Editorial

Nuclear reactor is a complex system with variety of materials (fuel, clad, coolant, moderator, etc.) under different conditions of pressure, temperature and concentration. Chemical behaviour of nuclear materials, particularly those which come in contact with water under hostile conditions, has a profound effect on the health of the reactor. It determines the extent of wear/ corrosion of the reactor components as well as the radiation levels on out of core system (PHT, moderator pipelines). It is, therefore, of prime importance to understand the water chemistry related to operating nuclear reactors. The present bulletin is aimed at putting together the knowledge and experience on water chemistry in one place. This will enable the budding young reactor chemists understand complex issues related to water chemistry and at the same time the radiochemistry fraternity might focus their efforts towards some of the challenges being faced by the station chemists, like the ^{124}Sb problem.

I thank Dr. S. Velmurugan to have agreed to be the guest editor of this bulletin. I am grateful to Dr. S.V. Narasimhan, who was the main source of strength behind this bulletin, to write the FOCUS.

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From the Secretary's Desk

Dear Members

Your association has initiated the process to elect the 10th Executive Committee for the period 2009-11. In view of the enthusiasm shown by members to be a part of the association to render their expertise and services, there is a contest for the membership in the Executive Committee.

The Chapter at Tarapur has become a reality on September 27, 2008. Our members at the centre have already drawn a programme to attend to the requests from various institutes in the vicinity of Tarapur by conducting a one-day workshops and help in meeting the objectives of the association in spreading the awareness about the subject of Radiochemistry and Applications of Radioisotopes for societal benefits. It is heartening to note that members from NPCIL at Tarapur have evinced keenness to support the activities of the association.

The Indo-US agreement has brought a bizarre of buoyancy in many premier academic institutes in India that impelled to launch new courses allied to Nuclear Technology while seeking support from the Department of Atomic Energy. Thanks to various reports that appeared in a section of newspapers on the entire gamut of the deal, many schools and colleges have written to IANCAS to conduct Workshops in and around Mumbai. Our Southern Chapter has broadened its base to cater to many such requests in the Southern Region particularly in Andhra Pradesh and Karnataka. This sudden surge in the requests from the academia makes the activities of our association more meaningful and responsible.

I must admit that the Editorial team of the association is working hard to bring out the bulletins on time and also to fill the accumulated delay. So far IANCAS has brought out 40 thematic bulletins on topics of contemporary relevance to the subject of Nuclear Technology and most of them are available in downloadable form in our website www.iancas.org.

IANCAS has conquered a mile stone in organizing a Workshop in Imphal, Manipur University against many testing security conditions that are prevailing in that part of the country. IANCAS compliments the authorities of the BARC for the encouragement and all the resource persons who have conducted the workshop with zeal and sense of duty.

G.A. Rama Rao

Water Chemistry in Nuclear Reactors

Guest Editor

Dr. S. Velmurugan
Water and Steam Chemistry Division,
BARC Facilities, Kalpakkam

FOCUS

Dr. S.V. Narasimhan

**Associate Director, Chemistry Group &
Head, Water and Steam Chemistry Division,
BARC Facilities, Kalpakkam**

Water cooled nuclear power reactors accounts for a significant percentage of electricity generated in the world. Chemistry plays an important role in the operation and maintenance of these water cooled nuclear power reactors. In these reactors, water plays several roles. It acts, as a moderator to slow down the fission neutrons, as a heat transfer fluid to transfer the fission heat to the steam generator to raise the steam, as steam to run the turbine and as cooling water in the condenser that dissipates the heat to the environment. In Pressurized Heavy Water Reactors (PHWRs), the mainstay of Indian nuclear power program, heavy water (D_2O) is used as moderator as well as primary coolant. The primary heavy water coolant transfers the fission heat from the fuel bundles to the light water in the steam generator. The steam generated in the steam generator turns the turbine generating the electricity. The steam coming out of the turbine is cooled by the cooling water in the condenser. The cooling water is sourced either from the sea or a river or lakes. The quality of water used varies from system to system. In the moderator system, the heavy water coolant is maintained under neutral condition and at a conductivity of $< 1 \mu S/cm$. The primary heavy water coolant is maintained under alkaline and de-oxygenated condition. All volatile treatment is followed in the secondary light water coolant. As the tertiary coolant system viz. the cooling water is sourced directly from the natural water bodies, it contains all the inorganic, organic and biological materials that are normally expected from these water sources. Similarly, the operating conditions of the various coolant systems also vary from system to system. The primary coolant is operated at $290\text{-}320^oC$ and at high pressure of $90\text{-}100 \ kg/cm^2$ pressure. Where as, the process water and cooling water systems are operated at close to ambient conditions. In addition, the nature of the problems encountered also vary from system to system. In the primary coolant system, the major problem is radiation field build-up which arises due to the interaction of water coolant with the system structural materials forming the corrosion products. Activation of the transported corrosion products by the neutron flux in the core generates the radioactive contaminants which in turn causes the radiation field and exposure of operating personnel to the radiation field. As this problem is unique to the nuclear power industry and as the industry has the mandate to keep the radiation exposure 'As Low As Reasonably Achievable' (ALARA), all efforts are being made to control the radiation field as much as possible. Similarly, corrosion of reactor coolant system is of concern to the nuclear power industry. As corrosion manifests in several forms and as all forms of corrosion are detrimental to the system, effort is made to keep the corrosion to the minimum. In addition, deposit accumulation in any part of the system especially on heat transfer surfaces is undesirable and should be prevented. It is good that Indian Association for Nuclear Chemists and Allied Scientists (IANCAS) is bringing out a special bulletin to highlight the importance the water chemistry in the efficient running of nuclear power stations.

