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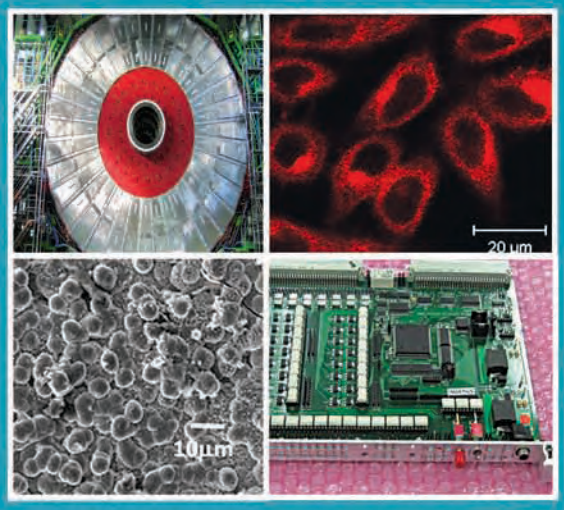
BARC NEWSLETTER



IN THIS ISSUE

In the Forthcoming issue

1. **Early Detection of Coronary Heart Disease using Peripheral Pulse Analyzer**
   G.D. Jindal et al.

2. **Development of Fluidized Bed Thermal Denitration**
   Neetu A. Baveja et al.

3. **Passive Gamma Scanning: a Powerful Tool for Quality Control of MOX Fuels**
   K.V. Vrinda Devi and J.P. Panakkal

4. **MetProSoft-10: Image Analysis Software for Metallographic Measurements**
   Lizy Pious et al.

5. **Studies on Improvements in Thoria Dissolution Process for Reprocessing Application**
   C. Srinivas et al.

6. **Characterization of Deformation Microstructure of TiAl alloys using Electron Microscopy**
   J.B. Singh et al.

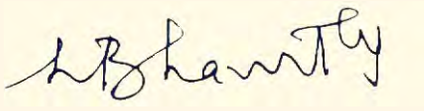
CONTENTS

From the Editor's Desk

We are happy to bring you the second issue of this year's BARC Newsletter. We have been getting good response to the feature "Brief Communication" introduced this year. We invite all BARC Scientists and Engineers to contribute to this feature and submit short one-page write-ups reporting the latest Scientific/Technical developments carried out by them in their respective areas of work. The proforma for submitting these short articles is available at the SIRD Divisional website under the hyperlink "Request Forms".

This issue carries seven articles and also six Brief Communications. The first article is from Dr. S. Kailas, Director, Physics Group, which features a very interesting and informative report of Physics research at BARC. The article gives a broad overview of Basic research in Physics, design and developmental activities relevant to the mandate of DAE and National Facilities made available by the Physics Group for R&D in various areas of Physics. One of the Research Articles describes a method of Solar photocatalytic water splitting for production of Hydrogen, the green energy source of the future. The second Research Article focuses on the development of Carbon-based materials used for nuclear applications. Three Technology Development Articles and a Feature Article are covered in this issue. We are sure this issue will also provide enough reading material in diverse areas.

We will be shortly inviting all the DAE Award winners for the year 2010, as well as other award winners for the year 2011, to submit their R&D contributions for the Founder's Day Special issue of the BARC Newsletter. It will be released in October this year, on the occasion of Founder's Day.



Dr. K. Bhanumurthy
On behalf of the Editorial Committee

Development of Peptide Mimic Shell Cross-linked Magnetic Nanocarriers for Theragnostic Applications

Chemistry Group

The combination of diagnosis and therapeutics (theragnostic) allows a large degree of control over the treatment of cancer. Magnetic nanoparticles provide a unique platform for theragnostic applications because of their biocompatibility, magnetic resonance (MR) imaging capability, heating ability under AC Magnetic Field (AMF), and their sizes which are comparable to that of functional biomolecules.

Water dispersible, pH responsive peptide mimic shell cross-linked Fe_3O_4 magnetic nanocarriers (PMNCs) were developed by facile soft-chemical approach. These nanocarriers are of an average size of about 10 nm, resistant to protein adsorption under physiological medium and transform from a negatively charged to a positively charged form in an acidic environment. The terminal amino acid on the shell of nanocarriers allows us to create functionalized exteriors with high densities of organic moieties (both amine and carboxyl) for conjugation of drug molecules (Fig. 1 given below).

The drug-loading efficiency of the nanocarriers was investigated using doxorubicin hydrochloride (DOX) as a model drug to evaluate their potential as a carrier system. Results showed high loading affinity of nanocarriers for anticancer drug, their sustained release profile, magnetic field induced heating and substantial cellular internalization. The confocal microscopy, flow cytometry and cell viability assay demonstrate that use of these nanocarriers as delivery vehicles could significantly enhance the accumulation of drug in target cancer cells leading to a high therapeutic efficacy which efficiently inhibit their proliferation. Moreover, the enhanced toxicity to tumor cells by DOX loaded PMNCs under AMF suggest their potential for combination therapy involving hyperthermia and chemotherapy. In addition, these nanocarriers exhibit excellent T_2 MR contrast properties (r_2 relaxivity: 217 $mM^{-1}s^{-1}$). Specifically, the developed novel nanocarrier can serve as base material for diagnosis as well as therapy.

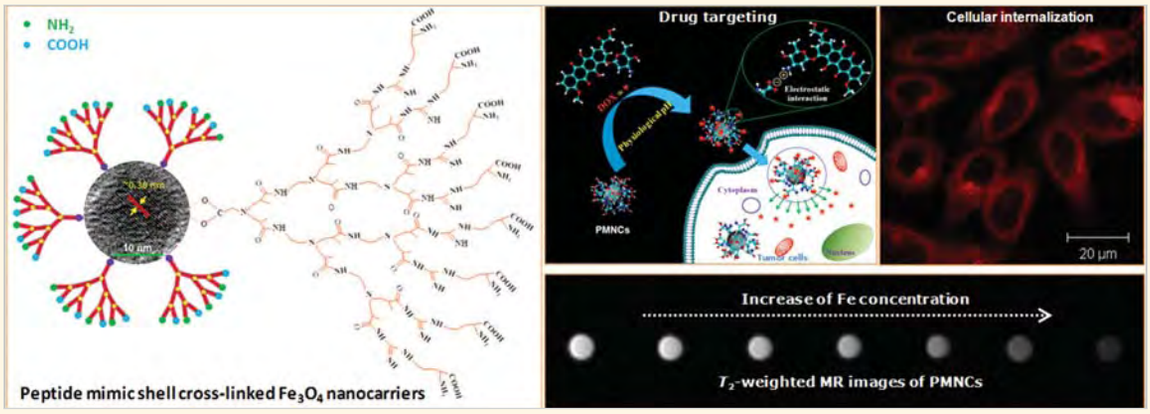


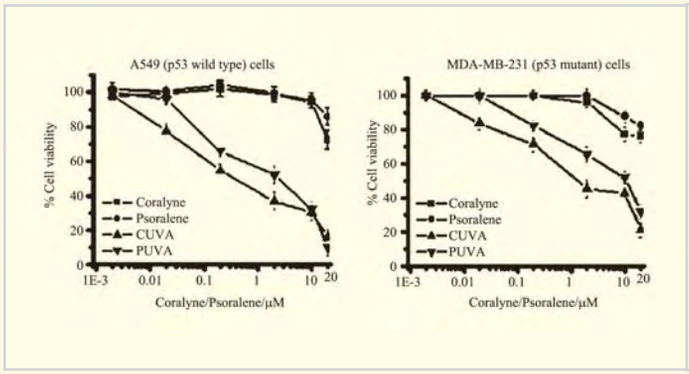
Fig.1: Peptide mimic shell cross-linked magnetic nanocarriers (PMNCs) and their drug targeting scheme, cellular internalization (red fluorescence from DOX loaded PMNCs) and T_2 weighted MR images

Photochemotherapy by Coralyne and UVA (CUVA): A Novel Strategy for Cancer Management

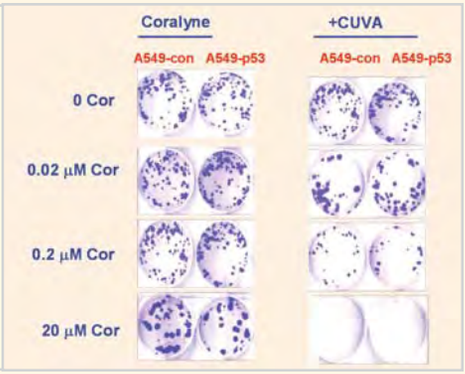
Chemistry Group

Photodynamic therapy (PDT) is recognized as a minimally invasive and non-toxic treatment strategy for a wide range of medical conditions, including cancers. However, PDT is useful only to treat localized but not metastatic cancers. Instead, photochemotherapy that combines the chemotherapeutic and photosensitizing properties of a drug might provide a promising modality in cancer treatment. To this end, our group has recently shown that a combination of the alkaloid, Coralyne and UVA (CUVA) could dramatically enhance DNA damage and a p53-independent apoptosis in different cancer cells compared to coralyne alone.

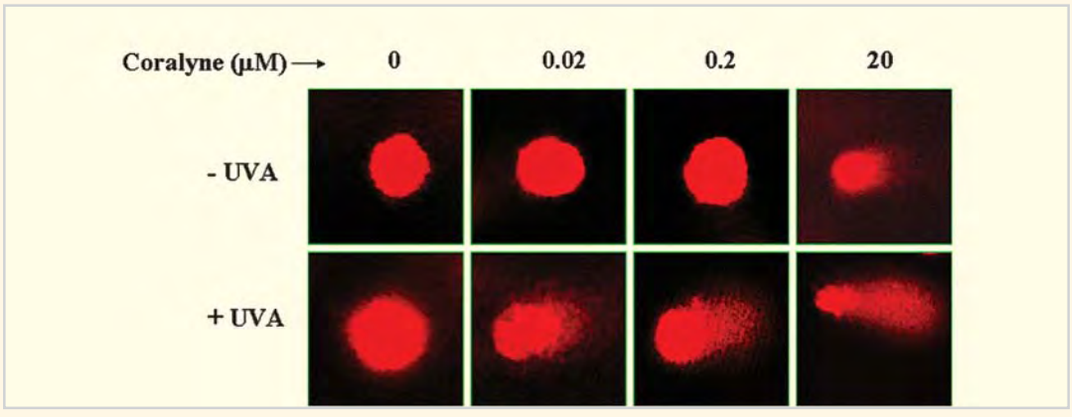
The CUVA treatment showed superior efficacy over the clinically-used Psoralene and UVA (PUVA) treatment in inducing apoptosis in human breast (MDA-MB-231 and MCF-7), skin (A431) and lung (A549) carcinoma cell lines. Thus, the CUVA treatment may represent a novel mechanism-based protocol for management of a wide range of tumors. Further, the ability of CUVA to sensitize cells regardless of the p53 status may be of clinical relevance given that approximately 50% tumors have defects in the p53-dependent apoptotic pathway.



Superior efficacy of CUVA over PUVA in p53-independent PDT-treatment clonogenic assay



Superior efficacy of CUVA over coralyne as revealed by clonogenic assay



CUVA induces better DNA damage than coralyne as revealed by comet assay

Controlled Uptake and Release of Phototherapeutic Porphyrin Dye using Surface Functionalized Silver Nanoparticle Conjugates

Chemistry Group

Nanoparticles provide a versatile intermediate between the molecular and macroscopic worlds. Recently there has been a growing trend towards making noble metal nanoparticle conjugates, particularly of coin metals like gold, silver or copper due to their extensive demand in molecular plasmonic devices, biosensing, catalysis, biomedical applications and so forth. Typically, modulation of surface plasmon features has been attempted by introducing modifiers or functional units to construct tailor-made functional devices. We report the synthesis of surface-functionalized silver nanoparticle (AgNP) conjugates with controlled size (5-30 nm) displaying different characteristic colours based on supramolecular approach involving macrocyclic host, cucurbit[7]uril (CB7). These AgNP conjugates (CB7-AgNP) display enhanced molecular recognition features for the phototherapeutic porphyrin dye, 5,10,15,20-tetrakis(4-*N*-methylpyridyl)-porphyrin (TMPyP). The uptake and release of TMPyP dyes with CB7-AgNP conjugates by external stimuli like amantadine hydrochloride has been demonstrated. Such supramolecular engineering of nanoparticle conjugates suggests prospective applications in biomedical sciences, especially drug delivery mechanism and therapeutic activation of drugs.

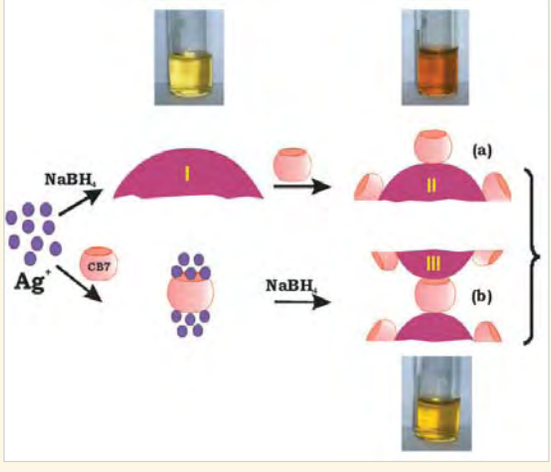


Fig. 1: Synthesis and characteristic colours of silver nanoparticle conjugates

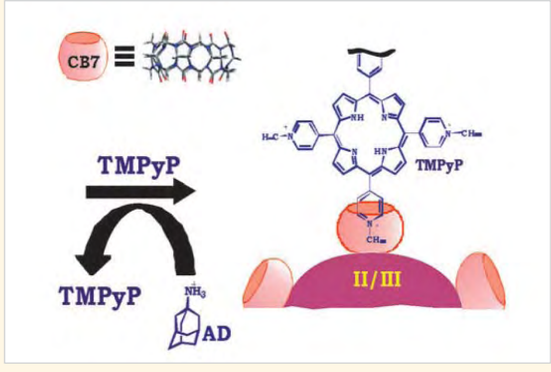


Fig. 2: Uptake & release mechanism

Designing Novel Nanomaterials for Application in Nuclear Waste Management

Chemistry Group

Understanding the behavior of radioactive nuclide elements in different environmental conditions is an active area of research. We have investigated the possible mechanism of interaction between carbon nanotubes (CNT) and uranyl ion through density functional theory based calculations. It is shown that functionalized carbon nanotubes can be used to bind uranyl ions much more efficiently as compared to their unfunctionalized counterpart. In this regard, we have considered various functional groups such as carboxylic acids, oxo and macrocycles. The uranyl binding energies are sensitive to the nature of the functional groups rather than the type of carbon nanotube. The binding takes place preferably at the functionalized sites, although pH could determine the strength of uranyl binding. Our predicted results correlate well with the uranyl sorption studies on CNT from experiments. Research is in progress to find a suitable host molecule which can bind actinyl cations selectively. These findings are new and can open up a new era for actinide speciation and separation chemistry using functionalized carbon nanotubes.

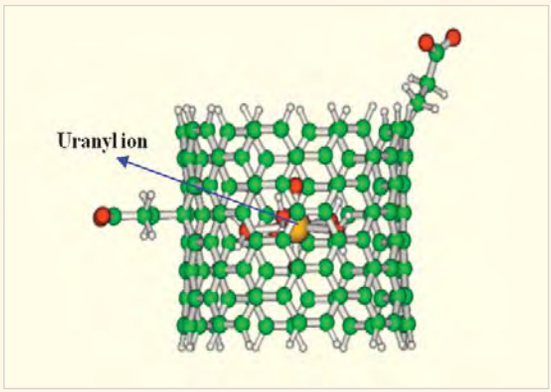


Fig. 1: Optimized structure of functionalized CNT encapsulating a uranyl ion.

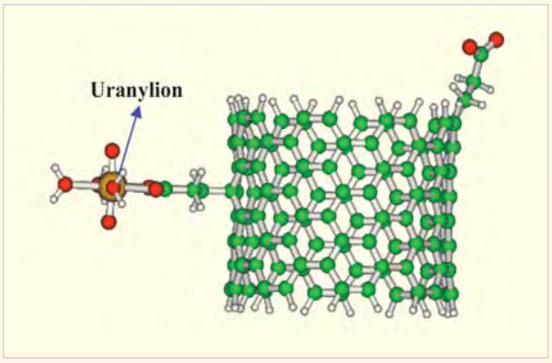


Fig. 2: Optimized structure of binding of uranyl ion at the functionalized CNT site.

Preparation and Characterization of $(U_{0.47},Pu_{0.53})O_2$ Microspheres for Test Pin Irradiation in FBTR

Radiochemistry and Isotope Group

Conventionally ceramic nuclear fuels are prepared in the form of cylindrical pellets by 'powder-pellet' route having several process steps e.g., milling, granulation, power compaction, etc. and is associated with radiotoxic dust hazard. On the other hand Sol-Gel process, being a wet chemical route, is dust-free, minimizes the problems of radioactive aerosols and is ideally suited to remote and automated manufacturing of highly radiotoxic plutonium and ^{233}U bearing mixed oxide fuels.

Vibro-compacted sphere-pac fuel pin is one of the methods for loading sol-gel derived fuel particles in a clad tube. The fuel is in the form of small spheres, normally in two or three different size fractions. Apart from the advantages during fabrication, sphere-pac fuel has exhibited comparable if not better performance during irradiation. In view of various positive aspects associated with sol-gel derived sphere-pac fuel and need of our own irradiation data, the task force on sol-gel vibro compaction technology, comprising scientists from BARC and IGCAR, has proposed to irradiate a capsule containing two sphere-pac pins and a reference pin with solid pellets in FBTR for 300 h. MOX fuel microspheres of 780 μm size containing 53 % PuO_2 prepared at BARC and natural UO_2 microspheres of 115 μm size are vibro compacted in the ratio 3:1 to achieve a smear density of 80 % TD. This is to be irradiated initially for 100 h at 205 W/cm and then for 200 h at 260 W/cm peak power.

The internal gelation process, which was originally developed at the KEMA labs Netherlands, was significantly modified to prepare high density MOX microspheres containing such high concentration of Pu for the first time. About 72 g of characterized MOX microspheres were sent to IGCAR for sphere-pac fuel pin fabrication and irradiation.

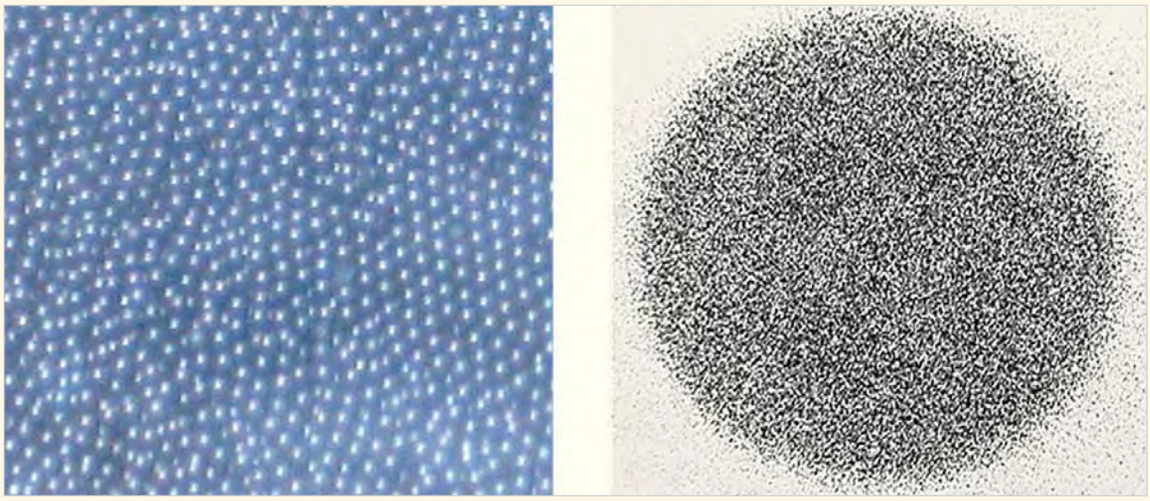


Fig. 1: (a) Sintered $(U_{0.47},Pu_{0.53})O_2$ Microspheres for Sphere-pac Fuel Pin fabrication
(b) Auto α Radiography of MOX microspheres Exhibiting Uniform Distribution of Pu

Hot Vacuum Extraction- Quadrupole Mass Spectrometry (HVE-QMS) for Ageing Management of Zr-Nb Coolant Channels

Radiochemistry and Isotope Group

Ageing management of coolant channels requires deuterium pick-up rate to be quantified for ensuring smooth operation of the reactor. The whole exercise involves determining deuterium pick-up in wafer thin (sliver) samples scrapped from the interior of the coolant channels (after removing the protective oxide layer) without sacrificing their integrity. Hot vacuum Extraction cum Mass Spectrometry (HVE-MS) is ideal for this task.

For this purpose, a HVE-QMS equipment was conceptualized, designed and fabricated indigenously with the help of local manufacturer M/s. Vacuum Techniques Pvt. Ltd., Bengaluru. A photograph of the equipment installed in RLG is shown in Fig. 1. Experimental conditions of the measurement methodology were optimized.

Fig. 1: HVE-QMS System

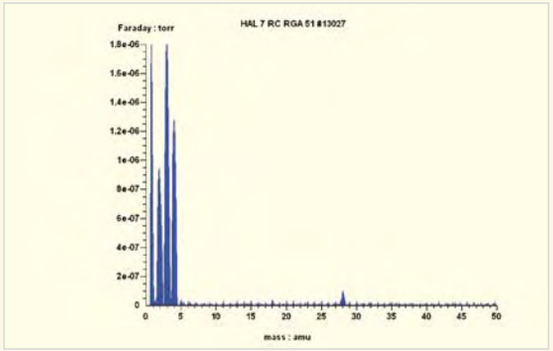


Fig. 3: Typical mass spectrum in HVE-QMS

Sensitivity factors for H_2, HD and D_2 obtained from the sensitivity plots shown in Fig. 2 were validated by analyzing mixture of H_2 and D_2 gases with known composition. Since no standards of deuterium are available, the method has been standardized by analyzing H_2 & D_2 charged Zr-Nb alloy coupons with known composition of H_2 & D_2 gases. The methodology has been validated by analyzing several hydrogen standards in various matrices like SS, Ti and Zr. Precision in the measurement was found to be 10%. Several sliver samples obtained from Indian PHWRs have been analysed. Typical mass spectrum obtained for one of the sliver samples is given in Fig. 3. The axial variation of D_2 content for a coolant channel operated for 8.5 EFPY is shown in Fig. 4.

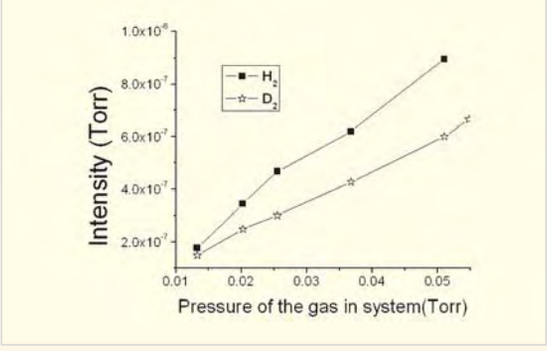


Fig. 2: Sensitivity plots of H_2 and D_2 in QMS

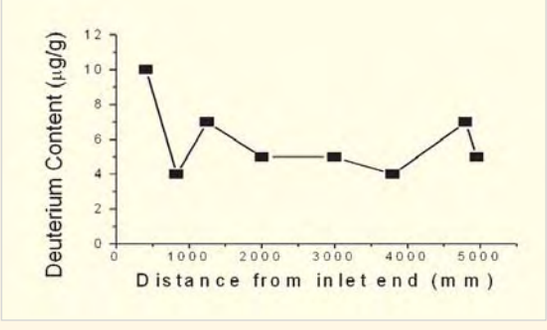


Fig. 4: Deuterium content in a typical coolant channel

Frontiers in Science & Cutting Edge Technologies: Physics Group in BARC

S. Kailas
Physics Group

Abstract

The Physics Group in BARC continues to pursue R & D programmes which are excellent and relevant to the DAE mandate. The Physics Group has an active basic research programme which spans a range of energy and length scales and includes a comprehensive study of matter at extremes. The indigenous development of technologies which include precision instrumentation, particle accelerators, synchrotron and neutron beam lines and high energy gamma ray telescope systems, is an intense activity of the group. The Physics Group also operates a number of national facilities for users from the DAE and universities for pursuit of frontiers in Physics.

Introduction

Right from inception of the DAE, the physics discipline has occupied a pride of place in the growth of atomic energy in the country. Over the years the Physics Group (PG) has contributed significantly to the various R & D programmes of BARC. The primary mandate of the PG continues to be pursuit of excellence in frontiers of physical sciences, spanning a wide dynamic range of length and energy scales, cutting across disciplines and investigation of matter at extremes of pressure and temperature. The PG programmes also include "directed basic research" and "applied research" in areas of relevance to the DAE. The scientific & technical personnel of PG are contributing to the operation and maintenance of national facilities like the 14 MV + SC Linac at TIFR, 6 MV FOTIA and PURNIMA fast neutron facility at Trombay, National facility for neutron beam research at DHRUVA, High energy gamma ray telescope TACTIC at Mt. Abu, Cosmic –ray neutron monitor at Gulmarg and Synchrotron beam-based set ups at INDUS, RRCAT, Indore. Further, the PG has a viable and sustained programme of indigenous development of detectors, crystals, sensors, beam line instrumentation, accelerator sub-systems, mass spectrometers, X –ray and neutron based imaging techniques, multilayer mirrors, sample analysis methodologies and these developments / services cater to the needs of many other units of DAE and also various divisions of BARC.

