

BASIC RESEARCH IN CHEMISTRY RELATED TO FAST BREEDER REACTOR TECHNOLOGY

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TECHNOLOGICAL progress is nurtured on research and development. Technology derives its strength directly from applied research which in turn draws upon the reservoir of basic knowledge. The development of high technology may call for the generation of basic information itself. On the other hand, organised attempts to solve technological problems provide the framework for focussing one's attention on selected basic phenomena. This stimulates the scientist to delve deeper into the subject and the consequent in-depth study would lead to a better understanding of the system. Technology also provides him with the necessary inputs in terms of facilities to carry out these studies.

The Chemistry Programme at the Reactor Research Centre has been built up on this premise. Our *raison d'être* is indeed the need to develop fast breeder reactor technology in the country and to tackle the chemistry related problems that arise in this process. However, within this framework we take our investigations deeper by asking fundamental questions so that the natural curiosity of the basic scientist is satisfied and his interest is kept alive. Thus, as far as we are concerned, there is hardly any conflict between basic and applied research. Our research is at once applied and basic.

The Reactor Research Centre (RRC) at Kalpakkam has been set up with the clear mission of developing fast breeder reactor technology. The major current project of RRC is the Fast Breeder Test Reactor (FBTR) which is an experimental fast reactor with a thermal output of 40 MW. This reactor will serve as a test bed for fuels and materials, in addition to giving us valuable experience. The design of a prototype fast breeder power reactor has been taken up. To support these activities, laboratories have been established for relevant research in chemistry, physics, metallurgy, reactor engineering, fuel reprocessing and safety studies. In this article, we will first consider fast reactors and their tech-

nological problems which come within the purview of chemists and then outline the basic research we are carrying out.

Fast Breeder Reactors

Fast breeder reactors are being developed with the idea of producing electricity through fission energy while conserving our uranium resources. Natural uranium contains only 0.72% of the fissionable isotope ^{235}U , which is what undergoes fission in thermal neutron reactors. However, in fast breeder reactors the more abundant ^{238}U (99.28%) isotope is converted to the fissile isotope of plutonium, ^{239}Pu , at a rate which is faster than the rate of consumption of this fissile nuclide and hence these are called breeder reactors. Thus fast reactors breed or produce more fuel than they consume.

The use of fast neutrons with their lower cross section for fission demands high fissile (plutonium) concentration in the fuel. In order to minimise fuel inventory and to keep the breeding gain high, the core is kept very compact. This demands fuels which can generate and transfer power at high density and a very efficient heat transfer fluid (coolant). Sodium is the preferred coolant in fast reactors and the fuel may be a mixed oxide or mixed carbide of uranium and plutonium.

Fast Reactor Fuels

The fast reactor core consists of essentially three materials: fuel, structural materials and coolant. A high density fuel will ensure that the fraction of the core (on atom fraction basis) occupied by the fuel is high and this is conducive to high breeding gains. The fuel must have high thermal conductivity in order to extract the maximum power from a given fuel pin. Further, it should have high melting point and thermal stability. This means that phase changes and chemical changes should not affect the perform-

ance of the fuel upto the high temperature limit set by the melting point of the material. These are some of the conditions that govern the choice of fast reactor fuels.

During the early years, it was thought that metallic fuels would be the best choice because of their high density and thermal conductivity. However, they have gone out of favour because of their lack of compatibility with the stainless steel cladding and their high swelling rate during irradiation. Because of the excellent experience with uranium oxide fuel in thermal reactors, the mixed oxide of uranium and plutonium has become the popular choice as fuel material in the current generation of fast breeder reactors. However, the mixed oxide has relatively low fissile atom density and thermal conductivity. Mixed carbides and nitrides, in which there is only one carbon or nitrogen atom per U, Pu atom in a close packed structure, are much superior in these respects. Table 1 lists the properties of the different types of fuel materials.

The fissile material in a large fast reactor is plutonium which is present upto a maximum concentration of 30% in the fuel. A small research reactor, however, requires much higher fissile content which is normally provided by enriching the uranium present in ^{235}U . In the case of FBTR this course is not open to us as enriched uranium is not readily available.