Guest Editorial

Dr. S. Velmurugan

The article on "Chemistry in operation of nuclear reactors" deals with the management of chemistry in different water circuits of water cooled nuclear reactors. The efficient management of chemistry domain addresses reduction in rate of radiation field build up in the primary coolant circuits, minimizes radiolytic degradation in moderator and ensures SG tube integrity while inhibiting primary coolant leaks. Several of these control measures happen by good chemistry specification based on action levels.

The article on "Corrosion of Primary Heat Transport system carbon steel material in PHWR" deals with the mechanism of activity transport in water cooled nuclear reactors. This is the only problem of serious concern in nuclear industry which has a direct link to man-rem budget, In international scene, every effort is made to have as low a man-rem exposure budget as possible per reactor per year. The paper discusses new method of radiation field control measures like metal ion passivation. The recently encountered problem of flow accelerated corrosion is also discussed.

The article on "Chemical Decontamination Strategies" discusses the methods of chemical decontamination successfully developed and applied in Indian PHWRs. Not only it elaborates the basis of initial process development but also it mentions some of the improvisations carried out to better the performance. Article also deals with two unique problems namely removal of stellite particulate activity from moderator system of PHWRs and removal of ^{124,122}Sb from PHT system of PHWRs.

There is an interesting article entitled "Role & Responsibilties of a station chemist in a nuclear power station – a perspective" in this issue from a Station chemist who is entrusted with a job maintaining good water chemistry domain while complying with an uninterrupted operation of the reactor within the allowed technical specification. Very clearly the job is of multidisciplinary nature and the task requires instant balanced judgment to implement corrective actions quickly while not compromising the plant life. Station chemist not only ensures efficient and safe operation but also ensures Plant Life Extension.

Another article dealing with "Removal of Turbidity from coolant systems using Electrochemical Filtration", describes a new method of turbidity removal employing physical filtration and charge based retention under an applied voltage. While the former is attributable to large surface area provided by the carbon felt, the latter is clearly due to charge carried by the particulates in the medium. The pressure drop, a main constraint in filters, is no longer a problem in the new technique. It has versatility in application. It can tackle turbidity and near nano levels, be it from iron, silica, antimony, indium etc and can be used in any of the water circuits from primary to tertiary !

Happy reading

Chemistry in the Operation of Nuclear Reactors

Dr. S.V. Narasimhan *Joined BARC in 1971, after Post Graduation in chemistry from Madras Univ. (1970). He did his Ph.D. (Phys.Chem.) in 1981 from Bombay University. He is presently the Associate Director, Chemistry Group and is also the Head, Water and Steam Chemistry Division, BARC Facilities, Kalpakkam, Tamil Nadu 603 102. In addition he is also Chairman of a DAE advisory Committee On Steam & Water Chemistry (COSWAC). His areas of specialisation are High temperature electrochemistry, Dilute chemical decontamination, Activity transport and surface analysis, Water chemistry, and Thermal ecology. He has 90 Journal papers apart from several presentations in symposiums. Presently he is guiding six PhD students in Madras University and in HBNI.*

Introduction

Water cooled nuclear power reactors are in general prevalent all over the world. They have been producing power very effectively and economically. Water, in its pure state, is used for transferring the heat generated in the core to the turbines to produce electricity. The properties of water are considerably affected not only by the high temperature but also by the radiation field. Nevertheless, the interaction of materials with water at high temperature is enhanced considerably. In addition, the radiolytic degradation of water and radioactivation of the corrosion products that is transported by the coolant water adds another dimension to the electricity generation scenario. In this paper, the water chemistry domains employed in NPPs are discussed with possible methods of control.