Currently the PG is taking a lead role in the development of the MACE gamma – ray telescope at Hanle and the state- of- the- art beam lines at INDUS, RRCAT, Indore. As a part of the Indian ADS programme, the PG is spearheading the design and development of Low Energy High Intensity Proton Accelerator (LEHIPA) and the PURNIMA fast neutrons coupled to a sub-critical U core. In addition, the PG is participating in several international programmes / performing / planning experiments at CERN – LHC, BNL(USA), GANIL(France), FAIR(GSI) , Fermi lab, ILL(Grenoble), PSI(Switzerland), Elletra(Italy). The PG is also actively involved in the setting up of the mega science project India-based Neutrino Observatory (INO) and the development of high intensity and high energy proton accelerator as a part of the Indian ADS programme. The S&T personnel of PG are contributing to HRDD / teaching activities at BARC Training school, Mumbai university – DAE Centre of Excellence in Basic Sciences at Mumbai university and BRNS programmes which strengthen the collaboration between the DAE and the teaching institutes.

In this article we shall summarise some of the highlights of the PG programmes under various heads - basic research, design and development, projects, O & M of facilities and services.

Basic Research

The basic research programmes in Physical Sciences involve investigation of phenomena which cover a range of energy scales , fraction of eV to a few TeV and length scales, a few fm to several light years. The basic motivation continues to be the understanding of the structure of matter and behaviour of matter at extreme conditions. The reaction mechanisms taking place in different time scales is another area of intense investigation. Both basic research and directed basic research programmes are being pursued.

In the area of astrophysics, the frontier areas are: discovery and measurement of high energy gamma ray emissions from the active galactic nuclei in particular, understand the origin and the acceleration mechanism of these high energy gamma-rays, establish connection between the phenomena of high energy gamma-ray emission and the energetic cosmic rays dominated by particles and finally bridge the gap between the ground based and the satellite based observations in terms of energy limits. Some of the recent observations include the flaring activity of extragalactic objects Mkn421 and Mkn 501 with the TACTIC (TeV Atmospheric Cherenkov Telescope with Imaging Camera) at Mt. Abu.

Nuclear physics research is expanding in three directions: Study of nuclear matter at high energy and density and observation of phase changes(QGP, hadron interactions, structure and medium effects); shape evolution of the nucleus as a function of excitation energy and angular momentum(high spin spectroscopy and GDR): Investigation of the nuclei away from the line of stability to map the nuclear landscape(stable and weakly bound projectile induced fusion and fission reactions) . Both the national (accelerator facilities at Kolkatta, Delhi and Mumbai) and international facilities at BNL, CERN, GANIL and GSI are being used. A number of state-of- the- art detector arrays(like the charged particle detector array) have been built for these investigations. Fission fragment spectroscopy facility at CIRUS/DHRUVA is an unique facility in the country. A state-of-the-art Resistive Plate Chambers (RPC) detector lab has been set up for LHC and INO programmes.

In the area of Atomic and Molecular physics research, multiwavelength investigation ranging from UV to IR is a recurring theme of the investigations. Some of the recent programmes include: investigation of molecules which are of atmospheric and astrophysical interest. VUV spectroscopy of solids - lanthanide doped glasses and radiation treated solids is another activity. For VUV spectroscopy studies of exotic molecules, free radicals and molecular solids, the PG has developed a full scale Matrix Isolation Spectroscopy set up at INDUS in collaboration with IGCAR, Kalpakkam and RRCAT, Indore. Laser spectroscopy is an important activity which is relevant for isotope separation programme of the department. One of the recent programmes is on nano-photonics- photonic band gap materials and self assembled photonic crystals. Ion traps and quantum optics are other areas of interest.

A state-of-the-art matrix-assisted laser desorption ionization (MALDI) technique in combination with TOF mass spectrometer has been established, for the detection, identification and characterization of peptides, proteins, DNAs and clusters in the mass range 1 to 50000 Da. In the macromolecular crystallography investigations, three dimensional structures of proteins – HIV -1 protease, PhoK and PSP94 have been determined.

Design and development of materials with desired properties is an important programme of the PG. The preparation and the characterization of Nano-materials, functional materials and thin films and investigation of their properties under different temperatures and pressures is an intense activity of the PG. Organic field effect transistors and organic and dye sensitized solar cells are being developed. High efficiency (8%) dye sensitized solar cells have been recently produced. Growth of high mobility

cobalt phatalocyanine films by molecular beam epitaxy technique is an ongoing programme. In the broad area of condensed matter physics, the research areas include : Diffusion in confined media, structures in magnetic nano-materials, mechanism of negative thermal expansion, structural evolution in protein solutions; mesoscopic structures in cement and SOFC materials, interfaces in magnetic multilayers, hydrogen bonding in novel ferroelectrics. The high pressure – static and dynamic pressure – investigations include study of magnetic and superconducting materials, low temperature spectroscopic studies, impedance and Hall coefficient measurements, shock studies with laser ablation, high strain rate dynamics in laser shocked materials, short pulse laser heating of shock compressed matter, hot electron transport in hot matter, characterization of targets for the maximum conversion efficiency used for the X-ray backlighter and time-resolved Raman spectroscopy of materials under laser driven shock. All these experimental programmes are supported by comprehensive and intense computational activity which has been an asset for the success of all the programmes of the PG. For a more comprehensive account of the ongoing basic research programmes, one may refer to the proceedings of the nuclear physics and solid state physics symposia and related theme meetings.

Design and Development

Some of the design and development activities have direct relevance to the nuclear power programme of our country. The PG has set up facilities to develop multilayer optical interference coatings for high power CW and pulse lasers in the wavelength region from deep UV to IR. The PG has expertise to make the Holographic transmission and reflection gratings. Further development of precision optical components and optical analytical instruments for various DAE programmes is another activity of the PG. Reactive electron beam PVD, co deposition PVD, ion beam sputtering, thermal evaporation are some of the techniques used for multilayer coatings.

A 10 meter long optical periscope has been designed and developed indigenously as an in-service inspection instrument for the visual inspection of Prototype Fast Breeder Reactor's (PFBR) main vessel internals including components and equipment installed inside. This project has been successfully completed with the collaborative efforts of Applied Spectroscopy Division (ASD), Division of Remote Handling & Robotics (DRHR), Centre for Design & Manufacture (CDM) of BARC and Reactor Engineering Group (REG) of IGCAR, Kalpakkam (Fig.1). A few hundred pieces of catalytic recombiner cards have been developed for NPCIL for safe recombination of hydrogen and oxygen. Thermoelectric devices are being developed for CHTR and space programmes. PbTe and TAGS alloy-based devices operating at 500 deg C have been developed with an efficiency of 6%. SiGe with n and p type doping has been prepared for use in this programme. Bottle double decapper gadget

Fig. 1: Periscope for PFBR facility

Fig. 2: Bottle double decapper for A3F, KARP

(Fig. 2) for handling bottles containing radioactive samples in hot cells to open the cap and pour the contents into reactants has been developed. It is compatible with the existing mechanism of tongs used in hot cell. The first units are in use in A3F and more are being made for KARP. A computerized and automated mechanical system that exposes biological cell samples to uniform and controlled doses of alphas from radioactive source- alpha irradiator - has been developed for Radiation Biology programme.

A large number of precision spectrometers have been designed, developed, installed and commissioned at various units of DAE, RMP, HWB and AMD. These instruments are continuously improved in performance and sensitivity to cater to the growing needs of the department. Development of portable gas chromatograph mass spectrometer for identification of chemical warfare agents, stable isotope ratio mass spectrometer and ion mobility spectrometer for explosive detection is underway.

One of the active areas of the PG is in the application of neutron and X-ray imaging techniques for nuclear energy, security and healthcare programmes. Both emission and transmission tomography techniques have been developed. The PG has developed an advanced digital imaging system using the flat panel technology. X –ray and neutron based phase contrast imaging technique is one of the recent advancements. Using neutron phase contrast imaging method it has been possible to quantify the presence of light elements in a matrix of heavy element (Fig.3). Neutron based tomography has been applied to various applications such as qualitative and quantitative evaluation of hydrogen in blistered zirconia tubes. It has also been possible to examine the fuel cladding using neutron tomography based technique.

Using X-ray-based phase contrast technique, it has been possible to characterize thin coatings (Fig. 4) of pyrocarbon, carbon composites, foams etc. The PG has developed an advanced digital imaging system using the flat panel technology.

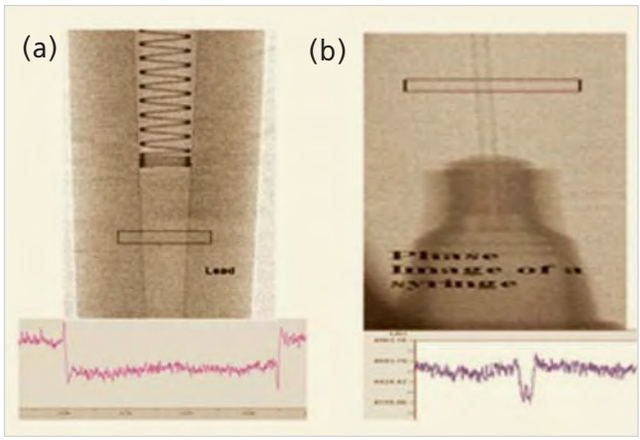


Fig. 3: (a) Neutron phase contrast image of a metallic spring inside drilled tapered hole in lead cylinder (dia~50 mm) The plot signifies the phase contrast feature at an interface (rectangular region in the image)
(b) Neutron phase contrast image of a medical syringe. The plot signifies the phase contrat feature across the fine needle edges (in the marked rectangular portion)

To carry out high pressure studies at very high temperatures (~ few thousands K) a laser-heated diamond cell facility, employing a 100 W air cooled ytterbium fibre has been set up at Purnima laboratories at BARC (Fig. 5). A Helium cryostat has been installed for the measurement of transport and optical

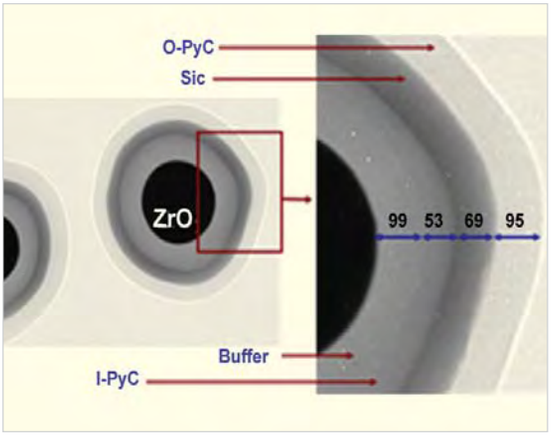


Fig. 4: X ray phase contrast imaging of Zirconia microsphere coated with four different materials

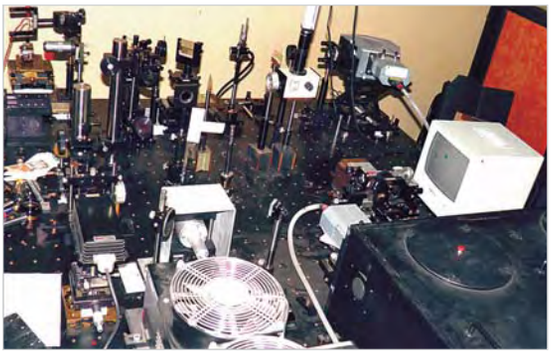


Fig. 5: Laser heated Diamond cell for high pressure high temperature measurements

properties of solids at high pressure and at low temperature. A facility for *in-situ* pressure measurements has also been developed.

As a part of the BARC contribution to the CMS detector upgrade at CERN, PG is developing RPC detectors (Fig. 6). While these RPCs are based on bakelite, similar RPCs being developed for the INO programme are made from glass. The RPC detectors are versatile and they can be also used for muon tomography programme as they can distinguish between different elements, like iron, lead and uranium.

Projects

The PG is spearheading the efforts to design and develop the next generation gamma – ray telescope, MACE (Major Atmospheric Cherenkov Experiment).

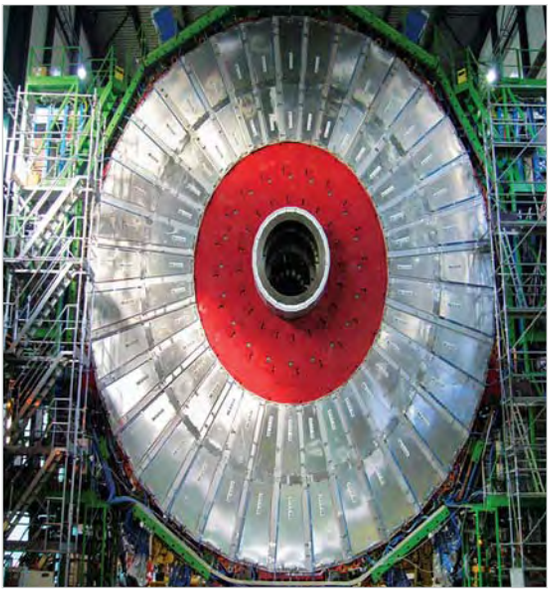


Fig. 6: RPC detectors for CMS upgrade at CERN

This will be located at Hanle at an altitude of 4200 m above sea level and is optimized for detection of gammas in the energy range 10 -100 GeV. This is a national effort involving IIA, TIFR and SINP and is being executed with the active involvement of ECIL (Fig. 7).

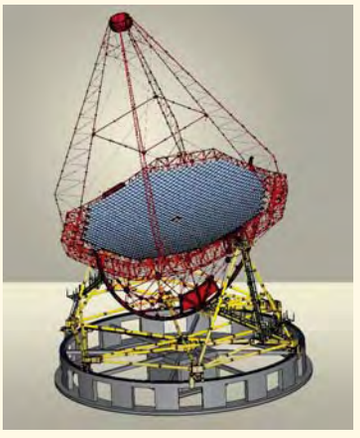


Fig. 7: Schematic of 21 m MACE Telescope at Hanle

A fast neutron facility based on D-D and D-T reactions is already in operation at PURNIMA, PG. It is proposed to couple the 14 MeV neutron source to a sub-critical U assembly (with BeO reflector and Polythene

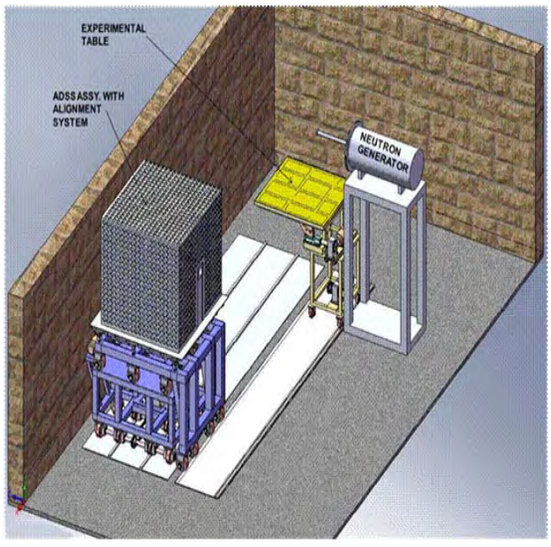


Fig.8: Schematic of PURNIMA subcritical facility

moderator) to carry out neutron multiplication and transport studies. The coupled operation of the accelerator and the sub-critical core is a forerunner to the ultimate ADS, a long term programme of the DAE (Fig. 8). Another flagship programme in which the PG is taking a lead role is the design and development of the LEHIPA (Low Energy High Intensity Proton Accelerator) which can serve as an injector of the high energy, high intensity accelerator (1 GeV, mAs) to be built as part of the Indian ADS programme. The LEHIPA consists of an ECR source, RFQ and DTL modules , high voltage power supplies, high power RF systems, precision temperature controlled LCW supply system and is designed to accelerate the protons upto 20 MeV with mAs intensity (Fig. 9). It is a challenging assignment and the project is planned for installation and commissioning at the basement of the Common Facility Building.

A project is underway to build a low energy heavy ion accelerator facility based on state -of –the- art high intensity, high charge state ECR ion source and RFQ modules. The Ion source is capable of delivering beams ranging from H to U and U ions with charge states 33 and 34 have been demonstrated (Fig. 10).

Generation of quality manpower, particularly in accelerator physics and technology, is crucial for the future programmes of BARC / DAE. This is relevant in the context of DAE with an ambitious plan to use accelerators not only for multidisciplinary basic research but also for applications which will include healthcare, nuclear energy and national security.

The PG is responsible for development and commissioning of several state- of- the- art beam lines at INDUS Synchrotron at RRCAT. Currently work is progressing well on the following beam lines – Photoabsorption (PASS), Infra Red FTS, SAXS, Imaging, and protein crystallography. When completed in the next one year, the user community will be able to pursue R & D programmes exploiting these beam lines.

O & M of facilities

The S&T personnel of the Physics Group operate and maintain a number of national facilities. Amongst them, mention may be made of the TACTIC high

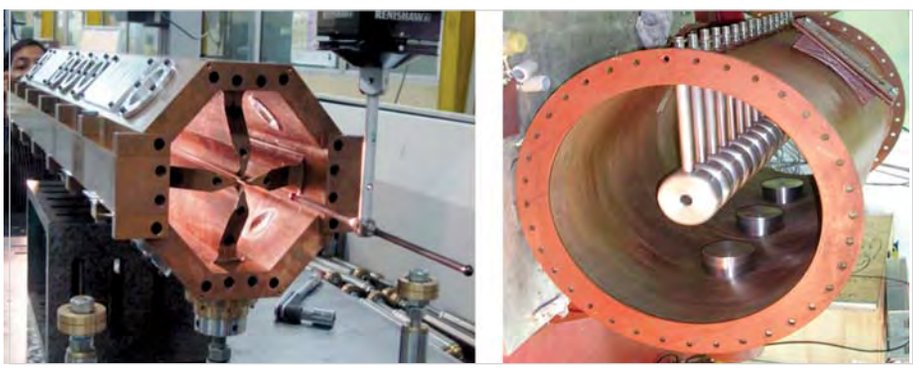


Fig. 9: Prototype versions of RFQ and DTL being built as part of the LEHIPA programme

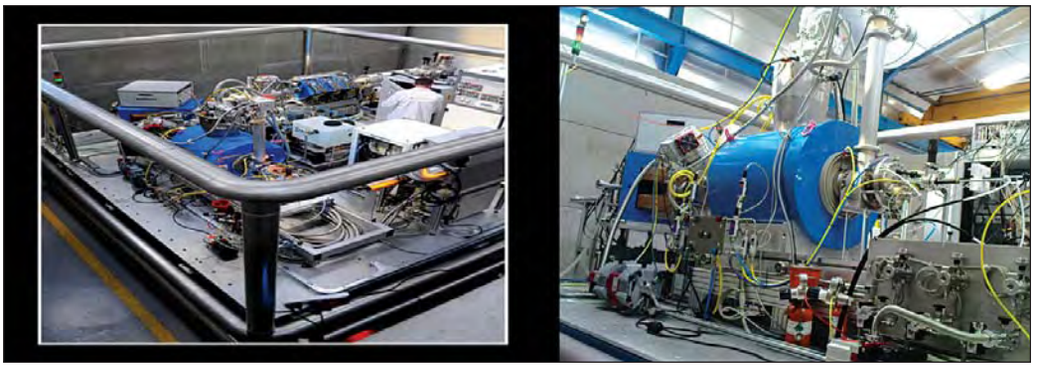


Fig.10: ECR Ion source capable of producing high intensity and high charge state ions from H to U

energy gamma ray astronomy facility at Mt. Abu (Fig.11), the National facility for neutron beam research at DHRUVA (Fig. 12), Low Energy Accelerator Facility (LEAF) at BARC, the 14 MV Pelletron + Superconducting LINAC at TIFR (Fig. 13), the 6 MV FOTIA at BARC (Fig. 14) and the fast neutron facility at PURNIMA.

Fig. 11: TACTIC facility at Mt. Abu

Fig. 12: National facility for neutron beam research at DHRUVA

The Physics group has been instrumental in setting up several beam lines at INDUS for users: The ones which are operated mainly by the Physics group are : Photo-physics, Extended X-ray Absorption Fine Structure (EXAFS) (Fig. 15), Angle Resolved Photoelectron Spectroscopy (ARPES), Energy Dispersive XRD (EDXRD) with an option to study material at high pressure and High Resolution Vacuum Ultraviolet (HRVUV) (Fig. 16) which are used for atomic, molecular and condensed matter physics investigations.

Fig. 13: 14 MV Pelletron + Superconducting LINAC

Fig. 14: 6 MV folded tandem Ion accelerator at BARC

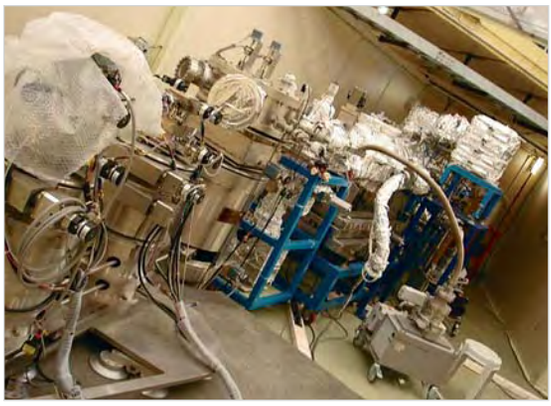


Fig. 15: EXAFS beam line

Fig. 16: HRVUV beam line

All these facilities are catering to a large body of users from the DAE and the universities.

Services

As part of the indigenous development of single crystals which are technologically important and of great relevance to DAE programmes, the Physics Group has a sustained programme of growing single crystals of different types. These include the laser ($PbMoO_4$, $NaBi(WO_4)_2$, Nd:YAG, $Pb_5Ge_3O_{11}$ and $Li_2B_4O_7$) and the detector (CsI(Tl) and LiF) materials. Silicon surface barrier semiconductor detectors of varying thicknesses (10 to 300 microns) and areas (50 to 250 mm sq) have been fabricated and supplied to the users. PG has a specialization in developing BF3 and He3 filled neutron proportional counters for many years and these have been employed successfully in our programme and also supplied to other users. The precision mass spectrometers –TIMS (Fig. 17), PGMS, ICPMS (Fig. 18), QMS and D/H ratio mass spectrometer- have been designed and indigenously developed to meet the growing needs of the department of DAE in general and RMP, AMD and HWB in particular. Over the years nearly, 25 mass spectrometers have been supplied to DAE users.

Powerful spectroscopic techniques (including PIXE, XRF) have been employed to characterize a large number of samples from different labs in DAE. Trace analysis of nuclear and detector grade material is being routinely carried out for various users. The Atomic Emission Spectroscopy, ICP-based technique and the Echelle Spectrometry are employed for this progamme.

Fig. 17: TIMS for AMD

Fig. 18: Multicollector ICP – MS for RMP

The PG is playing a leading role in the newly created Nuclear Data Physics Centre of India (NDPCI), which coordinates the nuclear data activities of the country and also interfaces with international agencies like the IAEA.

Summary

To sum up, the Physics Group has been making sustained and significant contributions to the R & D programmes of DAE in general and BARC in particular. The PG continues to hold a leading position in the country, in the pursuit of basic research addressed to frontiers in physics. In addition the PG also has the mandate to run severed national facilities catering to a large user community. One may consider the present article as just an overview of some of the important programmes of the Physics Group. It is only a representative account and is in no way exhaustive. Needless to say that much of the success achieved by the PG in the various R & D programmes would not have been possible without the active involvement and constant cooperation of colleagues from other Divisions / Groups of BARC but also other units of the DAE.

Acknowledgement

It is a pleasure to thank my colleagues Dr. S. L. Chaplot, Dr. A. Chatterjee, Dr. S. K. Gupta, Dr. B. N. Jagatap, Shri. R. Koul, Shri. P. K. Nema, Dr. N.K.Sahoo, Dr. S.M.Sharma, Dr. P. Singh and Dr. A. Sinha for their inputs and discussions. I am grateful to Dr. T. Mukherjee, Dr. K. Bhanumurthy and Dr. A. K. Tyagi for the kind invitation to write this article and useful suggestions.

Forthcoming Symposium

DAE – BRNS Interdisciplinary Symposium on Materials Chemistry

The 4th DAE – BRNS Interdisciplinary Symposium on Materials Chemistry will be held at BARC, Mumbai, from Dec 11-15, 2012. It is being organized by the Society for Materials Chemistry & Chemistry Division, BARC. The scientific programme of the Symposium will cover the following topics: Nuclear materials, High purity materials, Nanomaterials and clusters, Carbon based materials, Surface chemistry and thin films, Materials for energy conversion, Magnetic materials and electro-ceramics, Catalysis, Soft condensed matter, Biomaterials and polymers.

Important Dates

Last date for submission of abstract : Aug. 31, 2012
Acceptance notification : Sept. 28, 2012
Payment of registration fee : Oct. 31, 2012

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Photocatalytic Hydrogen Generation from Water using Solar Radiation

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Abstract

Solar photocatalytic water splitting is considered as a potential method for hydrogen production as both solar energy and water are renewable. The major task is the design of suitable photocatalysts, which can work efficiently under solar radiation, especially under visible light. The performance of the visible light active photocatalysts synthesized till date is far from satisfactory for any practical applications, which necessitates a lot more research and attention in this field. In the light of our recent findings, this article addresses the different problems associated with the development and efficient utilization of solar energy for the photocatalytic water splitting reaction.

