



# IGC Newsletter

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**Vertical** **Oblique**

~ 500 nm **Vertical Nanorods** **Oblique Nanorods** ~ 100 nm

Height of cover gas region (mm)

Cover gas temperature (°C)

250 300 350 400 450 500 550

Top organic phase  
Black ruthenium oxide at the interface  
Bottom aqueous

## *From the Editor*

### *Dear Reader*

It is my pleasant privilege to forward a copy of the latest issue of IGC Newsletter (Volume 102, October 2014, issue).

IGC Newsletter has been carrying a regular feature of interaction of young officers with eminent personalities. In this issue we are extremely happy to present the summary of the interaction with Dr. R. A. Mashelkar, National Research Professor and President of Global Research Alliance.

In the first technical article Dr. Sandip Dhara and colleagues have studied Raman spectroscopic imaging of single nanostructures such as indium nitride nanorods and gallium nitride nanotubes, in the diffraction limit and extended the study for determining the thickness of graphene layer.

In the second technical article Ms. Dipti Samantaray and colleagues have devised thixo-casting as an alternative manufacturing route to conventional process, for producing critical components of stainless steel and produced 304LSS ingot of ten kilograms weight.

In the young officer's forum, Shri Amit Kumar has shared his experience in theoretical simulation and experimental studies for determining the characteristics of sodium aerosol in the cover gas region of SILVERINA Loop.

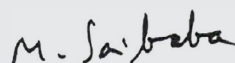
In the young researcher's forum, Dr. Pravati Swain has carried out parametric studies for the quantitative separation as well as recovery of ruthenium from simulated high level liquid waste by various chemical and electrochemical methods.

This Newsletter carries reports on the "BITS Practice School", "Summer Training in Physics and Chemistry (STIPAC-2014)", "Graduation Function of the Eighth Batch of Trainee Scientific Officers of BARC Training School at IGCAR" and "Quality Circle Annual Meet (QCAM) - 2014".

Dr. R. A. Mashelkar, National Research Professor & President of Global Research Alliance, Prof. K. R. Rajagopal, Distinguished Professor, Regents Professor, Forsyth Chair in Mechanical Engineering, Senior Research Scientist, Texas Transportation Institute and Dr. M. R. Srinivasan, Member, Atomic Energy Commission & Former Chairman, AEC, visited the Centre during the last quarter.

We are happy to share with you the awards, honours and distinctions earned by our colleagues. We look forward to your comments, continued guidance and support.

With my best wishes and personal regards,



(M. Sai Baba)  
Chairman, Editorial Committee, IGC Newsletter  
&  
Associate Director, Resources Management Group

## Interaction with Dr. R.A. Mashelkar



Dr. R. A. Mashelkar interacting with the team of Young Officers

Sir, how has been the journey from your childhood to Padma Vibhushan. Can you share with us any event that shaped your life?

Well, at the age of seventy one, it is very hard to pin point any single event but there are individuals who shaped my life. I feel it would be more appropriate to talk about individuals rather than events as such. The first individual who shaped my life, was my mother. I was born in a very poor family, my father passed away when I was six years old and then we moved from the village Mashel to Bombay. My ill-literate mother did menial jobs and brought me up. Though we had a challenge of getting two meals a day, my mother never made me feel inadequate as though something was missing. She taught me values and set high standards for me though she was uneducated.



**Dr. R.A. Mashelkar**, National Research Professor, is presently also the President of Global Research Alliance, network of not-for-profit R&D institutes from Asia-Pacific, Europe and USA with over 60,000 scientists.

*Dr. Mashelkar served as the Director General of Council of Scientific and Industrial Research (CSIR), with thirty-eight laboratories and about 20,000 employees for over eleven years. He was also the President of Indian National Science Academy and President of Institution of Chemical Engineers (UK).*

*When Dr. Mashelkar took over as the Director General of CSIR, he enunciated "CSIR 2001: Vision & Strategy". This was a bold attempt to draw out a corporate like R&D and business plan for a publicly funded R&D institution. This initiative has transformed CSIR into a user focused, performance driven and accountable organization. This process of transformation has been recently heralded as one of the ten most significant achievements of Indian Science and Technology in the twentieth century.*

*Dr. Mashelkar is only the third Indian engineer to have been elected (1998) as Fellow of Royal Society (FRS), London in the twentieth century. He was elected Foreign Associate of National Academy of Science (USA) in 2005, Associate Foreign Member, American Academy of Arts & Sciences (2011); Foreign Fellow of US National Academy of Engineering (2003); Fellow of Royal Academy of Engineering, U.K. (1996), Foreign Fellow of Australian Technological Science and Engineering Academy (2008) and Fellow of World Academy of Art & Science, USA (2000).*

*In August 1997, Business India named Dr. Mashelkar as being among the 50 path-breakers in the post- Independent India. In 1998, Dr. Mashelkar won the JRD Tata Corporate Leadership Award, the first scientist to win it. In June, 1999, Business India did a cover story on Dr. Mashelkar as "CEO OF CSIR Inc.", a dream that he himself had articulated, when he took over as DG, CSIR in July 1995. On 16 November 2005, he received the Business Week (USA) award of 'Stars of Asia' at the hands of George Bush (Sr.), the former President of USA. He was the first Asian Scientist to receive it.*

*Deeply connected with the innovation movement in India, Dr. Mashelkar is currently the Chairman of India's National Innovation Foundation, Reliance Innovation Council and Thermax Innovation Council and KPIT Technologies Innovation Council.*

*Thirty one universities have honoured him with honorary doctorates, which include Universities of London, Salford, Pretoria, Wisconsin and Delhi.*

*The President of India honoured Dr. Mashelkar with Padmashri (1991), with Padmabhushan (2000) and with Padma Vibhushan (2014), which are three of the highest civilian honours in recognition of his contribution to nation building.*

I would like to quote one example in this regard, I studied in Marathi medium school, and always stood first. Normally I would score 100 percent marks in Mathematics, once I scored 97 percentage and I did not bother about it. I showed my marks to my mother thinking that she would be happy, but she sat besides me and asked me as to where did I miss those three marks. I was really amazed by the way she questioned me. She kept on setting bench marks for me at different points of my life.

Another incident is a remarkable one. My mother used to go in search of a job. One day she went to Congress House in Bombay and waited in the queue for the job. The person in-charge, asked if she had the minimum qualification of third standard pass. She honestly said, "no" and was disqualified. She could have bluffed by saying she had gone to school, but she was honest in what she did and that is the value she taught me and my children. The realization that she was disqualified due to lack of proper education, reinforced her desire to educate me to the highest levels that were possible.

I was about to leave the school after completing SSC, I was about to look for a job, but my mother insisted that I should study further. Then I did my Inter-science, followed by Chemical Engineering. After completing Chemical Engineering I said, I would go for a job, she again said no as she had heard about Ph.D. Degree. After completing a Ph.D., I again said, this is the last degree and I would go for work, she refused, as she had found out that there is a Post Doctoral degree. An ill-literate lady setting standards of this kind was incredible!.

The second person who influenced my life was Principal Bhawe in my school, who taught me the importance of 'focus' in life. And the third individual was Prof. M.M.Sharma from University Department of Chemical Technology (UDCT). Being amongst the top of the class, I had offers of a number of fellowships in United States as well as in Canada. It was conventional at that time that the toppers would always go abroad for higher studies. But I had always done unusual things in my life. I looked at Prof. Sharma. He was just twenty seven, and had returned from Cambridge University. I thought where can I get a better guru than him and hence, decided to work with him. I completed my doctoral degree in three years. I learnt from him, about how to go about doing research with an almost zero budget and art of pursuing idea based research, as the annual contingency to spend on research was a meager amount of Rs.10,000 at that time. Second was the value system that he had. He was offered highest positions like Director General of Council of Scientific and Industrial Research (CSIR), Secretary of Department of Science and Technology and so on. He declined all those offers and remained a Professor all his life. Third thing about him was his exceptional courage and commitment. A tragedy happened in his life. His wife was returning from Rajasthan with her four year old son. While travelling, unfortunately he died on her lap because of acute gastroenteritis which could not be treated. I remember at that time, there was a Ph.D. student who had submitted the draft of his thesis, which needed to be cleared by Prof.M.M.Sharma before submission. Prof. Sharma came from the crematorium and within a few hours the student received the corrected thesis. Whenever I had pain in my life, I worked thinking as to what could be worse, than that happened to Prof. Sharma, losing his child. And yet he was so courageous.

My next guru is Prof. C.N.R. Rao. He taught me something, which was analogous to what my mother did, but it was in a different way. He taught how to never get satisfied with what I had achieved, so that I can always do things better. I became a fellow of the Royal Society. In three hundred and fifty years, only three Indian engineering scientists from India have received the honour, Prof.M.M.Sharma, Prof. Roddam Narashimha and myself. I went to Prof. C.N.R. Rao and said I became FRS and he said "not bad". I was disappointed. Then I became the Foreign Fellow of U.S National Academy of Science. I had been the first ever engineering scientist to have received this recognition, since 1863. For this too, Prof. Rao said "not bad". In 2011, I received Foreign Fellowship of World Academy of Arts and Science. From the year 1780 onwards, only seven Indians had become fellows and I was the seventh and I thought Prof. Rao would be happy. Again he said "not bad". Then I got disappointed. I asked him, what should I do to impress you, Sir? He gave me an interesting reply. He said 'do not forget that you are climbing a limitless ladder of excellence'. There are no limits to human achievements, excepting the limits that you set for yourself.

So I would say, rather than to mention any events, these four individuals have influenced my life.

**You taught at University of Salford and Delaware. Is there any specific incident that you recall which can be shared with us?**

It was interesting period at University of Salford. There, I taught courses like approximation techniques in chemical engineering mathematics like variational principles, etc., which I was not at all familiar with. I learnt these subjects on my own and taught the courses!

In the same way, I had another exceptional experience in my teaching at University of Delaware.

I was teaching a course on process fluid mechanics. There were ninety students. They were broken up in three batches with thirty students each. I had to teach the same course content for all the three batches. I used to get tired and bored listening to myself while repeating the same lecture. So I thought about doing things differently. I went to the library, got video cassettes on scientific subjects and played them in the classroom. At the end, I would just distribute the question paper. So, according to me, what is important in learning is observation, analysis and synthesis.

In that university, there was a 360 degree evaluation, which means not only teachers evaluated the students but the students also evaluated the teachers, I was amazed to see that I was ranked the best teacher that year. I was amazed to read a comment from one of my student who had written "I don't know how to thank Prof. Mashelkar, because he has helped me discover myself. May be, I will name my first child after him". We must practice such an education system and I wish, we create such an environment in India.

**Sir, you were talking about teacher and teaching, in your perspective how important is the role of a teacher in ones career?**

Teaching must be made an attractive career. I think, Government has to play a significant role in that. The Government has created a National Mission for Teachers and Teaching in the twelfth five-year plan for making teaching, an attractive profession. Ofcourse the current challenge is in the number and quality of teachers in the schools. This, I think can be solved by a combination of physical and digital learning. It would definitely make a difference. When large distance, large number and low income pose challenges, then physical and digital learning is the only solution.

**You have been the Director General of CSIR for eleven years, what in your opinion needs to be done so as to make research an attractive career for students?**

It is not research alone, it is research and innovation, because research converts money into knowledge. But innovation converts knowledge into wealth and social hood. We cannot just keep on producing knowledge by doing research.

As regards investment in R&D, in most of the countries, industries contribute 70-80% and Government contributes 20-30%, towards research and development. In India, this scenario is exactly the reverse and therefore Industries have to come forward and contribute more towards research and innovation to make research an attractive career.

Sir, is it true that our innovations are getting lost at some point, remaining only at the idea stage without moving into the field?

It is not a novel idea that matters, it is novel idea in practice that counts. Let me discuss about grassroots innovators, which means completely unaided. It could be a small farmer or an artisan or a school dropout or a house-wife who has an idea. To take them forward we have created what is called as "National innovation Foundation". I happen to be the Chairman, but the real spirit and inspiration behind this is Prof. Anil Gupta, Vice-Chairman of the foundation. Information on this is available on [www.nif.org.in](http://www.nif.org.in). We have created Grassroot Innovations Augmentation Network (GIAN) which helps unaided, unqualified, untrained individual innovator from the informal sector who have conceptualized/developed technological innovation and/or outstanding traditional knowledge practices to get noticed and recognized. At NIF, we have more than 200,000 such innovations, documented and recorded. But merely documenting these innovations wouldn't suffice. We need to take them forward to promote these innovations. Though if not all, some of the innovations are implemented through "Micro venture capital fund" that supports in creating business plan and helps them improve their design.

Similarly, we have created [www.techpedia.in](http://www.techpedia.in), where the undergraduate projects pursued by engineering students are documented and recorded. More than 100,000 such projects have been documented and we are trying to connect these projects with enterprises as some of the ideas would be of interest to the enterprises.

Sir, is it that students lack the knowledge of what to publish and what to patent? Also do you think it is the right time to introduce patenting rules and laws as a part of undergraduate curriculum?

Answer to your first question is, yes, to be honest, the awareness doesn't exist. There are legitimate reasons, as to why it did not exist. Because, till 1991, we had a closed economy. There was no new competition. Whatever we could produce we could sell in the markets, so there were no innovations and hence no patents. In 2007, when India celebrated 60 years of Independence, I celebrated 16 years of Independence since I look at 1991, when India liberalized itself, and became open to competition, as our second freedom. We are a late starter in innovation. A number of universities are now incorporating Intellectual Property (IP) related courses, as a part of the curriculum. There are schools which specialize in Intellectual Property Rights.

Awareness is increasing enormously. For instance, I was invited to lay a foundation stone of a new biotechnology based waste treatment project at Yerwada Jail, Pune which is having over 3,300 inmates. Around 10,000 chapathis needed to be prepared for their lunch and then again for their dinner. There was a dough making machine which had low productivity. So, two prisoners took the initiative, they were innovative. Then made some modification in the existing machine and made a difference in dough making process. The machine produced good dough of better consistency and did it faster. Apparently, they went to the Superintendent and said that it seems, "there is a person by name Mashlekar, who keeps talking about the patents and we want to patent this machine".

If this can reach the prisoners in Yerwada, I am sure it can reach industries in India too.

Sir, Can you compare the research eco system in corporate and Government R&D Labs. Corporate R&D Labs focus is in patenting and what they cannot patent, is published. What should be the focus for an government organization like us?

At the end, I wouldn't worry about whether I am in private or public. Your goals are to ensure that the proprietary knowledge that you have created remains with you as regards the right for exploitation is concerned. You do it for public good or private good, those should not be taken away by anybody else, that is fundamental. As long as the awareness of creating intellectual property rights is there, I am happy.

Does this not go against the concept of free flow of knowledge?

No, not at all, because what you do with the patent is upto you. If you wish you can donate the patent free. There are patent pools where even multinational companies have donated. The point is about you the inventor, holding the rights.