Primary heat Transport System (PHT)

The primary objective of the heat transport system is to transfer efficiently the heat generated in the core of the reactor by fission process to the steam generator. In PWRs and PHWRs the heat is picked up by water in single phase (liquid water) in the temperature range of 245°C to 310°C. The temperature dependence of specific heat of water allows maximum useful extraction of heat in this temperature range (Data). Natural interaction of metallic elements present in the alloys constituting the structural materials in the PHT system with the coolant water produces corrosion products and $H_2(g)$. Metal oxidation occurs with a corresponding complementary cathodic reduction of H^+ or Dissolved oxygen. The metallic ions so produced generally belong to the transition metal category. They are readily hydrolysed in the water medium and converted to insoluble metal hydroxides, oxy-hydroxides and oxides, which are termed as corrosion products. Many of these chemical reactions are kinetically enhanced by the temperature prevailing in the coolant. The thermal stability of the corrosion products is primarily dictated by the Pourbaix diagram. Their relative stability is thus decided by thermodynamics though several other factors like kinetic and hydrodynamic parameters also play a significant role. Since the corrosion products are insoluble and are produced at extremely slow pace, they remain in suspended particulate form in the size range 0.1 to 2 m with a maximum around 0.3 m. The distribution of particle size is controlled by size dependent removal by filtration and surface deposition.

It is also well known now that aqueous high temperature metal oxidation leads to the formation of two layers of oxide under quiescent or normal flow conditions. At the metal water interface, metal gets oxidized to oxide and released partly as metal ion to the coolant fluid. Across this in-situ formed oxide layer (called inner layer) there is a constant transport of metal ions outward and oxide ions inward. The relative rate of such ion transfers has a role to play in deciding the porosity, protectivity and structure of the oxide. It is matter of debate and

Dr. S.V.Narasimhan, Associate Director, Chemistry Group and Head, Water and Steam Chemistry Division, BARC Facilities, Kalpakkam, Tamil Nadu 603 102; E-mail:

mechanistic quantification as to whether the transport of the ions is decided by pore or grain boundary route. Nevertheless the transport does occur which keeps the inner oxide under dynamic equilibrium.

The outer layer of oxide over the metal is formed essentially by precipitation due to solubility and is also driven by forces of particle adhesion. There is a dynamic equilibrium between dissolved metal ions, suspended particulate oxides and deposited oxide.

It is this dynamic equilibrium which is a cause for concern in a nuclear power plant (in comparison to a thermal power station). In the core of the reactor where fission produced heat is released, both thermal and fast fission neutrons are present ($_f$, E_f, $_t$, E_t). The corrosion product ions and particulates present in the coolant reside in the core region for definite time period repeatedly. In this process, the nuclides of the metallic elements undergo nuclear transformation resulting in radioactive elements. Such transformation combined with the dynamic equilibrium described earlier results in the spread of contamination of out of core surfaces. As these nuclides are both and emitters with varying $t_{1/2}$ and Energy of the radiation, they have a significant impact on the man-rem problem faced by the power plant.

Antimony present in some of the fuel surfaces and pump seals in the heat transport system gets released due to mechanical wear. As the antimony chemistry is quite complex, its removal from coolant becomes very difficult. Majority of the inventory of antimony resides in the core on zircaloy surface during regular operation of the reactor. During shutdown and start-up, there is sharp release of antimony activity. It is known that there is oxygen excursion in the coolant along with temperature fluctuations during these periods. The radioactive antimony (^{122}Sb, ^{124}Sb) so released from the core gets easily deposited on out-of-core surfaces if not removed effectively by specific ion exchangers. This problem has been encountered in several PWRs. Specific shut down procedures have been worked out to minimize the release of radioactive antimony. which Prior to shut down, injection of

oxygen is carried out in the PHT system, followed by ion exchange removal of antimony.

In PHWRs also antimony problem has surfaced in reactors which used antimony as alloy element in moving parts. This problem is yet to be addressed fully in PHWRs. During full system chemical decontamination of PHWRs antimony problem had surfaced which further enhanced radiation field on out- of-core surfaces due to selective deposition on carbon steel pipes. Modified procedures have been evolved to address this issue.