1. Introduction

Hydrogen is considered as the energy carrier of the future as no green house gas like CO_2 is emitted when hydrogen is burnt and it can be generated from source like water. Attention was focused on photocatalytic generation of hydrogen from water after the discovery of Fujishima and Honda [1], who demonstrated that overall water splitting can be achieved using a photoelectrochemical cell made of a single-crystalline TiO_2 (rutile) anode and a Pt cathode under ultraviolet (UV) irradiation and operated with an external bias. Over the past few decades, lot of efforts have been made to produce hydrogen from water photocatalytically and a number of photocatalyts have been designed for this purpose. Though TiO_2 is an efficient, stable and cheap photocatalyst for hydrogen generation from water, its activity is limited to UV radiation, which is only 3-5% of solar radiation. Cadmium sulphide is another widely studied visible light active photocatalyst (bandgap 2.4 eV). However, the disadvantage of using CdS is that it undergoes photocorrosion in the absence of suitable sacrificial reagents. Current research efforts are directed towards the synthesis of visible light active and stable semiconductor photocatalysts. As solar radiation contains ~40% visible light and 3-5% uv-radiation, different modifications and band engineering of the UV-active photocatalyst are done, to make it visible light active.

The target is to develop a photocatalyst having a band gap (BG) of ~2eV for overall water splitting and a solar energy conversion efficiency of 10% (solar energy conversion efficiency is the ratio of the chemical potential energy stored in the form of hydrogen molecules to the incident radiation of energy). A technical estimation has shown that a one-third energy need in 2050 can be satisfied with 10000 "solar plants" of dimension 5x5km per plant with a solar energy conversion of 10% [2]. The total area needed for this is 250000 km^2, which corresponds to ~1% of the earth's desert land. These plants will generate 570 tons of hydrogen gas per day using an integrated solar energy of AM1.5G (Air Mass 1.5 global spectrum, it is the solar spectrum corresponding to 1.5 air mass and to a solar zenith angle of 48.2°) irradiation for a day. Hence, the primary focus has to be on the development of suitable photocatalysts for overall water splitting under solar irradiation with the required solar energy conversion efficiency.

2. Photocatalytic water splitting by semiconductors

When a semiconductor is exposed to a radiation having energy equal to or greater than the bandgap energy, an electron is excited from the valence band (VB) to the conduction band (CB) leaving a hole in the VB. The electron in the CB initiates the reduction of H^+ to hydrogen and the hole oxidises water to generate oxygen. For these reactions to take place, the VB potential must be more positive than the oxidation potential of water (1.23 V w. r. t. normal hydrogen electrode (NHE)) and CB potential must be more negative than the reduction potential of water (0.0 V w. r. t. NHE). A schematic illustration of the band structure of TiO_2 semiconductor and band potential requirements for overall water splitting reaction are shown in Fig. 1.

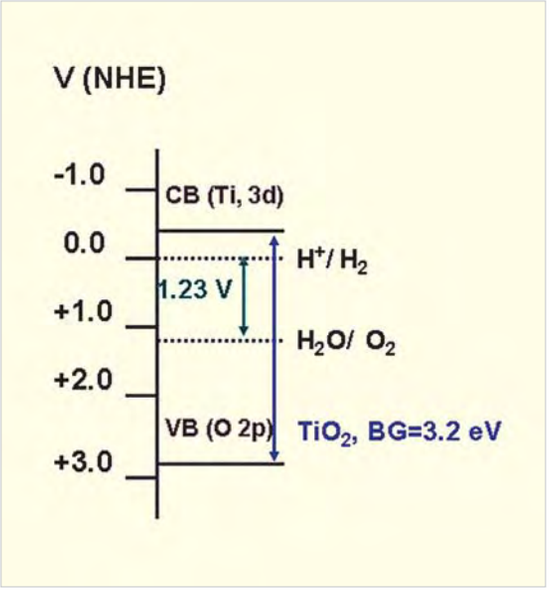

Fig. 1: Schematic presentation of the band structure of TiO_2 semiconductor

There are three important steps associated with the photocatalytic water splitting reaction as illustrated in Fig. 2. The first step is the excitation of the semiconductor. For the semiconductors to be visible light active, the BG has to be less than 3 eV. The next step is the migration of the charge carriers to the surface. This step is influenced by the crystallinity and particle size of the semiconductor. The higher the crystallinity, the better is the probability that the charge carriers can reach the surface without getting trapped by the defects. If the particle size is small, the charge carriers have to travel only a short distance to reach the surface, which can enhance their life time. The last step is the surface reaction of electron combining with H^+ to form hydrogen and hole reacting with water to form oxygen. A number of active sites on the surface will enhance these reactions and hence higher surface area of the catalyst is advantageous for this process.

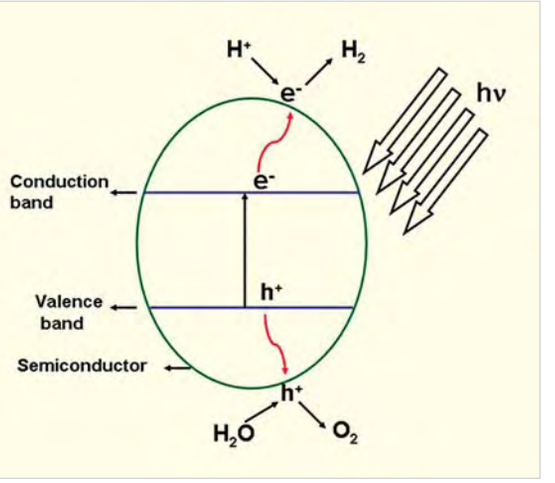

Fig. 2: Schematic presentation of the different steps involved in a photocatalytic process

Incorporation of noble metals like Pt, Pd, and Rh as co-catalysts on the surface of semiconductor photocatalyst improves the photocatalytic activity for hydrogen generation. The enhanced activity is due to the interfacial transfer of electrons from the photocatalyst to the metal when irradiated. This process enhances the electron-hole separation and minimizes the charge recombination. Besides using co-catalysts, sacrificial reagents like methanol, ethanol, etc. are used in photocatalytic hydrogen production reaction to suppress the electron-hole recombination.

3. Photocatalytic water splitting: current scenario

A number of oxide photocatalysts have been synthesized and tested for the photcatalytic water

splitting reaction. The oxide catalysts suitable for water splitting reaction are generally classified into two groups. Among these, one group belongs to cations with d^0 (Ti^{4+}, Zr^{4+}, Nb^{5+}, Ta^{5+} and W^{6+}) and other to d^{10} (Ga^{3+}, In^{3+}, Sn^{4+}, Ge^{4+}, Sb^{5+}) electronic configurations. An apparent quantum efficiency (product molecules formed per incident photon (polychromatic)) of 64% has been obtained for Pt/TiO_2 photocatalyst when irradiated with UV radiation of wavelength <300nm and in the presence of ethanol as sacrificial reagent. A few other oxides which exhibit photocatalytic activity for water splitting reaction under UV radiation are La doped $NaTaO_3$, $Sr_2M_2O_7$ (M=Nb, Ta) etc. Among these, $NiO/NaTaO_3$:La photocatalyst shows the highest activity with an apparent quantum yield of 56% at 270 nm [3]. Among the visible light active catalyst, the highest apparent quantum yield of 5.9% (420-440nm) was reported for $(Ga_{0.88}Zn_{0.12})(N_{0.88}O_{0.12})$ catalyst with $Rh_{2-y}Cr_yO_3$ as co-catalyst from water + H_2SO_4 at pH = 4.5 [4]. Among non-oxide photocatalysts, CdS is a highly active visible light photocatalyst in the presence of Na_2S and Na_2SO_3 as sacrificial reagents. When Pt and PdS are used as co-catalysts along with CdS, an apparent quantum yield of 93% was obtained at 420 nm in presence of Na_2S and Na_2SO_3 as sacrificial reagents. The disadvantage of CdS based photocatalyst is their instability in the absence of suitable sacrificial reagent leading to their photocorrosion.

4. Strategies employed for improving the photocatalytic activity of semiconductor photocatalyst

(i) Changing chemical composition

Doping with a suitable cation or/and anion can alter the bandgap rendering it visible light active. Though the cation doping can decrease the bandgap, it forms discrete levels within the bandgap forming trap levels. These defect/trap levels can act as recombination centres for the photogenerated electrons and holes leading to decreased photocatalytic activity. Cationic dopant like indium can contribute additional levels to the conduction band of the semiconductor, which decreases its bandgap. As the additional levels mix with the CB, they do not act as electron traps enhancing the photocatalytic activity. Doping of oxide semiconductors with anionic dopants like N or S leads to the mixing of the N 2p or S 3p orbitals with the O 2p orbitals and a new VB is created (Fig. 3). This process decreases the BG without affecting the CB level. As a result, band edge potentials are suitable for overall water splitting.

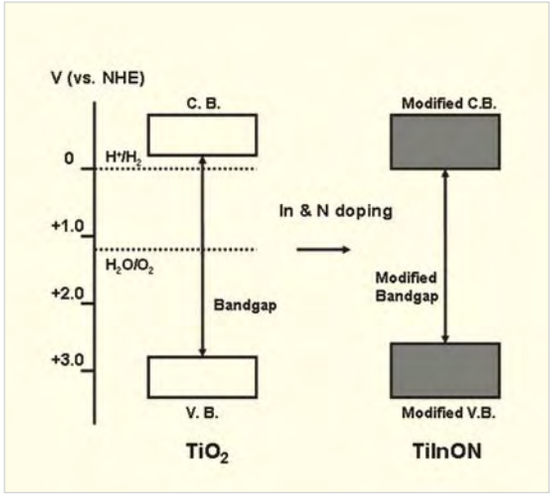

Fig. 3: Schematic presentation of the modification of the CB and VB of TiO_2 due to In and N co-doping

(ii) Altering Physical properties

Improving physical properties like surface area and crystallinity can enhance the photocatalytic activity. Nanometer sized photocatlysts can be prepared by solvothermal / hydrothermal synthesis, polyol-mediated route, sol-gel synthesis, gel combustion route etc. Calcination of these nanoparticles around 400^0C gives nanocrystalline semiconductors having a reasonably high surface area.

(iii) Minimizing the recombination of charge carriers

Use of coupled semiconductors or co-catalysts can enhance the activity of the photocatalyst. A composite of two semiconductors in which the CB potential of one is lower than that of the other can enhance the photocatalytic activity as the photogenerated electron can migrate to the CB of the semiconductor, whose CB potential is lower.

This process increases the life time of the charge carriers. Noble metal co-catalysts also increase the life time of the photogenerated electrons as stated earlier (section 3). Noble metals can act as a sink for the electrons, which enhances the liberation of H^+ as hydrogen gas from the noble metal sites.

5. TiO_2 and CdS based Photocatalyst systems

Photocatalytic systems based on TiO_2 and CdS have been studied in our laboratory. Some interesting results obtained from these studies are as follows.

(a) TiO_2 dispersed on different supports

Titania was dispersed on different supports like ZrO_2, Al_2O_3, NaY zeolite and CeO_2 to study the role of different supports on the photocatalytic activity [5]. As these different oxides exhibit surface acidity, it was of interest to investigate the role of surface acidic sites on the photocatalytic activity of TiO_2. The surface acidity of these supports, as measured by the pyridine adsorption method, decreases in the order zeolite>ZrO_2>Al_2O_3>CeO_2. TEM images indicated that TiO_2 was in a highly dispersed state on ZrO_2 support when compared to other samples (Fig. 4). TiO_2-ZrO_2 showed the highest activity among these samples (Fig. 5, Table 1). The enhanced activity of TiO_2 dispersed on ZrO_2 is attributed to the enhanced optical absorption due to the decreased band gap (~3.0 eV) and increased life time of the photogenerated charge carriers assisted by the surface acidic sites. Present study showed a new result that a highly dispersed phase of TiO_2 on a support having higher surface acidity exhibits enhanced photocatalytic activity. This strategy may be useful for the design of new catalysts yielding high photocatalytic activity.

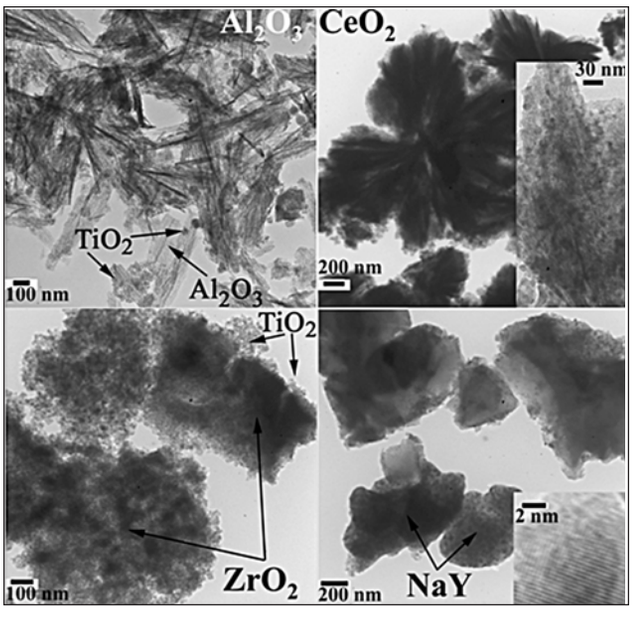

Fig. 4: TEM image of TiO_2 dispersed on different support oxides

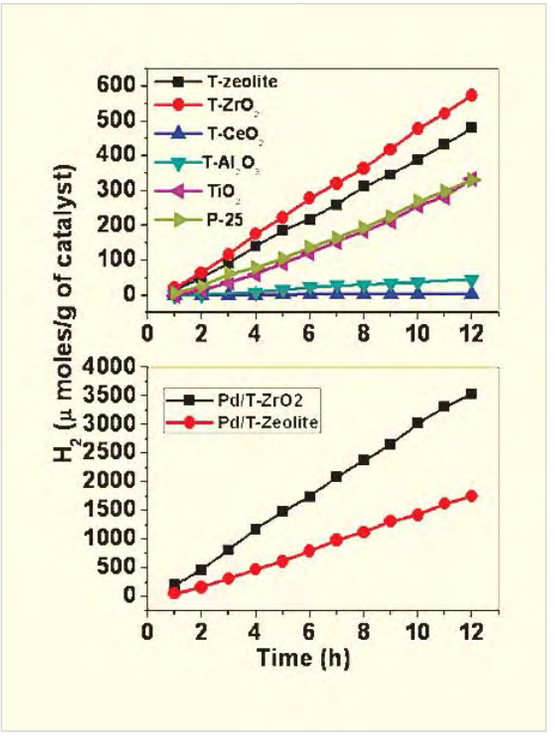

Fig. 5: Photocatalytic activity of TiO_2 dispersed on different supports. reaction conditions are given in Table 1

(b) Indium doped CdS dispersed on ZrO_2

Photocatalytic activity of In doped (2% by atomic weight) CdS dispersed on ZrO_2 (CdInS-Zr) was investigated, was compared the activity with that of undoped CdS and unsupported CdS [6]. The photocatalytic activity of CdS improved when it was dispersed on ZrO_2 and it was further enhanced when CdS was doped with indium (Fig. 6). Hydrogen generation rate and the apparent quantum efficiency are given in

Table 1. The apparent quantum efficiency as a function of wavelength for Pd-CdInS-Zr was studied, using Xenon arc lamp as light source. It is seen that an apparent quantum efficiency of 31% is obtained at $\lambda > 420$ nm. This system was found to be stable throughout the experiment

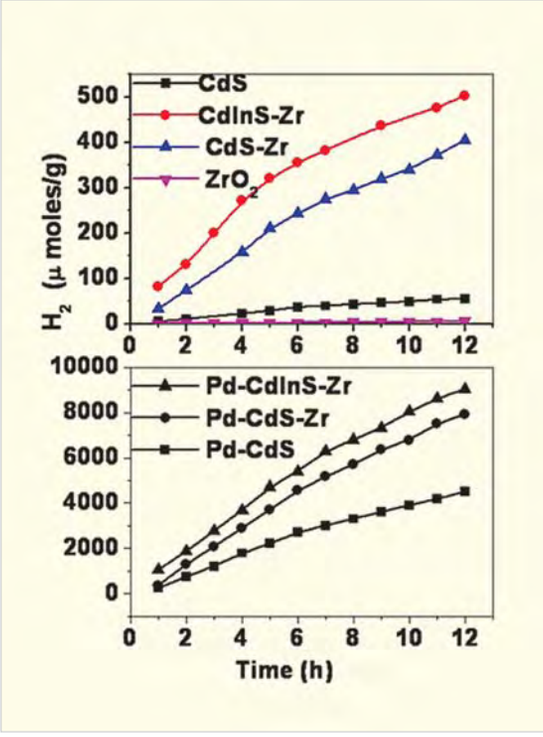

Fig. 6: Photocatalytic activity of different CdS samples dispersed on different supports. Reaction conditions are given in Table 1

(96 h) in the presence of Na_2S and Na_2SO_3 as sacrificial reagents. The enhanced photocatalytic activity of this composite sample is attributed to a synergistic combination of factors like enhanced life time of the photogenerated charge carriers, increased optical absorption compared to CdS-ZrO_2 and improved surface area. It is proposed that the increased life time of the charge carriers in the supported system is due to the transfer of the photogenerated electrons from the CB of CdS to the surface states of ZrO_2 (Fig. 7), which is substantiated by the increased fluorescence life time of the photogenerated charge carriers for the supported CdS.

The photocatalytic activity of different systems studied in our laboratory, the experimental conditions employed and the apparent quantum efficiencies obtained are summarized in Table 1.

6. Future scope

In order to meet the target of 10% solar energy conversion efficiency, considerable amount of research effort is required in the design of catalysts which can work efficiently under solar radiation. Careful choice of materials is required so that its band gap is around 2eV and at the same time it satisfies the band potential requirements. Sulphides meet the BG requirement, but they are not stable

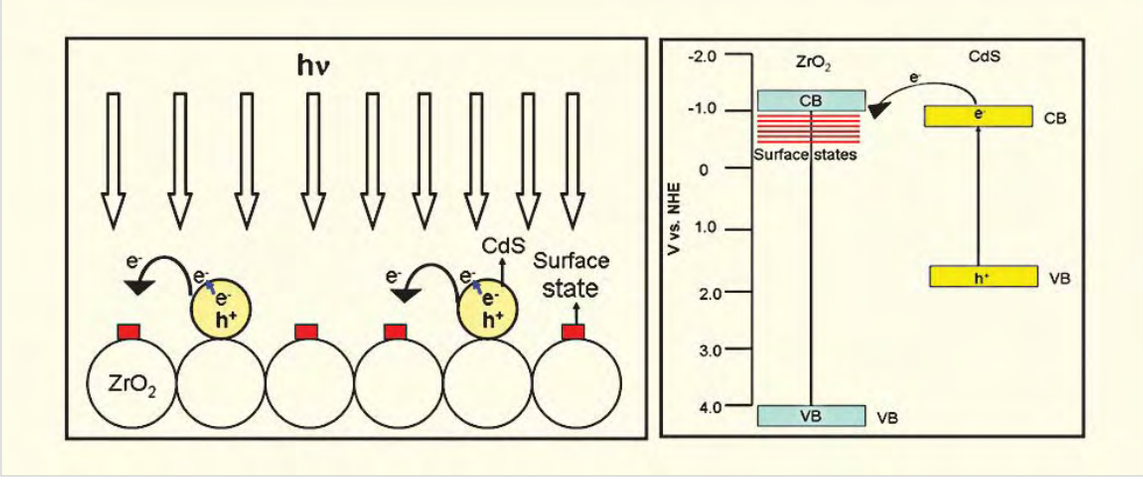

Fig. 7: (left panel) Schematic illustration of the photogenerated electron transfer process from CdS to the surface states of the ZrO_2 support. (Right panel) Schematic energy level diagram of electron transfer process from CdS to the surface states of ZrO_2

Table 1: Summary of the photocatalytic activity results obtained in our laboratory using sun light type radiation (*Spectrum of the lamp consisted of fluorescent emission predominantly in the visible region along with a UV contribution of ~3%)

No	Systems studied	Experimental conditions	H_2 generation rate ($L/h/m^2/g$)	AQE Light source: *fluorescent lamp (%)
1	TiO_2 doped with Sn &Eu: Pd co-catalyst	200mg catalyst, 25ml water, 5 ml CH_3OH	0.35	1.7
2	Ti^{3+} doped TiO_2 synthesized by solvothermal method:Pd co-catalyst	50mg catalyst, 25ml water, 5 ml CH_3OH	0.60	2.1
3	TiO_2- (2%)SnO_2 composite; Pd Co-catalyst	50mg catalyst , 25ml water, 5 ml CH_3OH	0.31	1.2
4	In & N co-doped TiO_2: Pd co-catalyst	50mg catalyst , 25ml water, 5 ml CH_3OH	0.28	1.1
5	30%TiO_{2-} dispersed on ZrO_2: Pd co-catalyst	50mg catalyst , 25ml water, 5 ml CH_3OH	1.1	3.3
6	In(2%) doped CdS 30(%) dispersed on ZrO_2: Pd co-catalyst	50mg catalyst, 12.5ml Na_2S + 12.5ml Na_2SO_3	2.8	4.0

in the absence of sacrificial reagents. Some oxynitrides and nitrides like TaON, Ta_3N_5 are reported to have BG of 2.4 and 2.0 eV respectively, but the quantum efficiency is far from satisfactory. $Rh:Cr_2O_3/Ga_{1-x}Zn_xN_{1-x}O_x$ is found to be active for overall water splitting, but the quantum yield is low. Though most of the oxides are stable catalysts, the VB and CB energy requirements for O_2 and H_2 evolution, make it inefficient for visible light photocatalytic reaction. Hence, it is important to develop a library of photocatalysts to clarify different factors influencing their photocatalytic properties. For example, there is no clear understanding of the role of different structures and shapes of the photocatalysts on the photocatalytic activity. Several detailed studies are required to understand these factors, which will be helpful for the design of new highly active photocatalysts for water splitting.

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References

1. A. Fujishima, K. Honda, *Nature* 238 (1972) 37-37.
2. K. Maeda, K. Domen, *J. Phys. Chem. Lett.* 1 (2010) 2655-2661
3. H. Kato, K. Asakura, A. Kudo, *J. Am. Chem. Soc.* 125 (2003) 3082-3089.
4. K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi, K. Domen, *J. Catal.,* 254 (2008) 198-204.
5. R. Sasikala, A.R. Shirole, V. Sudarsan, V.S. Kamble, C. Sudakar, R. Naik, R. Rao, S.R. Bharadwaj, *Appl. Catal. A: General* 390 (2010) 245-252.
6. R. Sasikala, A. R. Shirole, V. Sudarsan, K. G. Girija, R. Rao, C. Sudakar, S. R. Bharadwaj *J. Mater. Chem.,* 21 (2011) 16566 – 16573

Development of Carbon / Carbon Composites for Nuclear Reactor Applications

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Abstract

Carbon and carbon fiber reinforced materials are promising materials for use in nuclear reactors, due to their excellent thermal and mechanical properties. In the present studies, experiments were carried out to prepare carbon-carbon(C/C) composites using non-graphitizing precursors such as polyacrylonitrile (PAN) fiber and phenolic resin matrix. A typical sample of C/C composite at 40 vol% of PAN fibre showed to be amorphous. These fibers have been used to make a 2-D preform and phenol formaldehyde resin was impregnated, cured and carbonized to form the matrix. Impregnation was carried out under different conditions, and its effect was studied by XRD, Raman spectroscopy and XPS. The C/C composite samples have been irradiated by neutrons at neutron flux of $1x10^{12}$ n/cm^2/s with varying fluences at 40°C. The stored energy is very less about 23.4 J/g and 43.3 J/g as compared to irradiated graphite. The composites were coated with silicon carbide (SiC) for improved oxidation resistance by chemical vapor deposition technique.

Introduction

Carbon based materials due to their wide range of structures and several desirable neutronic properties are used in nuclear reactors and in the recent past there has been growing interest to develop speciality carbon for high temperature nuclear and fusion reactors. Graphite was used in the first nuclear reactor CP-1, constructed in 1942 at Stagg Field University of Chicago. Some of the emerging applications include their use as critical parts in advanced nuclear reactors. Efforts are underway to develop carbon materials with high density as well as amorphous isotropic carbon for use in thermal reactors. An amorphous structure is preferred in order to avoid accumulation of Wigner energy, which is the stored energy in graphite lattice due to dislocation of atoms induced by irradiation.

Carbon fiber reinforced carbon matrix composites or the so called carbon/carbon (C/C) composites are a generic class of synthetic materials consisting of carbon fibers reinforced in a carbon matrix. They possess densities ranging from 1600–2000 kg/m^3, much lower than those of metals and ceramics. They can be classified according to the type of reinforcement used and also depending on the type of process used for their manufacturing. Some of the most important and useful properties of C/C composites [1] are its light weight, high strength at high temperature (3000°C) in non-oxidizing atmospheres, low coefficient of thermal expansion, high thermal conductivity, high thermal shock resistance and low recession in high pressure ablation environments. The mechanical strength of C/C composites increases with temperature, in contrast to the strength of metal and ceramics. The main application areas of these are in defence, space and aircraft industries which include brake discs, rocket-nozzles etc. They also possess numerous applications in the field of general mechanical engineering. Carbon/carbon composite materials [2-5] as against conventional graphite materials are now contemplated as promising materials for the

fusion reactor, due their high thermal conductivity and high thermal resistance. C/C components materials may be the choice for the next generation Tokomak fusion reactors such as International Thermonuclear Experimental Reactor (ITER) which must endure severe environment including high-heat fluxes, high armor, surface temperature and eddy-current induced stresses during plasma disruption.