What should be the role of basic science in research at DAE?

Frankly speaking, you have a rich heritage because you had great leaders like Homi Bhabha and Vikram Sarabhai, who were leaders in

fundamental science. Secondly the Bhabha Atomic Research Centre, as far as I know, I have seen them thrive on basic science as some of the best works in physics, biology and chemistry etc., has come from BARC. So you already have that tradition.

When it comes to science, there are only two things. Science that has been already applied and science that is yet to be applied. We have to excel in both. When Raman effect was discovered, it was a great basic research breakthrough. But when 'Raman's scanners' were developed, it was the application of that fundamental science and mind you, this application was done abroad, not in India. How I wish that both happen in India. DAE has done good science, understood and promoted good science and also applied it very innovatively. That is your rich tradition. You should maintain it.

**Sir, how did you get into research and what was the starting point for the research?**

My research for doctoral degree was on mass transfer with chemical reaction in a bubble column. It was very empirical research, as there were no mathematical modeling or simulation accompanying that research. For the Post Doctoral degree, I had a choice of going either to U.S. or U.K. For some reason, I preferred U.K. I had two offers, one was at University of Manchester in Science and Technology, which was recognized as one of the top most universities in Europe at that time. There I was offered an Associate Lectureship, which really was a great achievement at that time, because it was very difficult to get a faculty position in U.K. But my challenge was that, I would have carried on the work in the same area that I was doing for my Ph.D. The second was the Post Doctoral Fellowship offer from Salford University, which was completely an unrecognized university. And yet I went to Salford university although it was a temporary fellowship, because the challenge I had was to do research in Non-Newtonian Fluid Mechanics, of which I knew nothing. And it was by doing research in this area that I won all my accolades. Many times, young people make mistakes of just carrying on the subject of their doctoral research being in the same field they can never make a difference. For young people to take a trodden or a safe path is very easy. But that shouldn't be done. They have to take up new challenges in life with full confidence.

**You are an administrator and scientist, which of the two roles, you enjoy the most?**

I have never looked at the job of an administrator in its true sense, because it is all about people management with the rule book that is there to help. I have never been burdened by the rule book though I have always gone by the objectives rather than the rules. Today, CSIR transformation is heralded as among the top ten achievements of India in the twentieth century in the book 'Scientific Edge' by Prof. Jayant Narlikar. Had I gone by the rule book, I wouldn't have achieved anything. I did things that were unheard of. I think from my heart and not just my mind.

Only concern, I have today is in the atmosphere. As I was mentioning to my friend Dr. Montek Singh Ahluwalia, the former Deputy Chairman of Planning Commission, today the country's problem is not budget deficit, it is trust deficit. The decision making becomes impossible due to lack of trust. We must restore it.

**Sir, do you think it is more difficult to manage scientists?**

Yes of course. It is the toughest job, because each scientist has a mind of his own. They don't do anything for themselves. They stand on certain principles. Indian National Science Academy (INSA) has just eight hundred chosen scientists in the country, which has a population of a billion. So they are very special people. Out of these eight hundred, thirty scientists were members of the INSA Council, when I was the president of INSA for three years. They all were individuals with strong convictions and there were honest differences. But managed the Council very well. How? I will let you in on a secret.

I have a granddaughter named Eshwari. She was four years. Normally in the morning, I would be reading newspapers- while seeping my tea. Eshwari will be fooling around. One day I wanted to test her capability in alphabets. She sat besides me. I wrote alphabet "A" and asked her what is it.? She said, its "A". I wrote "D", she said its "D". Then I wrote "Z", she said its "N". From the angle which I was looking it's "Z" and from the angle which she was looking, it looked "N". So, both of us were right. So, when it comes to managing different people, all that is required is an open mind to see as to how the other person looks at it.

I remember, in 1995, CSIR had forty independent labs, each running in its own directions and competing with each other. When I took over as Director General, CSIR, we had forty labs. Each lab behaved as though it was in its own. There was hardly any collaboration. Then we created "CSIR Vision – 2001", setting a common vision and strategy, for CSIR as a whole. That had a miraculous effect, which made every independent lab work with a common objective that was aligned with the overall CSIR vision.

**Sir, which technology do you think would dominate the world in the next two decades?**

Some technologies like mobile, internet, automation of knowledge work, internet of things, 3-D printing, advanced robotics, next-gen genomics, etc., will definitely dominate the world. It is becoming very clear that the digital way of life is just not for selected people and it is going to be for the masses. Today, we have 900 million mobiles, but the penetration of smart phones, as we move along with the cost dropping out, is going to be huge. That access is going to create a huge difference. And digital India will happen faster than we think.

When I was in Paris, I received a phone call from my daughter-in-law at 4:30 in the morning. I was worried. I picked up the call with anxiety. But it was my grandson, just two and half years old who has called me. I was amazed to see that he was able to scroll, find my image, press it, and connect with me!

I am founder professor at NIIT University, Shri Rajendra Pawar, the founder of NIIT wanted me to visit the University. On the way we were discussing on India going digital. I told him about my inspiration from the symbiosis schools of management on innovation and entrepreneurship, a course started by my paradigm. I was telling about, an individual Jan Koum, who was the originator of WhatsApp. Jan Koum was born in Kiev, moved to United States with his mother. He got a job in Yahoo but couldn't get a job in Facebook. It was in March 2009, he had an iPhone in his hand for the first time and by April 2014, he had half a billion customers on WhatsApp. It is a history that, Facebook that did not offer him a job had to buy his company for 17 billion dollars! So, the innovator is one who sees what everyone sees but thinks of what nobody has thought. This digital way is going to change the entire way we are going to read, write, interact, hire, transact, do commerce, entertain and this will not be just for few, it would be for everyone.

**Can you share with us the toughest period of your life ?**

On finishing primary school, I sought admission in a secondary school. I required twenty one rupees as admission fee. To gather this twenty one rupees, it took us twenty one days. My mother did not have the money. A lady, who herself was a housemaid in Mumbai, gave her savings to us. By then admission to most schools were over and I had to attend the Union high school again, in Marathi medium. I am glad that, I went to the Union high school because, had I not gone there, I would not have met Principal Bhawe.

**Sir we heard about, more from less for more (MLM) which is very innovative. Can you give an example where it has come from an organized research?**

Your MEG is a typical example, excepting that the capital cost is very high. You have to strive to bring down the capital cost and then we can start using it. So you have to pose yourself a challenge, how can I achieve magnetic shielding, which is 100 times cheaper. Today it is so expensive, because it is expensive and that requires disruptive thinking. A good example is chotukool, a rural refrigerator that costs just \$69. Godrej engineers said they wanted a new cooling technology and that is how a new one emerged, that works on solid state electronics based cooling as in our laptop. Had they continued with the traditional compressor, this sort of cost reduction wouldn't have emerged. So I strongly believe disruptive thinking is required.

**Talking about innovation, we think of China, right from vegetable peelers, toys to mats, everything is from China. Chinese have made the innovation in their own way, what do you think is the difference made by them and not made by Indians?**

China has the unique ability, to not to just limit at an idea but put idea into practice. This is missing here in India because of lack of innovation ecosystem. Some of the innovations are not counted as innovation, for example, missed call is an innovation by Indians, on a lighter side I would term this as an Indovation (innovation by Indians).



### What is your advice to youngsters?

There is no limit to achievement excepting the limit you put on your heads by yourself. I remember meeting our former Prime Minister Shri Atal Bihari Vajpayee in 1998, one month after the Pokhran test, he asked me, now that US has slammed sanctions on us and how would that affect our scientists? I said, as long as we don't put sanction on our minds, nobody can do anything. That has proved right after signing of the nuclear deal in 2008. So do not put limits.

Secondly you have to develop optimism that 'yes I can do this'. I would say don't get depressed when the sun sets and over excited when the sun rises, because failure and success will be part of your life. Mind, is best compared with a parachute, because parachute works only when it is open, likewise mind also works best when it is open.

I remember, once a famous badminton player Shri Nandu Natekar, invited me and Shri Sunil Gavaskar for dinner, as we had achieved something in our own fields. I am a fan of Sunil Gavaskar and we started sharing our experiences. While talking, Sunil Gavaskar told me one interesting thing, he said when he was playing tests against West Indies, tall bowler like Hall, twice his height would come from a long distance and bowl a ball which he would hardly see. He would be a defeated man at that time and the whole stadium would go into raptures. Sunil Gavaskar said, he developed an ability, of whipping out the memory of that ball from his mind as though it never happened and that is how he succeeded. The message is, "forget the failures of the past and design a positive future". People call me a dangerous optimist, because I don't see the half empty glass, but I see the half full glass.

### Sir, after having achieved so much, still do you feel you have a lot to achieve?

When I was stepping down from CSIR in 2006, in an event, the then prime minister Dr. Manmohan Singh said something very gracious. He said "I want to remind Dr. Mashelkar, that best is yet to come". That summarizes it. I am still waiting for my best. I work day after day, week after week, month after month, year after year and I hope to continue it till my last breath.



The team:

*Ms. Rimpi Dawar, Shri Anindya Bhattacharya, Dr. K. Prabakar, Shri Avik Kumar Saha, Shri Suddhasattwa Ghosh and Ms. K. Saipriya*

## Raman Spectroscopic Imaging of Single Nanostructures in the Diffraction Limit

Usually nanostructures with the dimension of a few tens of nanometer are visualized with the aid of either scanning and transmission electron microscopies (SEM and TEM) or using surface probe microscopes. Recently other spectroscopic techniques, namely, synchrotron based X-ray diffraction, photoelectron along with neutron diffraction, Raman and photoluminescence along with terahertz spectroscopies are also being used for imaging with nanometer resolution. However, laser based Raman spectral imaging is one of the most indispensable non-destructive tools to visualise the nanostructures for affordable, simple and quick data collection. Thus Raman spectroscopic imaging can be used as a unique tool for the direct observation of single nanostructures and introspect their physical properties in nanometric size to differentiate them from the corresponding bulk properties. In Raman imaging technique, the maps can be created based on the changes in the spectra involving characteristic Raman frequencies and several other important parameters e.g., intensity, polarization dependence, width, shift of the Raman peaks, collected from a material. The above mentioned changes in the Raman spectra generate the contrast which reveals the spatial distribution of the material properties for a line or areal mapping. However, there are certain limitations in imaging of nanostructures with Raman spectroscopy; first and foremost is the average separation between the nanostructures in overall distribution as it is limited by the optical resolution in the Rayleigh's criterion with two point sources regarded as just resolved when the principal diffraction maximum of one image coincides with the first minimum of the other. Secondly, spatial step size of micro-Raman spectrometer stage which is normally in the range of hundreds of

nanometers. The most important limitation, however, is the Abbe diffraction limit below which one cannot focus the light below a size  $d = \lambda/2\text{nsin}\theta$ , where  $\lambda$  is the excitation wavelength and  $\text{nsin}\theta$  is the numerical aperture of the focusing objective. Considering green light around 500 nm and a numerical aperture of 1, the Abbe limit is approximately  $d = \lambda/2 = 250$  nm which is large compared to most of the nanostructures. In the present report capability of Raman imaging for single nanostructures with 514.5 nm line of Ar<sup>+</sup> laser excitation with an objective of numerical aperture up to 0.9, is described. Micro-Raman stage movement resolution is 100 nm in both the X and Y directions.

Phase mapping was studied typically for single microbelts with GaN nanoprotuded shell of  $\sim 1000$  nm on Ga<sub>2</sub>O<sub>3</sub> core of  $\sim 5$   $\mu\text{m}$  (GaN@Ga<sub>2</sub>O<sub>3</sub>) grown in catalyst free chemical vapour deposition (CVD) technique. The intensity profile for 200 and 569 cm<sup>-1</sup> corresponding to Ga<sub>2</sub>O<sub>3</sub> and GaN phases, respectively over an area of  $10 \times 8$   $\mu\text{m}^2$  showed a clear image of the core-shell structure. The phases were confirmed in the detailed cross sectional high resolution TEM (HRTEM) analysis (Figure 1).

Radial Raman spectroscopic line scanning along the cross section of CVD grown single nanotips showed the presence of strain across the line. A differential Raman imaging along the cross sectional area of  $20 \times 20$   $\mu\text{m}^2$  showed presence of residual strain, due to the preferential crystalline orientation at the core which was different from the boundary surface (Figure 2). Chemical affinity makes diffusion rate of Ga lower in the polar surface (0001) with either Ga or N termination than that for the non-polar surface (10 $\bar{1}$ 0) with negligible chemical interaction on saturated Ga-N bonds. Hence growth of the GaN phase was pronounced at the non-polar surface.

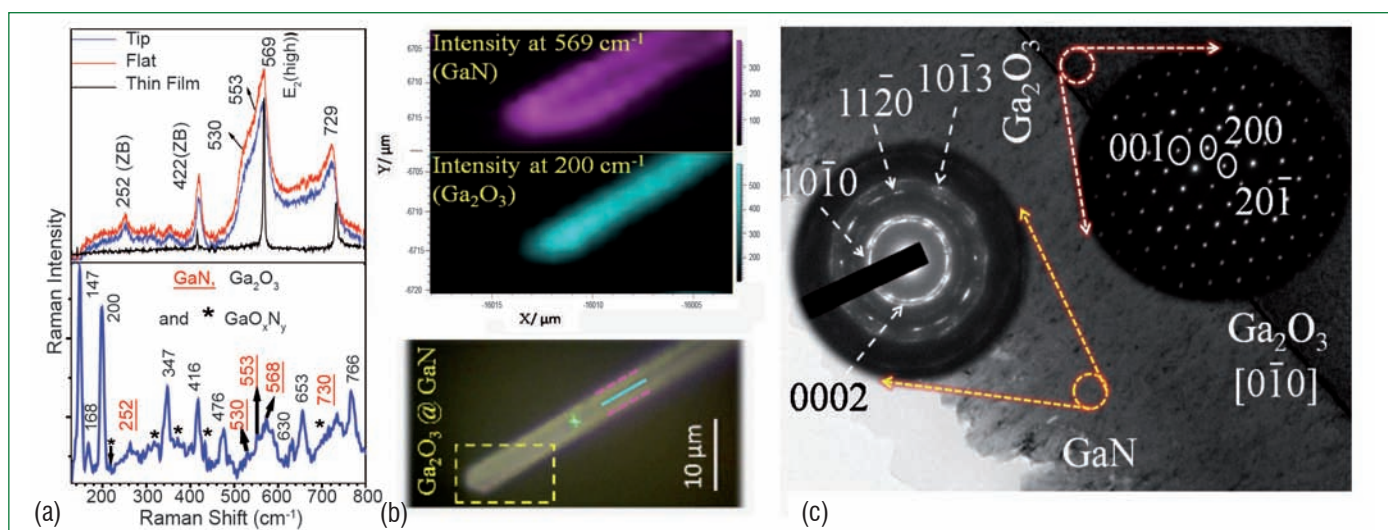


Figure 1: (a) Raman spectra of GaN@Ga<sub>2</sub>O<sub>3</sub> core-shell belt along the side wall for both the phases, (b) spectral image using 569 cm<sup>-1</sup> for GaN shell and 200 cm<sup>-1</sup> for Ga<sub>2</sub>O<sub>3</sub> core along with the optical image of the belt indicating the area scanned for different phases and (c) cross sectional HRTEM analysis for the evidence of crystalline phases present