The Chemistry of the coolant fluid in the primary heat transport system is maintained in the alkaline medium with lithium hydroxide. The dissolved oxygen in the water produced by radiolysis is kept under control by use of Hydrogen gas externally added to the system. The structure of different corrosion products present in the coolant system surface is altered significantly by variation in the concentration of dissolved hydrogen and H^+. The dependency is represented by the following equations.

$$Fe^{2+} + 2OH^- \quad \frac{1}{3}Fe_3O_4 + \frac{2}{3}H_2O$$
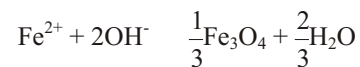
While the general corrosion is kept at minimum by the alkaline pH conditions, the transport and redistribution of corrosion products are not easy to control even though chemistry specifications are maintained within the specified ranges. This is attributable to the non-isothermal conditions prevailing in the PHT circuit. Compromising all these aspects, optimum pH region for the circuit is arrived at and it would ensure that inside the core the residence time of the corrosion products can be kept to minimum.

There is an alternative route to improve the protectivity of the oxide over structural materials surface. This is called metal ion passivation (MIP) technique. Selected metal ion is injected at very low concentration in the coolant. As the protective oxide layer is formed, these ions alter the structure of both inner and outer layer of the oxide. The transport of metal ion across by these oxide layers is thus hindered. In fact the origin of this technique is traceable to the behaviour of GE BWRs employing Zn as alloying element in condenser tubes. The

corrosion caused by condensate released ppb levels of Zn which upon incorporation in the protective ferrite/ chromite film rejected the Co activity. Nevertheless the mechanism of this technique in actual reactor system is not very clearly understood.

In the presence of radiation, the coolant water undergoes radiolytic de-composition producing hydrogen and oxygen as molecular products besides several oxidising and reducing radicals. The extent of the formation of molecular products is also dependent on partial boiling in the core near metal surfaces and the extent of stripping due to gas phase exchange and ion exchange purification. Metal - water reaction also produces hydrogen to some extent at elevated temperature which may be significant only in PHWRs as carbon steel is used as the major construction material.

Moderator System

The objective of moderator system is to thermalise the fission neutrons and also to remove heat deposited in the moderator. While in PWRs coolant acts as moderator also, in PHWRs these two systems are well separated in terms of design. This structural material of the moderator system is stainless steel and the calandria tubes are made of zirconium alloy. The total inventory of the moderator is residing in the core and interacts with the neutron. Thus the radiolitic degradation of the moderator is also significantly high. The radiolysis products are hydrogen and oxygen which get striped into cover gas prevailing over the moderator. The cover gas acts as transporting medium for the molecular products hydrogen and oxygen. The gases are recombined over palladium loaded alumina catalyst. The cover gas also prevents entry of moisture and oxygen into the moderator. The moderator system is operated between 50ºC and 70ºC. Considering the above physical and chemical features of the moderator system, the pH of moderator system is maintained in the neutral region. At low temperature and in neutral pH the SS is fully compatible. The addition of any type of pH maintaining agent is not desirable from the point of view of radiolysis.

In several PHWRs, no specific issue has surfaced in the moderator circuit. Ingress of nitrogen and oxygen(air) in cover gas, ingress of carbon (ingress of ion exchange fines) and ingress of cooling water impurities degrade the chemical quality of the moderator system. The specific conductivity of the moderator system is thus maintained at <1 S/cm to ensure that there are no harmful impurities in the system.

In a few selected PHWRs, due to mechanical interaction of stellite ball bearings present in the adjuster rod control mechanism, stellite powder got introduced into the moderator system. As the Co particulates circulated through the neutron zone in the core, ^{60}Co was produced. This radioactive cobalt got deposited in low flow areas as particulates resulting in high radiation fields. This problem was addressed by two methods:

1. Removing stellite containing ball bearings and replacing for non-stellite alloys.

2. Remove the existing radioactive deposits by chemical cleaning at low temperature.

Steam Water System

The steam required for turning the turbine is produced in the steam generator by using the heat from the primary heat transport system. The temperature domain of the secondary circuit ranges from 45 C (in condenser) to 110 C (in deaeartor) 195 C (in final feed water entering the SG. In addition the steam is raised at 250 C and 40 kg/cm^2 pressure. The SGs produce saturated steam with a natural recirculation of water. The steam is dried (<0.5) and sent to Turbo Generator (TG) set for power production. The materials in the secondary circuit consist of SG tubes (made of monel/ incoloy/ inconel 690 TT), carbon steel piping, feed water heater tubes (Stainless steel) and condenser tubes (SS, Ti, Al-brass- admiralty brass etc). The chemistry of the secondary circuit is maintained under alkaline reducing environment using volatile amine (Ethanolamine-ETA and hydrazine-N$_2$H$_4$). Over years of operational experience, it is learnt that the use of all volatile amine treatment is better to protect the water and steam circuits of the secondary system.