The main objective of the investigation was to fabricate C/C composites by impregnation method and to characterize the final microstructure. Thermo-physical properties of the carbon composite like density, co-efficient of thermal expansion have been evaluated. In the present studies, C/C composites were developed using non-graphitizing precursors such as polyacrylonitrile (PAN) carbon fiber and phenolic resin matrix. The desired non-graphitic composite material, having stability under irradiation, was obtained after a judicious control on the processing parameters.

Experimental

A suitable preform is the first step for manufacturing the C/C composites. The preform not only imparts the rigidity to the composite, but also incorporates the properties of fiber that eventually determine the properties of the composites. The preforms were made using PAN carbon fibers which were matted and stacked to a 2-D preform using phenol formaldehyde resin. Rectangular green preforms

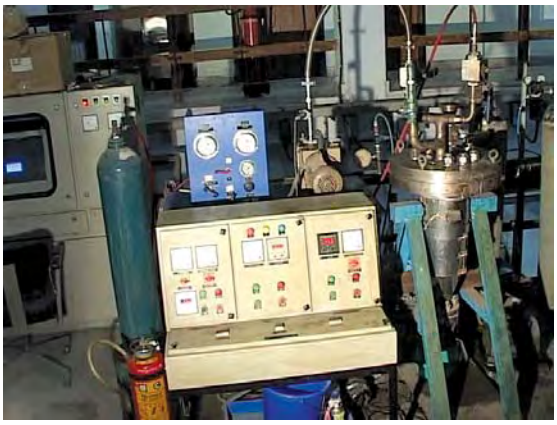

Fig.1: Indigenously fabricated Impregnator unit

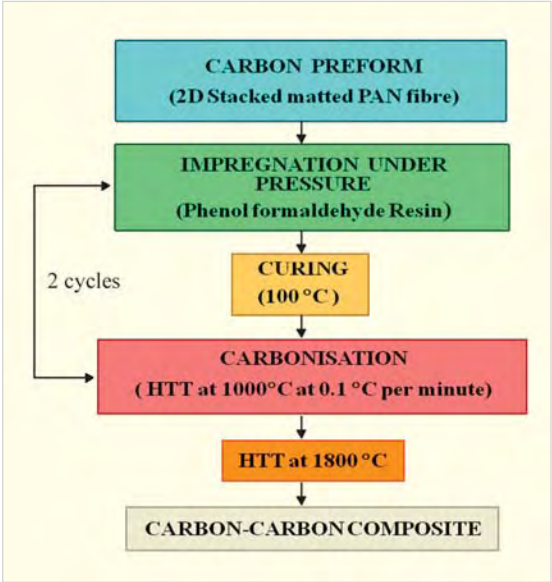

Fig.2: Flow-sheet for the preparation of C/C Composite

were cut into 1´´x 1´´ x 0.4´´ size and carbonized at a slow heating rate. The carbonized sample is highly porous and has been densified by impregnation (two cycles) with liquid phenol formaldehyde resin, under pressures in steps of 30, 50 and 70 bar and time duration in steps of 10, 15, 20 and 25 hours. The impregnation unit is shown in Fig. 1. The composite was densified by impregnating the 2D preforms with liquid phenol formaldehyde resin under high pressure and then carbonizing them by slowly heating at 1000°C as shown in Fig.2.

Characterization of the samples

The composites were thoroughly characterized by X-ray Diffraction (XRD), X-ray tomography and Raman Spectroscopy. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) have been used to estimate the ratio of sp^2 to sp^3 bonded carbon atoms (i.e. sp^2-C/sp^3-C) in a few representative composites impregnated at different pressures and for different times. The C/C composite samples have been irradiated with thermal neutrons at APSARA Reactor. These irradiated samples were characterized before and after irradiation for various structural parameters like extent of local ordering along c-axis, the average spacing of the $d_{(002)}$ i.e.

the (002) crystallographic planes using X-ray diffraction (XRD) technique. The salient observations were further validated using Raman spectroscopy. The fluences used were 2.52 x 10^{16} n/cm^2, 5.04 x 10^{16} n/cm^{2}and 7.2 x 10^{16} n/cm^2 at temperature of 313 K during the irradiation. The stored energy in the composites due to irradiation was measured using DSC.

All the composites were found to be amorphous in nature with no induced graphitization in them. The interlayer spacing (d_{002}) was calculated from the (002) peak maximum (under approximation of Gaussian line profile with a linear background) using Bragg's law [6,7]. The d_{002} values decreased almost linearly with pressure indicating an increased ordering in the samples at higher impregnation pressures. Local ordering in the composites at higher impregnation pressure is reflected in the concomitant grain growth along c-axis. Grain size (L_c) along c-axis has been approximately calculated from the (002) XRD peak broadening using Scherrer equation.

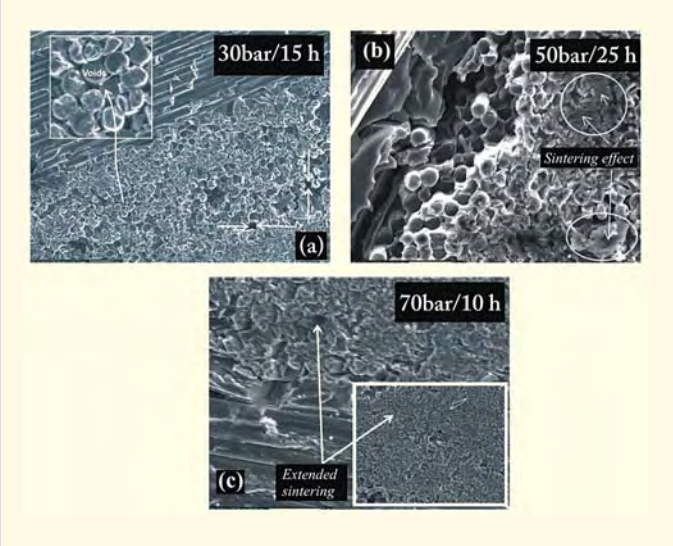

Fig. 3(a-c): SEM micrographs of three composites impregnated at different pressures

The derived material contains the disordered carbon phase which may contain both sp^2 and sp^3-bonded carbon atoms. Raman spectroscopy and XPS have been used to estimate [8] the ratio of sp^2 to sp^3 bonded carbon atoms (sp^2-C/sp^3-C) composites. The D/G ratio has been used to estimate sp^2-C/sp^3-C in the carbon composites from the Raman spectra of the samples which were fitted with multi-Lorentzian line-shape. In the XPS spectra, the peaks at 283.4 and 285eV are respectively attributed to sp^2 and sp^3 bonded carbon atoms. Ratio of the peak areas under the first two component curves provides a direct estimate of sp^2-C/sp^3-C in the composites. During the densification process there is increasing L_c and sp^2-C fraction.

Fig. 3(a-c) shows the scanning electron microscopy (SEM) images of three representative samples impregnated at 30, 50 and 70 bar respectively that illustrates the formation of carbon composite at the interface of PAN fibers. The micrographs also provide information on the population and 2D distribution of pores in the samples and hence on the effect of impregnation pressure on the growth of secondary carbon phase between two or more existing carbon particles.

The neutron irradiated carbon composite samples were characterized by XRD and Raman spectroscopy before and after neutron irradiation. DSC studies have also been carried out [9] to investigate the stored energy release behavior due to irradiation. From the XRD analysis of the irradiated and unirradiated samples, it is found that the value of d_{002} peak for the unirradiated samples is higher than that of the irradiated samples indicating the tendency to get ordered structure which was also inferred from the Raman spectroscopy. The stored energy release studies indicate, that simple defects created due to low fluence of irradiation are annealed by heating (accompanied by release of the stored energy at lower temperature) and on the other hand the complex defects which are formed require high temperatures for annealing. The flux/fluence used is lower than the actual scenario in the upcoming Compact High Temperature Reactor; however the present study could be an initial step in the direction of investigation of damage caused by neutrons on

carbon/carbon composite materials for its use in the upcoming reactor.

Although the C/C composites possess excellent properties, they are prone to oxidation at high temperatures when exposed to oxidizing atmospheres. Therefore, these composites were given protective coating [10-13]. SiC is a material with high temperature oxidation resistance along with good thermal shock properties and stability against hot corrosion. Among the different techniques to grow SiC on different substrates, the Chemical Vapor Deposition (CVD) is the most frequently used technique, as it can deposit materials with near theoretical density and good adherence to the substrate. SiC coating can be formed by using various Si and C compounds. In the present work, the coating was carried out with methyl trichlorosilane (MTS) as the SiC precursor. Extensive studies on coating with SiC by CVD technique using a hot wall reactor with methyl trichlorosilane was carried out at 1673 K. The effect of the operating parameters such as MTS, hydrogen flow rate and feed rate of MTS were studied.

The SiC coatings have been characterized using X-ray Diffraction (XRD) and Raman spectroscopy for phase identification. Scanning electron microscopy (SEM) analysis with EDS was also carried out for microstructure and elemental analysis. The photograph of coated sample and the SEM image

Fig. 4: Dense SiC coated C/C sample

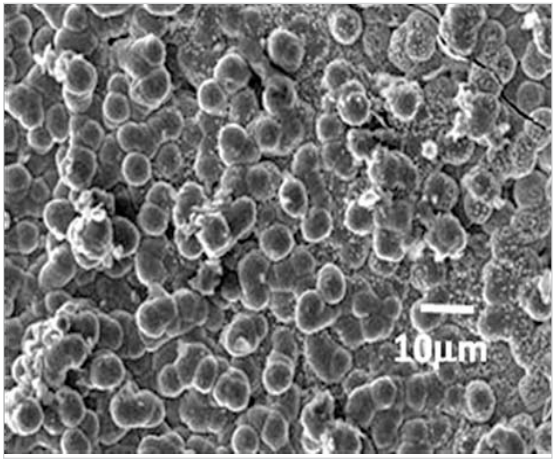

Fig. 5: SEM of SiC coated C/C sample

of the SiC coating are shown in Figs. 4 & 5, respectively.

Conclusion

C/C composites with density of 1470 kg/m^3 were developed with two cycles of impregnation and carbonization. These composites are amorphous in nature as revealed from the XRD even on heat treatment at 1800^{0}C. The concerted study on the effect of processing parameters on the porosity, structure and properties of carbon-carbon composites show that impregnation pressures, especially high pressure, is more effective in decreasing open porosity of the carbon/carbon composites and hence in their densification than impregnation time at relatively lower pressures. X-ray tomography showed visible decrease in the number of cracks and better matrix-resin bonding at higher pressures. Structural ordering takes place during the densification process as is evident from decreasing d_{002} and increasing L_c and sp^2-C fraction. Formation of micro/nano-scopic graphitic domains is believed to have been responsible for such short-range ordering and it was found to be more at higher impregnation pressures or when the samples were subjected to high temperature treatment. From the XRD analysis of the irradiated and unirradiated samples, it is found that the value of d_{002} peak for the unirradiated samples is higher than that of the irradiated samples indicating the tendency to get ordered structure. This is also inferred from the

Raman spectroscopy. The results of irradiation studies indicate that simple defects created due to low fluence of irradiation are annealed by heating accompanied by release of the stored energy at lower temperature. On the other hand the complex defects require high temperatures for annealing these defects. SiC coating on C/C composites was achieved using CVD technique. The coating were dense isotropic β-SiC phase. The major outcome of the above investigations was establishing the fact that the C/C composites are potential candidate structural materials for low temperature reactor applications.

Acknowledgement

Dr. Mainak Roy is thanked for useful discussion on Raman data.

References

1. Schmidt DL, Davidson KE, Theibert LS, Unique applications of carbon- carbon composite materials. *SAMPE J.* 35(3) (1999): 27, 35(4) (1999):51, 35 (5) (1999)47.
2. Graphite Moderator Lifecycle Behavior, IAEA – Tecdoc. 32 (1998) 32.
3. B. T. Kelly and T. D Burchell, *Carbon.* 499 (1994) 32.
4. R. E. Nightingale, Nuclear Graphite (Academic Press, New York, London) 1962.
5. T. D. Burchell, Carbon Materials for Energy production and Storage, In Design and Control of structure of Advanced Carbon materials for Enhanced Performance. B. Rand et al, editor. Kluwer Academic Publishers., 277-294, 2001
6. Marie J, Mering *J. Chem. Phys. Carbon.* 125 (1970) 6.
7. Warren BE. X-Ray Diffraction in Random Layer Lattices. *Phys. Rev.* 59 (1941) 693.
8. Yu O, Daoyong L, Cao W, Shi S, Chen L. A Temperature Window for the Synthesis of Single-Walled Carbon Nanotubes by Catalytic Chemical Vapor Deposition of CH_4 over Mo2-Fe10/MgO Catalyst. *Nanoscale Research Letters.* 4 (2009)574
9. Venugopalan R, Sathiyamoorthy D, Acharya R, Tyagi AK. Neutron irradiation studies on low density pan fiber based carbon/carbon composites. *J. Nucl. Mater.* 404 (2010) 19.
10. Fritze H, Jojie J, Witke T, Ruscher C, Weber S, Scherrer S, etal., *J. Eur. Ceram. Soc.* 18-23 (1988) 51
11. F. Smeacetto and M. Ferraris, Carbon.40 (2002) 583.
12. K. L. Choy, *Prog. Mater. Sci.* 48 (2003) 57.
13. Y. J. Lee, D. J. Choi, S.S. Kim, H. L. Lee, H.D. Kim, *Surf. Coat. Technol.* 177-178 (2004) 415.

Development and Fabrication of LEU Plate Fuel for Modified Core of APSARA Reactor

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Abstract

An indigenous Low Enriched Uranium (LEU: $U^{235}\cong17$wt%) based U_3Si_2 dispersed in aluminium matrix plate fuel has been developed, to replace the present imported High Enriched Uranium (HEU: $U^{235}\cong93$wt%) core of APSARA reactor. New plate fuel development and fabrication laboratory has been setup at the Metallic Fuels Division (MFD), BARC. The fabrication of LEU plate fuel for modified core of APSARA reactor has commenced in this facility in January 2012. With modified core, the power of APSARA reactor will increase from 1 MW to 2 MW and thermal neutron & fast neutron fluxes will be enhanced by almost 6.3 & 15 times respectively.

1.0 Introduction

Till mid 70's most of the research and test reactors worldwide were using High Enriched Uranium (HEU>85%U^{235}) plate type dispersion fuel elements, generally consisting of UAl_x (mainly UAl_3) or U_3O_8 dispersed in aluminium matrix and with Al-alloy clad [1]. In the late 70's, the Reduced Enrichment for Research and Test Reactor (RERTR) programme was initiated, to address the proliferation concerns and diversion issues. Since then it has become an international norm for both designing fuels for new reactors and for replacing the existing cores with Low Enriched Uranium (LEU<20%U^{235}) fuel.

The objective of using LEU as fuel is addressed by increasing the fuel volume fraction in the meat and by using higher density uranium compounds/alloys. It is also important to note, that achieving highest density in the fuel meat by using uranium as dispersoid is not feasible due to the poor irradiation and chemical stability of its lower temperature orthorhombic α–phase. It is also well known, that the cubic γ-phase of uranium has low swelling characteristics but it is thermodynamically unstable and cannot be retained at room temperature. The solid solubility of uranium is very poor with many elements of periodic table due to its 5f electron behaviour, however it shows some alloying characteristics with transition elements [2-4]. The density of various uranium compounds is shown in Table 1. The compounds of U_6X (X: Mn, Fe, Ni) and U_3Si have higher density than U_3Si_2 but they have not been favored for application as fuel because of their higher swelling behaviour. Some of these high density compounds are formed by peritectoid reaction as compared with U_3Si_2 which is a congruent melting compound. The moderate density and low swelling behaviour of U_3Si_2 compound has attracted fuel designers for its application as an alternate fuel in place of low density UAl_3 compound. However there is a limitation on increasing the fuel volume in the matrix beyond 55% [5-8]. Hence, in order to achieve the

Table 1: Density of various uranium compounds

Uranium compound	UAl_4	UAl_3	UAl_2	UO_2	U_3Si_2	U_3Si	U_6Mn	U_6Fe	U_6Ni
Density (gm/cc)	6.1	6.8	8.1	10.96	12.2	15.3	17.2	17.4	17.6

desired heavy metal density in the fuel meat to compensate loss of enrichment, higher density uranium compounds/alloys were developed.

At MFD, BARC, a new plate fuel development and fabrication laboratory has been setup and a suitable process flow sheet has been developed to fabricate LEU based U_3Si_2 dispersed plate fuel elements for modified core of APSARA reactor. Two model fuel assemblies with natural uranium and conforming to specifications of modified APSARA core have been fabricated using standardized process parameters. The new facility has been inaugurated by Director, BARC on January 16, 2012 (see Fig. 1) and has started receiving LEU metal powder for further processing.

Fig. 1: Photograph of inauguration of plate fuel fabrication facility by Dr. R. K. Sinha, Director, BARC on January 16, 2012

2.0 Fabrication Work

2.1 Preparation of U_3Si_2 compound

The starting material used for the synthesis of U_3Si_2 compound is uranium metal powder and high purity & low boron grade silicon powder. Silicon powder was prepared by crushing silicon chunks in a jaw crusher followed by sieving. Extreme care was taken throughout the powder handling operation to avoid any oxidation of powders for which the entire powder handling operation was carried out inside a train of glove boxes maintained under high purity argon atmosphere. The process flow sheet for the preparation of U_3Si_2 granules was initially standardized to one kilogram batch size which has now been scaled up to a batch size of around 2.5 Kg (see Fig. 2).

To start with, uranium metal powder and silicon powder were weighed in the required proportion

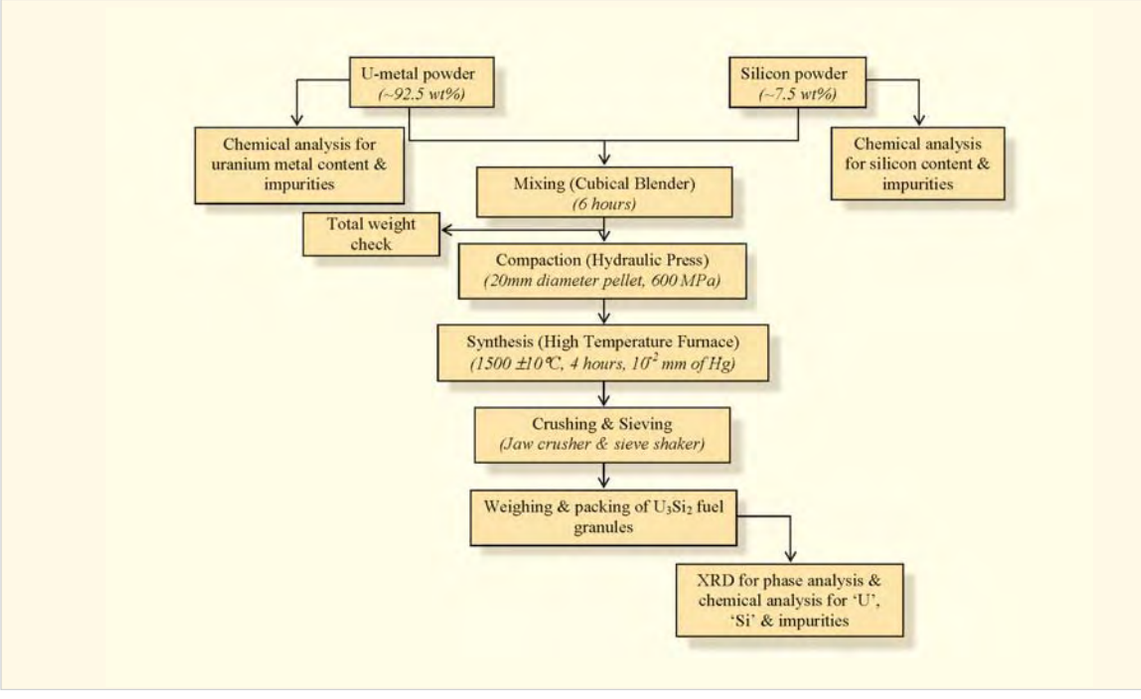

Fig. 2: Flow-sheet for fabrication of U_3Si_2 fuel granules by powder metallurgy route

and were mixed in a cubical blender for 6 hours to ensure good homogeneity between the constituents. The mixture was then compacted in a hydraulic press in the form of cylindrical pellets. During compaction, no admixed binder/lubricant was added to the mixture and only die-wall lubrication was used. The pellets were compacted at 600 MPa pressure in a 20 mm diameter pellet with L/D ratio at around 0.5 to 0.75. The green pellets were then loaded in molybdenum trays coated with plasma sprayed yttria and were heated inside 10 kW resistance heating furnace with graphite as heating element. Synthesis was carried out under vacuum of ~1.33 Pa at 1500±10^{0}C for 4 h. During the heating cycle, intermittent soak was given at 1100^{0}C and 1400^{0}C for one hour each. The synthesis temperature was kept well below the melting point of U_3Si_2 to avoid formation of any liquid phase and hence to eliminate any impurity pickup.

After cooling the furnace to room temperature, the synthesized U_3Si_2 clinkers were taken out and crushed to required size. Crushing was done in glovebox maintained under argon atmosphere due to the pyrophoric nature of the silicides, particularly in powder form [9]. A photograph of fuel granule production facility is shown in Fig. 3.

2.2 Fabrication of fuel plates

The fuel plates of U_3Si_2 particles dispersed in aluminium matrix and with Al-alloy clad were fabricated by mixing U_3Si_2 granules and aluminium metal powder in the required proportion. This mixture was then compacted in 800 ton single action hydraulic press at 900 MPa to get fuel meat. The press was enclosed inside glovebox for inert argon gas cover. The fuel meat was then picture framed (see Fig 4) followed by welding along edges to prepare fuel sandwich. A gap of around 20mm was kept open at one side during edge welding of sandwich to allow gases to escape out during hot rolling. The sandwich was then soaked inside a resistance heated furnace at 450^{0}C for 4 hours under vacuum and then hot rolling was carried out in multiple passes with intermittent soaking. Final plate dimension was achieved by cold rolling operation.

Fig. 3: Photograph of U_3Si_2 fuel granule production facility

Fuel plates passed through blister test were cleaned chemically in a 2.5 N NaOH solution for 5 minutes to remove any embedded contamination and the stains. Then X-ray radiography was carried out to locate fuel meat boundary and uranium distribution

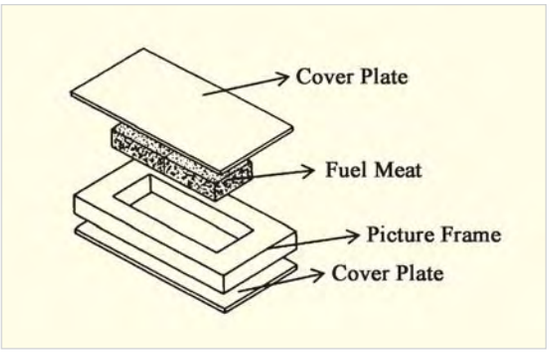

Fig. 4: Sketch of fuel-clad sandwich showing picture frame, fuel meat and cover plates

in the meat at 32.0 KV and 96.0 KV respectively. Based on the X-ray image, the outer boundary was located and trimming was carried out to get required dimension fuel plate.

2.3 Fabrication of fuel assembly

The finished fuel plates were then subjected to roll swaging operation to fabricate square cross section fuel boxes of Standard Fuel Assembly (SFA) and Control Fuel Assembly (CFA). Once these fuel boxes were prepared by swaging, the end fittings were welded for fabrication of complete fuel assembly.

Process flow sheet developed for fabrication of Al-alloy clad U_3Si_2-Al plate fuel assembly is shown in Fig. 5.

The photograph of plate fuel development and fabrication laboratory with process equipment has been shown in Fig. 6. The facility was inaugurated by Director, BARC on January 16, 2012 (see Fig. 1).