Supported with HRTEM analysis, the finding of residual strain close to the core resolved the issue of differential growth dynamic of GaN phase at different crystalline planes present in the polar core and on the non-polar surface of the nanostructure, as the reason for the growth of tip shape. In case of InN nanorod array, we could uniquely resolve the growth orientation, by simple observation of the distribution of  $E_1(\text{LO})$  mode at  $589\text{ cm}^{-1}$  over an area of  $3 \times 2\ \mu\text{m}^2$  (Figure 3a). Raman peaks at 489 and  $589\text{ cm}^{-1}$  correspond to symmetry allowed  $E_2(\text{high})$  and  $E_1(\text{LO})$  modes, respectively, for the wurtzite phase of InN. In addition to these peaks a surface optical (SO) mode at  $561\text{ cm}^{-1}$  is also observed. Field emission scanning electron microscopic (FESEM) morphologies of distinct growth orientation are shown in the outset (Figure 3a). Intensity distribution  $E_1(\text{LO})$  mode of vertical nanorods reveal the distribution of the nanorods (Figure 3b) and resembles the distribution of the nanorods as shown in FESEM image (Figure 3a). This may be due to the reason that separation of vertical nanorods ( $\sim 500\text{ nm}$ ) is sufficient to be distinguished in the Raman area mapping since we have performed the mapping with a step size of  $100\text{ nm}$  and the optical resolution of  $\sim 180\text{ nm}$  with  $514.5\text{ nm}$  excitation and  $100\times$  objective with numerical aperture =  $0.9$  using the Rayleigh's criterion. Mapping of oblique nanorods with  $E_1(\text{LO})$  mode intensity (Figure 3b), however does not show distinct distribution of nanorods. This may be owing to the fact that  $E_1(\text{LO})$  mode originates from the bulk of the material and cannot distinguish the nanorods having tip separation  $\sim 100\text{ nm}$  or less as shown in the FESEM analysis (Figure 3a). Moreover,  $E_1(\text{LO})$  mode contributed also from sides of the nanorods due to oblique alignment, schematically shown in the outset (Figure 3b).

Crystallographic orientation of a highly anisotropic square shaped

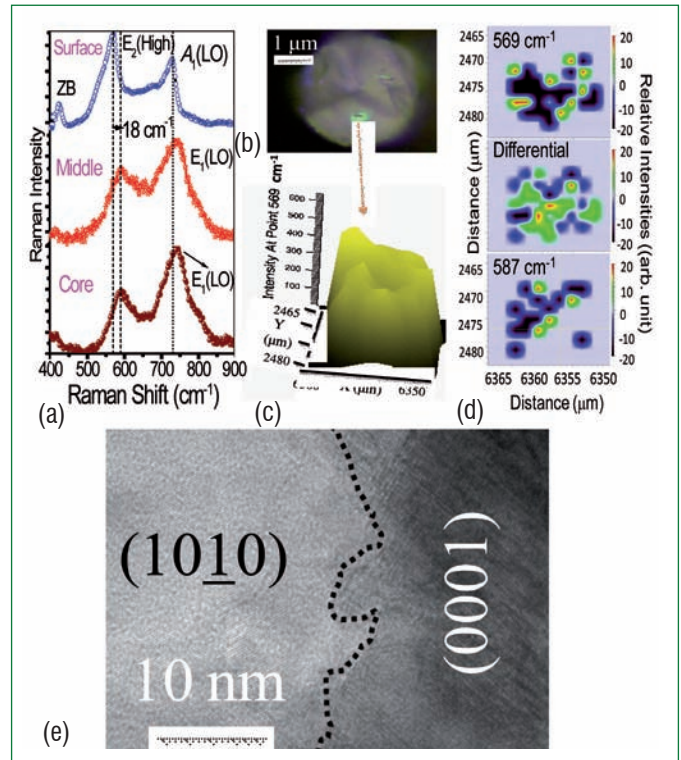


Figure 2: (a) Raman spectra of GaN nanotip for a radial scan covering surface to core region, (b) optical image of cross section of the nanotip, (c) 3-D Raman intensity image for  $569\text{ cm}^{-1}$  peak showing surface region alone, (d) 2-D Raman intensity images for  $569, 587\text{ cm}^{-1}$  peaks and their differential image and (e) HRTEM analysis for the evidence of crystalline orientations of wurtzite GaN phase present at the surface and core regions

single wurtzite GaN nanotube facet was probed by polarized Raman imaging. The polarization dependent Raman intensities are collected for an area of  $400 \times 600\text{ nm}^2$  in two mutually orthogonal directions  $Z(\text{XX})Z$  and  $Z(\text{XY})Z$  with respect to the nanotube long

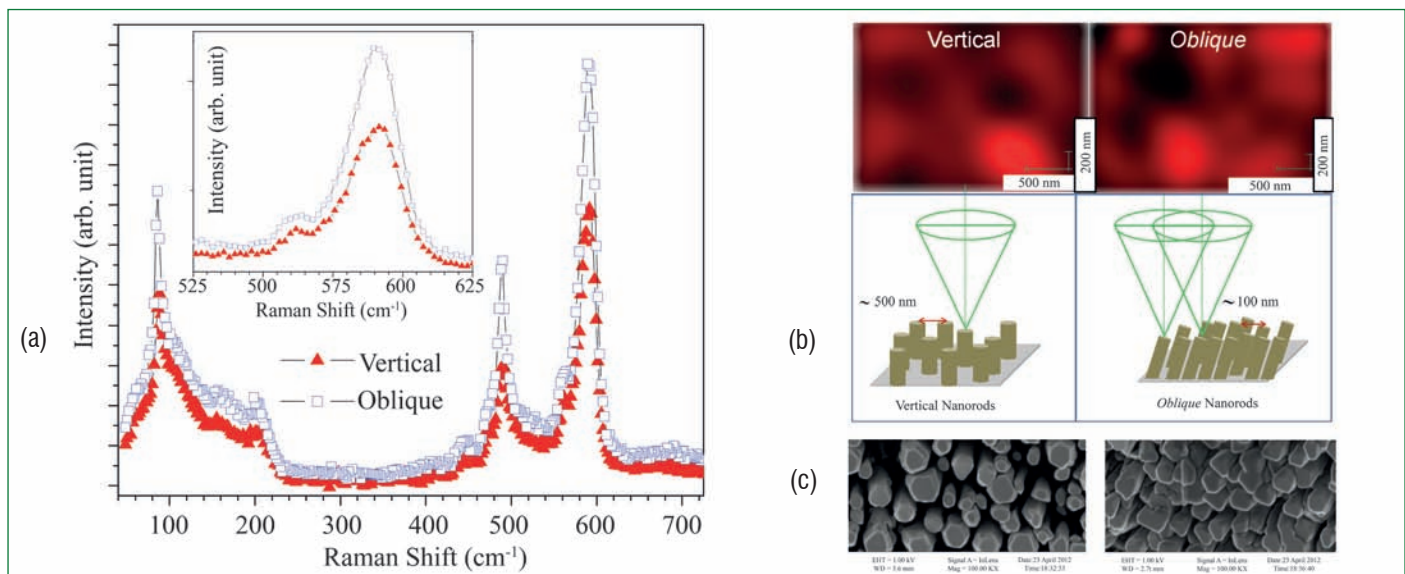


Figure 3: (a) Raman spectra and corresponding FESEM images of vertical and obliquely oriented InN nanorods. at the outset, (b) Raman images using  $E_1(\text{LO})$  mode for both the samples showing well resolved nanorods in case of vertical orientation alone and (c) schematic of the vertical and oblique nanorod morphologies with the limitation of optical resolution in the image processing is depicted at the outset

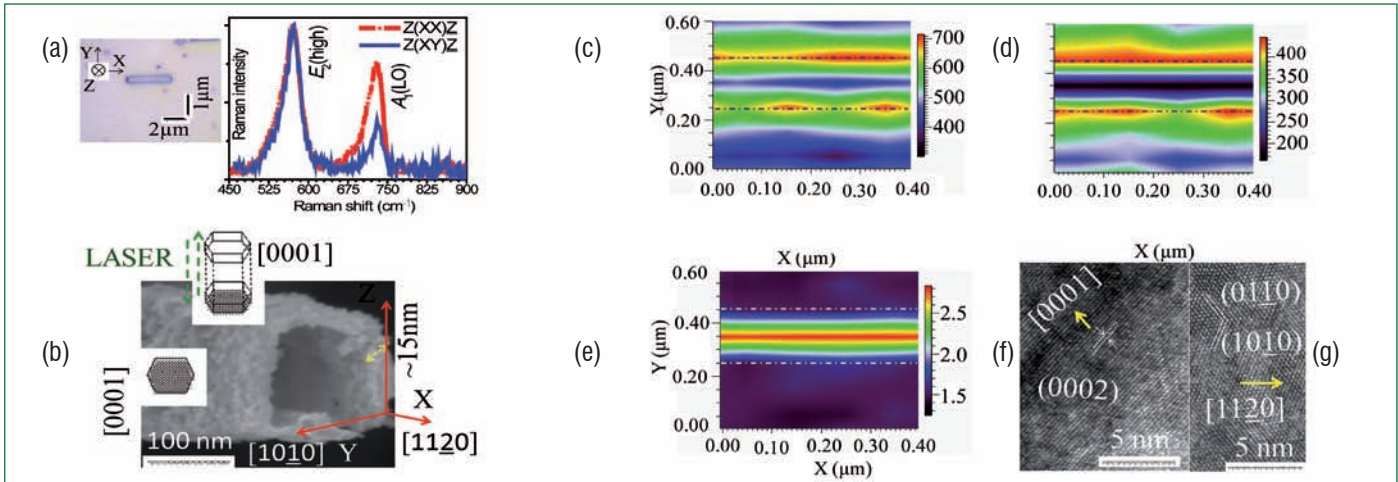


Figure 4: (a) Optical image and the Raman spectra of GaN nanotube for two orthogonal polarizations in the back scattering geometry (b) TEM image of the nanotube and possible crystalline orientation for the facet and growth direction as interpreted from the Raman study. Raman intensity images for (c)  $E_2(\text{high})$  mode, (d)  $A_1(\text{LO})$  mode and (e)  $E_2(\text{high})/A_1(\text{LO})$  HRTEM analysis as an evidence of (f) [0001] crystalline facet orientation and (g) growth direction along [1120] for the wurtzite GaN nanotube

axis. Variation in intensities of symmetry allowed  $A_1(\text{LO})$  mode (only in the Z(XX)Z configuration) with respect to that for the  $E_2(\text{high})$  mode of wurtzite GaN with two different polarization directions reveal the possible crystalline orientations of [0001] in the facet and growth direction along [1120]. The polarized Raman spectral imaging illustrates the fact of inhomogeneous crystalline orientations along the edges of the nanotube facets owing to its finite wall thickness (Figure 4). While describing the process of identifying the orientation of crystalline facets in a non-destructive polarized Raman study we also emphasize the role of polarization leaking in the nanostructures for the optical measurements in the diffraction limit with our nanostructure width around 200 nm while optical resolution is barely  $\sim 180$  nm.

In another unique study, we could resolve layers of graphene grown in the electron cyclotron resonance plasma technique. Graphene is a two-dimensional single layer of  $sp^2$  bonded carbon atoms arranged in a hexagonal honeycomb structure with a typical thickness of 0.335 nm. The Raman spectrum of the single

layer graphene shows dominated peaks around  $1580\text{ cm}^{-1}$  (G) corresponding to  $E_{2G}$  phonon at Brillouin zone centre and is due to bond stretching of all pairs of  $sp^2$  carbon atoms in the ring and a very intense peak around  $2678\text{ cm}^{-1}$  (2D) which originates due to the double resonance of inter-valley transition at K point of the zone boundary. The intensity ratio of G and 2D peaks ( $I_{2D}/I_G$ ) is reported to be greater than or equal to 4 for a single layer graphene. As the number of layers in the graphene increases the ratio of  $I_{2D}/I_G$  decreases. Depending on the values of  $I_{2D}/I_G$  ratios single layer, bilayer and trilayer graphene were imaged using the Raman intensity ratio mapping technique over an area of  $20 \times 30\ \mu\text{m}^2$  in the Streamline Raman imaging mode (Figure 5) facilitating large area imaging. The cross sectional and tilted views are shown along with the optical images for single layer, bilayer and trilayer graphene in a unique way for the first time.

In conclusion, we have described Raman spectroscopic imaging of single nanostructures for its phases in the core-shell morphology, differential strain to understand growth mechanism in for the tip shape, and optical phonon modes emanating from the bulk for morphological analysis. Polarized Raman imaging of a faceted nanotube is also studied for identifying the crystalline orientation. The dimensions of these nanostructures or their separation from each other for longitudinal optical mode and polarized Raman imaging in InN nanorods and GaN nanotubes, respectively are in the diffraction limit  $\sim 200$  nm for  $514.5$  nm excitation. The study is also extended to define thickness of graphene layer including a 3-D map for the stacked layers of graphene where a monolayer thickness is only about  $0.34$  nm. An indirect technique of intensity ratio of 2D and G band is used for the analysis of thickness of graphene layer.

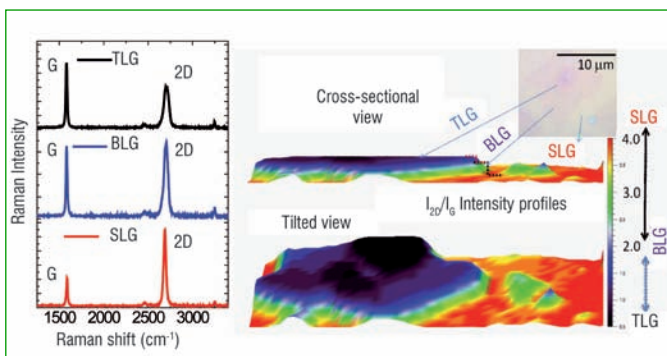


Figure 5: Raman spectra of single layer (SLG), bilayer (BLG) and trilayer (TLG) graphene located at different regions for the film as indicated in the optical image. Corresponding 3-D cross sectional and tilted Raman images using  $I_{2D}/I_G$  ratio shows clear vision for the stacking layers

Reported by

Sandip Kumar Dhara and Colleagues, Materials Science Group

## Thixo-Casting: An Alternative Manufacturing Route to Conventional Casting Process for Manufacturing of Austenitic Stainless Steel

This article outlines the works carried out by IGCAR and Indian Institute of Science (IISc), Bengaluru to demonstrate the feasibility of thixo-casting of austenitic stainless steel (SS). Using an indigenously designed and manufactured adjustable cooling slope, a thixo-cast 304LSS ingot of ten kilograms weight was successfully produced for the first time in the country.

