V$  is measured by forcing a diamond pyramid-type (with apex angle  $136^\circ$ ) indenter into the surface of the specimen and is defined by

$$H_V = 1.854 * P_H / d^2 \quad (15)$$

where  $d$  is average diagonal length in micron and  $P_H$  is indenter load in Kg.

Average Micro hardness,  $H_V$  for  $UO_2$  and SIMFUEL calculated by using above relation is 5.423 GPa and 3.638 GPa for  $UO_2$  and SIMFUEL respectively. The Vicker's hardness of  $UO_2$  (5.423 GPa) is in good agreement with  $6.4 \pm 0.5$  GPa of  $UO_2$

**TABLE 1. Elastic constants of UO<sub>2</sub> and SIM fuel**

Sl. No.	Property	UO <sub>2</sub>	SIMFUEL
1	Shear modulus, (Gpa )	76.3	70.24
2	Elastic modulus, E (Gpa )	201.10	181.64
3	Bulk modulus, K (Gpa )	185.07	147.94
4	Poisson's ratio, $\gamma$	0.321	0.294

**TABLE 2. Elastic Constants of UO<sub>2</sub> as compared to Literature data**

Property	UO <sub>2</sub> (Present study)	UO <sub>2</sub> (Literature data)
Shear modulus, G (Gpa)	76.3	76.11(94.7 % TD) [9], 76.77 (94.7 % TD) [9]
Elastic modulus, E (Gpa)	201.10	193.8 (94.7 % TD) [9], 199.9 (95.9 % TD) [10], 204.7 (96.1% TD) [10], 214±2.9 [11], 229.55 [12], 228 [13], 223.47 [14], 217.6 [15], 223.37 [10], 223.4 [13], 223 [16].
Bulk modulus, K (Gpa)	185.07	171.7 (95.9 %TD) [10], 183.4 (96.1 %TD) [10], 198.5 [11], 166 [17], 205 [18].
Poisson's ratio, $\gamma$	0.318	0.317 [10], 0.319 [19], 0.317 [13], 0.316 [20], 0.320 ±0.003 [11], 0.326 [18], 0.306 (95.9 % TD) [10], 0.314 (96.1 % TD) [10].

(0 % porosity) and 4.3 Gpa (14% porosity) and with hardness of single crystal UO<sub>2</sub> (5.9 ±0.5 Gpa). [22]

#### ***Yield stress and Yield Strain***

Yield stress, Y of ceramics can be obtained from hardness measurements. The relationship between H<sub>v</sub> and Y for ceramics with ionic bonds is approximately given by the following equation: [21]

$$P_H / Y = H_V / Y \sin\phi = 1 + 1.2 * \ln[(E/Y) * \pi^{0.5} * \cot\phi / 8(1-\gamma^2)] \quad (16)$$

In this equation,  $\phi$  is half of the indenter apex angle, E and  $\gamma$  are Young's modulus and Poisson's ratio of the material. and P<sub>H</sub> is indenter's load.

Yield stress, Y is calculated by using above formula and elastic modulus, E and Poisson ratio values from Table 2, which comes out to be 1.393 Gpa for UO<sub>2</sub> and 0.842 GPa for SIMFUEL Yield stress of UO<sub>2</sub> (1.393 Gpa) is in good agreement with the values obtained by Yamada [14] for UO<sub>2</sub>, as 1.7 and 1.35 Gpa for 0% and 14% porosity respectively.

Yield stress of SIMFUEL (0.842 GPa) is found to be less than yield stress of UO<sub>2</sub> (1.393 GPa), this is analogous to the result obtained by Yamada [22] where Yield stress of UO<sub>2</sub> decreases with CeO<sub>2</sub> addition, and with the results obtained by Yamanaka [21] where Yield stress of (U, Ce)O<sub>2</sub> decreases with Nd or Zr addition simulating fission product in MOX fuel.

#### ***Yield Strain***

$\epsilon$  is obtained from the calculated values of Y and E, as 0.693 % and 0.464% for UO<sub>2</sub> and SIMFUEL respectively. Generally, as the value of the elastic strain  $\epsilon$  at the yield stress is about 1%. The values of  $\epsilon$  for UO<sub>2</sub> (0.693%) and SIMFUEL (0.464%) are reasonable. Fig.11 show the stress-strain diagrams for UO<sub>2</sub> and SIMFUEL obtained from the calculated values of Y and E.