Table 1 Properties of Fuel Materials

	Mixed Oxide (U,Pu)O ₂	Mixed Carbide (U,Pu)C	Mixed Nitride (U,Pu)N
Density (g/cm ³)	11.0	13.6	14.3
Metal Atom Density	9.7	12.7	13.5
Thermal Conductivity (W/cm ² C, 1100°C)	0.022	0.17	0.19
Thermal Expansion	$14 \times 10^{-6}/^{\circ}\text{C}$	$11.4 \times 10^{-6}/^{\circ}\text{C}$	
Melting Point	2675°C	2360°C	2630°C
Boiling Point	3500°K	4100°K*	
Specific Heat	340J/g°C	250J/g°C	
Heat of Fusion	280J/g	186K/g	
Critical Pressure	2200 atm	7680 atm*	

* Data for UC

Therefore, a fuel with upto 70% concentration in plutonium has to be used. Since a mixed oxide of this composition has unfavourable properties in terms of phase stability, stoichiometry and compatibility with the clad, an appropriate mixed carbide has been chosen as the fuel for FBTR. As very little information is available in the open literature on a fuel of this composition, the required data has to be generated in our own laboratories.

The fast reactor fuel is normally used in the form of cylindrical pins, of about 5 to 8 mm diameter. The ceramic fuel, in the form of pellets, is filled in thin stainless steel cladding tubes which provide a barrier between the fuel and the coolant, at the same time helping to maintain the geometrical shape of the fuel elements. A cluster of such fuel pins are assembled together to form a sub-assembly which is contained in a stainless steel duct. Many such sub-assemblies together constitute the core of the reactor. The fuel must be compatible with the cladding throughout its life in the reactor.

The fuel is subjected to very hostile thermal and radiation environments during its life in the reactor. The centre of the fuel pellet sees a temperature close to its melting point ($\sim 2800^{\circ}\text{C}$ for the mixed oxide) while the surface temperature remains at 700–1000°C. Such high temperatures and thermal gradients become driving forces for many chemical changes which are not normally encountered in the laboratory.

Fast reactor fuel must undergo high "burn-up" (10 to 15 atom percent) in order to be economical. A ten atom percent burn-up results in the fissioning of 10% of the heavy element atoms in the fuel. This drastically alters the chemistry of the fuel as about 20 atom percent of fission products have been produced (each fission event gives rise to two fission products). The effect of these fission products not only on the fuel but also on the compatibility of the fuel with the clad must now be understood.

Chemistry of the Mixed Oxide Fuels

The high thermal gradient existing in an operating fuel pin causes not only a restructuring

the fuel (changes in grain sizes, porosity etc) but also the redistribution of the oxygen in the fuel. It must be remembered that the mixed oxide of uranium and plutonium can exist with a wide range of stoichiometry. The starting composition of the fuel is hypostoichiometric ($O/M = 1.97$) so that the oxygen potential of the fuel is not high enough to cause significant oxidation of the clad. Under the temperature gradient prevailing in the fuel pellet, the oxygen redistributes in such a way that the surface tends to stoichiometry ($O/M = 2$) and the centre shows significant deviation from stoichiometry.

In addition to oxygen, uranium and plutonium also get redistributed—the centre of the fuel getting enriched in plutonium. In order to model these processes to predict the behaviour of the fuel in the reactor, we require a good deal of high temperature thermodynamic data.

Let us now examine the effect of fission products. There are about 30 fission product elements having a significant yield in the fission processes. Their chemical states under reactor irradiation conditions are not easy to predict. (When the fuel is examined after irradiation, it is under conditions quite different from that in the reactor and the chemical state of some of the fission products could well have changed.) The prevailing temperature and oxygen potential conditions determine the oxidation state of the fission products. Some like alkaline earths, rare earths and zirconium form oxides, but one must ask the further question whether they go into solid solution with the fuel matrix, form separate phases or form compounds such as barium zirconate. Noble metals palladium, ruthenium and rhodium form metallic phases. Molybdenum may form oxide or molybdate at high oxygen potentials, but remains as metal at low oxygen potentials. Volatile fission products like Cs, Te and I migrate to the clad where they participate in clad corrosion. Rare gases, of course, do not form chemical compounds, but they form tiny bubbles in the fuel and this leads to fuel swelling.

Thus the behaviour of fission products has a strong influence on the performance of the fuel. The presence of fission products in the fuel lattice

and the precipitation of some of them as separate phases causes the fuel to swell during irradiation. The diffusion of fission gases to form bubbles and the collection of these bubbles at grain boundaries lead to a much higher degree of swelling. The expansion of the fuel stresses the clad, though the oxide fuel is sufficiently plastic at high temperatures to alleviate this problem.