Thixo-casting is an alternative to conventional manufacturing techniques such as casting and forging. This technology combines the benefits of both conventional casting and forging processes. Near-net shape products are manufactured using thixo-casting with minimum intermediate process steps compared to the forging process. The products manufactured using this technology show better mechanical properties compared to its conventional cast counterparts. Thixo-casting is carried out in the temperature range where the material shows “thixotropy”, a property by virtue of which the material flows like fluid when agitated and, it thickens up and retains its shape like solids when allowed to stand still. As alloys exhibit thixotropy in the semi-solid stage, thixo-casting requires the alloy in its semi-solid state, rather than in solid state as used in forging process or in molten state as used in conventional die casting technology. Though, there are many requirements imposed on the potential feedstock for semi-solid processing, the key feature which determines its suitability for the above processing is the formation of unique microstructure that contains solid spheroids in a liquid matrix. These solid spheroids in the liquid matrix translate and rotate about adjoining spheroids in contact in response to applied force and thereby are responsible for thixotropic behavior of the alloy. The resultant microstructure responsible for better property in the material is obtained by breaking of the growing dendrites in the solidifying alloy. The growing dendrites during solidification are broken by employing methods such as mechanical stirring, electro-magnetic stirring, ultrasonic vibration, cooling slope etc.

Thixo-casting was restricted to materials with relatively lower melting points, such as aluminium-based and magnesium-based alloys. The use of this technology for steels is often considered challenging due to high process temperature, complex phase formation, possibility of oxidation and difficulty in controlling parameters in the narrow semi-solid processing window. However, in view of significant advantages such as the reduction in the number of the intermediate processing steps, energy input and

potential for improving component complexity, different research groups based in UK, Germany, China and Japan are currently working on the development of technology for semi-solid forming of steels. For the last few years IISc, Bengaluru has been involved in the development of indigenous semi-solid forming technology at National Facility for Semi-Solid Forming (NFSSF). IISc has successfully developed the technology for manufacturing of components of non-ferrous alloys in laboratory scale. However, considering the complexity involved with the processing of steel, thixo-casting of steel was not tried earlier.

To demonstrate the amenability of thixo-casting for manufacturing of stainless steel, a project was initiated by IGCAR in collaboration with IISc., Bengaluru. Based on the literature survey, cooling slope technique was chosen to obtain the required microstructures in the billet. In this method, the alloy in low superheat condition, usually at 10° C above the liquidus temperature is poured over an inclined cooling plate made of ceramic material that is maintained at a relatively lower temperature than the melt. As the molten metal flows over the plate, large numbers of nuclei form on the relatively cooler plate surface. However, due to continuous fluid movement, the newly formed nuclei are washed away and collected in the mould kept at the lower end of the cooling slope. After solidification, microstructures with fine spheroids are ensured in the slug due to presence of large number of nuclei. This method has been

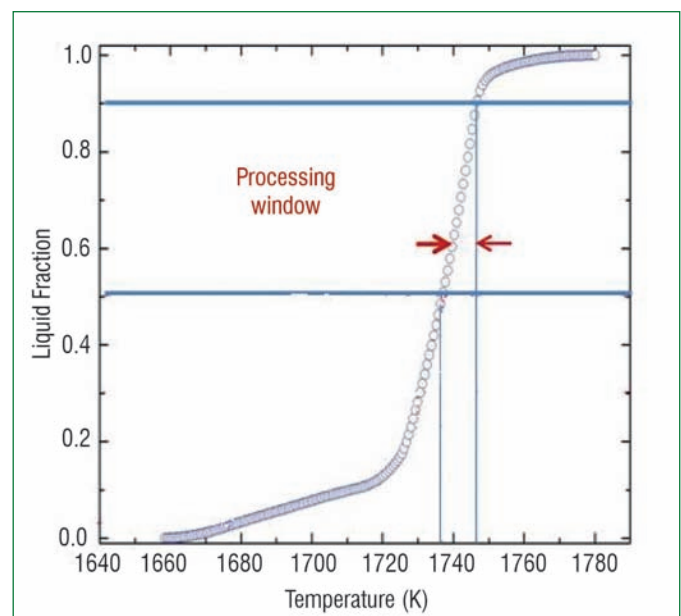


Figure 1: Processing temperature window for thixo-casting operation

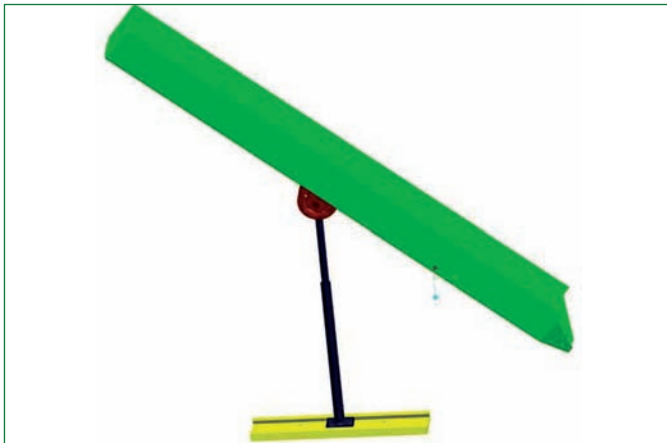


Figure 2: Schematic of the cooling slope

successfully used for producing non-dendritic billets for several non-ferrous alloys and M23 high speed steel ferrous alloys.

304LSS was used for this investigation as a representative of the 300 series austenitic stainless steels, often chosen as a model alloy for various studies on stainless steels. To obtain the liquidus and solidus temperatures, liquid fraction evolution during melting of the steel and information about solidification behavior of 304LSS, Differential Scanning Calorimetry (DSC) experiments were carried out. The solidus and liquidus temperatures (1653 and 1752K, respectively) were measured from DSC endotherms. Then the thixo-casting temperature was decided from the liquid fraction evolution. The window for thixo-casting of SS304L is shown in Figure 1. Using the experimental data obtained from the DSC experiments, CFD analysis of the metal pouring process was carried out. A cooling slope was designed and manufactured based on the results obtained from the CFD analysis. The schematic of the cooling slope is given in Figure 2. Using this indigenously developed cooling slope, the thixo-casting of 304LSS was carried out. Melting of the steel for this process was carried out using the

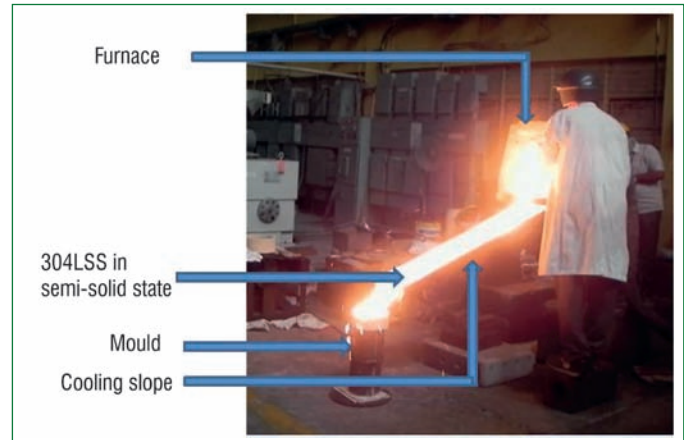


Figure 3: Thixo-casting of 304LSS

furnace at Defence Metallurgical Research Laboratory, Hyderabad and a thixo-cast ingot of ten kilograms weight was produced. The thixo-casting process carried out is shown in Figure 3. To compare the microstructure of the steel and subsequent analysis, an ingot of ten kilograms weight was also produced by conventional casting route using the same furnace. The microstructure of the cast 304LSS is shown Figure 4a. The long chains of dendrites can be seen in this figure. The thixo-cast microstructure shown in Figure 4b shows small clusters of skeletal  $\delta$ -ferrites in the matrix. Comparison of these microstructures demonstrates the effectiveness of cooling slope to produce non-dendritic structures in the stainless steel. The dendritic microstructure in stainless steel castings is often considered as detrimental for long term usage of critical components. Thixo-casting can be used as an alternative manufacturing route to conventional casting process, for producing critical components of stainless steel.

*Reported by  
Dipti Samantaray and colleagues  
Metallurgy and Materials Group*

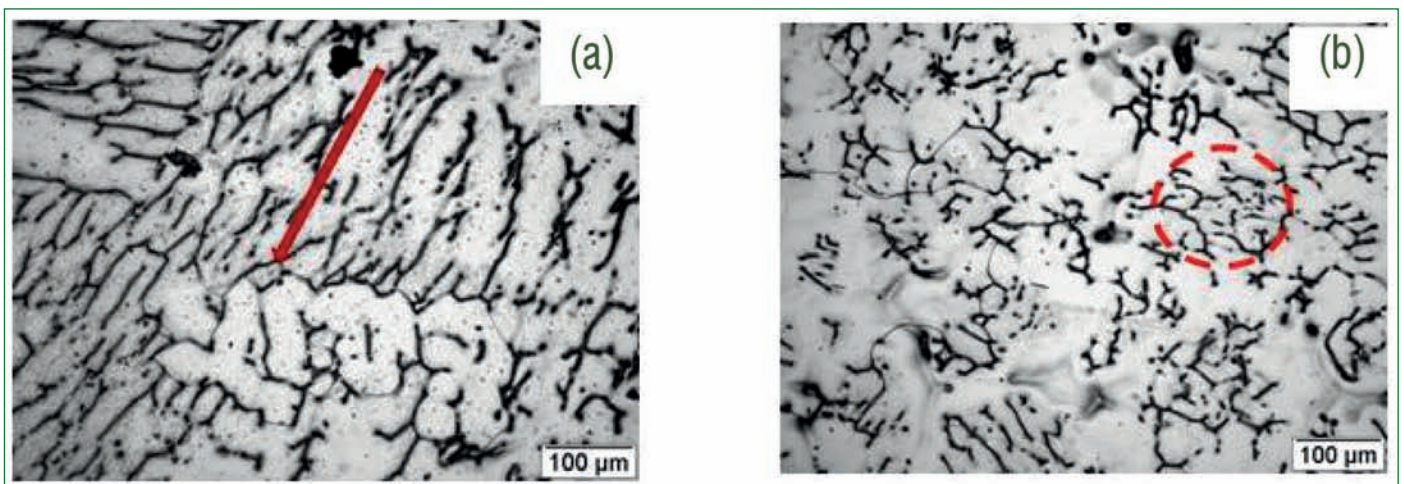


Figure 4: Microstructure of 304LSS obtained by (a) conventional casting; arrow shows a dendrite chain and (b) Thixo-casting, circle shows a cluster of skeletal  $\delta$ -ferrite

## Young Officer's FORUM

### Characterisation of Sodium Aerosol in Cover Gas Region of SILVERINA Loop



Shri Amit Kumar obtained his M.Sc. from Chatrapati Sahu Jee Maharaj University, Kanpur, Uttar Pradesh. He is from the third batch of BARC Training School at IGCAR campus and currently working as Scientific Officer in Radiological Safety Division. His current area of interests include aerosol study related to Fast Reactor Safety. He has published four papers in peer-reviewed journals and six national and international conference papers. Currently, he is doing Ph.D. in the area of sodium aerosol characterisation in cover gas region under the guidance of Dr. R. Baskaran with HBNI.

During operation of sodium cooled fast reactor (SFR), evaporation of sodium from the hot pool surface and subsequent condensation results in the formation of sodium aerosols within the cover gas space. When the aerosols get accumulated in sufficient concentration, they will participate in the radiative exchange within the cover gas space and modify the total heat transfer to the cooled roof structure by radiation absorption and scattering mechanisms. Further, the mass transfer occurs due to condensation of sodium vapour on the cooler surfaces like annular gaps, roof top, control plug, rotating plug and fuel handling machine and results in deposition of aerosols. This deposition hinders the rotational movement of rotating plug and operation of fuel handling machine. The sodium aerosols also affect the operation of the cover gas purification system, decrease its efficiency (flow through cold trap circuit) and reduce the visibility of the cover gas region.

During the design of the reactor and roof structure, necessary care has been taken to account for the heat and mass transfer phenomena. However, it is important to know the concentration of aerosol and size distribution of droplets, in order to predict the heat and mass transfer phenomena effectively, which can get changed due to interaction of thermal radiation with aerosols and mass transfer due to condensation of aerosols. Further, sodium aerosol properties would get modified due to (i) difference in temperature between the sodium pool surface and the bottom of roof top plug, (ii) spatial variation of cover gas region, (iii) geometric dimension

(diameter of the sodium pool surface, height of the argon cover gas and shape of roof top) of the cover gas system and (iv) possible enhanced coagulation of sodium aerosols upon interaction with gamma radiation, resulting in increase of the size. Hence in order to understand various processes of sodium aerosols in the cover gas region and their role on heat and mass transfer phenomena, determination of characteristics of sodium aerosols (physical) and theoretical simulation of aerosol parameters for a given condition (temperature, geometry etc.) assumes significance and it would modify the cooling requirement of roof slab design. Hence, theoretical simulation and experimental studies have been initiated to determine the characteristics of sodium aerosol in the cover gas region of SILVERINA Loop.

The aerosols in the cover gas region are formed due to the condensation of sodium metal vapour (liquid droplet). The sampling of such aerosols is very critical and it requires sophisticated methodology (without exposing to atmosphere) unlike sodium combustion aerosols, where, sodium fumes are generated and sampled in the open atmosphere. The sampling of aerosols in cover gas region involves (i) drawing of aerosols, (ii) trapping in a suitable medium without exposure to atmosphere and (iii) analysis of the trapped aerosols for determination of its characteristics. Taking into consideration the above aspects, a suitable technique for the characterization of sodium aerosols has been developed and qualified in Aerosol Test Facility (ATF). Subsequent experiments

were conducted in SILVERINA Loop of FRTG and sodium aerosol parameters were determined. In this article description of sampling system for aerosol sampling in SILVERINA loop, details of results and analysis of characteristics of sodium aerosols, theoretical simulation of mass concentration of sodium aerosol for the given pool (loop) condition and validation of model with experimental results, temperature profiling of cover gas region and future work on sodium aerosol characterisation are presented.