Elastic strain (0.464 %) at yield stress, and yield stress (0.842 Gpa) of SIMFUEL are less than elastic strain (0.693 %) at yield stress, and yield stress (1.393 Gpa) of UO<sub>2</sub> which indicates that

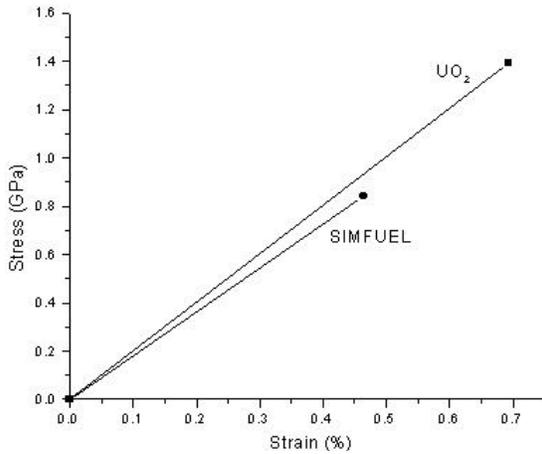


Fig. 11 Stress-strain diagram of  $UO_2$  and SIMFUEL

SIMFUEL is broken at lower stress than  $UO_2$  when the fracture toughness is not taken into account.

#### Hot Hardness

Hardness is defined as the resistance to deformation under a compressive load. The extent of deformation depends upon the type of indenter used. The indenter could be a ball indenter, pyramid indenter or conical indenter etc. In case of high temperature hardness (hot hardness or thermal toughness), hardness is a strong function of temperature and time and it decreases with increasing time and temperature. At lower temperatures, decrease in hardness with temperature is relatively sluggish; however, beyond a temperature of  $0.5 T/T_m$ , ( $T_m$  is the homologous temperature) it decreases rapidly and there is a change in slope indicating onset of deformation by dislocation glide and climb which are thermally activated processes. For ceramic material having a range of melting point, the transition occurs at lower temperatures ( $0.35$  to  $0.45 T/T_m$ ) due to the presence of porosity and impurities.

Plot of hardness, as a function of temperature could be a good indicator for determining the temperature for onset of creep deformation. Hot hardness is a temperature and time dependent parameter at a particular load and hence from the plot of hot hardness vs. time, activation energy of creep

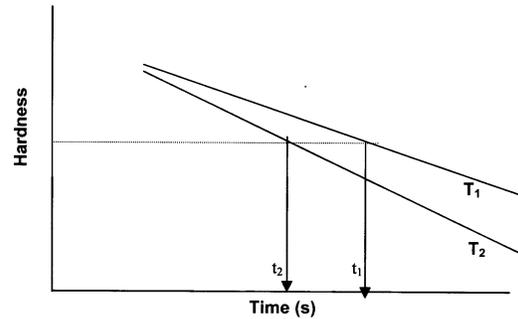


Fig. 12 Hardness as a function of time and temperature.

could be obtained using the following relation of Andrade and Mott [23,24].

$$H^m = k. \exp (-Q/ R.T). t \quad (17)$$

Where  $m$  is the stress coefficient,  $k$  a constant,  $t$  is the time of deformation.  $Q$  is the activation energy of creep.

$$\log t_1 - \log t_2 = (Q/R.t) [ ( 1/T_1) - ( 1/T_2) ] \quad (18)$$

At any two temperatures  $T_1$  and  $T_2$  and the corresponding time of deformations  $t_1$  and  $t_2$  the following relation could be derived

Hot hardness has been measured using a Nikon's micro Vickers hardness tester with diamond pyramid indenter. In these measurements, both the sample and the specimen are heated independently to the same measurement temperature and the indenter is allowed to stay for five seconds or more. After the indentation is made, the diagonals of indentation are measured on a CC TV and hardness is calculated using;

$$H_T = 1.854 P/d^2 \quad (19)$$

Where  $P$  is the load in kg and 'd' is the average diagonal length. A number of indentations are made and the averages of the hardness are taken as the hardness data. Fig.10. shows the hot hardness data of mixed (U,Pu) carbide for FBTR (Mark II). It is seen from these plots that for mixed carbide fuel containing 55% PuC (Mark II) the transition occurs at 648 K. indicating onset of creep deformation. Fig.11 shows the hot hardness data of  $UO_2$  containing 0.1%  $TiO_2$  (as a grain growth promoter)