3.0 Acceptance criteria

The uranium silicide compound (U_3Si_2) prepared by powder metallurgy route is characterized by

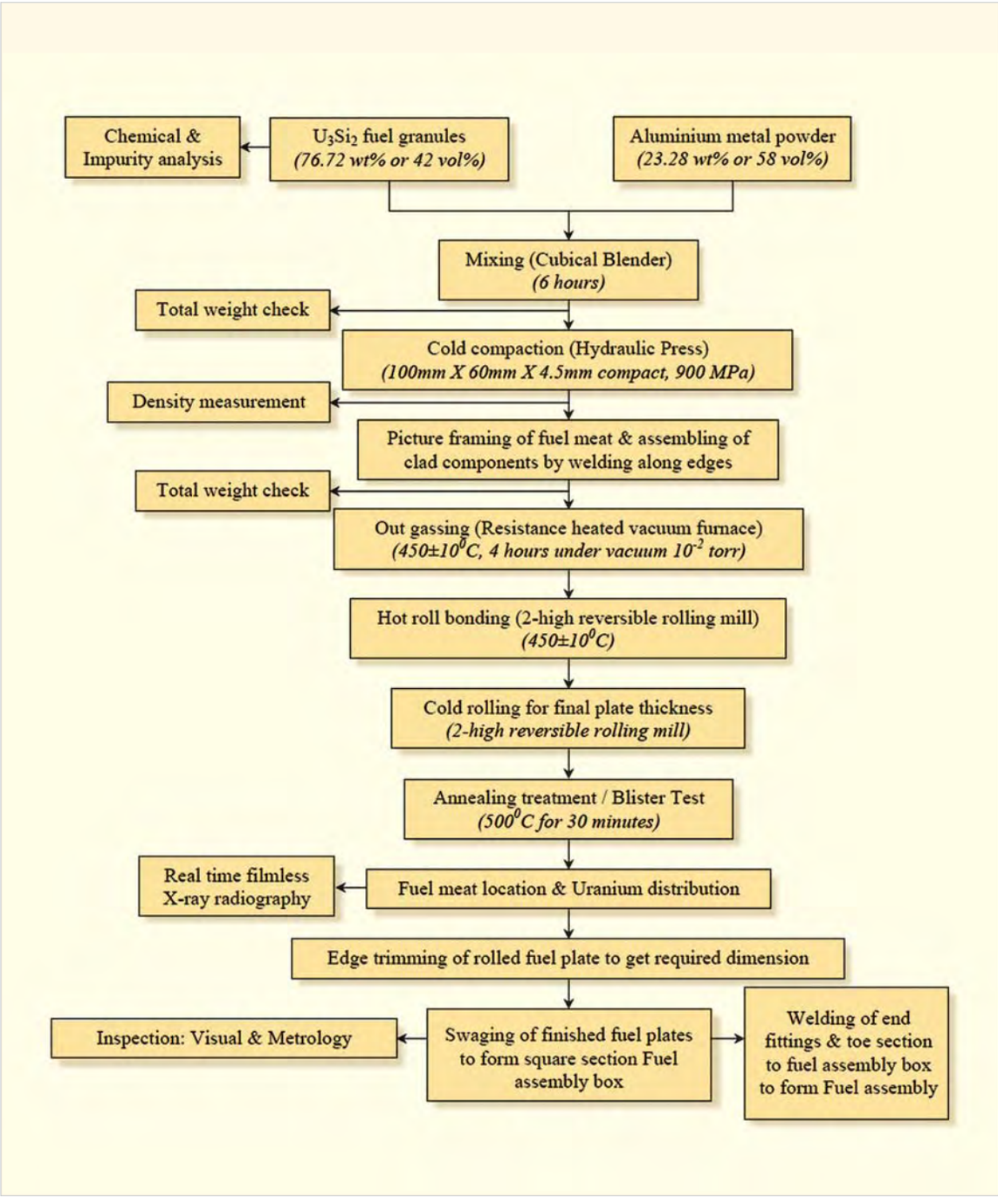

Fig. 5: Process flow sheet followed for fabrication of Al alloy clad U_3Si_2-Al plate fuel assembly

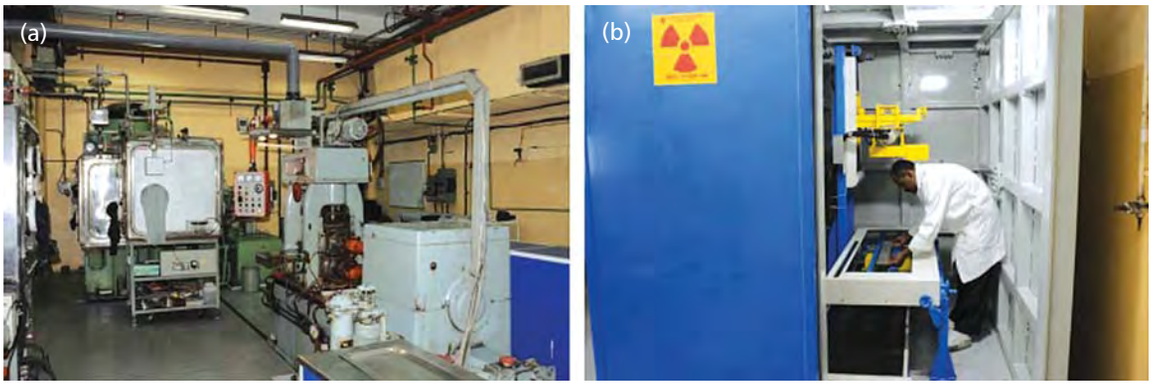

Fig. 6: Photograph of (a) plate fuel development and fabrication laboratory, (b) Real time X-ray radiography system

chemical analysis to determine uranium, silicon and impurity contents. Typical chemical analysis of a batch of U_3Si_2 clinker is given in Table 2. Phase analysis was also carried out by X-ray diffraction technique (see Fig. 7). The XRD pattern (Fig. 7) confirms the presence of U_3Si_2 as major phase and no other silicides are present in significant quantity. Powder metallurgy route employed for synthesis of U_3Si_2 compound results in homogeneous product. Metallography was carried out and microstructures were developed using optical and electron microscopy (Fig. 8). In addition, the microstructures have revealed the presence of intragranular porosity in the fuel compound. The results of X-ray radiography (see Fig. 9) on fuel plates have shown around 4.4 gm/cc of uranium loading in the fuel meat. The plates were also examined metallographically for the clad and fuel meat thickness (see Fig. 10). A Standard Fuel Assembly (SFA) photograph is shown in Fig. 11.All fuel plates were blister tested at 500^{0}C for 30 minutes under

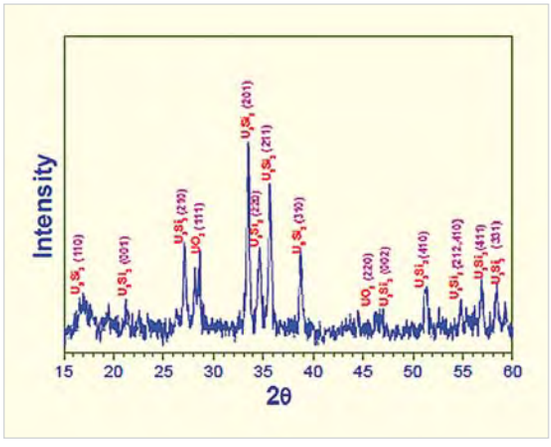

Fig. 7: X-ray diffraction pattern of U_3Si_2 clinker

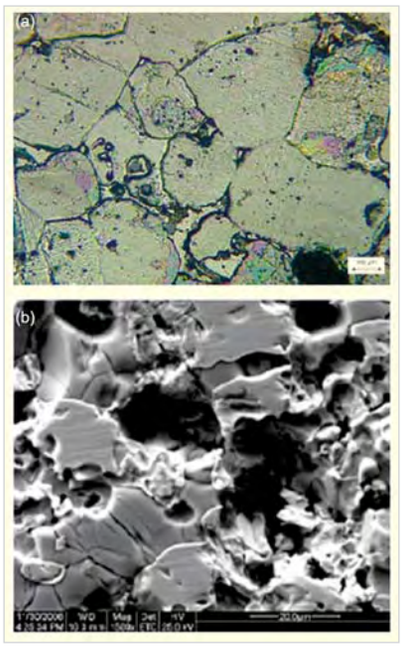

Fig. 8: Microstructure of U_3Si_2 clinker (a) Optical, (b) SEM

Table 2: Chemical analysis of U_3Si_2 compound

Element	U	Si	C	O	N	B
Concentration (wt%)	92.5±0.1	7.1±0.1	0.178	0.138	0.025	0.0001

Fig. 9: X-ray radiography of plate fuel at (a) 32.0 KV, (b) 96.0 KV

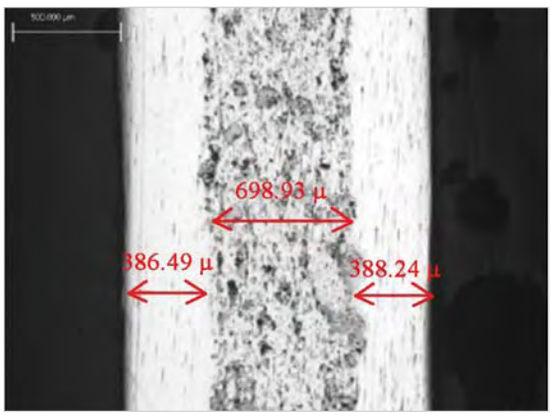

Fig. 10: Metallography examination of fuel plate in longitudinal direction

vacuum and then each plate has been examined visually for presence of any blister. Presence of any blister will lead to rejection of fuel plate. Fuel plates were also checked for presence of any loose and fixed contamination. Metrology of hardware components and final fuel assembly were also carried out to qualify it as per the dimensional specification of modified Apsara core.

4.0 Conclusion

Synthesis of U_3Si_2 fuel granules by powder metallurgy route was developed successfully. The product (U_3Si_2) prepared by powder metallurgy route does not require any additional step for homogenization unlike in melting casting route. A process flow sheet was also developed and established for the fabrication of fuel plates with 4.4 gm/cc of uranium loading in the fuel meat. Fuel plates were fabricated with minimum dog bone region which complies with the specifications. Blister test was carried out to determine non bond region in the fuel plate. The calibration of digital radiography grey value with uranium density was also established for online determination of uranium density in the fuel plates.

This work marks an important development which can be used for proposed research reactor and core conversion of existing reactors in the near future.

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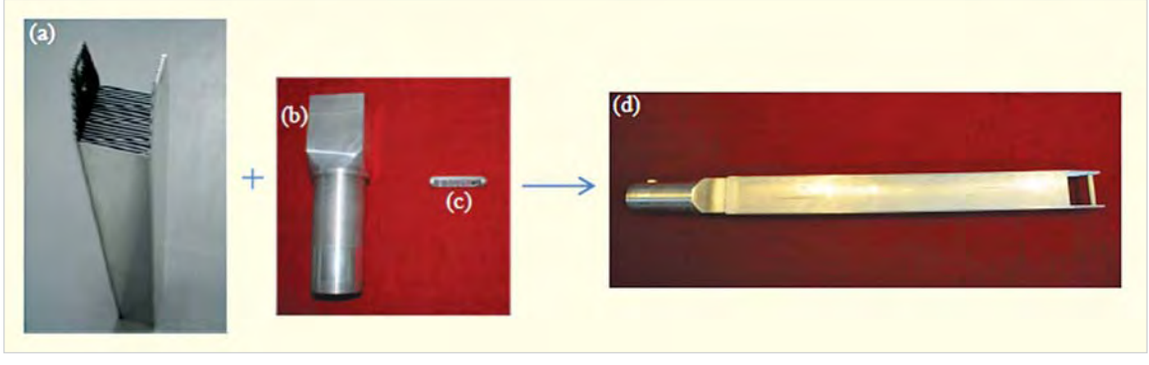

Fig. 11: Photograph of components and standard fuel assembly of modified core of APSARA reactor (a) Fuel box, (b) Toe section, (c) Handling pin, (d) SFA

out this work. The authors deeply acknowledge the support and help provided by Dr. K. L. Ramakumar, Director, RC&IG and Head, RACD in carrying out chemical characterization. The authors also acknowledge the timely support given by Shri Manjit Singh, Director, DM&AG and Head, CDM in the fabrication and supply of various hardware components required for the project. The authors acknowledge the help and engineering support provided by Shri K. N. Mahule, Head, ED&DD, S/ Shri R. S. Prasad and R. K. Mittal of ED&DD in the course of commissioning of plate fuel laboratory. The authors would take to place on record their deep gratitude to S/Shri H. S. Kamath and R. P. Singh, former Directors of NFG for providing useful guidance and encouragement. The authors gratefully acknowledge the team effort and hard work by all the scientific and technical staff members of MFD especially S/Shri S. K. Pal, G. P. Mishra and R.M Malagi.

References

1. R.F. Domagla, T.C. Wiencek and H.R. Tresh, *Nucl. Tech.* 62 (1983)353.

2. G.L. Copeland, Performance of Low Enrichement U_3Si_2-Aluminium dispersion fuel elements in the Oak Ridge Research Reactors, Argonne National Laboratory Report, ANL/ RERTR/TM-10 (1987).

3. V.P. Sinha, G.J. Prasad, P.V. Hegde, R. Keswani, C.B. Basak, S.Pal, and G.P.Mishra, Development, Preparation and Characterization of uranium molybdenum alloys for dispersion fuel application, *J. Alloys and Comp.* 473(2009)238.

4. Jeong-Soo Lee, Chang-Hee Lee, Ki Hwan Kim, Vyacheslav Em, Neutron diffraction study of U-5.4wt% Mo alloy, *J. Nucl. Mater.* 280(2000)116.

5. J.P. Durand and Y. Fanjas, LEU fuel development at CERCA: status as of October 1993, Proceedings of the 16th International Meeting on Reduced Enrichment for Research and Test Reactors, Japan Atomic Energy Research Institute Report, Oarai, Japan, JAERI-M 94-02, 71-78.

6. J.P. Durand, P. Laudamy and K. Richter, Preliminary developments on MTR plates with uranium nitride, Proceedings International Meeting on Reduced Enrichment for Research and Test Reactors, 18-23 September, Argonne National Laboratory Report, ANL/RERTR/TM-20, Williamsburg.

7. V.P. Sinha, P.V. Hegde, G.J. Prasad and H.S. Kamath, Development of high density uranium molybdenum alloys by powder metallurgy route for dispersion fuel application in research and test reactors, 17th Plansee Seminar, Reutte, Austria, Vol. 1, (2009), RM 78/1-16

8. G.I. Snelgrove, The use of U_3Si_2 dispersed in aluminium in Plate-type Fuel Elements for Research and Test Reactors, Argonne National Laboratory Report, ANL/RERTR/TM-11 (1987).

9. V.P. Sinha, G.P. Mishra, S. Pal, K.B. Khan, P.V. Hegde and G.J. Prasad, Development of powder metallurgy technique for synthesis of U_3Si_2 dispersoid, *J. Nucl. Mater.* 383(2008)196.

Zinc Oxide Nanowires for Gas Sensing Application

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Abstract

We present the growth of ZnO nanowires (NWs) using vapor phase and hydrothermal methods. In order to investigate the gas sensing characteristics, two types of sensors were prepared: (i) mat-type and (ii) as-grown random network of ZnO NWs. Mat–type sensors detected H_2S at room temperature with fast response and recovery times of 250 and 700 s, respectively. On the other hand, as-grown random network of ZnO NWs were less sensitive to H_2S. However, modification of random networks by CuO layer improved the sensing properties, which is explained on the basis of the formation and destruction of p-n junction among p-type CuO and n-type ZnO.

1. Introduction

One dimensional nanostructures of metal oxides namely nanowires (NWs) have emerged as a general platform for ultra-sensitive direct electrical detection of biological and chemical species[1,2]. NWs in particular, offer various advantages that include high surface area to volume ratio, Debye length (the distance over which a local electric field affects the distribution of free charge carriers) comparable to the target molecule, low power consumption, possibility of high integration densities and ease of incorporation into microelectronic devices. Among various semiconducting oxide materials, ZnO has generated a great deal of interest due to its direct wide band gap of 3.37 eV, large exciton binding energy of 60 meV, and processing advantages for its nanostructures[3]. There are two different approaches to the production of 1D structures: top-down and bottom up technologies. The first one is based on standard micro fabrication methods with deposition, etching and ion beam milling on planar substrates in order to reduce the lateral dimensions of the films to the nanometer size. Electron beam, focused ion beam, X-ray lithography, nano-imprinting and scanning probe microscopy techniques can be used for the selective removal processes. The advantages are the use of the well developed technology of semiconductor industry and the ability to work on planar surfaces, while disadvantages are their extremely elevated costs and preparation times. Furthermore the 1D nanostructures produced with these techniques are in general not single-crystalline. The second approach, bottom-up, consists of the assembly of molecular building blocks or chemical synthesis by vapor phase transport, electrochemical deposition, solution-based techniques or template growth. Its advantages are the high purity of the nano-crystalline materials produced, their small diameters, the low cost of the experimental set ups. The main disadvantage is their integration on planar substrates for the exploitation of their useful properties, for example transfer and making contacts can be troublesome.

Providing electrical contacts to NWs is often considered as a complex and tedious process. An electrical contact to sensors based on single NWs is often realized using a 'pick and place' approach. In this, NWs are first drop-casted or spin-coated onto the substrates containing predefined electrodes and then aligned using dielectrophoresis technique. To assure proper contact, additional electrode material

is often deposited connecting NW and electrode using Focused Ion Beam techniques. One of the promising approaches is to use ordered or random networks of NWs. Herein NWs can be selectively grown between the predefined electrodes or electrical contacts can be provided by depositing the electrodes with known dimensions on the NWs network itself. This method is advantageous over the one involving the 'pick and place' approach as it removes the complexity involved towards a longer extent. Besides, it is easy and can assure reproducible measurements. Accordingly, in the present work, ZnO NWs have been investigated in detail for possible gas sensing application.

2. Growth of ZnO nanowires

NWs have been synthesized using two approaches namely vapor phase deposition and hydrothermal method[1,2]. For vapor phase deposition, Zn metal powder was heated in a quartz boat placed inside a quartz tube at 900°C under controlled Ar and O_2 atmosphere. Zn was found to evaporate and deposit in the quartz tube in the direction of the gas flow. For hydrothermal growth, ZnO nanoparticles (NPs) were first synthesized using chemical route and then spin coated onto the substrate which acts as a seed[3]. NWs growth was accomplished by suspending NP coated substrates upside-down in an open beaker filled with an aqueous equimolar (0.025 M) solution of zinc nitrate hydrate and hexamine at 90°C. The aspect ratio of NWs was controlled using the duration of the reaction. Fig. 1 shows the corresponding SEM images of the ZnO NWs grown using both the methods. ZnO NWs grown at 700°C after heating Zn powder for 5 h have diameters $\leq$ 100 nm. On the other hand, hydrothermally grown NWs exhibit diameter between 50 and 200 nm and length 1-2 μm forming a dense network over the substrate. The quasi-hexagonal ends of the ZnO-NWs indicate that their main axis is preferentially oriented along the [0001] direction, which is in accordance with the growth habit of wurtzite crystals.

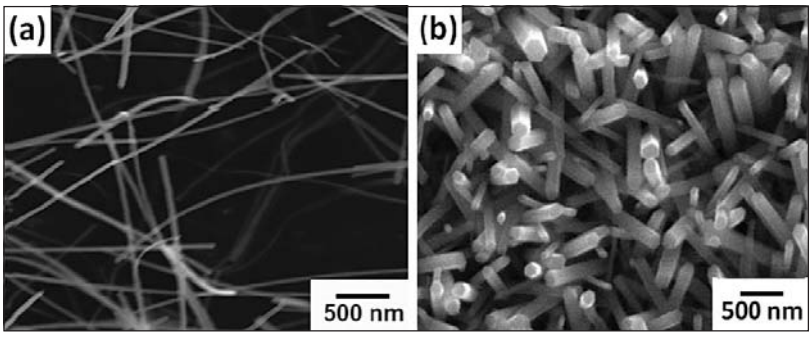

Fig. 1: SEM images of ZnO NWs (a) vapor phase grown at 700°C after heating Zn powder for 5 h and (b) hydrothermally grown for 6 h growth time.

3. Gas sensing measurements

Gas sensing properties of NWs were investigated in a static gas sensing set-up as shown in Fig. 2. In brief, sensor films were mounted in a stainless steel test-chamber (volume: 250 cm^3) equipped with a temperature control unit. The desired temperature was achieved using a Pt-wire based heater attached to the backside of the sensor film. The desired concentration of the test gas was achieved by injecting the measured quantity of commercial gas inside the chamber. The resistance of the film was

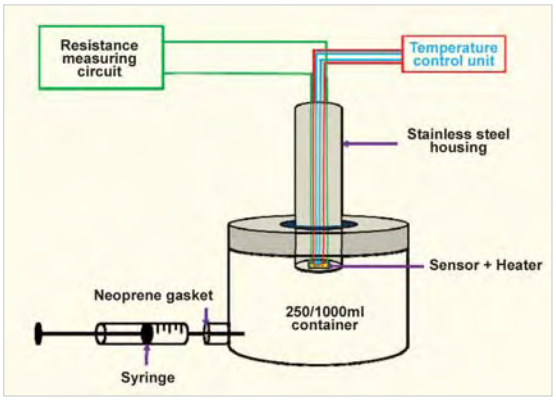

Fig. 2: Static environment gas sensing set-up

monitored and acquired as a function of time using a personal computer equipped with Labview software. Recovery of the sensors was achieved by opening the housing to the atmosphere.

3.1. Drop-casted mat-type ZnO NW films

NWs films were prepared by first making a paste in methanol and painting them on substrate containing predefined electrodes followed by annealing at 500°C. NWs were aligned di-electrophoretically between the microelectrode gaps under the application of electric field of 20 Vpp at 100 KHz. Consequently, NWs were trapped and aligned along the electric field lines bridging the electrode gap where the electric field becomes higher. As shown in Fig. 3, sensor films exhibited good sensitivity ($S = R_a/R_g$) towards H_2S and NO gases at room temperature with very little or no response towards other gases. Typical response and recovery times for 10 ppm concentration are 250 and 700 s for H_2S and 250 and 150 s for NO, respectively. The response and recovery times were found to increase with concentration.

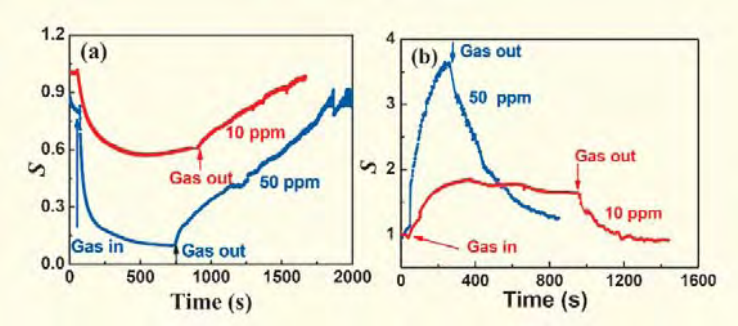

Fig. 3: Response (*S*) of a typical ZnO NW film to different concentrations of (a) H_2S and (b) NO. The measurements have been

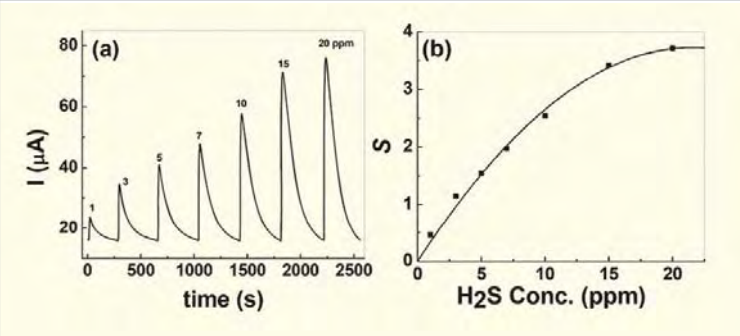

Fig. 4: (a) Response curves of ZnO NW-film towards different concentrations of H_2S at 350°C and (b) corresponding concentration dependence of sensor response.

3.2. ZnO NPs and hydrothermally grown NWs

Fig. 4 shows the response curves of NW-films towards different concentrations of H_2S at 350°C with corresponding concentration dependence of response. NW-films can reliably detect H_2S at 1 ppm concentration. Sensor response [$S = (I_g - I_a)/I_a$] is also observed to increase with concentration saturating at around 15 ppm. It exhibits a power law dependence on concentration given as:

$$S = AC^{\alpha} \quad (1)$$

where, A is constant. From the fit of Fig.5 (b) the value of α was found to be 0.7. The power law dependence arises from receptor and transducer functions i.e., the adsorption or interaction of H_2S with the sensor surface and the change of surface potential, respectively.

Response of NP-films (size:10 nm) was also studied on exposure to H_2S and Cl_2 gases at 350°C as shown in Fig. 5. NPs are found to have lower response to the gases and interestingly the change in resistance is in opposite direction to that of NWs indicating p-type conduction.

The formation of n-type NWs and p-type NPs were independently confirmed by hot probe and Kelvin probe Contact Potential Difference (CPD) measurements, respectively. For hot probe measurements, thin films of required nanomaterial (with two Au electrode contacts) were

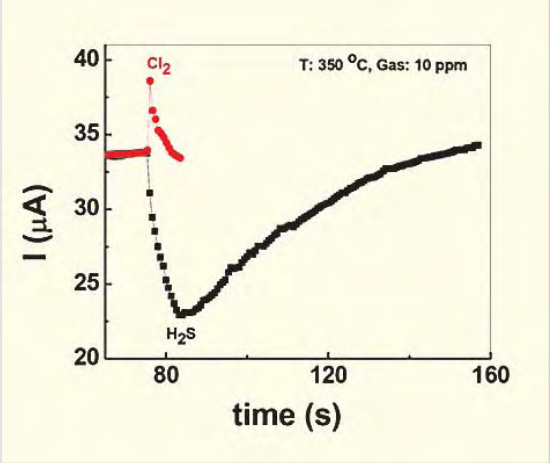

Fig. 5. Response curves of ZnO NP-film towards 10 ppm of H_2S and Cl_2 gases at 350°C

heated from one end and the developed thermo-e.m.f was measured. With the hot and cold probes connected to positive and negative terminal of the voltmeter respectively, a negative voltage for NP-films and positive voltage for NW-films were obtained, confirming the p-type and n-type nature of NPs and NWs, respectively. Fermi level of a semiconductor is close to conduction band for n-type and to valence band for p-type materials. Therefore, it is expected that the work function of a material should increase when the nature of conductivity changes from n to p-type. To confirm difference in nature of conduction for NPs and NWs, work function was scanned across the samples by Kelvin probe. The average work functions of 4.8 and 5.3 eV for NW- and NP-films respectively is obtained, which is in accordance with the change in nature of conductivity from n to p-type.