### Theoretical Modeling

A theoretical model is developed using standard mass and number concentration decay equation (First order Ordinary Differential Equation) to predict the equilibrium mass and number concentration of aerosols in the cover gas region. Taking size of the aerosols as an input from the experimental results, the equilibrium mass concentration is evolved by solving rate equation of mass concentration and number concentration numerically by finite difference method. In this model, the input parameters are temperatures of sodium pool surface, bottom surface of roof and bulk cover gas, geometry of the vessel (diameter of the pool, height of the cover gas region) and radius of aerosol. The steady state equations for mass concentration, number concentration and inter-relating equation of mass and number concentration of the

aerosols are given below:

$$\frac{dC}{dt} = -\lambda C + \delta C + Se \quad 1$$

$$\frac{dN}{dt} = -\lambda N - KN^2 + Sn \quad 2$$

$$C = \frac{4}{3}\pi r^3 \rho N \quad 3$$

Where C – Mass concentration (g/cm<sup>3</sup>)

$\lambda$  – Decay rate (gravitational, wall plating and ventilation) (1/s)

$\delta$  – Convective source rate (1/s)

Se – evaporative source term (g/cm<sup>3</sup>seconds)

N – Number concentration (1/cm<sup>3</sup>)

Sn - Source term for number concentration  
(no. of particles/cm<sup>3</sup> seconds)

K – Coagulation rate (1/s)

$\rho$  – Particle density (g/cm<sup>3</sup>)

r – Radius of particle (cm)

t – Time (seconds)



Figure 1: Photograph of aerosol sampling system integrated with test pot-1 of SILVERINA loop



To begin with, the source terms  $S_n$  and  $S_e$  are calculated using system geometry and other operating parameters. At  $t=0$ , the value of  $N$  and  $C$  are equal to zero. By taking sodium particle radius ' $r$ ' from the experimental value, the  $\lambda$ ,  $\delta$ ,  $E$  &  $K$  values are calculated. Next, for a small time increment of  $t < 1$  s, the value of  $C$  and  $N$  are calculated using equation 1 and 2 and particle radius ' $r$ ' is calculated by using equation 3. Using all the current values of  $C$ ,  $N$  and  $r$ , the new set of  $\lambda$ ,  $\delta$ , &  $K$  values are calculated. This process is continued till the concentration mass converges. The program for solving these equations through iterative method is written in MATLAB.

### Sampling and Analysis

The sampling system for aerosols consists of (a) aerosol sampling tube (b) aerosol sampling bottle (c) line heaters and controller and (d) aerosol flow controlling device.

The photograph of aerosols sampling system integrated with test pot-1 of SILVERINA loop is shown in Figure 1. The sampling tube is divided into two parts. One part of the sampling tube is inside the test pot-1 and other part is outside. Both the parts are connected with a flange. The sampling tube placed inside test pot-1 has been fabricated with three different lengths (215, 415 and 715 mm) to enable the sampling at three different levels. Before starting the experiment, tube of required length is attached with the flange and inserted into the test pot-1. The outer tube is connected to the sampling bottle through a needle valve. The value of the outer tube is wound with heating coil and temperature is maintained at about  $110^\circ\text{C}$  to prevent solidification of aerosols during sampling. The aerosol sampling tube is made of SS316 with internal diameter of

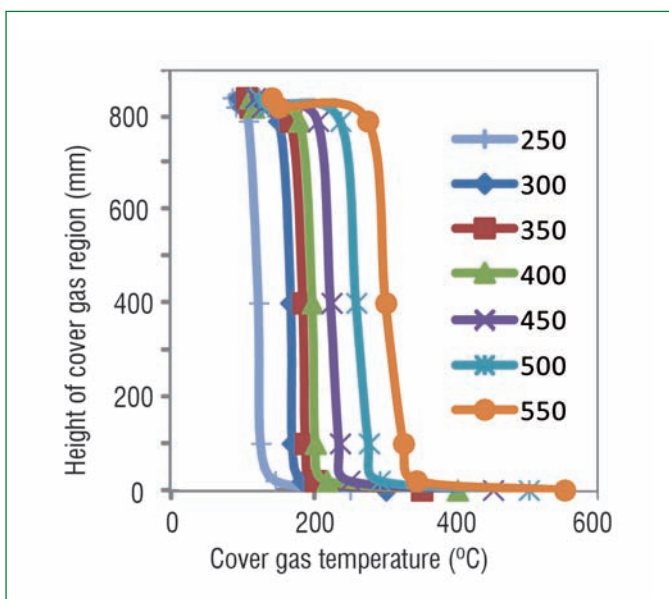


Figure 2 : Variation of temperature in cover gas region

10 mm (1.5 mm wall thickness). The maximum particle diameter that can be collected is  $20\ \mu\text{m}$ , without having bias due to wall deposition by impaction for a flow rate of 2 lpm. The samples are drawn in to sampling bottle (made of Perspex) filled with paraffin oil ( $\sim 600$  ml) and maintained at ambient temperature. The sodium aerosol laden cover gas is made to pass through the bottle, thus solidification of aerosol particle would occur as the cover gas enters into the paraffin oil. The cover gas coming out from the first sampling bottle is made to pass through the second sampling bottle so as to remove escaped aerosols, if any, from the first bottle. After the sampling, the sample bottles are removed from the loop and paraffin oil is drained for further analysis.

The sodium pool temperature was varied from  $250$ - $550^\circ\text{C}$  and argon gas was bubbled through liquid paraffin oil. Since the concentration of sodium aerosols increases with increase of sodium pool temperature and in order to avoid coagulation of aerosols trapped in the paraffin oil, the sampling time was set as 20 minutes for the pool temperature of  $250^\circ\text{C}$  and progressively reduced to two minutes for the pool temperature of  $550^\circ\text{C}$ .

The size distribution of sodium aerosols was determined by measuring the particle size distribution (sodium aerosol) hovered in a liquid dispersant (paraffin oil) by using ensemble diffraction technique. The scattered intensity and angle with respect to background measurement (without aerosol) gives the number concentration and particle size distribution. The mass of sodium aerosols trapped in liquid paraffin is measured by transferring them into water (to become NaOH) and measuring the change in conductivity of the NaOH solution. Mass concentration of sodium is estimated using a pre-established calibration graph plotted between changes in conductivity vs concentration of NaOH.

### Temperature measurement

The pool, roof and cover gas temperature are required for the theoretical simulation of mass concentration of aerosol in the cover gas region. Hence, a temperature measurement system has been fabricated, installed at the top flange of SILVERINA loop test pot-1. The temperature profiling was carried out at (i) the pool surface (820 mm), (ii) near to the pool (790 mm), (iii) roof surface (0 mm), (iv) near to the roof surface (20 mm), (v) two locations on the middle of the region with 300 mm difference in height (400 and 100 mm).

The temperature profile of cover gas region in SILVERINA loop was measured by varying sodium pool temperature from  $250$ - $550^\circ\text{C}$ . and is shown in Figure 2. The temperature started decreasing from

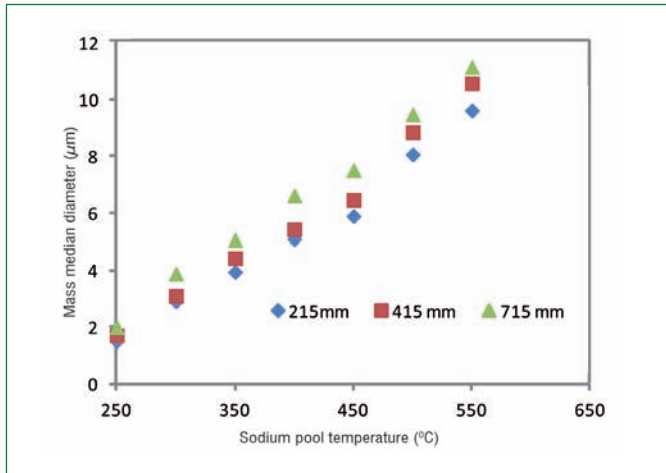


Figure 3: Variation of mass median diameter of sodium aerosol with pool temperature

the pool surface upto 20 mm, then reaches uniform temperature over region upto 750 mm height and converges towards roof temperature at the height of 820 mm. The temperature of the roof top was found to vary from 90 to 150°C for the sodium pool temperature of 250 to 550°C respectively.

### Size distribution

The Mass Median Diameter (MMD) of the sodium aerosol distribution was determined for three different sampling levels and for all the pool temperatures and it is shown in Figure 3. It is observed that it varied from 1–16 µm and increased with increase of sodium pool temperature. It can also be noted that for all the pool temperatures, the value of MMD is found to be higher near the pool surface (715 mm) when compared with that of near the roof (215 mm) and middle level of cover gas region (415 mm).

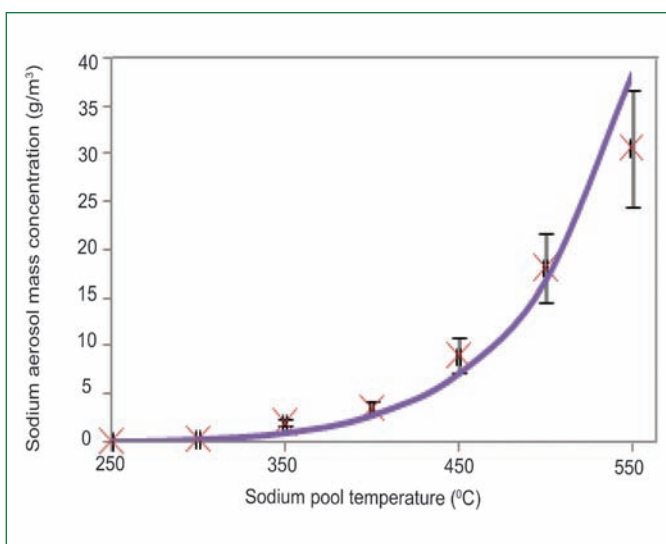


Figure 5: Theoretical and experimental comparison of sodium aerosol mass concentration (× 415 mm — Theoretical)

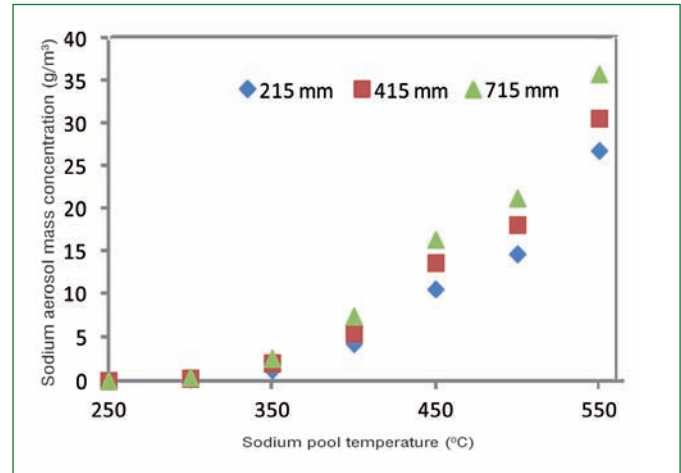


Figure 4: Variation of sodium aerosol mass concentration with pool temperature for three different levels

### Mass Concentration

The mass of sodium aerosols trapped in the bottle for all the samples was estimated and found to vary from 0.026 – 35.6 g/m<sup>3</sup>. The variation of mass concentration of sodium aerosol with pool temperature is shown in Figure 4. It is observed that the mass concentration increases exponentially with increase in sodium pool temperature. It is also observed that for all the pool temperatures, the sodium aerosol mass concentration is higher near the pool than that of near the roof and middle level of cover gas region.

### Theoretical simulation

The mass concentration of sodium aerosols in the cover gas region is predicted using the model. Figure 5 shows the predicted mass concentration versus various pool temperatures along with experimental values (at the middle level – 415 mm). The experimentally determined mass concentration of aerosols and the theoretically predicted concentrations are in good agreement ( $\pm 20\%$ ) for the pool temperatures (250-550°C).

Further work is in progress to determine the mass concentration of sodium aerosols for different geometry of cover gas region and the model will be optimized in predicting the mass concentration of sodium aerosol for any geometrical input and temperature of the sodium pool. The study would be extended to determine the sodium aerosol characteristics in the presence of gamma radiation and study the possible enhanced coagulation and settling of sodium aerosols within the cover gas space.

Reported by Amit Kumar  
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## Young Researcher's FORUM

### Parametric Studies on the Separation and Recovery of Ruthenium

The most commonly adopted aqueous method for the reprocessing of spent fuels discharged from nuclear reactors is the PUREX (Plutonium Uranium Extraction) process. The noble metal ruthenium (Ru) is one of the major fission products produced during the fission of plutonium-rich fuels in fast breeder reactors (FBRs). Ruthenium is also one of the important nuclides to be considered in the reprocessing of spent fuels, because of its large fission yield, relatively long half lives of  $^{103}\text{Ru}$  and  $^{106}\text{Ru}$  isotopes and its many oxidation states ranging from 0 to +8, some of which are fairly extractable in the solvent extraction conditions employed in PUREX process. It also creates problem in the nuclear waste management processes owing to the formation of highly volatile and radio-toxic  $\text{RuO}_4$  that decomposes and deposits on the cooler parts in the off gas stream, resulting in increasing the radiation field. Hence, separation of ruthenium is a desirable step in reprocessing as well as in the waste management of high level liquid waste (HLLW). On account of the existence of several oxidation states, formation of a large number of co-ordination complexes, slow rate of reactions, interfering effect from the other Platinum Group Metals (PGMs) namely Pd and Rh and the associated radioactivity, it is a challenge to separate and recover ruthenium from HLLW. Studies have been undertaken for the quantitative separation as well as recovery of ruthenium from simulated high level liquid waste (SHLLW) by various chemical and electrochemical methods.

#### Ruthenium in Nuclear Reactors

The fission yield (the fraction of a fission product produced per fission) of ruthenium is directly proportional to the fuel burn-up, fuel enrichment in  $^{235}\text{U}$  in the case of uranium-based fuels and the yield is more in U, Pu mixed oxide (MOX) fuel than in  $\text{UO}_2$



Dr. Pravati Swain joined Reprocessing Group, IGCAR as a Research Scholar in the year 2007, after obtaining her M.Sc. degree in Chemistry from Ravenshaw University, Odisha. She was awarded Ph.D. degree in Chemical Sciences by HBNI, in the year 2014 for her work on the 'Separation and Recovery of Ruthenium' under the guidance of Dr. C. Mallika. Currently, she is working as a Research Associate at IIT-Madras in a research project supported by Global Research Outreach (GRO) program. She is extremely passionate about electrochemistry and its application to real world problems and her research interest is in battery technology.

fuel. In a fast breeder reactor, because of the high burn-up (about  $100 \text{ GWd.t}^{-1}$ ) and with different neutron spectrum for Pu fission, about nineteen kilograms of Ru, Rh and Pd per tonne are produced. Among the three fission products, ruthenium exhibits higher intrinsic radioactivity, caused by the isotopes  $^{103}\text{Ru}$  (0.0036 wt.%;  $t_{1/2}$ : 39 days) and  $^{106}\text{Ru}$  (3.8 wt. %;  $t_{1/2}$ : 1.02 years).  $^{103}\text{Ru}$  emits beta particles with  $E_{\text{max}} = 0.76 \text{ MeV}$ , gamma radiation (0.05, 0.61 MeV) and decays to stable  $^{103}\text{Rh}$ .  $^{106}\text{Ru}$ , a soft beta emitter ( $E_{\text{max}} = 0.039 \text{ MeV}$ ) decays to  $^{106}\text{Rh}$  ( $t_{1/2}$ : 30 s), a hard beta emitter ( $E_{\text{max}} = 3.54 \text{ MeV}$ ) and also a gamma emitter of energy in the range 0.51-0.62 MeV.