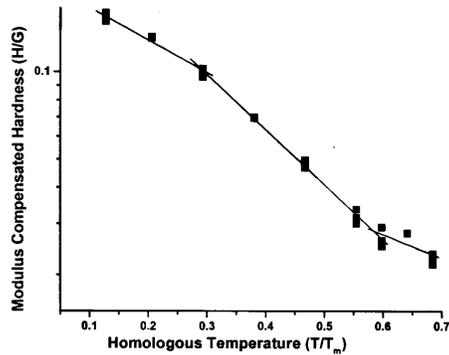


Fig. 13 Hot hardness profile of (a) hyperstoichiometric mixed carbide fuel (Mark II) for FBTR

as a function of temperature indicating a distinct change in slope at around 800K. A microstructure showing a Vicker's Indentations at high temperature on  $UO_2$  with 0.1%  $TiO_2$  is also seen. [25].

### Conclusions

The importance and need for the different thermal properties of nuclear fuels for fast and thermal reactors have been emphasized in this paper. The database generated for some of the important fuels for our thermal and fast reactors have been highlighted.

### Acknowledgements

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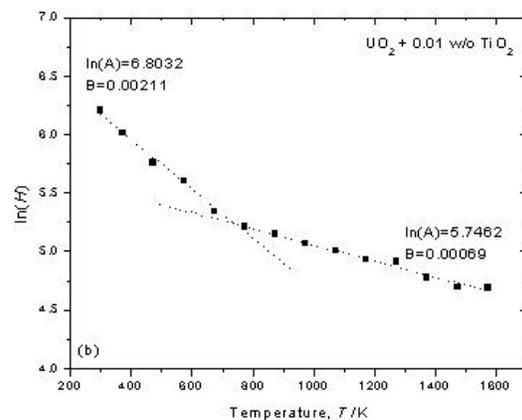
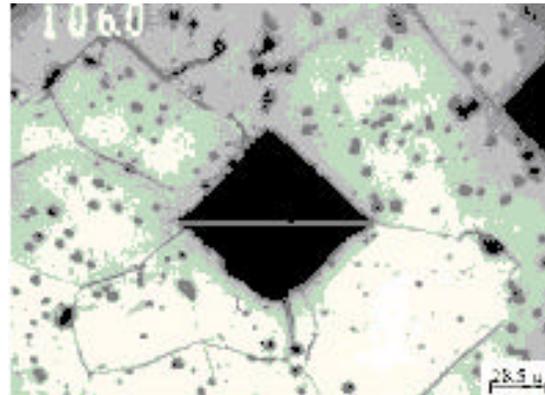


Fig. 14 Hot hardness data of  $UO_2$  containing 0.1%  $TiO_2$  (as a grain growth promoter); indicating a distinct change in slope at around 800K. A typical microstructure showing a Vicker's Indentations at high temperature is also seen [25].

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## Development of Boron and other Boron compounds of Nuclear Interest



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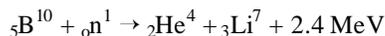


### Introduction

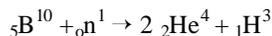
Boron is one of the few elements to possess nuclear properties, which warrant its consideration as neutron absorber material. Boron and its compounds are extensively used in nuclear industry for application as control rod, human shielding against neutrons and as sensor elements [1,2]. Boron has two principal isotopes,  $B^{10}$  and  $B^{11}$  and the effectiveness of boron as neutron absorber is due to the high absorption cross section of  $B^{10}$  isotope (3835 barns for thermal neutrons). Neutron absorption of boron is sufficiently high in the low neutron energy range to make it an excellent candidate for use in thermal reactors. At higher

energies, the cross section of most other elements becomes very small, often abruptly as in the case of cadmium, where as that of  $B^{10}$ , decreases monotonically with energy. Absolute values along the entire energy spectrum are of sufficient magnitude to make it very effective in the intermediate and also in the high-energy range. Boron has another advantage over other potential neutron absorber materials. The reaction products of neutron absorption namely helium and lithium are formed as stable, non-radioactive isotopes. As they do not emit nuclear radiation, decay-heating problems during reactor shutdowns and transfer of depleted control rods are minimal. The  $(n, \alpha)$  reaction

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however leads to release of helium, which needs attention in the design of control rods. With fast neutrons ( $E > 1.2 \text{ MeV}$ ) there is a secondary reaction as given below.