Cu is known to be an excellent promoter for H_2S causing an enhancement of both the sensitivity and the selectivity of the sensor towards H_2S. Accordingly, we have investigated the effect of Cu on H_2S sensing properties of ZnO NWs[7]. The sensor modified with 10 nm of Cu responded with maximum sensitivity at an operating temperature of 250°C. Fig. 6 shows the response curves recorded towards increasing concentration of H_2S. The sensor exhibited a fast response and recovery times for example, towards 5 ppm of H_2S response and recovery times were 62 and 150 s, respectively. This fast response kinetics could be attributed to the effective electron conduction pathway provided by NWs.

In order to investigate the nature of interaction between ZnO-NWs and CuO, we have carried out photoluminescence (PL) studies (Fig. 7 (a)). Both the ZnO-NW and CuO(10nm):ZnO-NW random networks exhibit a peak at 384 nm corresponding to a Near Band edge Emission (NBE). ZnO-NWs network exhibited a broad band peak at 595 nm attributed to oxygen vacancies. For CuO(10nm):ZnO-NWs network, this peak broadens, intensifies and shifts to higher wave length (i.e. 627 nm). The origin of such a peak has been attributed to the plasma resonances of oxidized copper aggregates. Interestingly on CuO deposition NBE peak quenches by ~42%. This can be explained based upon the formation of p-n junction between p-type

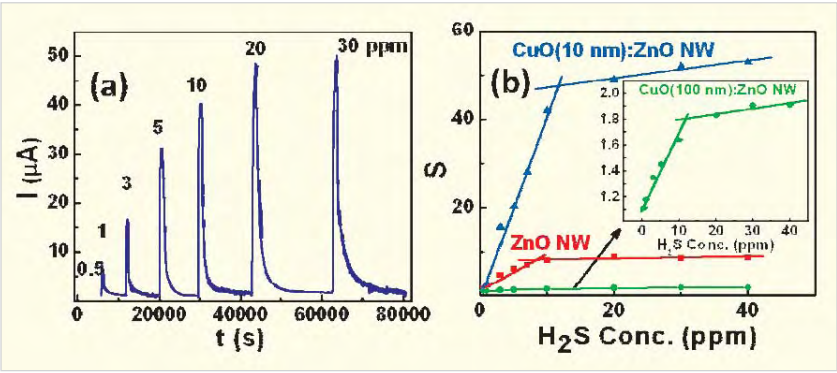

Fig. 6. (a) H_2S response curves of CuO (10nm):ZnO-NWs measured at 200°C (b) Variation of the sensitivity as a function of H_2S concentration. Inset shows enlarged view for CuO (100nm):ZnO-NWs sensor.

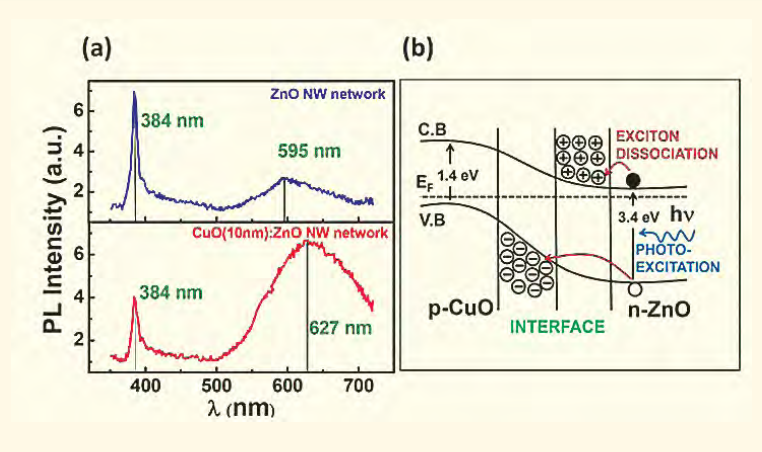

Fig. 7: (a) Room temperature PL spectra recorded for ZnO-NWs and CuO (10nm):ZnO-NWs random networks. (b) Schematic representation of the formation of p-n junction between CuO and ZnO and quenching of near-band edge emission of ZnO due to dissociation of excitons.

CuO and n-type ZnO, as schematically shown in Fig. 7 (b). When a photon is incident on the sample, electron gets excited into the conduction band leading to the formation of an exciton. The p-n junction enhances the dissociation of excitons as ZnO transports electrons away and CuO transports the holes. Dissociation of excitons greatly suppresses the electron-hole recombination necessary for PL emissions.

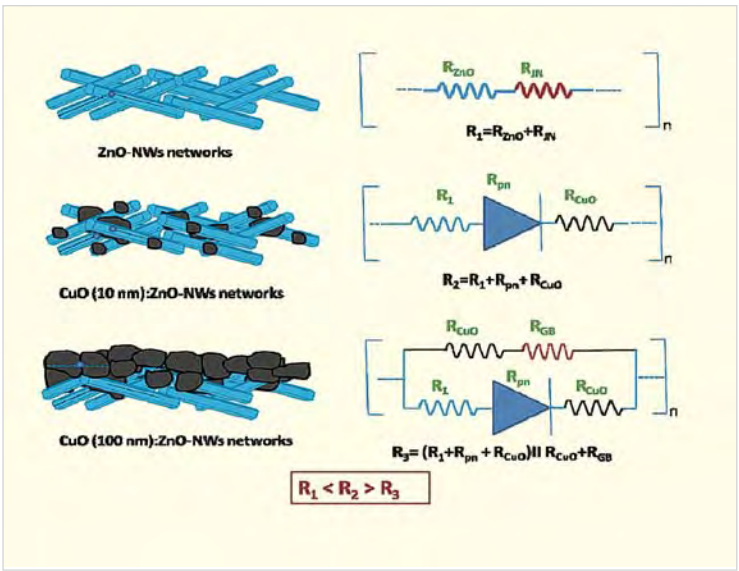

Fig. 8: Schematic representation of the equivalent electrical circuit of different CuO:ZnO-NWs random networks

In order to further investigate the effect of p-n junction, we have measured the room temperature electrical resistance as a function of CuO layer thickness. The results unambiguously show that the resistance increases sharply upto a nominal thickness of 10 nm and then decreases monotonically. The electrical resistance (R_1) of bare ZnO-NWs network can be represented as the series resistance of the ZnO-NWs (R_{ZnO}) and the junction resistance formed between the NWs (R_{JN}) (Fig. 8). The resistance (R_2) of ZnO-NWs network modified with a CuO layer upto a nominal thickness of 10 nm can be represented as a series equivalent to that of R_1, p-n junction and CuO aggregates. Due to the presence of p-n junction, the value of R_2 is expected to be very high. However, at very high nominal thickness, CuO fully covers the ZnO-NWs network. Thus a continuous CuO layer acts as a parallel resistance, which reduces the total resistance (R_3) of the sample. Herein the CuO layer contributes two resistances one corresponding to CuO layer (R_{CuO}) and the other corresponding to the grain boundary (R_{GB}) resistance between CuO grains. Thus $R_1 < R_2 > R_3$ is in accordance with experimental results.

Modification of ZnO NWs network with CuO (10 nm) results in the formation of random n-p-n type junctions. The potential barrier formed at the ZnO/CuO/ZnO heterojunction results in a very high resistance of the film. Exposure to H_2S causes the potential barrier to disappear. CuO reacts with H_2S forming CuS as per the following reaction:

$$CuO + H_2S \rightarrow CuS + H_2O \quad (2)$$

CuS being metallic will destroy the n/p/n junction as well as the potential barrier, and a new type of n-ZnO/metallic-CuS/n-ZnO heterojunction will be formed. The destruction of potential barrier results in a sharp decrease in the electrical resistance. During recovery, CuS reacts with oxygen forming once again CuO. The potential barrier reappears due to the formation of n-ZnO/p-CuO/n-ZnO heterojunctions, and original high resistance is regained.

4. Summary

ZnO NWs grown using both the physical as well as the chemical methods have been investigated for gas sensing applications. In particular, techniques like vapor phase deposition and hydrothermal growth were used effectively to realize these nanostructures. Proper electrode contacts were realized using dielectrophoresis technique and by directly depositing the electrode over NW network film. ZnO NPs exhibited a p-type response towards gases while NW film detected H_2S with faster response and recovery time of 13 and 78 s, respectively towards 20 ppm at 350°C. Cu incorporation over NW surface has been demonstrated to improve both the sensitivity and the selectivity towards H_2S. Our results clearly illustrate that ZnO NWs are the potential candidates for the realization of next generation of sensors. Hopes are high that significant practical devices will soon evolve from the integration of these structures with conventional microelectronics.

Acknowledgements

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References

1. Aswal, D.K., Gupta, S.K. (eds), Science and Technology of Chemiresistive Gas Sensors, Nova Science Publisher, NY, USA, 2007. ISBN: 978-160021-514-8.
2. Ramgir, N. S., Datta, N., Kaur, M., Debnath, A. K., Aswal, D. K., Gupta, S. K., "Semiconductor nanowires and heterostructures based gas sensors", in Vincent Lefevre (Ed), Nanowires: Properties, Synthesis and Applications, Nova Science Publisher, NY 11788, USA ISBN 978-1-61470-129-3 (2011) 1-46.
3. Ramgir, N. S., Rikka, V., Kaur, M., Kailasa Ganapathi, S., Mishra, S. K., Datta, N., Aswal, D. K., Gupta, S. K., Yakhmi, J. V., "ZnO nanowires as H_2S sensor", CP1313 International Conference on Progress in Emerging Functional Materials, PEFM-2010,: 322-324.
4. Gupta, S. K., Ramgir, N. S., Kaur, M., Datta, N., Saxena, V., Joshi, A., Singh, A., Aswal, D. K., "Studies on polymer-ZnO nanowires composites for gas sensing application", *World Journal of Engineering,* 7 (2010): 379-380.
5. Datta, N., Ramgir, N. S., M., Kailasa Ganapathi, S., Debnath, A. K., Aswal, D. K., Gupta, S. K., "ZnO nanowires coated with CuO films as highly sensitive H_2S sensors", TFST-2011, Indian Vacuum Symposium on Thin Films: Science and Technology, at BARC, Mumbai.
6. N. S. Ramgir, S. Kailasa Ganapathi, M. Kaur, N. Datta, K. P. Muthe, D. K. Aswal, S. K. Gupta, and J. V. Yakhmi, "Growth and gas sensing characteristics of p and n-type ZnONanostructures", *Sens. Actuators B* 156 (2011): 875-880.
7. Datta, N., Ramgir, N. S., Kaur, M., Kailasa Ganapathi, S., Aswal, D. K., Gupta, S. K. "Selective H_2S sensing characteristics of hydrothermally grown ZnO-nanowires network tailored by ultrathin CuO layers" *Sens. Actuators B* 166-167(2012): 394-401.

Design and Application of a Formal Verification Tool for VHDL Designs

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Abstract

The design of Control and Instrumentation (C & I) systems used in safety critical applications such as nuclear power plants involves partitioning of the overall system functionality into subparts and implementing each subpart in hardware and/or software as appropriate. With increasing use of programmable devices like FPGA, the hardware subsystems are often implemented in Hardware Description Languages (HDL) like VHDL. Since the functional bugs in such hardware subsystems used in safety critical C&I systems have disastrous consequences, it is important to use rigorous reasoning to verify the functionalities of the HDL models. We describe our work on developing a software tool named VBMC (VHDL Bounded Model Checker) for mathematically proving functional properties of hardware designs described in VHDL. It is based on the principle of bounded model checking. Although the design of VBMC is still evolving, it is currently also being used for the functional verification of FPGA based intelligent I/O (EHS) boards developed in Reactor Control Division, BARC.

1. Introduction

Computer-based Control and Instrumentation (C&I) systems used in nuclear power plants are mandated to undergo a rigorous verification process commensurate with the safety class of the system. The design of such systems involves partitioning of the overall system functionality into subparts, and implementing each subpart in hardware and/or software as appropriate. Needless to say the verification support for these systems has to be tool-based, to make it rigorous, repeatable and fast. We had identified various areas in the system development life cycle where such verification tools needed to be deployed. Although commercial solutions are available in some areas for verification of software and hardware, scalability, technological obsolescence and supply availability from foreign vendors always remain in question. This is the main motivation behind the ongoing programme at the Reactor Control Division to develop indigenous tools for software and hardware verification.

Many C&I systems are now increasingly using FPGA devices, which allow configurability by the hardware designer. The configurability is enabled by the capability of "field programming" such hardware devices using Hardware Description Languages (HDL) like VHDL. Since the functional bugs in such hardware subsystems used in C&I of safety critical systems have disastrous consequences, it is very much required that verification techniques of equal rigour as the software should also be applied to the design of such hardware components. In fact, this is also mandated by AERB safety guide D-25. This was the motivation to develop a verification tool for hardware designs which are synthesized and configured into Field Programmable Gate Arrays (FPGA). In this article, we discuss our efforts towards the development of a verification tool called VBMC for VHDL-based hardware design. We also discuss few applications of this tool in BARC. The tool has been developed in collaboration with CFDVS, IIT Bombay, Mumbai.

2. Background of Hardware Verification

Traditionally, the functional verification of HDL designs has been done by simulation or testing. However, exhaustive testing covering the entire behaviour space of the design is impractical for designs of even medium size and complexity. It is now recognized that formal verification provides a complementary approach to simulation and testing by unravelling the corner cases of the behaviour space quickly.

Hardware designs fall into two different domains: *Control-dominated and Data-dominated*. A common definition of a "control-dominated" design is one which is realized by interacting finite state machines e.g. memory controller hardware. On the other side "data-dominated" designs like digital filters involve multi-bit data and its word level interpretation.

The formal verification techniques for data-dominated designs differ significantly from those used for control-dominated designs. Control-dominated designs are normally verified using model checking. Model checking involves an exhaustive search of the entire state space of the design to ensure that the design can never be in an undesirable state. Model checking is typically fast and fully automatic. Unfortunately, the number of states in the state spaces of real-world designs is prohibitively large particularly due to the wide data paths present in the designs. This restricts the scope of model checking techniques in formal verification of data-dominated designs. Data-dominated designs are normally verified using proof-based approaches that focus on mathematically proving/refuting properties of the designs using proof engines called Theorem Provers. Theorem proving often requires human insight and creativity to complete proofs and is not fully automatic.

Real-life designs are a mix of both control and data dominated subparts and it is very difficult to separate them. Hence, it is usually left to the verification engineer to carve out suitable parts of the design that are then subjected to appropriate verification techniques. This makes the process tedious, error-prone, and highly dependent on the ingenuity and skills of the verification engineer. Hence, it is important to develop automated verification tools which can verify hardware designs with both control-dominated and data-dominated subparts.

There are some commercial as well as academic tools for the formal verification of HDL designs. The tools in the commercial domain include FormalCheck [1] and RuleBASE [2]. However these tools operate at bit-level which pose serious scaling issues when reasoning about designs with wide data paths. VCEGAR [3] is an academic tool for formal verification of Verilog programs which works at word-level. This tool is based on an idea called predicate abstraction. The identification of right set of predicates is crucial in the successful application of this tool, which is an undecidable problem in general.

VBMC (VHDL Bounded Model Checker) is a tool for mathematically proving/refuting functional properties of hardware designs with both control-dominated and data-dominated subparts described in VHDL. It is based on the principle of bounded model checking. In bounded model checking, the model checker looks for a violation of the stated property while exploring a depth of k (integer) of the state space. If no bug is found in this depth of k, then one can increase k until (i) violation is found, (ii) the entire space is searched, or (iii) the computation time becomes prohibitive. In case of (ii), it has been proved that the design does not violate the property under all possible executions.

3. Conceptual Framework and Design of VBMC

VBMC performs the verification of functional properties of VHDL designs with both control-dominated and data-dominated subparts by combining three powerful techniques used by the formal verification community, namely symbolic

simulation [4], word-level constraint solving [5], and counterexample guided abstraction refinement [6].

Symbolic simulation involves simulating a design's behaviour using symbols for the design's inputs. This helps in deriving relations between inputs, outputs, and internal variables of the design as symbolic expressions. By substituting concrete values for the symbols in these symbolic expressions, the result of traditional (concrete valued) simulation can be obtained. This technique has been shown to be effective in reasoning about designs with wide data paths as well as significant control complexity.

The symbolic expressions generated by symbolic simulation can be used to derive the transition relation (R) of the design. Transition relation of a design is a relation between present and next states of the design. As an example, let us say that we want to ensure that the design has a functional property P for k cycles of operation. This can be done by unrolling the transition relation k times, conjoining the unrolled relation with the negation of the property P, and then checking for satisfiability of the resulting constraint using a word-level constraint solver. The process of checking for the satisfiability of such a constraint (called verification condition C) gives one of the two outcomes: (i) either we get a set of assignments of values to the signals in the design that demonstrates a concrete execution of the design violating the property, called a counterexample, or (ii) we infer that the verification condition cannot be satisfied, implying that the design satisfies the property under verification up to k cycles of operation.

The process of checking the satisfiability of the verification condition C can pose serious scaling issues if one tries to reason about all variables and expressions at the greatest level of detail. We alleviate this problem using an abstraction (over-approximation) C' of the verification condition C which is simpler to reason about compared to C. C' is obtained from the transition relation R in the following way: We initially obtain an abstraction of the transition relation (R') from the transition relation R by hiding the details of selected internal signals of the design. C' is obtained by unrolling the abstract transition relation k times and conjoining the unrolled relation with the negation of the property P. The set of solutions of R' is a superset of the set of solutions of R; hence the set of solutions of C' is a superset of the set of solutions of C. If C' does not have any solution then, C also does not have any solution, and the design satisfies the property up to k cycles of operation. However, if C' has a solution π, then π may or may not be an execution which the design can follow violating the property. If π is an execution of the design which violates the property, then π is called a real counterexample. Otherwise π is called a spurious counterexample. Hence, if a counterexample is obtained, it needs to be analyzed to check if it is a real or spurious counterexample. If it is a real counterexample, we have proved that the design violates the property under verification. However, if it is a spurious counterexample, it needs to be eliminated by refining the abstraction R' (and consequently C') using hints from the spurious counterexample. This process of checking for the satisfiability of the abstract verification condition and refining it continues iteratively, until (i) a real counterexample is obtained, or (ii) it is proved that the design satisfies the property. This technique of starting from an initial abstraction and refining it iteratively in a counterexample guided manner is called CounterExample Guided Abstraction Refinement (CEGAR).

As the transition relation R is in general a bit-vector (word-level) formula, the problem of generating an abstraction of the transition relation boils down to variable elimination (more commonly known in literature as quantifier elimination) problem for bit-vector formulas. VBMC uses a novel quantifier elimination algorithm *QuaLMoDE* [7], which tries to keep

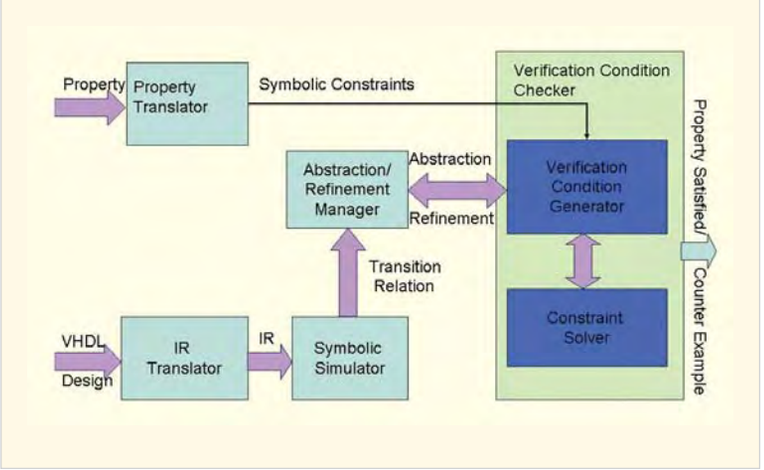

Fig. 1: Architecture of VBMC

the quantifier-eliminated formula at word-level as much as possible, resorting to blasting only when it is absolutely necessary. This helps in keeping the abstract transition relation and the abstract verification condition at word-level. Keeping the abstract verification condition at word-level is appealing, as it allows efficient word-level reasoning to be applied by the back-end word-level constraint solvers. This improves the overall scalability of the verification scheme particularly when verifying designs with wide data paths.

The block diagram in Fig. 1 shows the internal details of VBMC. A brief description of the internal components of VBMC is given in Table 1.

Table 1: Components of VBMC

Components	Description
IR Translator	The IR translator translates the VHDL design into an Intermediate Representation (IR).
Symbolic Simulator:	The symbolic simulator performs the symbolic simulation of the design generating symbolic expressions and generates transition relation of the design from the symbolic expressions.
Abstraction/Refinement Manager:	Abstraction/refinement manager generates an abstraction of the transition relation by hiding/eliminating the details of a selected set of internal variables of the design. The degree of abstraction depends on the set of internal variables chosen for elimination. The larger the set of internal variables chosen for elimination, the larger is the degree of abstraction.
Property Translator	Property translator converts the property (in Bounded Property Specification Language [8]) into the input language of the constraint solvers called the SMTLIB format
Verification Condition Generator/Checker	Verification condition generator/checker (i) generates the abstract verification condition, (ii) checks the satisfiability of the abstract verification condition using a word-level constraint solver, and (iii) either reports that the property is proved/refuted or finds the set of internal variables in the design to be exposed (not to be eliminated) while generating the next abstract transition relation.

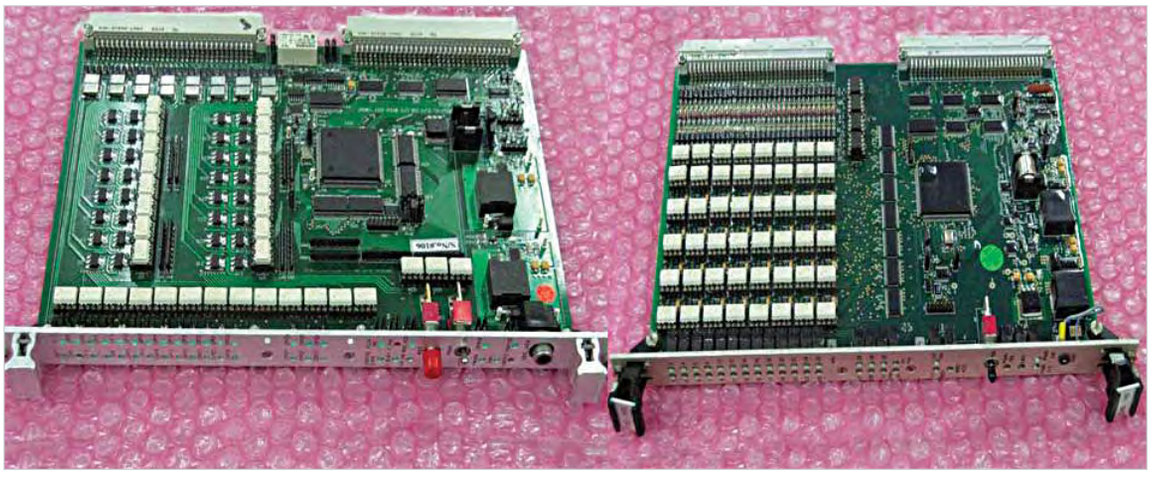

Fig. 2: Digital input and output boards

4. Applications

The Reactor control Division has a programme of in-house development of hardware boards (EHS Boards) for use in safety-critical I&C systems. There are four categories of EHS boards: Power PC based Processor Board, Dual Ethernet Communication Board, Protocol Translator Board and Field Interfacing (I/O) Boards (Fig. 2). The I/O boards are intelligent and designed based on present day technology and components, and the intelligence of these boards is implemented in FPGA/CPLD using VHDL.

These boards have been designed following design life cycle as mandated by AERB-D25 safety guide. As a part of this, FPGA Requirement Specification (FRS) Document was prepared. VBMC has been used for the functional verification of VHDL programs developed for the FPGAs used in these I/O boards. The functional properties specified in the FRS document were taken up for verification. The verification cycle followed was iterative and is shown in Fig 3. Properties were initially written in English, followed by their translation into Property Specification Language (PSL) which was then submitted for verification. In cases, where the tool reported the falsification of the property in the design, we have examined each of the counterexample produced by the tool and the design to understand the reason for failure. The results produced by the tool have helped in increasing precision in specification. As explained earlier, if verification of a property fails, the tool generates a counterexample. The GUI displays the counterexample in the form of waveforms for input and output signals. An example screenshot of such a waveform is shown in Fig. 4.

5. Conclusions and Future Work

We have also evaluated the performance of VBMC on a set of other benchmark VHDL designs. This included a set of public domain VHDL designs [9]. Using VBMC, we could check functional properties of these designs up to 2000 cycles of operation within 1800 seconds on a 1.83 GHz Intel(R) Core 2 Duo machine with 2GB RAM running Ubuntu 8.04, with "simplifyingSTP" as the back-end constraint solver. This outperformed the existing techniques, which were unable to scale beyond a few tens of cycles with a time limit of 1800 seconds.

At present, the Graphical User Interface (GUI) of the tool is not very user friendly and it requires expertise on the underlying technology. We are extending the GUI which will allow the design engineer to work with the tool with minimum expertise.