In the irradiated  $\text{UO}_2$  and  $(\text{U,Pu})\text{O}_2$  fuels, ruthenium is present in the form of white metallic inclusions of Mo-Tc-Ru-Rh-Pd alloys. Post irradiation examination of (U,Pu) carbide fuel revealed that ruthenium was present in the form of  $\text{CeRu}_2$  (lanthanide-noble metal intermetallic compound) and a dicarbide phase of the type  $(\text{U,Pu})_2\text{RuC}_2$ , regardless of the C/U ratio, at all burn-ups. During the dissolution of irradiated fuel in nitric acid, ruthenium passes into solution mainly in the form of various nitrato, nitro and nitrato-nitro complexes of trivalent ruthenium nitrosyl  $[\text{Ru}(\text{NO})]^{3+}$ . These are complexed with hydroxo and aqua ligands and are of the general formula  $[\text{RuNO}(\text{NO}_3)_x(\text{NO}_2)_y(\text{OH})_z(\text{H}_2\text{O})_{5-x-y-z}]^{3-x-y-z}$ . After conditioning, the dissolver solution is subjected to solvent extraction for the purpose of separating U and Pu and the resulting HLLW (called as aqueous raffinate) contains the major fraction of ruthenium as ruthenium nitrosyl complexes.

#### Problems Associated with Ruthenium in Reprocessing and Waste Management

Among the variety of ruthenium nitrosyl complexes formed in the

dissolver solution in nitric acid medium, trinitrato, tetranitrato, nitronitrato and nitro complexes exhibit varying distribution behaviour between the aqueous (nitric acid) phase and the organic (tri-butyl phosphate/dodecane, TBP/DD) phase and a few of them remain in TBP/DD after stripping. Therefore, it is difficult to completely separate ruthenium from U and Pu, which results in the possible contamination of the product as well as increase in the radioactivity of the environment and warrants for a modification in the flowsheet for extraction runs.

For long term storage, the radioactive waste is vitrified with glass materials and converted to a relatively insoluble and compact solid which will neither react nor degrade for extended periods of time. As a solid, the waste becomes easy to store and handle; reduction in the volume is desired because of the less space requirement for long-term storage before ultimate disposal and keeping the solubility as low as possible, reduces the chance of leaching by groundwater. The concentrated HLLW is added to molten glass mass and vitrified. During this process, ruthenium is oxidized to volatile  $\text{RuO}_4$  by  $\text{HNO}_3$  and the oxide escapes to the vapour phase. Gaseous  $\text{RuO}_4$ , on contact with the cooler parts of the surface of the stainless steel equipment decomposes to a non-volatile black deposit of  $\text{RuO}_2$ . As a result of this deposition, the ducts carrying the off-gases become the source of radioactivity and radiation field around these pipes and ducts increases, leading to radiation exposure to the operators. Moreover, the platinum group metals are partially precipitated and accumulated at the bottom of the melter, since their solubility is low in the molten glass. Sedimentation of PGMs leads to local over-heating, high viscous glass formation and low rate of vitrification, which are mainly caused by the existence of needle like crystals of electrically conducting  $\text{RuO}_2$ . Thus, separation of ruthenium species before vitrification could be advantageous.

#### Techniques for the Separation and Recovery of Ruthenium

Various methods reported in the literature for the removal of ruthenium from HLLW include volatilization, precipitation, solvent extraction, chromatography, sorption and electro-oxidation/reduction. Volatilization of ruthenium during evaporation and calcination of fission products could be suppressed by providing about 0.1 M phosphite or hypophosphite ion in the solution. This method is not effective for Zr bearing solutions, as about 0.3 M Zr reacts with phosphite or hypophosphite to form a precipitate and handling of the precipitate containing solutions is then required. Ruthenium can also be separated by oxidizing with  $\text{O}_3$  or  $\text{KMnO}_4$

and subsequently treating with  $\text{HCO}_2\text{H}$  or hydrazine to reduce  $\text{RuO}_4$  to  $\text{RuO}_2$  or Ru. Increasing the temperature and decreasing the acidity were found to favour the volatilization of ruthenium with  $\text{KMnO}_4$ . The complex ruthenium species formed during the nitric acid dissolution can be eliminated by coprecipitation with ferrocyanide in an excess of  $\text{Cu}^{2+}$  (as nitrate). However, all these processes introduce corrosive ions in the waste stream, in addition to handling precipitates at higher temperatures.

Pyrometallurgical extraction of noble metals from the waste with molten lead calls for exotic construction materials, as temperatures of 1000K and above are involved in the process. Ruthenium could be separated from an aqueous solution by solvent extraction using organic solvents like ethers, esters, ketones and alcohol with a common structural property of having an atom capable of donating an electron pair to a coordination bond in the presence of nitrite anions such as  $\text{NaNO}_2$ . In the presence of nitrite, the distribution ratio (organic/aqueous) of ruthenium is significantly increased, probably due to the formation of ruthenium-nitrite complex. An increase in nitrite content brought about a considerable improvement of ruthenium extraction. Ion-exchange chromatography is being used for separation of noble metals. However, the only promising candidate is a mixture of activated carbon and zinc powder, as about 97 % ruthenium could be removed. Sorption methods are suitable for the separation and pre-concentration of ultra trace amounts of noble metals from solutions containing large excess of non-noble metals.  $^{106}\text{Ru}$  can be removed from the effluents of fuel processing plants by bringing the effluent into contact with finely divided iron at pH 6.

The simple and inherently safe electrochemical method for the separation of ruthenium is attractive since it does not require the addition of external corrosive reagents, which would induce the trans-passive corrosion of 304L stainless steel waste vault tanks. In the electrochemical method, easy control of the process parameters is possible and separation of ruthenium is accomplished in a single step, though the Faradaic efficiency of this process is poor. Ruthenium can be separated either by deposition as metal on the cathode or by electro-oxidation to  $\text{RuO}_4$  at the anode.

Two relatively simple processes employed for the separation of ruthenium from pure nitric acid medium as well as from a simulated HLLW and the systematic parametric studies performed to optimize the process parameters for achieving improved separation efficiency are described. The redox behaviour of ruthenium nitrosyl species in nitric acid medium was also evaluated using the potentiostatic electrolysis techniques namely

cyclic voltammetry and chronopotentiometry.

### Separation of Ru from Simulated HLLW using Normal Paraffin Hydrocarbon

The removal of ruthenium was accomplished by making use of the high volatility of  $\text{RuO}_4$ . The principle involved in the volatilization method for the separation of ruthenium consists of oxidizing the ruthenium species to  $\text{RuO}_4$  vapour using strong oxidizing agents and subsequently, removing the  $\text{RuO}_4$  formed as  $\text{RuO}_2$  or Ru in the presence of reducing agents. Volatilization method was adopted for the separation of ruthenium using ammonium ceric nitrate as the oxidizing agent. As Ce is one of the fission products, its use as the oxidizing agent will not make any significant change in the vitrification process. Depending on the various chemical forms of Ru present in the solution, the percentage removal of ruthenium varied and a low percentage of ruthenium was removed in the case of ruthenium nitrosyl nitrate,  $\text{RuNO}(\text{NO}_3)_3$  solution in 4M nitric acid. Addition of  $\text{H}_2\text{O}_2$  and subsequent heating of the ruthenium solution for longer durations enhanced the removal of ruthenium from  $\text{RuNO}(\text{NO}_3)_3$  solution. However, implementing this process in the actual plant is practically difficult. The purpose of the present study is to improve the separation percentage of Ru from  $\text{RuNO}(\text{NO}_3)_3$  solution by optimizing the process parameters in a systematic way, in the oxidation of Ru species using ammonium ceric nitrate and without adding  $\text{H}_2\text{O}_2$ . Experiments were conducted with pure  $\text{RuNO}(\text{NO}_3)_3$  solution as well as with a synthetic non-radioactive waste solution simulated with all fission product elements to investigate the effect of different concentrations of nitric acid and ammonium ceric nitrate, temperature and ageing of the ruthenium bearing solutions on the separation of ruthenium.

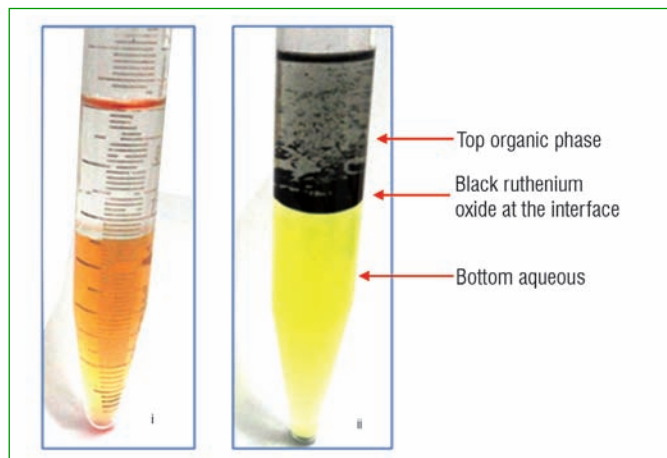


Figure 1: Black Ru suspension at the organic and aqueous interface: (i) before and (ii) after adding ammonium ceric nitrate

In the presence of ammonium ceric nitrate ruthenium in the aqueous phase was oxidized to volatile  $\text{RuO}_4$ . The  $\text{RuO}_4$  vapour was trapped by n-paraffin hydrocarbon (NPH, organic phase on the top of aqueous layer) and the black coloured precipitate of lower ruthenium oxide formed at the organic-aqueous interface (Figure 1) was filtered off using cellulose fiber filter paper. The concentration of Ru in the aqueous phase before and after the separation was estimated by ICP-OES analysis. About 80 % of ruthenium could be separated from nitrosyl nitrate solutions, at low concentrations of nitric acid in the range 0.5–1 M using 0.02-0.04 M Ce(IV) as the oxidizing agent and at ambient temperature. The black ruthenium oxide suspension at the interface between the organic and aqueous phases was characterized by XRD, TEM, EELS and XPS techniques. The XRD and TEM results revealed the ruthenium based powder to be amorphous phase and the presence of Ru and O in the powder

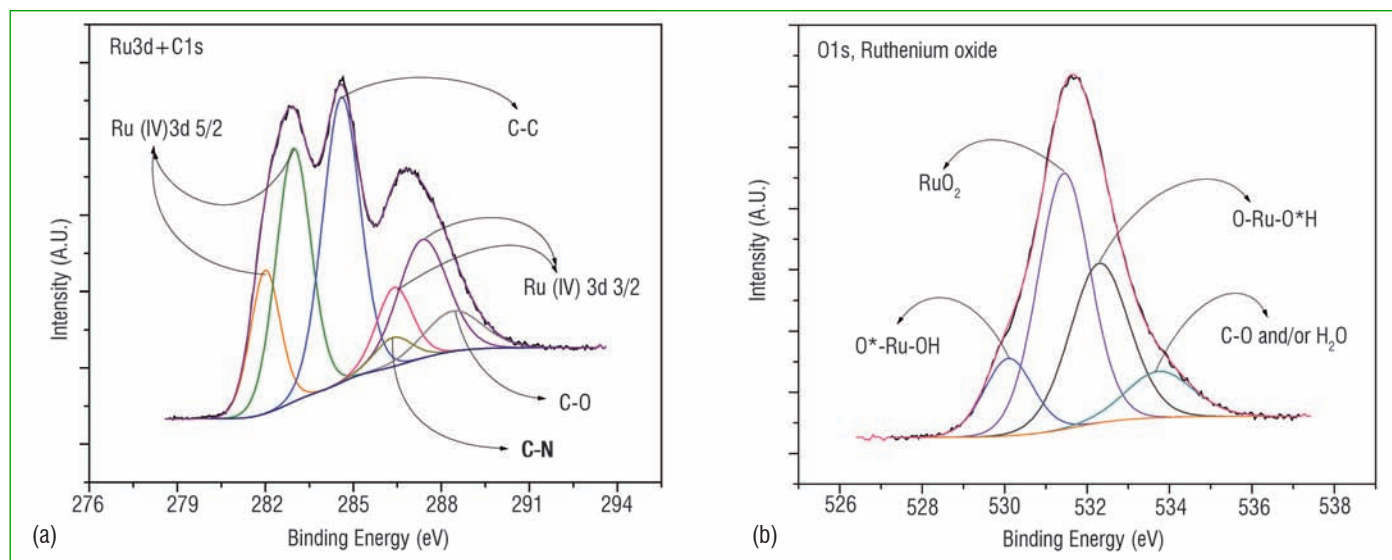


Figure 2: XPS spectra of: (a) Ru 3d core level lines; (b) O 1s on ruthenium bearing species

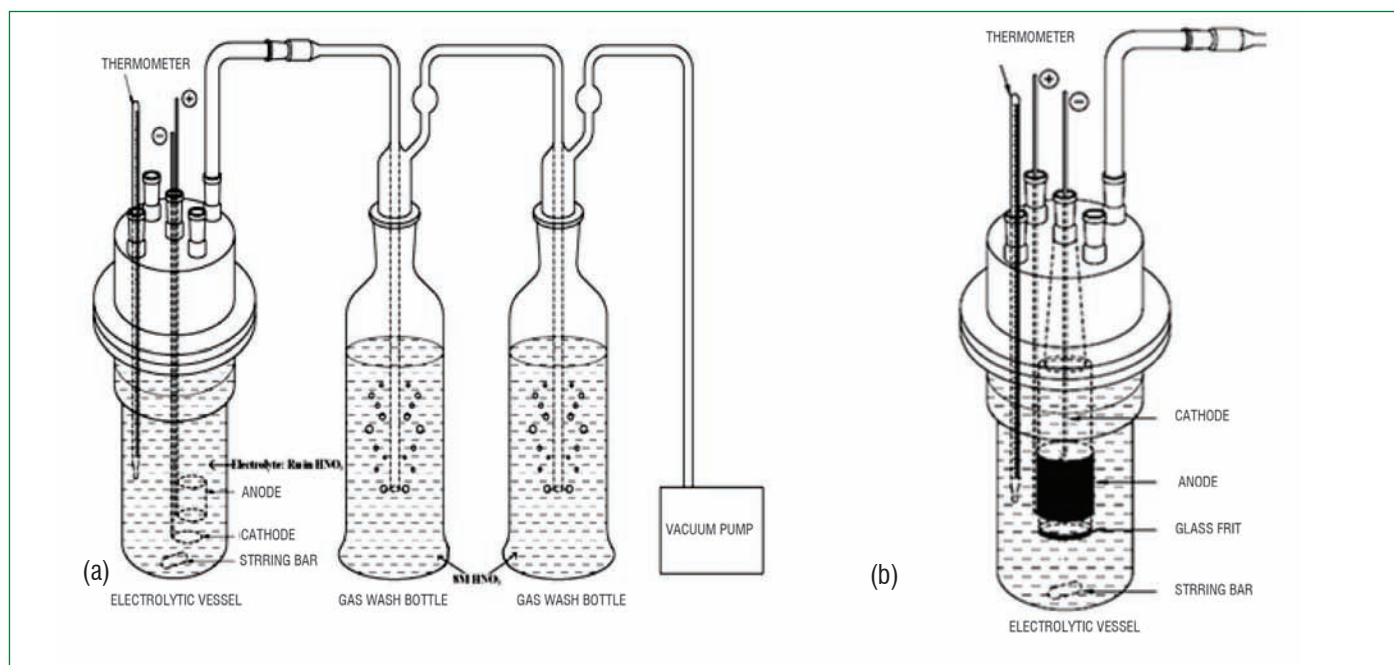


Figure 3: Schematic of (a) undivided electrolytic cell; (b) divided electrolytic cell

was confirmed from EELS. The XPS results (Figures 2a and b) showed the Ru species present in the black suspension to be in +4 oxidation state corresponding to RuO<sub>2</sub> and oxy-hydroxide species of Ru(IV) to some extent over the surface.