Though this reaction has a very less probability compared to  $n, \alpha$  reaction, it has great importance from the viewpoint of reactor waste, since it constitutes one of the major sources of tritium production in the reactor core.

Elemental boron, its compounds boron carbide and titanium boride are the three most important substances widely used in nuclear industry. This article traces the development of technologies and production of these materials and other associated products for the Indian nuclear energy programme [3].

### **Boron**

Boron is the 51<sup>st</sup> most common element in the earth's crust at a concentration of three grams per metric ton. Tourmaline,  $\text{Na}_4\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  is the most common mineral containing about 10% boron. The most important ore of boron is Kernite,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ . Commercial deposits are rare; the two principle ones are Mojave Desert in California and in Turkey [4].

### **Properties**

Boron is an extremely hard refractory solid with a hardness of 9.3 on Moh's scale and has a very electrical conductivity of  $1.5 \times 10^{-6} \text{ ohm} \cdot \text{cm}^{-1}$  at low temperatures. Hence boron is classified as a metalloid or semiconductor. Physical and chemical properties of elemental boron are significantly influenced by the purity and crystallinity. Amorphous boron exhibits various shades of brown, due to the presence of boron suboxide. Amorphous boron has a density of 2.35g/mL, m.p of  $\sim 2100^\circ\text{C}$ , and sublimates at approximately  $2500^\circ\text{C}$ . Crystalline boron is very inert but amorphous boron oxidizes slowly in air even at room temperature and burns spontaneously at about  $800^\circ\text{C}$ . Boron is not affected by either hydrochloric or hydrofluoric acid even on

prolonged boiling. Boron reacts with a majority of metals at high temperatures to form metallic borides.

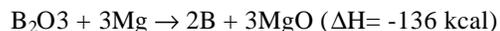
### **Uses**

In addition to its role as a neutron sensor in nuclear instrumentation, elemental boron has an important military application. Mixed with an oxidizer, boron is used as pyrotechnic in missiles and rockets. Boron is considered as a possible fuel for solid fuel ramjets.

### **Preparation**

It is extremely difficult to prepare pure boron due to its high reactivity with other metals and gases at high temperatures. Due to extreme hardness, pulverization of boron introduces impurities from the crushers and causes superficial oxidation.

In the laboratory, boron can be produced by thermal decomposition of boron hydrides such as diborane,  $\text{B}_2\text{H}_6$ , or by thermal/electrolytic reduction techniques. The Moissan process, reduction of boric oxide with Magnesium, is the most widely used commercial method of boron production. This process is strongly exothermic.



This reaction is exothermic in nature and is initiated at a temperature of  $700\text{-}800^\circ\text{C}$ . Magnesium metal reacts with boron resulting in the formation of mixture of borides  $\text{MgB}_2$ ,  $\text{MgB}_4$ , and  $\text{MgB}_{12}$ . At higher temperatures, however magnesium boride decomposes into its elements. On the other hand calcium and aluminium form stable borides and hence cannot be used as reductants. For preparation of pure boron, use of raw materials in as pure form as possible is recommended, since all the impurities get reduced and join the final product.

In the electrolytic process, fused electrolytes containing borates or metal fluoroborates are electrolysed. In our laboratory two electrolytic routes for the extraction of boron have been developed [5]. The methods are extraction of boron by fused salt electro winning from  $\text{KCl-KF-KBF}_4$  electrolyte and electroextraction from soluble  $\text{B}_4\text{C}$  anodes in  $\text{NaCl-KF-KBF}_4$  melt. The electrolytic cell essentially consists of a cylindrical inconel reactor provided with a graphite crucible which holds the