The effective oxygen potential of the fuel depends on the chemical nature of the fission products. As the fission products together succeed in tying down less of oxygen than the uranium and plutonium atoms which have disappeared on account of fission, the oxygen potential of the fuel increases with burn-up. It has not been possible, so far, to arrive at an exact relationship between the variation of oxygen potential and burn-up.

Fresh oxide fuel is compatible with its stainless steel clad. However, after a burn-up of about 4 to 5 atom per cent, significant chemical attack of the clad from the inside is noticed. Fission products are evidently responsible for this corrosion and Cs, Te and Mo are the major suspects. However, their role is not clearly understood, though conflicting theories have been put forth involving the formation of Fe, Cr, Ni tellurides, cesium chromate and cesium molybdate.

Chemistry of the Carbide Fuel

The mixed carbide fuel [(U,Pu)C] behaves quite differently from the mixed oxide. It exists only in a narrow range of stoichiometry. If the fuel is hyperstoichiometric, then the sesquicarbide phase of U_2C_3 would be present which would tend to carburize the clad. If it is hypostoichiometric, then the metallic phase appears and this is not compatible with the clad. The carbide is quite reactive and is pyrophoric in the powder form. Therefore, special handling techniques are required to prepare this fuel material.

It is when fission products are produced on account of burn-up that the differences are more pronounced. Fission products tend to tie up carbon more effectively than the fissioning heavy element atoms. Though the actual chemical states of many fission products are not well

defined in this case also, it is clear that the C/M ratio of the fuel decreases with increasing burn-up. Thus, if we start with stoichiometric fuel, it becomes hypostoichiometric as burn-up proceeds with the result that metallic phase gets formed. Therefore, the fuel is made to be slightly hyperstoichiometric to start with, the extent to which the sesquicarbide phase is present being computed on the basis of the anticipated burn-up.

The cubic closed pack structure of the carbide accommodates fission products in the lattice much less readily than the oxide and consequently the carbide fuel swells much more under irradiation than the oxide. Swelling due to fission gases is also more pronounced in the case of carbide and this increases drastically at high temperatures ($> 1500^{\circ}\text{C}$). Further, the carbide fuel does not creep even at high temperatures. These problems are taken care of in the design of the fuel pin wherein sufficient room is provided for fuel swelling and central temperatures are kept low.

The fission products in the carbide fuel are less hostile to the clad than in the case of the oxide fuel. However, carbide fuel causes carburization of the clad. Though this has not turned out to be a severe problem, it must still be better understood to evaluate what limitations it would impose on peak fuel performance.

Fuel Reprocessing

The fuel is discharged from the reactor when it has reached the designed limit for safe operation in the core. The plutonium (and uranium) contained in the fuel must now be extracted efficiently in order to refabricate the fuel. There is sufficient economic incentive for doing this very efficiently ($> 99.9\%$ yield of plutonium) and in as short a time as possible. However, the fuel is terribly radioactive. An aqueous reprocessing method, called PUREX process, is commonly employed in processing spent fuel from thermal reactors. This has been extended to the mixed oxide fuel of fast reactors, but many problems remain. Reprocessing of the carbide fuel is a new technology and much work is needed especially

in the head end treatment by which the fuel is brought into solution. It would be desirable to develop non-aqueous or pyrochemical processes which are less affected by the high radiation levels and which can shorten the cycle time required to put the plutonium in the irradiated fuel back into the reactor in the form of re-fabricated fuel.

Chemistry of the Liquid Sodium Coolant

Liquid sodium, which is used as the coolant in the fast breeder reactor, is quite compatible with the stainless steel structural materials in the pure state. However, traces of impurities play an important role in the corrosion, mass transport and other processes taking place in the heat transport loops of the reactor. Even parts per million levels of oxygen causes corrosion in the high temperature sections of the loop and the corrosion products get transported through the liquid sodium medium to cooler parts. Some of these corrosion products and fission products which find their way into sodium can cause high radiation levels when they deposit on parts like heat exchangers and pumps which have to be periodically maintained. Thus one must not only control and monitor the oxygen impurity level, but also understand the transport and deposition of radionuclides in the reactor. Carbon in sodium causes carburization or decarburization of structural steels depending on the temperature and concentration. What is really important is the thermodynamic activity of carbon in sodium, but it is not yet well established as to what chemical forms carbon takes in sodium and what their inter-relationships and transformation kinetics are.