#### Separation and Recovery of Ruthenium by Electro-Oxidation

Separation of Ru from ruthenium nitrosyl, [RuNO]<sup>3+</sup> species and from simulated HLLW in nitric acid medium was achieved by electro-oxidation method, in which constant current was applied in undivided and divided cells and oxidation was carried out in the presence/absence of cerium redox catalyst. The schematic of the cell assemblies is presented in Figure 3. Electro-oxidation of Ru to volatile RuO<sub>4</sub> using cerium was carried out in an undivided cell configuration and the amount of RuO<sub>4</sub> collected in 8 M nitric acid as well as in alkaline trap was compared under different experimental conditions. A divided cell fabricated using borosilicate glass frit as the separating membrane was employed for separating ruthenium from SHLLW without adding metal ions as the redox catalyst. The influence of experimental conditions like different concentrations of nitric acid, current density, temperature and concentration of cerium on the separation of ruthenium was investigated. The separation percentage of ruthenium was observed to increase with decrease in nitric acid concentration, which is due to the formation of easily oxidizable ruthenium nitrosyl complexes in lower concentrations of nitric acid. Maximum separation of 95% ruthenium could be achieved from ruthenium nitrosyl nitrate in 1 M nitric acid using 20 mA.cm<sup>-2</sup> as the anodic current

density and with 0.02 M Ce at 318 K, when electro-oxidation was performed in an undivided cell. The amount of ruthenium separated from simulated waste was only 54 % under identical experimental conditions; a possible cause could be the interference by Pd in the waste solution. To minimize the deleterious effect of nitrite ions produced at the cathode on the separation of Ru, the divided cell with glass frit as the diaphragm was employed and about 80 % ruthenium could be separated from simulated HLLW, in 4 M HNO<sub>3</sub> without any redox catalyst. Cyclic voltammetric (CV) study in nitric acid medium revealed that oxidation of Ru to RuO<sub>4</sub> takes place in the potential range 1.28-1.49 V on gold electrode. The reference electrode in all these experiments was Ag/AgCl. With Pt as working electrode, there was a surge in anodic current from 1.2V onwards corresponding to the oxidation of ruthenium along with water oxidation. The RuO<sub>4</sub> formed during electro-oxidation was sucked via a vacuum pump and trapped either in alkaline (NaOH) or in nitric acid medium. A portion of RuO<sub>4</sub> decomposed to lower oxide and got deposited on the inner wall of the electrolytic vessel. In an electro-oxidation experiment of RuNO(NO<sub>3</sub>)<sub>3</sub> solution in 1 M nitric acid, performed with 10 mA.cm<sup>-2</sup> as the anodic current density in the presence of 0.02 M cerium ions as the redox catalyst, the initial concentration of ruthenium in the electrolyte was 75.9 mg and after electrolysis for 10 hours, the amount of Ru remained was 23.4 mg, amounting to the total conversion of 52.5 mg of ruthenium to RuO<sub>4</sub>. The amount of ruthenium collected in the nitric acid trap was 44.3 mg, which accounted for the recovery of 84 % of ruthenium in the acidic trap; the remaining would have got deposited as lower oxide

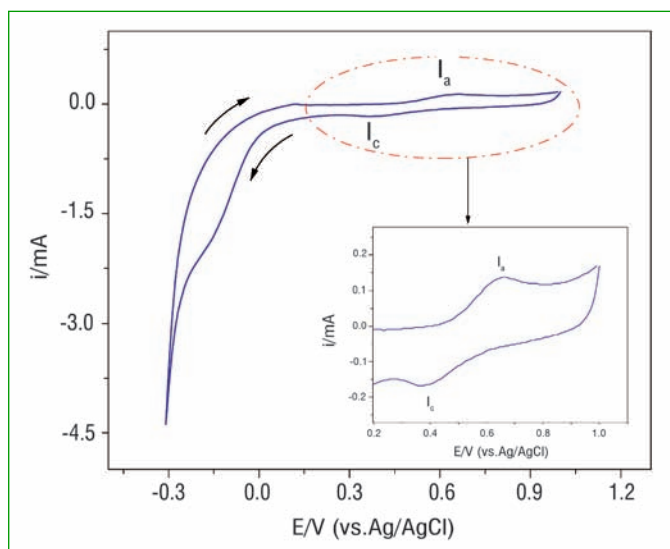


Figure 4: Cyclic voltammogram of 40 mM ruthenium nitrosyl ( $[\text{RuNO}]^{3+}$ ) solution in 1M  $\text{HNO}_3$  recorded with  $0.05 \text{ V}\cdot\text{s}^{-1}$  scan rate at platinum working electrode and at 298 K

of ruthenium. To prevent the deposition of  $\text{RuO}_2$  over the wall of the vessel, keeping a layer of NPH above the electrolyte was observed to serve as a better trap for gaseous  $\text{RuO}_4$ .

#### Oxidation and Reduction Behaviour of Ruthenium Nitrosyl Nitrate in Nitric Acid

Separation of Ru from  $[\text{RuNO}]^{3+}$  and from simulated HLLW was carried out by electro-oxidation, applying a constant potential using a divided cell and the reduction behaviour of  $[\text{RuNO}]^{3+}$  in nitric acid medium was also investigated by different electroanalytical techniques. Cyclic voltammetric experiments with  $[\text{RuNO}]^{3+}$  solution (containing 20 mM of Ru) using Pt as working and counter electrodes and Ag/AgCl as reference electrode revealed that water oxidation and Ru to  $\text{RuO}_4$  oxidation occurred simultaneously and when the potential was higher than 1.2 V, there was a surge in anodic current. The current was observed to increase with increase in concentration of ruthenium, temperature and decrease in the concentration of nitric acid. Separation of ruthenium was carried out by chronoamperometric method using Pt mesh as working and counter electrodes and by applying three different potentials 1.25, 1.45 and 1.65 V in a divided cell with glass frit as diaphragm. When the applied potential was 1.25 V (vs Ag/AgCl), the separation of ruthenium increased from 17 to 23 and 35 % with decrease in acidity from 4 to 2 and 1 M respectively, after electrolyzing for 10 h. Increasing the applied potential to 1.45 V, the separation percentage was found to increase from 21 to 46 and 60 % and at the applied potential of 1.65 V the separation of Ru increased from 26 to 48 and 74% with decrease in the concentration of nitric acid from 4 to 2 and 1 M respectively after 10 hours of electrolysis. Though

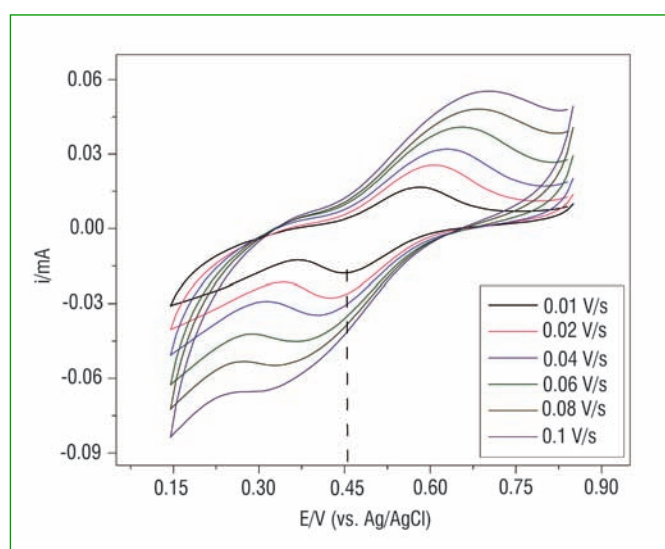


Figure 5: Cyclic voltammograms of 40 mM of ruthenium nitrosyl solution in 1 M  $\text{HNO}_3$  recorded at Pt electrode with different scan rates; T: 298 K

separation percentage of ruthenium increased with increase in the applied potential, the current efficiency was found to decrease from 52 to 25 and 10 % when the applied potential was raised from 1.25 to 1.45 and 1.65 V. In order to obtain better separation from 1 M nitric acid solution at 1.25 V, experiments were carried out at a higher temperature and the percentage of ruthenium separated could be increased from 35 to about 68 % by increasing the temperature from 300 to 333 K, for the same duration of 10 hours of electrolysis. Separation of ruthenium was also carried out in the presence of 0.04 M Ce from 1 M nitric acid solution. Since oxidation of Ce in 1 M nitric acid occurs above 1.4 V, separation of Ru was investigated at the potentials 1.45 and 1.65 V and 89 and 97 % could be removed after 10 h of electrolysis.

Separation of Ru was quantitative in the electro-oxidation method; however, separation percentage of ruthenium by electro-deposition technique was found to be very low and a large portion remained in the solution. In order to understand the low recovery of ruthenium by electro-deposition technique, it was essential to investigate the behavior of the lower oxidation states of ruthenium. Hence, the reduction behaviour of ruthenium nitrosyl complex  $[\text{Ru}^{2+}(\text{NO})^+]^{3+}$  and its kinetics in nitric acid medium have been investigated using CV and chronopotentiometry (CP), at Pt and glassy carbon working electrodes. The cyclic voltammogram of 40 mM of  $[\text{RuNO}]^{3+}$  solution in 1 M nitric acid recorded at the scan rate of  $0.05 \text{ V}\cdot\text{s}^{-1}$  using Pt electrode at 298 K is shown in Figure 4. One distinct reduction peak (Ic) at about 0.4 V and one oxidation peak (Ia) at about 0.6 V were observed and these could be due to the redox couple  $[\text{RuNO}]^{3+}/[\text{RuNO}]^{2+}$ . The peak corresponding to the

**Table 1: Comparison of kinetic parameters derived for reduction of  $[\text{RuNO}]^{3+}$  species in 1 M  $\text{HNO}_3$  at Pt and GC working electrodes**

Kinetic parameters	40 mM $[\text{RuNO}]^{3+}$ solution in 1 M $\text{HNO}_3$	
	Platinum electrode	Glassy carbon electrode
$D_0$ ( $\text{cm}^2\cdot\text{s}^{-1}$ )/CV expt.	$2.95 \times 10^{-8}$	$1.65 \times 10^{-8}$
$D_0$ ( $\text{cm}^2\cdot\text{s}^{-1}$ )/CP expt.	$1.10 \times 10^{-8}$	$1.57 \times 10^{-8}$
$k_s$ ( $\text{cm}\cdot\text{s}^{-1}$ )	$2.06 \times 10^{-5}$	$6.73 \times 10^{-5}$

reduction of ruthenium nitrosyl complex was validated by carrying out a controlled potential electrolysis of a solution containing 160 ppm of Ru in 1 M nitric acid at 0.4 V and recording the UV-Visible spectra of the solutions before and after electrolysis. The reversibility of the electrode process corresponding to the peaks  $I_c$  and  $I_a$  in Figure 4 was examined by evaluating the effect of scan rate on the current-potential behaviour in the electro-reduction of ruthenium nitrosyl ions. Figure 5 represents all the scans from 0.01 to 0.1  $\text{V}\cdot\text{s}^{-1}$  for the reduction of 40 mM of  $[\text{RuNO}]^{3+}$  solution in 1M nitric acid within the selective potential window of 0.15 to 0.85 V at 298 K. This figure revealed that the cathodic peak potential,  $I_{p,c}$  shifted significantly from 0.457 to 0.387 V, as the scan rate was increased from 0.01 to 0.1  $\text{V}\cdot\text{s}^{-1}$ , which is not the characteristics of a reversible reaction. For the reduction of  $[\text{RuNO}]^{3+}$  ions in 1M nitric acid medium, peak potential shift and broadening of peak shape with scan rate were observed in CV runs. The difference between the cathodic and anodic peak potentials ( $\Delta E_p$ ) increased with scan rate and the average of the peak potentials  $1/2(E_{p,c} + E_{p,a})$  was nearly constant at different scan rates indicating that the process was quasi-reversible.

The value of heterogeneous electron transfer rate constant ( $k_s$ ), and the diffusion coefficient values determined from the results of CV and CP experiments for the reduction of  $[\text{RuNO}]^{3+}$  species in 1 M  $\text{HNO}_3$  are compared in Table 1. The very low diffusion coefficient value revealed the complexing nature of Ru(II). As Ru(II) exists as different complexes instead of bare Ru(II) ions in nitric acid medium, the separation percentage of ruthenium from ruthenium nitrosyl nitrate solution by electro-deposition technique will be very

low. Hence, it is advantageous to separate and recover Ru as  $\text{RuO}_4$  from liquid waste, by electro-oxidation method.

Removal of Ru by chemical volatilization method using ammonium ceric nitrate as the oxidizing agent was found to be quantitative, simple and cost effective method. This method of separation of ruthenium using ammonium ceric nitrate as oxidizing agent will not increase the waste volume and would not involve any additional issue in waste fixing as Ce is anyway one of the fission products. However, quantitative separation is possible from 1 M nitric acid solution only. Hence, the HLLW in 4 M nitric acid solution requires to be diluted. In the electro-oxidation method, by applying a constant current or potential to a divided cell with glass frit as diaphragm, quantitative separation of ruthenium was possible both from pure  $[\text{RuNO}]^{3+}$  and from simulated HLLW prepared in 4 M  $\text{HNO}_3$ , without any redox mediator. However, the current efficiency in this method of separation, by applying constant current was very low due to the simultaneous reaction of water oxidation. In order to obtain improved current efficiency, based on the results of CV studies, electrolysis was conducted by applying constant potentials in the divided cell. With 1.25 V as the applied potential, the current efficiency could be increased to only 52 % for pure  $[\text{RuNO}]^{3+}$  solution in 1 M acid, though conversion efficiency was quantitative. As Ru(II) exists as different complexes instead of bare Ru(II) ions in nitric acid medium, the separation percentage of ruthenium from ruthenium nitrosyl nitrate solution by electro-deposition technique will be very low and it will be beneficial to separate and recover ruthenium as  $\text{RuO}_4$  from liquid waste by electro-oxidation method.