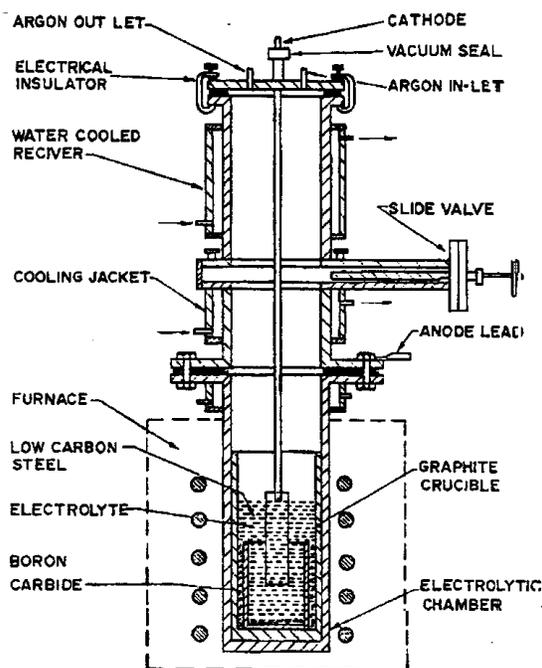


Fig. 1 Electrolytic cell

molten electrolyte and also acts as anode. A water-cooled top flange provided with facilities for introduction of cathode as well as gas ports is used to close the reactor. The winning cell differs from the soluble anode cell in two respects. It does not contain the anode feed namely  $B_4C$  and the perforated graphite basket, which holds the feed. Sketch of electrolytic cell used for electro extraction of boron from boron carbide is shown in Fig. 1.

In electro winning, the following overall reaction can be assumed to take place.



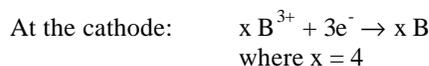
During electrolysis, build up of KF is found to be detrimental, as it results in the decrease in conductivity of the electrolyte. To a great extent this effect can be nullified by the periodical addition of KCl. Under optimum operating conditions, it is possible to obtain a current efficiency of about 84% and a boron yield of >90%.

In the soluble anode process,  $B_4C$  packed in graphite basket acts as anode. The following two



Fig. 2 Electrodeposit of boron

reactions can be assumed to be taking place during electro deposition.



Hence in this case, electrolysis is conducted at a low voltage of just above 1V. In this process, 98% current efficiency is achievable and boron yield of about 82% under the optimum operating conditions. Photo of cathode with boron deposit is presented in Fig. 2.

The cathodic deposit of boron needs to be washed with water to dissolve accompanying salt. It is further ground to required size and aqueous processed to obtain pure boron. As boron is a very hard material, size reduction is extremely difficult. The grinding operations can be carried out by using either low speed ball mills for a prolonged time or high-energy equipments such as attritor or planetary mills in a comparatively shorter time. When the grinding media and the container is made of ordinary metals or alloys, the ground boron is highly contaminated with the grinding media and requires an additional acid leaching step to purify the powder. Alternately expensive equipments with tungsten carbide lined reactors and grinding media can also be used for fine grinding of boron with out much contamination.

Technology for the production of boron powder from boron carbide, developed by our laboratory has been transferred to defense units at

Dehu Road and Khamaria. Boron powder produced at these factories has been found to be of superior quality for defense application compared to that of magnesium reduced powders.

A colloidal solution of boron powder is used for the fabrication of coated elements used as sensors in neutron counters. Specification of boron powder for this purpose is stringent in terms of particle size and purity, to obtain a uniform coating thickness of 0.8 to 1.2 mg/cm<sup>2</sup>. Neutron sensor elements fabricated from boron powders of natural isotopic composition as well as enriched in B<sup>10</sup> prepared in our laboratory are being used in neutron counters at various locations of different types of reactors [6].

### **Boron Carbide**

#### *Properties*

Boron carbide is one of the most important compounds of boron for reactor applications. Boron carbide is chemically inert and contains high content of boron (nearly 80%). It is generally accepted that in B-C system, one binary phase B<sub>13</sub>C<sub>2±x</sub> exists with a wide homogeneity range of 8.8 to 20.0 at % carbon. It is a very hard material, and only diamond and cubic boron nitride are known to be harder than boron carbide.

Upto 1200°C, the oxidation is limited by the diffusion of reagents through the oxide layer. Boron carbide is not attacked by cold chemical reagents but gets oxidised by hot oxidizing acids such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub> etc. It reacts with many metals to form carbides or borides at 1000°C. Al and Si form substitution compounds.

#### *Uses*

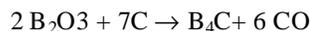
Boron carbide is used as control rod material in boiling water reactors and also as shut off rods in various types of reactor configurations. For fast breeder reactors, boron carbide with enriched B<sup>10</sup> isotope is the most preferred material for control of neutrons. For neutron shielding, boron carbide is used as powder, compacts and as composites with aluminium, rubber/ polythene etc. Boron carbide is an important starting material for the preparation of borides. Other industrial uses of boron carbide are as abrasives for lapping, grinding, polishing media for

hard materials, wear-resistant components and in light weight armor.