When there is a leak in the steam generator of a fast reactor, water (or steam) leaks into sodium. Such leaks must be quickly identified so that remedial action can be taken before they worsen. One of the first indications of such a leak is the (dissolved) hydrogen or rather hydride level in liquid sodium. Thus monitoring hydrogen levels in sodium with high sensitivity is an important task.

In the event of a breach in the clad, the fuel gets

exposed to sodium. The oxide fuel then reacts with oxygen containing sodium to form a compound, sodium uranoplutonate, which is rather a voluminous compound compared to the mixed oxide and hence may cause problems such as flow blockage. It is, therefore, important to understand the conditions of its formation and rate determining steps that would inhibit the growth of this product. The carbide fuel is in general more compatible with sodium but the nature of any interaction between a highly "burnt" fuel and sodium must be well understood.

Areas of Basic Research

In the process of our attempt to gain an insight into the technological problems outlined above, several areas of basic research open up. These can best be illustrated by means of examples.

Thermophysical Properties: As we have already seen, properties such as thermal conductivity and heat capacity are very important in evaluating fuel performance. Now these properties change with burn-up which introduces more and more fission products into the lattice. Therefore, we have a programme to study the variation of thermal conductivity at high temperatures as a function of these compositional changes. Here we start with fresh fuel materials and progressively dope it with specific fission products. One starts with simple systems first and then proceed to more and more complex systems, and then try to correlate these thermophysical properties with structure. One can then ask the more basic question of how to predict the properties of such complex systems, starting from the properties of simple systems. This study has necessitated the development of a laser flash technique for the measurement of thermal conductivity and heat capacity at high temperatures and under controlled environment.

Basic Thermodynamic Data: Basic thermodynamic information is required to build models and predict chemical behaviour. In the case of the mixed oxide, we must know how the oxygen potential depends on temperature, stoichiometry

and composition. As fission products are injected into the fuel the oxygen potential changes. These are studied by doping the fuel with fission product elements first individually and then collectively. In addition, the relevant phase equilibria must be established. Other data required include diffusion constants, vapour pressures and the nature of the chemical species in the vapour phase. Similarly in the case of the mixed carbide also, we must establish phase relationships, free energies of formation of various carbides, variation of carbon potential with stoichiometry and impurity (especially oxygen and nitrogen) content etc.

The techniques used in these studies include thermogravimetry, gas equilibration, solid electrolyte EMF measurements and x-ray diffraction. Partial pressures of different vapour species are measured using Knudsen effusion coupled with mass spectrometry. The vapour pressure data also yields thermodynamic information on the condensed phase with which the vapour is in equilibrium. The underlying objective is to establish correlations and build models which can then be applied to similar systems.

Chemical State of Fission Products

It is fairly easy to establish the oxidation states of some fission products. For example, elements such as alkaline earths, rare earths and zirconium will be formed as oxides under the oxygen potential conditions in the oxide fuel. However, they can exist as solid solutions, separate phases or compounds. To analyse this situation, one has to establish the limits of their solid solutions taking into account the influence of one solute on the other. One must examine the conditions of formation of all other possible compounds. For instance, does zirconium form ZrO_2 in solid solution with $(U,Pu)O_2$ or does it form $BaZrO_3$? Does molybdenum exist as metal, oxide, Cs_2MoO_4 or $BaMoO_4$? Such questions have to be answered before a proper assessment of the technological problem can be made. The situation with respect to the carbide fuel is even less clear. Thus these investigations take us to the basic properties of solid solutions of oxides and

carbides and the conditions of formation of different chemical states and phases.

Fuel-Clad Chemical Interaction

We have seen that the oxide fuel at high burn-ups attacks the clad and that fission products such as Cs, Te and Mo are suspected to be instrumental in these attacks. One hypothesis suggests that Fe, Cr, Ni tellurides are formed when liquid cesium containing tellurium attacks the clad. To examine the validity of this one needs basic data on the thermodynamics of the tellurides of Fe, Cr, Ni and Cs. This is precisely what we are doing using Knudsen cell mass spectrometry and x-ray diffraction as the main techniques. One must similarly examine other possible compounds. In the case of the carbide fuel, one must study the carburization of stainless steel and its possible enhancement through the agency of fission products such as cesium.

Process Chemistry

In order to reprocess the fuel by aqueous processes it must first be brought into solution. When the carbide fuel is dissolved, a number of organic compounds are produced, which can affect the efficiency of reprocessing. These compounds are not well characterized nor are the mechanisms of their formation understood. The fission product carbides may lead to a different distribution of compounds. This opens up an interesting study on the hydrolysis of carbides. Solvent extraction of plutonium, uranium and fission products and their mutual interference at high plutonium concentrations, and the influence of the degradation of the solvent extraction chemicals under the high radiation levels are other problems to be investigated.