The parametric studies conducted for the separation of ruthenium can be implemented in the plant for the removal of ruthenium from the actual HLLW and also in continuous mode. Constant potential electrolysis using a redox mediator with lower oxidation potential requires to be carried out in order to get good separation percentage as well as current efficiency. Designing suitable electrolytic cells and demonstrating the performance of these cells in separating ruthenium from actual HLLW are also within the scope of future work.

*Reported by Pravati Swain  
Reprocessing Group*



## Conference and Meeting Highlights

## BITS Practice School

May 27 – July 17, 2014



Dr. P. R. Vasudeva Rao, Director, IGCAR interacting with the students from BITS Practice School during the inaugural function

Twenty five students from BITS Pilani, Hyderabad and Goa campuses underwent BITS Practice School at our Centre during May 27-July 17, 2014. The course aimed at exposing the students to industrial and research environments, how the organizations work, to follow and maintain work ethics, study the core subjects and their applications in the organization, participate in the assignments given to them in the form of projects.

The students were from various disciplines like Chemical Engineering, Computer Science & Engineering, Electrical & Electronics Engineering, Electronics & Instrumentation Engineering, Electronics & Communication Engineering, Mechanical Engineering and Master in Information Systems. Dr. P. R. Vasudeva Rao, Director, IGCAR inaugurated the

Practice School at IGCAR on May 27, 2014. Dr. P. Srinivasan, Programme Coordinator, BITS Practice School Division participated. Students carried out challenging projects in various Groups of the Centre in line with their discipline. During the period of their stay, they visited various facilities at IGCAR, BHAVINI and MAPS. As a part of the curriculum, Quiz, Project work presentations, group discussions and report writing were done in the Practice School. The valedictory function was held on July 17, 2014. Dr. R. Natarajan, Director, Reprocessing Group & Project Director, Fast Reactor Fuel Cycle Facility delivered the valedictory address and distributed the certificates to the students.

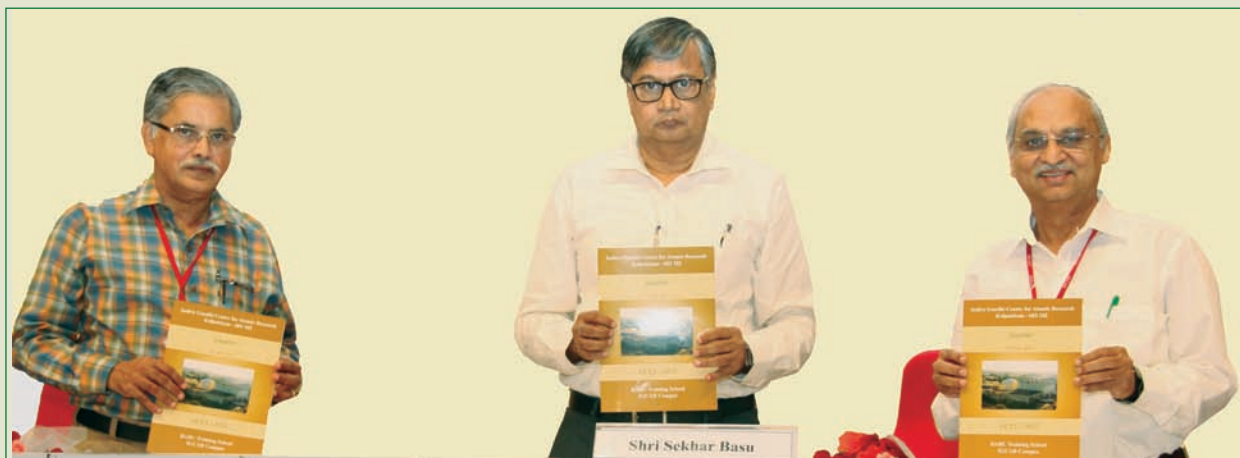
*Reported by M. Sai Baba,  
Coordinator-BITS Practice School*



Students from BITS Practice School with Dr. R. Natarajan, Director, RpG and Project Director, FRFCF and senior colleagues of the Centre during the valedictory function

## Graduation Function of the Eighth Batch of Trainee Scientific Officers of BARC Training School at IGCAR

July 24, 2014



Shri Sekhar Basu, Director, Bhabha Atomic Research Centre, Dr. P. R. Vasudeva Rao, Director, IGCAR, Dr. M. Sai Baba, Associate Director, RMG, during the release of souvenir at the graduation function

The eighth batch of fifty four TSOs from the BARC Training School at IGCAR have successfully completed their training and were graduated in a special ceremony that took place on July 24, 2014 at 11.00 hrs in the Sarabhai Auditorium, Homi Bhabha Building, IGCAR. Shri Sekhar Basu, Director, Bhabha Atomic Research Centre, Mumbai, was the Chief Guest. Dr. P. R. Vasudeva Rao, Director, IGCAR welcomed the gathering. Dr. Vidya Sundararajan briefed the audience about the Orientation Course in Engineering and Sciences programme. Shri Sekhar Basu released the souvenir featuring the training school programme in the previous academic year and Dr. P. R. Vasudeva Rao received the

first copy. Shri Sekhar Basu gave away the prestigious 'Homi Bhabha Prize' comprising of a medallion and books worth Rs.5000 to the meritorious toppers from all the disciplines and delivered the presidential address. He also gave away the course completion certificates to all the graduate passing out. A few of the Trainee Scientific officers passing out shared their experience, gave a feedback on the academic programme and their stay at hostel. Dr. M. Sai Baba, AD, RMG, proposed the vote of thanks.

*Reported by M. Sai Baba,  
Associate Director, RMG*



Eighth Batch of Graduates of BARC Training School at IGCAR with Shri Sekhar Basu, Director, Bhabha Atomic Research Centre, Mumbai, Dr. Prabhat Kumar, Chairman and Managing Director, BHAVINI, Dr. P. R. Vasudeva Rao, Director, IGCAR and senior colleagues of the Centre

## Quality Circle Annual Meet (QCAM) - 2014

August 25, 2014



Dr. T. Jayakumar, Director MMG, IGCAR delivering the Presidential address during quality circle annual meet

Quality circle is a small group of employees doing similar or related work who meet regularly to identify, analyze, and solve work related problems usually led by a senior team member. After completing their analysis, they present their solutions to management for implementation and to improve the performance of the organization. Thus, implemented correctly, quality circles can help the organization to reduce costs, increase productivity, and improve employee morale.

In IGCAR, every year Quality Circle Annual Meet (QCAM) is conducted and the QC case studies are presented by the QC teams. QCAM – 2014 was conducted on August 25, 2014 at Convention Centre and SRI Seminar hall, Anupuram in parallel sessions. Welcome address was delivered by Shri G.Srinivasan, Director, ROMG, The Presidential address was delivered by Dr. T. Jayakumar, Director, MMG. Dr. R. Raju, Professor, Department of Industrial Engineering, Anna University, Chennai delivered the Inaugural address and vote of thanks by Shri G. Kempulraj, Head, Central Workshop Division.

Totally Thirty Quality Circles (about 300 members) from IGCAR, schools from Kalpakkam and neighborhood presented QC case studies in a wide spectrum of topics

covering Technical, Research & Development, Services and Education. Professional judges from Quality Circle Forum of India, Chennai chapter, adjudged the QC case study presentations. Under the Mechanical and Manufacturing' stream, the STAR QC Team bagged 'Dr. Placid Rodriguez memorial trophy', while PLUTONIUM QC team bagged the 'Shri M.K. Ramamurthy memorial trophy' for Plant Operation and Services category. KURUMBU QC, Government HSS, Vengappakkam won the 'Dr Sarvepalli Radhakrishnan memorial trophy' for School category.

During the valedictory function, the events were summed up by Shri K. G. Subramanian, Convenor, QCAM-2014. The programme was concluded with the valedictory address and the prizes were distributed to the participants by Shri G. Srinivasan, Director, ROMG and Shri A.Jyothish Kumar, Associate Director, ESG, IGCAR. Vote of thanks was proposed by Shri T.V Maran, Member secretary, Organising Committee.

*Reported by G. Kempulraj,  
Member Secretary, Apex Steering Committee on  
Quality Circles, IGCAR, QCAM 2014*

## Summer Training in Physics and Chemistry (STIPAC - 2014)

May 26 - July 4, 2014



STIPAC students with Dr. P. R. Vasudeva Rao, Director, IGCAR & senior colleagues during the inaugural function

IGCAR has been, for over a decade and a half, successfully running summer training for the pre-final Post Graduate students in Physics & Chemistry. The programme is conducted, generally, from the last week of May to the first week of July of each year. Students from across the country apply for this programme and are selected on the basis of a one page write up on an assigned topic and academic track record. If needed, even a telephonic interview is held. Care is taken to ensure that there is representation from across the states, universities and colleges.

The 16<sup>th</sup> Summer Training In Physics and Chemistry (STIPAC 2014) programme commenced on May 26 and ended on July 4, 2014. The programme was steered and mentored by Dr. P. R. Vasudeva Rao, Director, IGCAR, Dr. C. S. Sundar, Director, MSG and Dr. K. Nagarajan, Director, CG.

There were 20 students each in Physics and Chemistry, from across the country, for this year's programme. The write up assigned for screening was "Crystallography and its impact on understanding properties of materials". The courses were run on the theme "Materials: Structure & Properties".

The students were assigned projects / experiments and were encouraged to have hands on experience in various areas of research carried out at the Materials Science and Chemistry

Groups. The students also gave a presentation on the projects they did carried out.

The inaugural address by Prof Kamanio Chattopadhyay, IISc, Bengaluru covered various aspects of Quasicrystals.

Apart from the lectures by in house experts, the students were also exposed to experts from other institutions. Expository lectures were delivered on Crystalline Order and Symmetries by Dr. V. K. Wadhawan, Bengaluru, Applications of Synchrotron Radiation by Dr. Sanjay Rai of ISUD, RRCAT, Indore, Physics of Biological Materials by Prof. P. B. Sunil Kumar, IIT Madras, Chennai, Long Walk in the Woods and the Light at the End: Looking Back at Laue's Experiments by Dr. Saibal Basu of SSPD, BARC, Mumbai, Molecular Dynamics Simulation of Lipases by Prof. P. Gautam, Director, Centre for Biotechnology, Anna University, Chennai, Thermodynamics of Fuels by Dr. V. Venugopal, Raja Ramanna Fellow, BARC, Role of Chemists in Reactors by Dr.S.V. Narasimhan, Chairman, COSWAC, DAE and Happy Accidents in Chemistry by Dr. K. S. Viswanathan, IISER, Mohali.

The students visited BHAVINI, MAPS & FBTR and got an overview of the challenging work being carried in the area of energy production.



Prof. U. V. Varadaraju, IIT Madras, Chennai distributing certificate to STIPAC student during the valedictory function

Dr. Prabhat Kumar, CMD, BHAVINI, elucidated on the Challenges in Large Scale Project Management, and Dr. S Radhakrishnan, RPS, MAPS opened up their minds to the various issues involved in harnessing Nuclear Energy.

The valedictory address by Prof. U.V.Varadaraju, IIT Madras, Chennai dwelt on Electrochemical Energy Storage Systems.

*Reported by  
Course Coordinators of STIPAC 2014*

## Visit of Dignitaries



Dr. R. A. Mashelkar, National Research Professor & President of Global Research Alliance delivering the Vikram Sarabhai Memorial Lecture

Dr. R. A. Mashelkar, National Research Professor & President of Global Research Alliance visited IGCAR on August 12, 2014. He met Dr. P.R.Vasudeva Rao, Director, IGCAR, senior colleagues of the Centre and discussed about various programmes in progress. During his visit he delivered the Vikram Sarabhai Memorial Lecture on "Reinventing India as an Innovation Nation". He visited the Madras Atomic Power Station and construction site of PFBR, BHAVINI.



Prof. K. R. Rajagopal, Distinguished Professor delivering the IGC Colloquium

Prof. K. R. Rajagopal, Distinguished Professor, Regents Professor, Forsyth Chair in Mechanical Engineering, Senior Research Scientist, Texas Transportation Institute, delivered the IGC Colloquium on “Art, Craft & Philosophy of Science” during his visit to IGCAR on August 26, 2014.



Dr. M. R. Srinivasan, Member, Atomic Energy Commission & Former Chairman, AEC delivering the Diamond Jubilee Colloquium

Dr. M. R. Srinivasan, Member, Atomic Energy Commission & Former Chairman, AEC, visited the Centre on September 04, 2014. During his meeting with DAC members, he was briefed about the activities of IGCAR by Dr. P.R.Vasudeva Rao, Director, IGCAR, and status of FRFCF by Dr. R. Natarajan, Project Director, FRFCF. After the meeting he delivered the Diamond Jubilee Colloquium on “Evolution and Ethos of DAE”. He then visited the Interim Fuel Storage Building at Reactor Operation & Maintenance Group and various facilities/laboratories at Metallurgy & Materials Group, Materials Science Group, Chemistry Group and Reactor Design Group.

 Awards & Honours 

Dr. R. Natarajan, RpG has been conferred with VASVIK Award for the year 2014 for his outstanding contributions in the field of Chemical Sciences & Technology

Dr. U. Kamachi Mudali, MMG has been conferred with VASVIK Award for the year 2014 for his outstanding contributions in the field of Material & Metallurgical Science & Technology

 Best Paper/Poster Award 

Electrochemical and Corrosion behavior of Zirconium and Titanium Alloys in Nitric Acid and Simulated Dissolver Solution

Shri Jayaraj, Shri K. Thyagarajan, Dr. C. Mallika and Dr.U. Kamachi Mudali from MMG

International Conference on Electrochemical Science and Technology – 2014 (ICONEST 2014) held at IISc, Bangalore during August 7-9, 2014

Best Poster Presentation Award

Evaluating Degree of Sensitization in Nitrogen Modified 316L Stainless Steel-Comparison of AC and DC Electrochemical Techniques

Shri Srinivas Mannepalli, Shri A. Vinod Kumar, Dr. N. Parvathavarthini and Dr. U. Kamachi Mudali from MMG

17<sup>th</sup> National Congress on Corrosion Control (NCCI 2014) held at Central Electrochemical Research Institute, Karaikudi during August 21-23, 2014

Best Poster Presentation Award



*Spathiphyllum*

**Dr. M. Sai Baba,**

Chairman, Editorial Committee, IGC Newsletter

Editorial Committee Members: Dr. K. Ananthasivan, Shri M.S. Chandrasekar, Dr. N.V. Chandra Shekar, Dr. C. Mallika, Shri K. S. Narayanan, Shri V. Rajendran, Dr. Saroja Saibaba and Dr. Vidya Sundararajan