#### *Preparation*

Boron carbide is usually prepared by carbothermic or magnesiothermic reduction of oxide in presence of carbon as per the following reactions [7,8].

#### *Carbothermic reduction*



This process is generally carried out at temperatures in the range of 1900°C - 2500°C.

#### *Magnesiothermic reduction:*



This reaction is highly exothermic in nature. As the reductant magnesium has high vapour pressure at the reaction temperatures of above 1000°C, enough care has to be taken in carrying out this process such that, the reaction does not become explosive in nature. The products of magnesiothermic reduction have the following disadvantages, namely, the carbide obtained is of sub micron size, as magnesium oxide acts as grain growth inhibitor and the magnesium content of the carbide is high due to the formation of magnesium boride during the reduction. The reaction products also have to be purified by acid leaching to remove magnesium oxide and excess magnesium.

Carbothermic reduction route was developed using a graphite resistance furnace [9]. A typical boron carbide production run, using a heating element of 37 mm diameter and 1000 mm long graphite rod is described below. Charge consisting of boric acid and petroleum coke (-325 mesh) in the ratio of 10:3 by weight is mixed thoroughly in a double cone mixer and placed around the heater rod. Electric power to the heater is increased in steps to attain a final voltage of 30-32V (1800-2000A) in an hour from start. As the charge melts, a mixture of fresh and old material is added. Appearance of burning CO at the top of the furnace indicates the onset of vigorous reaction. Furnace with the reacted mass is allowed to cool. Boron carbide formed close to the high temperature zone and the surrounding

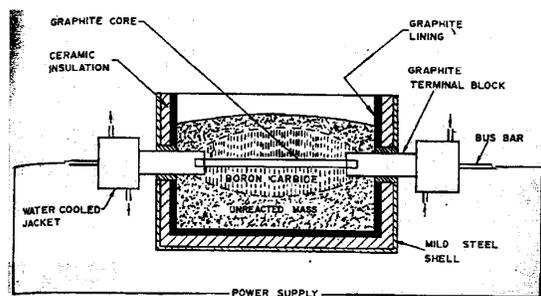


Fig. 3 Graphite resistance furnace for production of boron carbide

partially reduced mass are visually separated and collected. About 12kgs. of boron carbide is obtained in each batch. Sketch of graphite resistance furnace for boron carbide production is shown in Fig. 3.

Though boron carbide can be prepared by simple methods, serious problems are encountered in further processing for size reduction. Boron carbide lumps, as obtained from the furnace, are crushed to small pieces in a jaw crusher and then to a fine powder in a pulveriser. This powder needs purification to remove the small amounts of unreacted / partially reduced charge and contaminants picked up during the size reduction operations. Aqueous leaching to remove the impurities is carried out using hydrochloric acid in polypropylene tanks, using silica-cased heaters for heating and air for agitation. Washed, dried and graded powder is stored in airtight drums. Mixture of graded powders is packed by vibro compaction in stainless steel tubes for use as control rods and shielding elements.

Technology for the production of abrasive grade boron carbide powder has been transferred to private industries. One of the producers, namely Boron Carbide India Ltd. has been successfully marketing this product in our country, under the trade name Vajrabor for the last two decades.

For capture of fast neutrons, boron carbide with higher amounts of  $B^{10}$  isotope than naturally occurring composition (19-20%) is needed. During the production of boron carbide by carbothermic reduction substantial amount of boron is lost due to high volatility of boron oxides and also locked up in

the partially reduced stock of the furnace returns. This method is not suitable for production of enriched boron carbide, as loss of enriched boron is not tolerated due to high costs of enrichment. An alternate method, developed in our laboratory involves the production of enriched boron by electrolytic process followed by synthesis of enriched boron carbide from the elements. Control rod elements for the forthcoming Prototype Fast Breeder Reactor (PFBR) at Kalpakkam, Tamil Nadu are proposed to be fabricated through this method.

### Densification of Boron Carbide

Due to the presence of high fraction of strong covalent bonding, low plasticity and high resistance to grain boundary sliding, sintering of stoichiometric boron carbide ( $B_4C$ ) powder is extremely difficult. In our laboratory experimental studies were conducted on pressure less sintering of boron carbide. Effect of addition of carbon, titanium boride ( $TiB_2$ ) and zirconium dioxide ( $ZrO_2$ ) on densification was investigated [10].