As already indicated, investigation into possible pyrochemical reprocessing methods as an alternative to aqueous reprocessing methods offers a whole new field of basic studies. Essentially these processes would involve the distribution of Pu, U and fission products between high temperature molten phases of salts, alloys etc. The behaviour of these elements in these molten phases (solubilities, distribution

coefficients, chemical states and their transformations) offer possibilities of interesting basic research, though special techniques have to be devised to carry out these experiments.

Chemistry in the Liquid Sodium Medium

Solubilities of many metals and non-metals in sodium and the nature of the chemical species in sodium are not well established. For example, solubilities of metals like Fe, Cr, Mo etc are important to understand corrosion and activity transport processes. These solubilities are strongly dependent on the oxygen concentration in sodium. We still do not know in what chemical form these metals exist in solution. Carbon can possibly exist in many chemical forms in sodium (*e.g.* carbonate, atomic carbon, carbide, acetylide, cyanide etc.) and each of these would give a different chemical activity. Oxygen dissolves as oxide and hydrogen as hydride in sodium. However, when oxygen, hydrogen, carbon and nitrogen are present together, their mutual interactions and the equilibria between the various species formed make an interesting study. Experiments to understand such interactions in liquid sodium are in progress in our laboratory.

On-line Monitors

From the point of view of reactor operation, it is important to monitor the concentrations or thermodynamic activities of oxygen, carbon and hydrogen in the sodium loops of the reactor. Developing on-line meters that would function at the operating temperatures of these loops is one of our activities. Electrochemical meters have been developed for all the three impurities. For carbon and hydrogen on-line meters based on diffusion through metals have also been developed. The electrochemical oxygen meter, for example, is based on a oxide-ion-conducting solid electrolyte. One face of this electrolyte is in equilibrium with liquid sodium and the other with a reference electrode. An EMF measured between these electrodes gives a measure of the oxygen concentration in sodium. Similarly the electrochemical carbon meter is based on a liquid electrolyte consisting of a eutectic mixture of

lithium carbonate and sodium carbonate, while the electrochemical hydrogen meter makes use of a hydride ion conducting solid electrolyte. The development of these meters is, indeed, applied research, but a detailed look at the processes taking place at the electrode interfaces and in the electrolytes take us to basic electrochemistry.

Development of Techniques and Skills

A research programme of the type described here depends on a wide variety of techniques and skills. Some experimental techniques such as thermogravimetry, x-ray diffraction, high temperature galvanic cells and Knudsen effusion mass spectrometry have already been mentioned. Well characterised samples have to be made and sintered into high density pellets. Inert atmosphere preparation facilities, sintering furnaces, analytical techniques for characterisation etc., are essential ingredients of the programme. Extremely high purity environments are necessary to handle liquid sodium in the pure form. In many cases, the techniques and the necessary skills had to be specifically developed. For instance, oxygen meters were first based on imported yttria-doped-thoria solid electrolyte. As this became unavailable, we proceeded to pre-

pare this on our own. The design and fabrication of the laser flash equipment for thermal conductivity measurement, an out-of-pile simulation unit for generating the thermal conditions seen by the fuel pellet etc are other examples.

Because of the mutual dependance of many skills, a programme of this type must have a minimum critical size. It is our commitment to the fast reactor technology which has made available to us the resources to reach this critical size and to develop all the necessary skills and techniques. These inputs now serve a research programme which is at once both applied and fundamental in nature.

16 April 1984

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ANNOUNCEMENTS

NOBEL PRIZE IN CHEMISTRY FOR 1984

The 1984 Nobel prize in Chemistry has been awarded to Prof. R. Bruce Merrifield of Rockefeller University in New York. Prof. Merrifield is noted for

his work "development of methodology for chemical synthesis on a solid matrix".

NOBEL PRIZE IN PHYSICS FOR 1984

The 1984 Nobel prize in Physics has been awarded to two Nuclear physicists from Italy and Holland, Prof. Carlo Rubbia and Simon van Der Meer respectively. The two scientists are noted for their important

contributions leading to the discovery of the "field particles W and Z communicators of weak interaction" which is one of the four fundamental force fields in the universe, operating deep inside the matter.