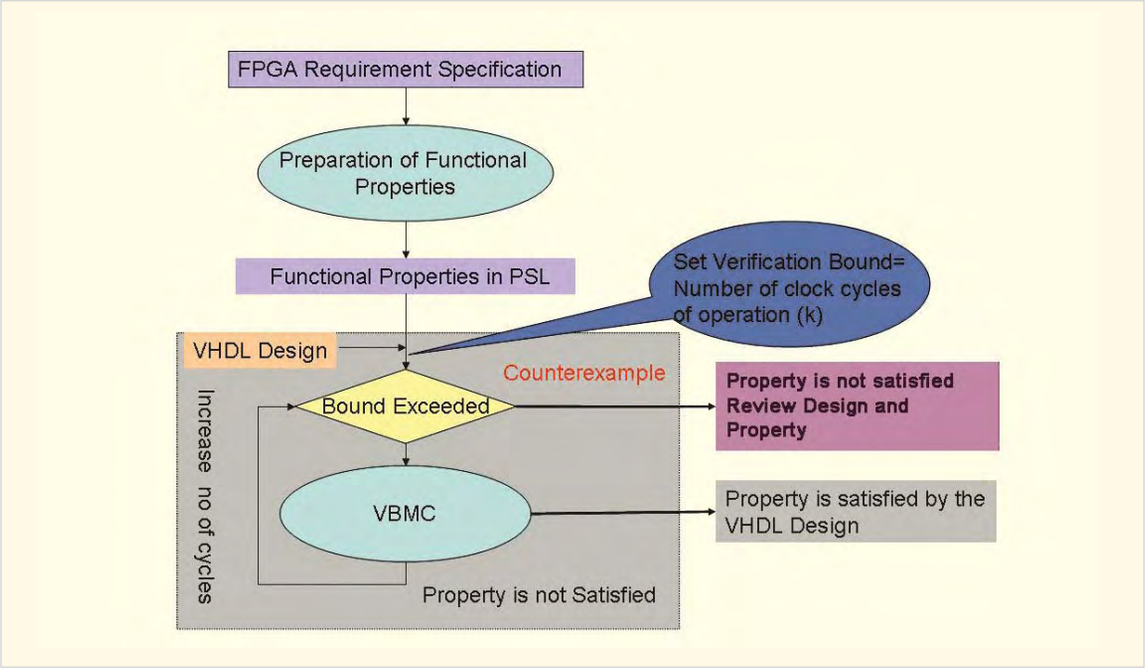

Fig. 3: Verification steps

Given a VHDL design and a property in Property Specification Language (Bounded), VBMC either generates a counterexample, or infers that the design satisfies the given functional property for the given cycles of operation. It can be observed that, in the latter case, VBMC provides a guarantee that the design satisfies the property for a bounded number of cycles of operation. We are working on the design of a framework in which VBMC can be extended to give

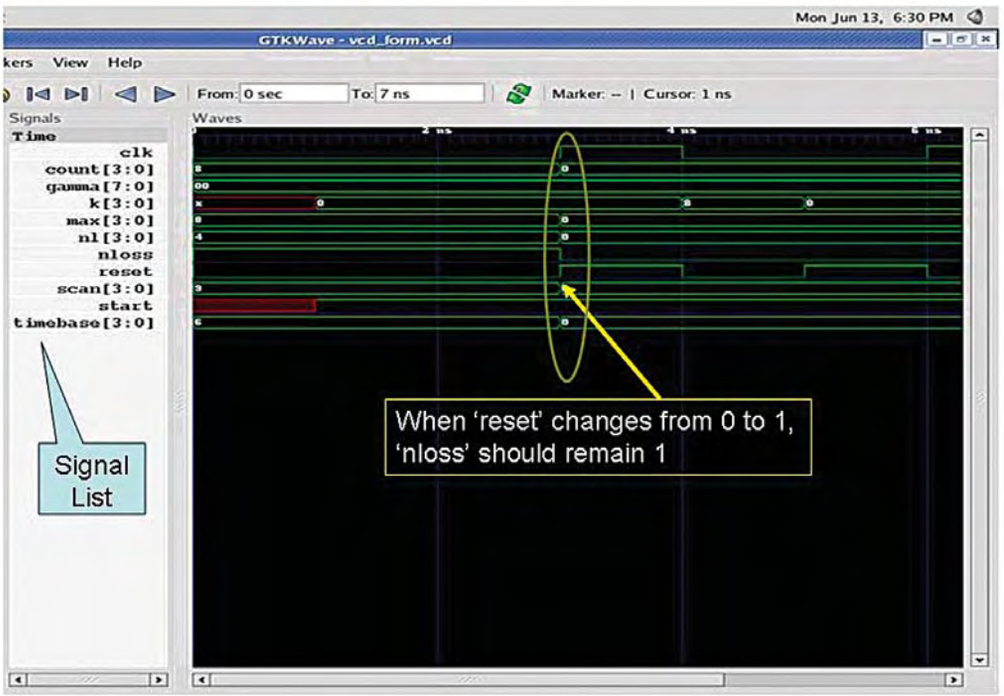

Fig. 4: Counterexample in waveforms generated by VBMC

unbounded guarantees. This will also involve academic research in algorithms for model checking.

Acknowledgements

We sincerely acknowledge the technical guidance provided by Prof Supratik Chakraborty, Centre for Formal Design and Verification of Software (CFDVS), IIT Bombay, Mumbai in the design and development of the tool. The authors wish to thank Shri G..P. Srivastava, Director, E&I Group and Shri R.K. Patil Associate Director, E&I Group for their constant support during this work.

References

1. Cadence website. http://www.cadence.com (accessed March 13, 2012)
2. IBM research website. http:/ www.research.ibm.com (accessed March 13, 2012)
3. VCEGAR tool website. http:// www.cs.cmu.edu/modelcheck/vcegar (accessed March 13, 2012)
4. R. Bryant. "Symbolic simulation—techniques and applications". *Proceedings of 27th ACM/ IEEE Design Automation Conference (DAC 1990)*
5. SMTLIB website. http://www.smtlib.org (accessed March 13, 2012)
6. E. Clarke, O. Grumberg, S. Jha, Y. Lu, and H. Veith. "Counterexample-guided abstraction refinement". *Proceedings of International Conference on Computer Aided Verification (CAV 2000), Lecture Notes in Computer Science*, 2000, Volume 1855/2000
7. Ajith John and Supratik Chakraborty. "A Quantifier Elimination Algorithm for Linear Modular Equations and Disequations". *Proceedings of 23rd International Conference on Computer Aided Verification(CAV 2011), Lecture Notes in Computer Science* 6806 Springer 2011, ISBN 978-3-642-22109-5
8. Ajeetha Kumari, "Property Specification Language Tutorial", http://www.project-veripage.com/psl_tutorial_1.php (accessed March 13, 2012)
9. ITC'99 benchmarks website. http:// www.cad.polito.it/downloads/itc99.html (accessed March 13, 2012)

Searching for the Proverbial Needle in a Haystack: the Information Dilemma

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Abstract

Information is a prerequisite for the development of a Society. We are now in the information overload mode, with instant access to billions of pages of information at our fingertips. Yet the paradox remains that the right kind of information is still not available to the serious researcher working in an R & D organisation. The tools to retrieve this vast amount of information are unable to cope with the exponential growth in information. The present article traces the origin and development of Information / Knowledge Organization & Retrieval (KO&R) tools, the current status of R&D in this area and some recent initiatives at BARC in this direction.

1. Introduction

Ever since the dawn of civilization, Man has been motivated by his innate need to record and preserve History (His+Story) for posterity. The beginnings go back to the Egyptian Civilization, where leaves of the Papyrus plant were used to record History. The Aryans, Greeks, Romans and the Chinese perfected the art and utilization of Stone, Clay tablets and scrolls of Silk to record their day to day lives as well as major events. But the real impetus to preservation and use of recorded (Explicit) knowledge, was given through the invention of printing, by Gutenberg in Germany in 1439. Several scientific discoveries in the 19th Century and rapid industrial and technological developments around the world saw the growth of scientific and technical literature. Universities, Specialized laboratories and research institutions started publishing results of their R&D activities through journal articles, technical reports and conference papers. Patents and trademarks followed. Books were no longer things to be preserved but information to be disseminated. Accordingly, the focus of libraries shifted from being *object-centric* to *user-centric*. This fundamental shift in focus, led to the need for better organization of the collection of books and other printed material for quick reference and use.

2. The Systematic Organization of Knowledge

When the question of organization of Knowledge was raised and debated in learned circles everywhere, it was universally recognized and accepted that subjects or the topics covered in a particular book have to be the main criterion for arranging them systematically on shelves. This would also ensure that books on the same subject would be together and readers could easily browse through the collection. Therefore almost all the tools for organizing knowledge are based on subject approach to information.

2.1 Traditional Tools for KO&R

2.1.1 Classification Schemes: Classification schemes began to be developed around the beginning of the 19th Century, to group and classify the entire Universe of Knowledge. Every Classification scheme uses a system of notations to represent the subject contents of books and on the basis of which all books are systematically arranged on the shelves. Creators of Classification schemes use epistemological, literary, scientific / philosophical and cultural warrants (theories of justification) for inclusion of new subjects in the Classification of recorded knowledge as and when needed.

Classification schemes can be General organizing the whole of recorded knowledge or they can be Special, organizing only a small domain of knowledge.

2.1.2 Indexing Systems: Rapid advances in computerization in the late 1960s and early 1970s, led to the development and growth of various indexing systems. These indexing systems used simple natural language terms called index terms to represent the subject contents of a book. The fundamental difference between these systems pertained to the theoretical basis for fixing the significance order of index terms in the form of a string for composite subjects. Parallel to the string indexing systems, another type of indexing called Co-ordinate indexing was also developed by several indexers. These systems were more flexible as they circumvented the dependence upon a linear sequence of terms for expressing relationships between index terms. Here, relationships were based on combination rather than permutation. The modern day indexing systems gradually evolved from this concept. No longer based on single-word terms, they may be regarded as pre-coordinate terms that are post-coordinated at the time of searching.

2.1.3 Thesauri: The need for a "Controlled vocabulary" was strongly felt due to the semantic pitfalls of using natural language terms during machine translation, mostly at the time of searching through computerized indexing systems. Thesauri are coordinate indexing tools wherein terms are post coordinated at the time of searching using Boolean operators (AND, OR, NOT) to combine different terms in a search strategy. A thesaurus is called a controlled vocabulary tool as only a single term is used as a valid and unique descriptor and other terms related to it are placed under it. A common thesaurus word block thus comprises the Descriptor (the preferred term) and other terms which are broader in scope, narrower in scope or are semantically related to it. Thus some form of control is exercised in the organization and management of natural language both during indexing and retrieval of information.

3. Internet as the largest source of Information

The beginnings of the Internet can be traced back to a project sponsored by the US Defense Advanced Research Projects Agency (DARPA) in 1969, which would enable researchers and defense contractors to share information. The Internet was created in 1990 by Tim Berners-Lee, a computer programmer working for CERN (European Organization for Nuclear Research, Geneva). Prior to the WWW (World Wide Web) also called Web, accessing files on the Internet was a challenging task, requiring specialized knowledge and skills. The Web (comprising tools like HTTP, HTML and URL also created by Berners-Lee) made it easy to retrieve a wide variety of digital files using the hypertext linking facility. The Internet has grown and continues to grow at a tremendous pace. According to the *worldwidewebsize.com*, the Indexed Web contains at least 11.78 billion pages (as on 8th May, 2012).

3.1 Development of search engines as KO&R tools for the Internet: Although sophisticated search and Information Retrieval (IR) techniques date back to the late 1950s and early 60s (Section 2.1.2), these techniques were used for closed systems. The early Internet search and retrieval tools lacked even the most basic capabilities mainly because it was felt that traditional IR techniques would not work on an open unstructured information base like the Internet. Accessing a file on the Internet was through a programme, called the FTP (File Transfer Protocol). Files on FTP servers were organized in hierarchical directories, similar to the files on the personal computers. This structure made it easy for the FTP server to display a listing of all the files stored on the server. The first servers were located at CERN, in Geneva.

Initially navigating the web was difficult as it lacked a cohesive, uniform structure. The early search engines extensively used simple programmes called Web Crawlers to gather new links to web pages and add them to their lists. Simultaneously, on the other hand, the number of new pages kept multiplying and the search engines appeared to be

inadequate for the purpose. Even the most sophisticated search engines can retrieve only between 20-50% [1] of the information from the *Visible Web*. The rest called the *Invisible Web* (comprising Content in Relational databases, Real-time content, Dynamically generated content, Executable and Compressed files etc.) remains inaccessible even today. This chaotic situation led to the development of the *Semantic Web* [2] initiative by the World Wide Web Consortium (W3C,) the Internet body responsible for developing standards to realize the full potential of the Web.

4. Development of Ontologies as modern tools for KO&R

4.1 Ontologies and Philosophy: Ontology (ontos = being and logos = study) means "the study of being". It is the theory of objects and their ties. Traditionally, Ontology as a subject, was the focus of Philosophers and Logicians [3], who used the term to denote the study of what is, i.e. what exists, the kinds and structures of objects, properties and other aspects of reality of the universe. Ontology is the first part that actually belongs to Metaphysics. It is a pure doctrine of elements of all our *a priori* cognitions; or it contains the summation of all our pure concepts that we can have *a priori* of things.

4.2 Ontologies and Artificial Intelligence: In the field of Artificial Intelligence, an Ontology is a theory concerning the kinds of entities and specifically the kinds of abstract entities, that are to be admitted to a language system. The concept was developed and implemented since the early 1990s. AI researchers use Ontologies (in plural) for two basic purposes: Problem Solving Methods (PSMs) and Knowledge Based Systems (KBSs).

4.2.1 Types of Ontologies: AI researchers have classified ontologies using different criteria. According to van Heust, [4], ontologies can be classified into two main types based on a) Amount and type of structure of the conceptualization and b) Subject of conceptualization. Terminological ontologies such as Unified Medical Language System (UMLS) of the National Library of Medicine, Informational ontologies which specify the record structure of databases, for e.g. the medical records of patients and Knowledge Modelling ontologies (for AI applications.) fall under the first type. Domain ontologies that express conceptualizations specific to a particular domain, Generic ontologies which are general in nature and Representational ontologies providing lexical representation of concepts fall under the second type.

4.3 Ontologies and the Semantic Web Initiative by the W3C: The ultimate goal of the Web is to enable computers to do more useful work and to develop systems that can support trusted interactions over the network. The term "Semantic Web" refers to W3C's vision of the Web of linked data. The Semantic Web is the communication platform between computers and people operable via semantically encoded information. It is an extension of the current Web, in which meaning of information is clearly and explicitly linked from the information itself, better enabling computers and people to work in cooperation. Ontologies are an integral part of this communication platform.

Semantic Web technologies enable people to create data stores on the Web, build vocabularies and write rules for handling data. To build vocabularies which will make information exchange more meaningful, Ontologies need to be developed. Ontologies are therefore increasingly being used as KO&R tools, by Web-based information services. The Web Ontology Language (OWL) is one such initiative by the W3C to develop Ontologies. According to the OWL document [5] "An Ontology defines the terms used to describe and represent an area of knowledge. Ontologies are used by people, databases and applications, that need to share domain information. Ontologies include computer-usable definitions of basic concepts in the domain and the relationships among them. They encode knowledge in a domain and also knowledge that spans domains. In this way, they make that knowledge reusable". The Semantic Web Advance Development (SWAD) and the DARPA (Defense Advance Research Project Agency) Agent Metadata Language / Ontology Inference Layer (DAML+OIL) are other initiatives of the W3C, for the creation and deployment of components for the

Semantic Web. All these initiatives aptly demonstrate the significant role of semantics in search and retrieval of information.

4.4 Ontologies and Information Science: Conventional knowledge organization tools like Classification schemes and Thesauri resemble Domain Ontologies in a way that they define concepts and relationships in a systematic manner, but they are less expressive when it comes to machine language. Ontologies represent a domain of knowledge and permit relationships such as the definition of classes, relations and functions. Despite their high level of specification, they allow a great deal of flexibility. One of the earliest reported associations between Ontologies and Information Science, was made by Dahlberg. In her "Ontical structures and Universal Classification", she established the link between Cognitive [6] processes, objective knowledge, concepts and their relations and laid the ontological foundations of a modern Classification system. The use of Ontologies as KO&R tools, began around late 1990s. A few projects have been undertaken in recent years to develop them. There is as yet no standard definition of an Ontology in the field of Information Science. But there has been a steady increase in R&D on various methods [7, 8] to develop Domain Ontologies.

The basic difference between other KO&R tools and Ontologies is the ease of explicit specification of relationships between keywords either free-text or controlled. Through Ontologies, Associative or Related term relationships can be better expressed. This is particularly important in developing Ontologies in interdisciplinary subject domains, where related term relationships are very significant for search and subsequent retrieval of information.

In the conventional KO&R tools, a subject is treated in a uni-dimensional manner, where mainly literary warrant (published literature) is taken into consideration. Ontologies provide the additional facility to incorporate Organizational or Institutional Warrant. This means, Domain Ontologies tailored to the KO&R needs of a particular organization or user community, can be specifically created by Ontology developers. The process of conceptualization is at the core of developing Domain Ontologies. Conceptualization is done through the identification and interlinking of keywords in the selected domain. A keyword in combination with other keywords semantically related to it is transformed into a more comprehensive 'Concept'. Using theoretical principles of Classification and Indexing, keywords can be grouped into Concepts through generation of one-to-many correspondences or linkages between them. These associations or linkages are developed according to user requirements by Ontology developers and thus every Ontology is unique since it represents a part of the reality of the Universe conceptualized by it. These concepts can then be grouped into clusters based on user requirements. Concept mapping is an intellectual process wherein basic knowledge about the domain as well as a deep understanding about the needs of the user community is required.

5. Ontology Language

Any type of ontology has to be represented by a predefined machine language. The current ontology representation languages are of three types: Logic-based (using First Order Logic), Frame-based (using Frame Logic) and Web-based (using RDF, XML, HTML formats). An ontology language should ideally incorporate the advantages of all the three types of representative languages.

6. Developing Domain Ontologies for BARC

The very nature of interdisciplinary and multidisciplinary R&D in BARC, makes it an ideal experimental platform for developing domain ontologies. A simple Generic Ontology on Nuclear Energy is shown in Fig. 1.

Once the core areas of R&D are identified, concept mapping and interlinking would lead to the development of multiple domain ontology layers. These semantically-rich layers of interconnected concepts can be created, using standard interoperable metadata tools, so that search and retrieval become more meaningful both in intranet and internet environments.

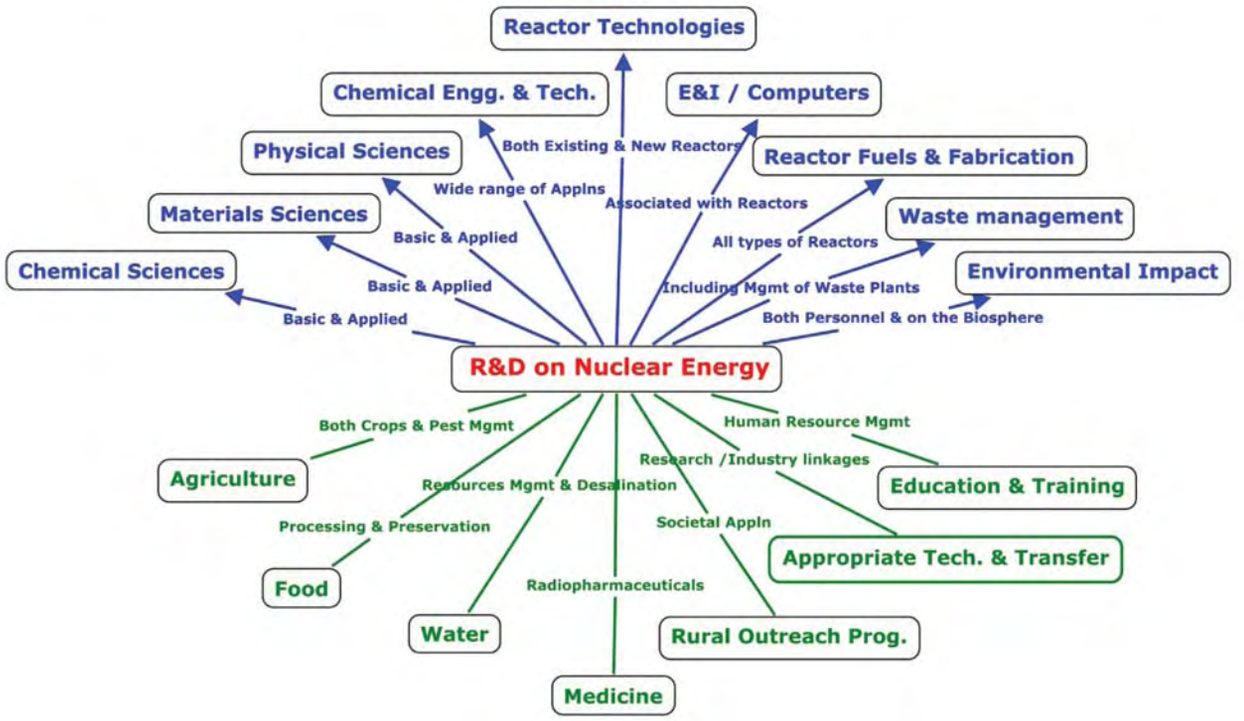


Fig.1: A Generic Ontology

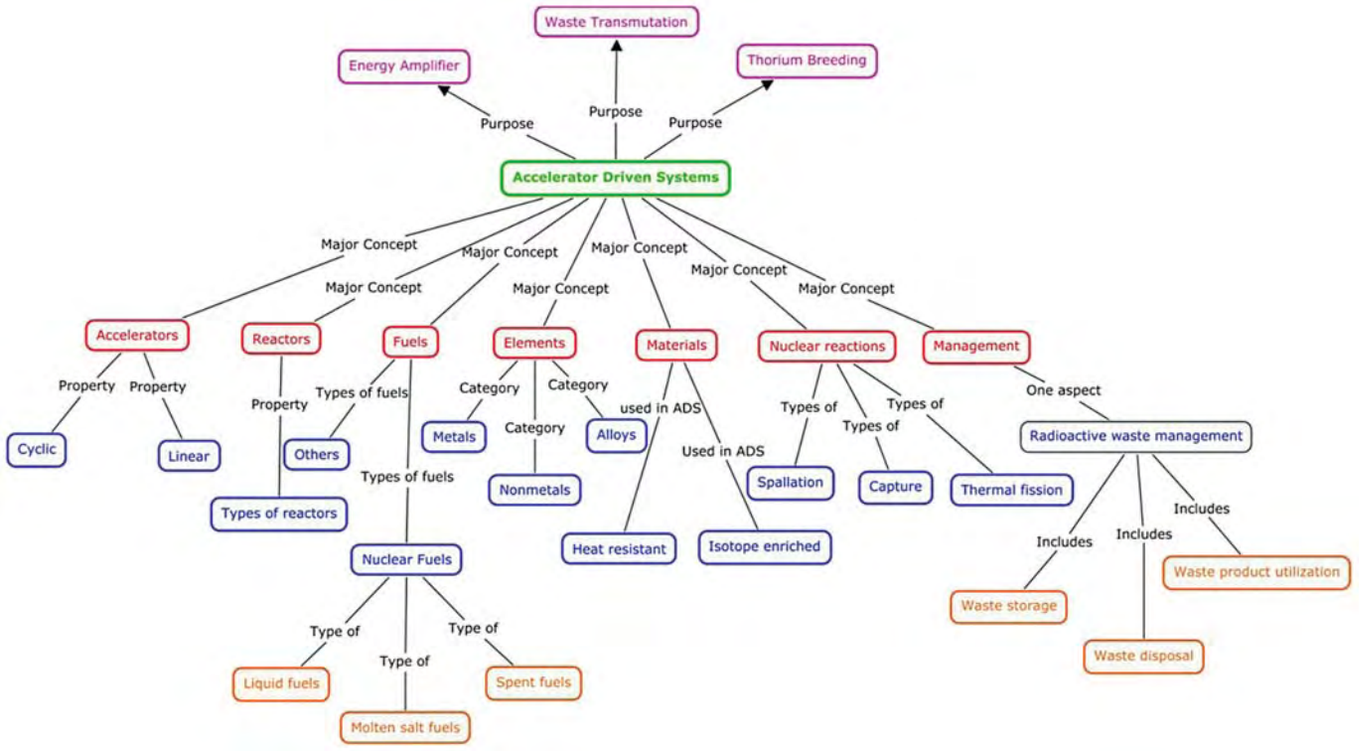


Fig. 2: Basic conceptualization of the prototype Domain Ontology on ADS

For e.g. if we have to develop a domain ontology on Reactor Technologies, we would first need to identify basic concepts or core areas in this domain, which could be done under expert guidance. Then each of the core concepts could be further subdivided into narrower subject areas. Projects,

Experts, publications and institutions associated with those areas could then be linked and brought together onto a single web-based platform. This would portray the various aspects of reality of the object "Reactor Technologies" as perceived in BARC. Thus a domain ontology on Reactor Technologies unique to BARC can be developed.

In the field of Nuclear Science & Technology, a standard vocabulary control tool, the INIS thesaurus being extensively used for KO&R, for several decades now. It provides a rich corpus of doscripters that can be used as starting points in developing domain ontologies in R&D areas of interest at BARC. A beginning has made in the form of a prototype domain ontology on Accelerator Driven Systems. The basic outline is shown in Fig. 2. Another effort has been made recently in the area of Test Blanket Module (TBM) for the ITER programme.