Some of the salient results of sintering studies are presented below. Particle size of boron carbide powder and sintering temperature are two most important parameters for densification by pressure less sintering. While sintering particles with a size range of 0.5 to 2.0  $\mu m$  median diameter at temperatures below 2300°C, density obtained was less than 85%  $\rho_{th}$ . Higher sintering temperature of 2375°C and a fine particle size of median dia. 0.5/0.8  $\mu m$  gave a density > 90%  $\rho_{th}$ . Addition of carbon helped in obtaining densities of >90%  $\rho_{th}$  at a slightly lower sintering temperature of 2325°C as well as in grain refinement.  $TiB_2$  addition was not found to be helpful in sintering of boron carbide.  $ZrO_2$  as sintering additive was found to be very effective in reducing the sintering temperature. Density of 93%  $\rho_{th}$  could be achieved by sintering with 5wt%  $ZrO_2$  at a comparatively lower temperature of 2275°C. Knoop hardness ( $HK_{100}$ ) of sintered pure boron carbide pellets was measured to be 24-25 GPa and that with  $ZrO_2$  as 32 GPa. Fig. 4 and 5 present the structure of sintered boron carbide under optical and Scanning Electron Microscope.

Sintering by hot pressing is the most preferred industrial method for production of near net shape

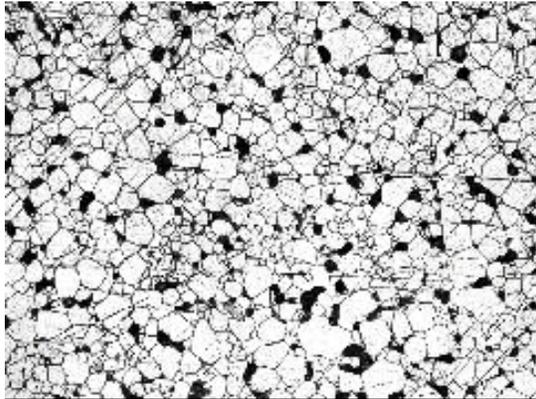


Fig. 4 Microstructure of sintered  $B_4C$

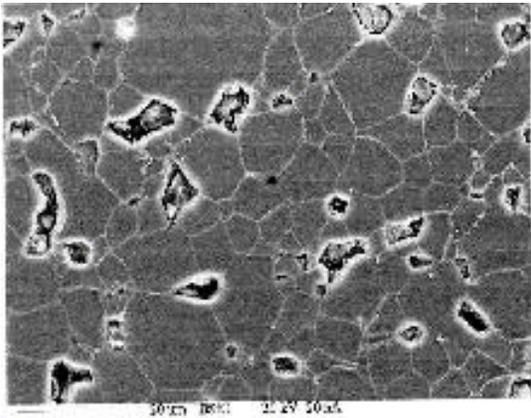


Fig. 5 SEM of sintered boron carbide

products but it has the drawback of low productivity and higher investment. In our laboratory, facility exists for preparation of sintered discs of boron carbide of diameter up to 126mm. Optimisation of powder characteristics and sintering parameters for production of boron carbide pellets for use in research and prototype reactors are being carried out using this facility.

#### **Boron Loaded Products**

##### ***Borated Rubber Sheet***

For plugging neutron leak surrounding beam holes in research reactors and also in the storage of radioactive materials, flexible rubber sheets containing boron carbide are effectively used. Our laboratory has developed the process for production of Bocarsil, a composite of silicon rubber and boron

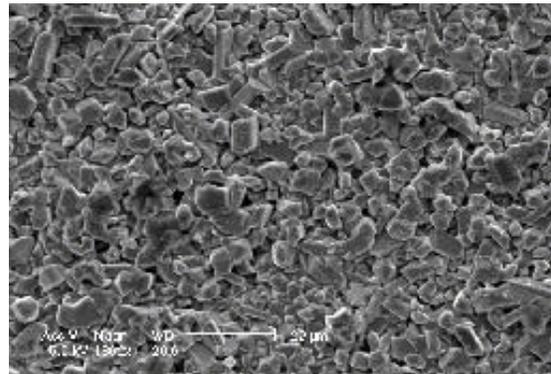


Fig. 6 SEM of hot pressed  $TiB_2 + MoSi_2$

carbide. Silicon rubber was chosen for its longer shelf life. Fine boron carbide powder with a median particle size in the range of 10-20 $\mu m$  is thoroughly mixed with silicon rubber in a sigma kneader, rolled into sheets of required thickness and then cured at a temperature of 150 $^{\circ}C$ . A maximum loading of 50 % of boron carbide by weight can be incorporated into these sheets. It has excellent flexibility and a neutron absorption cross-section of 30 barns, for thermal neutrons.

##### ***Boron Carbide/Aluminium Composite***

For application at higher temperatures, boron, a composite made of boron carbide and aluminium powders is in use. This material is fabricated by powder metallurgy route. Powders of boron carbide and aluminium in the required ratio are mixed thoroughly and hot pressed at a temperature close to the melting point of aluminium. The sintered compact is sandwiched between aluminium sheets and picture framed all around. This block is then hot rolled to produce boron sheets of required thickness. Boron sheets with a maximum boron carbide content of 50-60 wt% could be produced with good adhesion. Boron and borated rubber sheets produced in our laboratory were used in the construction of Dhruva, a research reactor at Trombay, Mumbai.

##### ***Poly Boron Blocks***

Composites with boron content of less than 10% are also useful for neutron shielding in instruments using radioactive isotopes. Polyboron is a composite, made up of boron compound such as boric acid in polythene matrix. The procedure for

fabrication of polyboron shapes consists of mixing of the chosen polymer with a boron compound, melting the mixture and casting into moulds of requisite shape. These cast blocks can be easily cut, drilled, worked in lathes etc. to meet the complex final shapes. Hydrogen content of the polymer also acts as a good moderator for neutrons.

### **Titanium Di-boride**

Borides are considered suitable control rod materials, especially for high temperature reactors. Titanium boride is one of the candidate materials for such an application, due to its high melting point of  $3225 \pm 25^\circ\text{C}$ , low density of  $4.5 \text{ gm/cm}^3$  and a good thermal conductivity.

### **Preparation**

In our laboratory borothermic process involving reduction of titanium dioxide by boron carbide has been developed for the production of titanium boride.



This carbide-oxide reaction is the simplest method of preparation of compound, when both reactants are available in pure and finely divided form. Accurately weighed charge components are intimately mixed in a planetary mill for homogenization and compacted using a hydraulic press. The pellets are heated in a vacuum induction furnace to a temperature of  $1600\text{-}1800^\circ\text{C}$  under a dynamic vacuum of  $1 \times 10^{-5}$  m.bar. The product, a loosely sintered boride, is easily crushed and ground to fine powder. Quantity of impurity contents 'O' and 'C' in the product depends on the charge composition and the operating parameters such as temperature, pressure and period of soaking. The process has been optimised for obtaining a pure boride with these impurity elements less than 0.5% each.

### **Densification of Titanium Boride**

Due to its high melting point, sinter addition is essential for consolidation of titanium boride. Studies on the densification of titanium boride with and without the addition of moly- disilicide were carried out [11]. Molydisilicide was synthesized from its elements in the laboratory. Pressures less

sintering experiments were conducted in a graphite resistance heated furnace in an atmosphere of argon and hydrogen. Hot pressing experiments were carried out in a 50-ton capacity press with graphite resistance heated furnace. Salient features of experimental studies are given below.

Dense  $\text{TiB}_2$  of  $\sim 98\%$   $\rho_{\text{th}}$  with fine microstructure ( $\sim 1\text{-}2 \mu\text{m}$ ) could be obtained by hot pressing  $\text{TiB}_2$  powders at a temperature of  $1800^\circ\text{C}$ . By the addition of  $\text{MoSi}_2$  (10 wt%), hot pressing temperature could be brought down to  $1700^\circ\text{C}$ . In case of pressure less sintering process, a maximum of  $91\%$   $\rho_{\text{th}}$  could be obtained even with addition of  $\text{MoSi}_2$  and a higher sintering temperature of  $1900^\circ\text{C}$ . The optimized composite ( $\text{TiB}_2\text{-}10 \text{ wt } \% \text{ MoSi}_2$ ) exhibited a hardness value of  $\sim 26 \text{ Gpa}$ . Fig.6 presents SEM picture of hot pressed Titanium boride with molydisilicide.

The recent publications indicate the revived interest in the preparation of boron, its compounds and preparation of components. Efforts are directed towards the preparation of pure and fine powders in less number of steps, mechanical alloying, direct synthesis of mixed compounds, explosive compaction etc.

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