7. Conclusion

In the present scenario, digital information including information on the Internet is growing at a break-neck speed. The tools for KO&R will have to be faster, more accurate and cover a wider range of content. National organizations such as the Documentation Research & Training Centre (DRTC), Indian Statistical Institute and the Sarada Ranganathan Endowment for Library Science (SRELS) are actively engaged in R&D on various aspects of Knowledge Organization. At the international level, ISO, International Federation of Library Associations (IFLA), International Information Centre for Terminology (Infoterm), Unesco and the International Society for Knowledge Organization (ISKO) are deeply involved in research, development and cooperative programmes on KO&R. At SIRD, we are also making modest efforts to develop domain ontologies in core areas of R&D at BARC.

Information and Communication Technologies, Human Machine Interactions, Artificial Intelligence, Computational Linguistics and Cognitive Psychology have been impacting KO&R and will continue to impact the organization and retrieval of all forms of Explicit Knowledge. Ontology, in its philosophical meaning, is the discipline investigating the frame work of reality. This reality [9] is structured into a series of integrative levels, which in turn, forms the basis for representing knowledge and developing new models of Knowledge Organization. Therefore, future Ontological methods will be shaped by this philosophical perception and the subsequent semantic representation of various levels of reality. KO&R in the domain of Information Science is rooted in Philosophical foundation and can thus provide a sound theoretical basis for representing this reality. The answers to the development of intelligent KO&R tools in the near future, may lie at the intersection of all these domains.

8. References

1. Sherman, C. and Price, G.: The invisible Web; uncovering information search engines can't see. Medford, Information Today Inc., 2003
2. Semantic Web: http://www.w3.org/standards/semanticweb
3. Kant, I. *Lectures on Metaphysics.* Edited and translated by Karl Ameriks and Steve Naragon. Cambridge, Cambridge Univ. Press, 1997. (Cambridge edition of the works of Immanuel Kant in Translation
4. van Heust, G., Schreiber, A.T. and Wielinga, B.: Using explicit ontologies in KBS development. *International Journal of Human Computer Studies,* 46, 1998, p.183-292.
5. OWL 2 Document Overview. http://www.w3.org/TR/owl-features/
6. Dahlberg, I.: Ontical Structures and Universal Classification. Bangalore, Sarada Ranganathan Endowment for Library Science, 1978.
7. Deokattey, Sangeeta, Neelameghan, A. and Kumar, V.: A method for developing a Domain Ontology; a case study for a multidisciplinary subject. *Knowledge Organization*, 37 (3), 2010, 173-184.
8. Gokhale, Pratibha; Deokattey, Sangeeta and Bhanumurthy, K.: Ontology development methods.*DESIDOC Journal of Library & Information Technology*, 31(2), 2011, pp. 77-83
9. Gnoli, C. and Poli, R.: Levels of reality and levels of representation. *Knowledge Organization*, 31 (3), 2004, 151-160.

Workshop on Photon and Ion induced X-ray Emission Spectroscopy, PIXS 2012

A workshop was organized on Photon and Ion induced X-ray Emission Spectroscopy at the Karnataka University, Dharwad during 23-25, February 2012. Around 200 participants attended. The workshop was inaugurated by Dr. S. Kailas, Director, Physics Group and was presided by Dr. M.I. Savadatti, Emeritius Professor, Karnataka University and former Vice-Chancellor, Mangalore University and also by Dr. H.B. Walikar, Vice Chancellor, Karnataka University. The Convener was Dr. N.M. Bediger, Professor, KU and the Co-convener was Dr. Daisy Joseph, Nuclear Physics Division. The invited speakers were Dr. R.K. Choudhary (Key note address), former Head, NPD, BARC, Dr. Thomas Calligaro, Centre of conservation of art and cultural heritage, France, Dr. M.K. Tiwari, RRCAT, Indore, Prof. L. Tribedi, TIFR, Dr. S.N. Jha, Spectroscopy Division, BARC, Dr. D. Bhattacharya, Spectroscopy Division, BARC, Dr. Daisy Joseph, NPD, BARC, Dr. V.S. Raju, CCCM, Prof. I.M. Govil, Punjab University, Dr. N.L. Misra, FCD, BARC, Dr. Dhrubajyoti Gupta, SINP, Dr. B.R. Kerur, Gulbarga University and Dr. S. Narayana Kalkura, Anna University, Chennai. It was a technically fruitful workshop for the all the participants especially the students.

Inauguration of the workshop by Dr. S. Kailas, Director, Physics Group, BARC

"Workshop on Hadron Physics & India-PANDA Discussion Meeting: a report

A five day workshop on Hadron Physics was held at the Training School Complex, BARC, Anushaktinagar, Mumbai, from October 31 to Nov. 4, 2011. It was organized by BRNS, DAE and DST & India-FAIR coordination Centre, Kolkata. The aim was to present and discuss / review the latest experimental & theoretical results on various topics in the field of intermediate energy nuclear physics. The topics covered were (i)Nucleon structure and resonances, (ii)Meson-nucleon interactions, (iii)Nucleon-nucleon and nucleon-nucleus interactions, (iv)Strangeness physics, hyperon-nucleon interactions and hypernuclei and (v) Medium effects in nuclei. There were about 80 participants including 9 experts in this field from foreign research laboratories, many senior and young scientists from national labs & universities and students. The format of the workshop was review lectures by experts and presentation of advanced research results by young researchers. The present workshop was fifth in the series sponsored by BRNS, DAE.

In addition, there was a technical session devoted to Indian participation in the detector development and physics studies with anti-protons at the upcoming international facility FAIR, Germany. The aim of this special session was to have a discussion amongst the India-PANDA members to present collaboration status and work plan. The meeting was attended by more than 30 people including some of the key members of PANDA collaboration from abroad. A number of presentations were made which were followed by a detailed discussion on various issues related to the interest from different groups, ongoing R&D activities at NPD, BARC on SiPM based scintillation detector, and at IIT-Bombay on luminosity detector.

Group photograph of the participants

DAE-BRNS Theme Meeting on Nuclear Reaction Data Evaluation: a report

The DAE-BRNS theme meeting, sponsored by BRNS, was held at the Homi Bhabha National Institute, from 13th to 17th February, 2012. The topic covered were installation and benchmarking of the EMPIRE (a nuclear reaction model code) System, output options and data formatting, introduction to the nuclear data evaluation, EMPIRE input preparation for Monte Carlo covariance calculation, GANDR (Global Assessment of Nuclear Data Requirements) System, GANDR Preparation of prior evaluation and experimental data, GANDR setting up of PENDF (Point Evaluated Nuclear Data File), GANDR running with default prior PENDF and covariance matrix and GANDR comparison of the results from different options. Dr. Andrej Trkov from the Jozef Stefan Institute Slovenia and Dr. R Capote Noy from the IAEA gave a series of lectures on the EMPIRE nuclear reaction code and the GANDR error analysis. They also gave practical demonstrations and training to the participants in connection with the use of these codes. The theme meeting was attended by participants from various Universities, National laboratories and BARC. In all, 19 participants from various universities, 16 from BARC and 4 from other units of DAE were present. The source codes were distributed to the participants. The participants could acquire a working knowledge of the computer simulations to be carried out for generating and evaluating nuclear reaction data.

Group photograph of the participants

56th DAE Solid State Physics Symposium 2011: a report

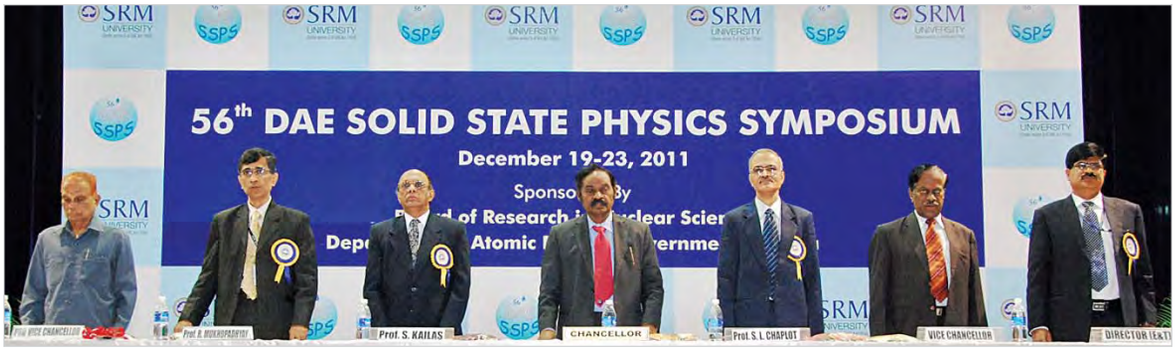
The 56th DAE-Solid State Physics Symposium (DAE-SSPS) was held at SRM University, Kattankulathur (~30 km south of Chennai) during December 19-23, 2011. Dr. R. Mukhopadhyay, SSPD, BARC, was the Convener of the symposium and Dr. R. Mittal, SSPD, and Dr. A.K. Chauhan TPD, BARC were the scientific secretaries. Prof. S. Kailas, Director, Physics Group, BARC, inaugurated the symposium on Dec 19, 2010 and Dr. T. R. Pachamuthu, Chancellor, SRM University, presided over the inaugural function while Dr. M. Ponnavaikko, Vice Chancellor, Prof. T P Ganesan, Dr. Pro-Vice Chancellor, SRM University and Prof S.L. Chaplot, Head, Solid State Physics Division, BARC, graced the occasion.

This symposium, sponsored by The Board of Research in Nuclear Sciences (BRNS), is an annual, very popular and prestigious scientific event, covering almost all aspects of solid state physics. This annual symposium is the largest gathering of solid state physicists in the country and the number of researchers attending the symposium is growing every year. This year we received about 1150 contributed papers. This includes 33 papers in the PhD thesis award category, 11 papers in the Young Achievers award category and 13 papers in the MSc Projects award category. A panel of experts chosen from various institutes and universities across the country reviewed all the papers. After evaluation, 748 papers were accepted for presentation in the symposium. The number of registered participants was 775, and 627 contributed papers were presented in poster sessions spread over four days, out of which 28 papers were also presented in oral sessions.

The highlights of the symposium were the theme seminars, 1) Superconductivity, to commemorate the 100 years of superconductivity discovered by Kamerlingh Onnes in 1911, 2) Chemistry of Materials, commemorating the international year of chemistry, 3) Organic Semiconductor, 4) Amorphous Solids and Glasses, and 5) National facilities existing in the country for condensed matter physics research and several other important topics. In addition to these seminars, there were 12 invited talks on subjects of current interest by eminent scientists from India and abroad.

An Evening talk entitled "Quasicrystals-Nobel prize 2011 and Indian Science" delivered by Prof. K Chattopadhyay, IISc, Bangalore on 22nd December was really enchanting. Prof Chattopadhyay sailed the audience through the days when the quasicrystal was in the highlightand most talked about.

The American Institute of Physics will publish the proceeding of the symposium online. Overall the symposium was very successful both academically and socially.



Inauguration of the 56th DAE-SSPS at SRM University, Kattankulathur, Tamilnadu. From left to right: Prof. T P Ganesan ProVice Chancellor, SRM University, Prof. R. Mukhopadhyay, Convener, DAE-SSPS 2011, Prof. S. Kailas, Director, Physics Group, BARC, Dr. T. R. Pachamuthu, Chancellor, SRM University, Prof S.L. Chaplot, Head, SSPD, BARC, Dr. M. Ponnavaikko, Vice Chancellor, SRM Universtiy and Prof C. Muthamizhchelvan, Director (E&T) SRM University.

Ninth Supervisory Training Programme on "Radioactive Waste Management": a Report

The Ninth supervisory training programme on Radioactive Waste Management was designed, formulated and conducted at BARC, Trombay during January 9th to 20th, 2012, for the supervisors who are associated in waste generation in various plants / facilities / research labs and also those who are engaged in waste management. This training programme covered various aspects of Radioactive Waste Management, radiation protection and industrial & fire safety. The training programme was carried out by way of classroom lectures, demonstrations and visits to various plant / facilities at Trombay such as Plutonium Plant, Waste Immobilization Plant, RSMS, ETP and Dhruva reactor. Faculty members were invited from Trombay, Tarapur and Kalpakkam sites of NRG and NRB and from AFD, ROD, IHSS, Tombay Dispensary, Fire Station, etc. to deliver the lectures. The topics covered were radioactive waste management of different types of waste; matrices for immobilization and their quality assurance; near surface disposal systems; deep geological disposal; radiation, industrial and fire safety; radiation monitoring; health physics; first aid; ventilation aspects; off-gas cleaning; aspects of remote handling; waste management database; future projects related to waste management; process instrumentation and control; plant process flow-sheets of various waste management plants; minimization of waste; etc. Few more subjects such as regulation, dose apportionment, waste assaying, waste compaction, various remote gadgets, special techniques for separation of useful isotopes from waste, cold crucible technology, etc, were also covered.

During the inaugural programme, on 9th January 2012, Shri P. N. Patil welcomed the gathering. Shri R.G. Yeotikar, Officer-in-Charge, Training, NRG

Inaugural function of Ninth Supervisory Training Programme. Mr. R.G. Yeotikar, officer-in-charge, training, Nuclear Recycle Group & organizer of this training programme; is giving brief account of the training programme and the selection of the subjects. Others on the dais (from left to right) are Mr. P. K. Wattal, Head, PSDD; Mr. S. Basu, Chief Executive, NRB; Mr. Kanwar Raj, Head, WMD and Mr. K.N.S. Nair, Head, TDD

and organizer of this programme, introduced the syllabus of the programme and explained the importance of the selected subjects. Shri K.N.S. Nair, Head, TDD; Shri Kanwar Raj, Head, Waste Management Division; Shri P. K. Wattal, Head, Process Development Division and Shri S. Basu, Chief Executive, Nuclear Recycle Board, addressed the trainees and emphasized importance of training and its usefulness in updating knowledge in various aspects of radioactive waste management.

Shri Kanwar Raj, in his invited talk, presented the philosophy of radioactive waste management & indicated that we should also consider waste as a source of wealth. He appealed to the participants to follow simple methods and practices (i)to minimize the wastes, (ii) to segregate the wastes and (iii)to reuse and recycle the waste so that they help waste managers directly or indirectly for reduction of waste volume and enhancement of safety of environment and of future generation. Vote of thanks was given by Shri P. Patange.

The Valedictory Function of this training programme was held on 20th January 2012 and was presided over by Shri Kanwar Raj, Head, Waste Management Division. Shri K.M. Singh, Plant Superintendent, WMF, Trombay, and other senior officers attended the valedictory function. During this valedictory function a feed back session was arranged for participants from all the sites. Shri R. G. Yeotikar, Officer-in-Charge, Training, answered and responded to this feedback. Thereafter the certificates were awarded to all the participants.

Photograph of participants of Ninth Supervisory Training Programme on Radioactive Waste Management

School on Analytical Chemistry (SAC-2011): a Report

The BRNS - AEACI sponsored Second School on Analytical Chemistry (SAC-2011) was held at the National Centre for Compositional Characterization of Materials (NCCCM), Hyderabad during 21- 27th August 2011 and in JNTU on 25-26 August 2011. A total of 67 young scientists, academics and research scholars from different units of DAE and various Universities participated in this school. The inauguration function was held at Gurukul, BARC Training School, NFC, Hyderabad on Sunday, 21st August 2011 which was presided over by Dr. Tulsi Mukherjee, Director Chemistry Group, BARC and Chairman, National Advisory Committee. Shri R.N. Jayaraj, Chief Executive, NFC, Hyderabad inaugurated the school. The dais was also shared by Shri P. B. Maithani, Director, AMDER, Hyderabad, Prof. M. Lakshmi Narasu, Director, Institute of Science and Technology, JNTU, Hyderabad, Dr. A. V. Reddy, Head, Analytical Chemistry Division, BARC, Mumbai and Chairman, Technical Committee and Dr. J. Arunachalam, Head, NCCCM, Hyderabad and Chairman, Local Organizing Committee. Dr. Arunachalam welcomed the guests, resource persons and participants. Dr. Reddy explained the theme of the school. He spoke on the necessity of introducing an examination so as to make this series of schools as a certification course in the near future and thanked the BRNS for financial support. Dr. Mukherjee in his presidential address spoke about the importance of imparting quality training and continued education. Shri Jayaraj urged the participants to utilize the opportunity to learn from experts as well as to visit various facilities. In his key note address on *"Role and future needs of analytical chemistry in nuclear fuel fabrication"*, he gave an overview of the NFC programme stressing the role of analytical chemistry and contributions made by NFC chemists.

From Left to Right: Shri P.B. Maithani, Director, AMDER, Shri R.N. Jayaraj, Chief Executive NFG, Dr. T. Mukherjee, Director, Chemistry Group, BARC, Dr. A.V.R. Reddy, Head, ACD and Dr. J. Arunachalam, Head NCCCM, Hyderabad

Dr. Mukherjee released a monograph on sample preparation, prepared by scientific staff of NCCCM. Inaugural function ended with vote of thanks by Dr. A. C. Sahayam, Secretary, Local Organizing Committee.

The course consisted of lectures in the morning session and experiments in the afternoon sessions. A wide variety of lectures were delivered by experts and experiments belonging to various aspects of analytical chemistry and environmental analytical chemistry were conducted by Colleagues from NCCCM and JNTU. The topics covered were trace and ultra trace analysis, QA/QC, accreditation and reference materials, importance of organic and inorganic mass spectrometry, neutron activation analysis and ion beam analysis, spectrometric techniques such as atomic absorption and ICP-OES, chromatographic techniques, electroanalytical chemistry, thermal analysis, X-Ray fluorescence, environmental analysis and elemental speciation in analytical chemistry. Lectures and experiments related to environmental analysis and statistical treatment of data and uncertainties in analytical measurements were held at Centre for Environment, JNTU, Hyderabad during 25, 26 August 2011. Experiments namely i) multi elemental analysis by ICP-OES, ii) determination of Hg in environmental samples using CVAAS, iii) determination of Cr (VI) using Ion Chromatograph, iv) determination of Cd using ELCAD and v) ion bean analyses using tandem accelerator were conducted in NCCM. The experiments vi) Analysis of gaseous samples for Methane, CO_2 and Hydrogen in GC, vii) Analysis of organics in waste waters and contaminated soils by GC MS, viii) measurement of COD, DO and BOD in waters and waste water sample and ix) determination of Ammonia in water samples were conducted at JNTU. Five Special lectures were delivered by (i) Dr. Tulsi Mukherjee on "safety in chemical laboratories", (ii) Shri. N. Saibaba, ACE, NFC on "Activities of NFC" on 21-08-2011, (iii) Shri. G. V. S. Hemantha Rao, DCE, NFC on "Nuclear Material Accounting (NUMAC)" on 22-08-11, (iv) Shri. P. S. Parihar, AD (operations), AMDER on "The role of AMD in nuclear power program" on 23-08-11 and (v) Shri Narayana Rao, ECIL, Hyderabad on "Analytical Instrumentation" on 27-08-11.

Valedictory function was chaired by Dr. J. Arunachalm and spoke about the importance of the school, its utility etc. Dr. A. V. R Reddy delivered the valedictory lecture on "Atoms for peace" giving an emphasis to DAE's three stage programme. All the participants were given certificates by Dr. J. Arunachalam. Vote of thanks was proposed by Dr. R. K. Singhal, Secretary, SAC.

Report on DAE-BRNS National Workshop on Materials Chemistry (Functional Materials) (NWMC 2011- FUNMAT)

The DAE-BRNS National Workshop on Materials Chemistry (Functional Materials) (NWMC 2011-FUNMAT), organized by the Chemistry Division and Society for Materials Chemistry, was held at BARC during 7-8 December, 2011. The workshop received an overwhelming response from various academic and R&D institutes, across the country. About 200 registered participants from different disciplines such as chemistry, physics and materials science attended the technical sessions. The workshop was convened with 17 invited talks, spanning across diverse topics relevant to advanced functional materials. Some of the topics were magnetic materials, glasses and glass ceramics, hydrogen production and storage, synthetic materials chemistry, electrical materials, sensors, soft materials, optical materials etc. The topics were selected based upon recent upsurge in the research and development in materials relevant to advanced technologies, energy production, sensors and devices, nuclear waste management, health sciences etc.

The workshop began with a keynote address by Dr. V. C. Sahni, DAE Homi Bhabha Chair Professor and former Director, RRCAT, Indore. In his inaugural address Dr. Sahni mentioned about new innovations in several key areas of materials science and emphasized the importance of multidisciplinary research in materials development programmes. Molecule based magnetic materials for future electronic applications and multifunctional magnetic particles for drug delivery were some of the key functional materials discussed during the workshop. Invited speakers presented their research work and perspectives on several functional materials for diverse applications such as glass formation and applications in nuclear waste management, materials development for hydrogen generation and storage, high purity materials preparation for electronics, synthetic chemistry for tuning crystal structure and function. Application of novel experimental tools like dielectric spectroscopy and impedance spectroscopy in characterizing materials for super-ionic conduction, multiferroics etc. were discussed. Development of thin film materials for sensors of gases and biomolecules, design of soft materials via self assembly, optical materials for solid state lighting etc. were also discussed.

The workshop concluded with a valedictory function chaired by Dr. T. Mukherjee, Director Chemistry Group. Many participants gave their feedback about the workshop and appreciated the diversity and interdisciplinary nature in the topics. The workshop offered an excellent platform for young researchers to discuss among various delegates and experts in the field. This could lead ways to strengthen their research by interdisciplinary and multi-institutional cooperation.

From Left: Dr. P. A. Hassan, Dr. T. Mukherjee, Dr. V. C. Sahni and Dr. D. Das

"Status of Vitrification Technology for Treatment of High Level Liquid Waste": Report of a Theme Meeting

A one day theme meeting on "Status of Vitrification Technology for Treatment of High Level Liquid Waste" was arranged by the Nuclear Recycle Board in coordination with the Board of Research in Nuclear Sciences (BRNS) at BARC, Tarapur on February 22, 2012. The objective of the theme meeting was to summarize all recent developments on high level waste management with respect to technology, matrix and process development on a single platform. Experts in the field briefed the participants about the recent developments in the field. About 175 delegates from different units of BARC participated in the deliberations. Following topics were covered in the theme meeting:

- Development and deployment of various vitrification technologies
- Processing of HLW using various vitrification techniques
- Recovery of valuables, Development of actinide partitioning and ceramic matrices
- Challenges in treatment of HLW arising from reprocessing AHWR and FBR spent fuels.
- Remote control aspects in HLW management and its transportation.
- HAW management aspects at Integrated Recycle projects

Shri. S.D. Misra, Director Nuclear Recycle Group inaugurated the theme meeting in the presence of Shri S. Basu, Chief Executive, Nuclear Recycle Board.

Shri Kanwar Raj, Head Waste Management Division gave a key note address covering the overview of development of Vitrification technology in India. Dr. C.P. Kaushik briefed about the challenges in waste management with respect to the HLW arising from reprocessing of AHWR and FBR spent fuels. Ms. Smitha Manohar gave a broad idea about the need of actinide partitioning as well as recovery of various valuables from HLW. Shri Y. Kulkarni, CS, TNRPO shared his practical experience on the Joule Heated Ceramic Melter for processing of HLW and its decommissioning features. Dr. G. Sugilal gave a brief introduction to futuristic vitrification technology making use of the cold crucible method. Shri K.K. Haldar gave an overview of the Integrated Recycle projects for HLW management of Nuclear Recycle Board. Various aspects of remote control in management of HLW and transportation were covered by Shri. K.M. Singh. Plant Superintendent, WMD, BARC, Trombay.

Shri S.D. Misra, Director, NRG giving the inaugural address. On the dais from left to right: Shri Y. Kulkarni, Chief Superintendent Tarapur based Nuclear Recycle Plant operations, Shri S. Basu, Chief Executive, NRB, Shri G.J. Prasad, Director,NFG and Shri Kanwar Raj, Head, WMD.

BARC Scientists Honoured

Name of the Scientist	:	**Tulsi Mukherjee** **Director, Chemistry Group**
Conferred	:	Lifetime Contribution Award in Free Radical Research
Conferred by	:	Society for Free Radical Research, India, at SFRR Conference, Kolkata during 12-14, Feb, 2012

Name of the Scientist	:	**K. Srinivas** **Architecture & Civil Engineering Division**
Award	:	9th Vishveshvaraiya Construction Excellence Award, 2012 for outstanding contribution in Engineering & Infrastructure Sector
Presented at	:	Inaugural Session of the International Conference "Rail Asia 2012", Mumbai, 4th May, 2012.

Name of the Scientist	:	**A.K. Tyagi** **Chemistry Group**
Conferred	:	CRSI CNR Rao National Prize in Chemical Sciences (2012) for significant and outstanding contributions in Chemical Sciences
Conferred by	:	Chemical Research Society of India, Bengaluru at the 14th CRSI National Symposium in Chemistry at NIIST, Thiruvananthapuram, during Feb. 3-5, 2012

Name of the Scientists	:	**S. Mukhopadhyay, L. S. Danu, D.C. Biswas, P.N. Prashanth, A. Goswami, A. Chatterjee and R.K. Choudhury**
Title of the Paper	:	Yrast and near-yrast spectroscopy of Neutron-rich fission fragments using Thermal Neutrons from Reactor
Award	:	First Prize in Poster Presentation
Presented at	:	DAE Symposium on Nuclear Physics at Department of Nuclear Physics, Andhra University, Visakhapatnam from December 26-30, 2011

Name of the Scientist	:	**H.N. Ghosh** **Radiation & Photochemistry Division**
Conferred	:	CRSI Bronze Medal (2012) for outstanding contribution in Chemical Research
Conferred by	:	Chemical Research Society of India, Bengaluru at the 14th CRSI National Symposium in Chemistry at NIIST, Thiruvananthapuram, during Feb. 3-5, 2012

V. R. Chavan
Wooden Art Work

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