The pH is maintained by the hydrolysis reaction of the amine giving rise to OH$^-$. Since the amine is a weak base, there is an equilibrium existing between the free amine and the dissociated form.

The free amine reacts easily with acid (generated by ingress of impurities or by thermal hydrolysis of organics) to produce amine salt which alters the pH of the medium as per the BL-equation. The amine has a definite distribution coefficient between steam and water. The condensate contains varying amount of amine depending on the location in the SG circuit. This offers protection to the structural material in the steam circuit as well. The hydrazine is added at the boiler feed pump suction to provide reducing atmosphere and to remove traces of dissolved oxygen from the system. Excess hydrazine could thermally decompose to ammonia and enhance the pH of the system in addition to the role played by the amine. The mixture of ammonia and amine will have a different impact in the condensation along with the first drop of water in the steam circuit.

The integrity of the SG tube is very important in nuclear reactors because it acts as a boundary between the radioactive primary coolant and the environment. Due to the steaming on the secondary side of the SG tubes, large amount of salts get deposited on the tubes, tube sheets etc. Such coating formation is deleterious to the heat transfer process and can result in excess localised attack on SG tubes resulting in catastrophic failures. In order to prevent such deposit formation ingress of cooling water in the SG circuit is to be totally avoided or the condensate should be fully purified by ion exchange process. In addition soluble corrosion product iron can get generated in the steam- water circuit and hence iron can find its way into the SG tube. It will further complicate the deposit formation on SG tubes and tube sheets. Hence iron input to SG is a very important parameter that should be kept to a minimum at all times.

Blow down of SG water reduce sludge build up. However, it results in loss of heat and purified water. Hence both heat and the water are recovered in boiler blowdown recovery system. Similarly the use of full flow condensate polishing unit for purifying the condensate free of soluble impurities has been quite successful in preventing the entry of salts. However, the regeneration methodology employed in the condensate polishing units has itself introduced some slip of low concentration of chloride or sodium. Better methods are now available for preventing such slips of Cl^- and Na^+.

Chemistry control specification

The management of chemistry parameters in the primary and secondary circuit of nuclear reactors is very critical for the efficient and economic operation. This carries additional significance because of the fact that the primary coolant containing radioactivity should be contained at all times and can not be allowed to escape to environment from radiation hazard point of view. The chemical constituents are of many types as detailed below:

1. Intentionally added chemical to maintain a certain chemistry domain;

2. Impurities entering into the system due to ingress of process cooling water, ion exchange resins, oils, etc

3. Impurities generated in the system due to radiolysis

4. Impurities generated in the system due to corrosion of materials

Some of these parameters are of immediate relevance to safety of the plant and personnel while some of the parameters may have long term implication on the life of the reactor components. The variation in the concentration of the parameters in reactor systems occur at different rates depending upon several factors involved in the operation. Similarly the control of these parameters within a preferred domain is also expected to take a definite duration as the system is designed essentially to operate for power production and not for containing the impurity ingress. Considering these aspects the technical specification has been arrived at. The parameters are divided into control parameters and diagnostic parameters. Control parameter is one which decides whether the reactor should continue operation at full power or not when it is found to be outside a normal range of values (NRV). When the value of the control parameter is outside the NRV, the value is expected to fall in any one of the three action levels. The action level (AL) prescribes a certain band width for the magnitude of the chemical parameter which is also associated with a certain allowable time span. The combination of AL and T is so chosen as to minimize the deleterious impact of the impurity on the structural material. Similarly the action level 2 and 3 are designed followed by a

direction to shut down the plant. The details are given below:

Action Level 1

In this action level, damage to the system can occur over a long period of operation. Hence action is to be initiated to improve the chemistry in a reasonable time mentioned therein. Sampling frequency should be increased as deemed fit.

Action Level 2

Damage to the system can occur to a certain extent as a consequence of operation in this action level. Hence prompt action is necessary within the duration specified. The corrective action should be such as to restore the value of the parameter to NRV. A technical review of the incident should be documented. An incident report should be prepared and discussed at SORC. Sampling frequency should be increased as deemed fit.

Action level 3

It is not advisable to prolong the operation of the plant, if the value of the chemical parameter is in this action level. For parameters related to safety, action is to be initiated to lower the power and shut down the reactor within 4 hours. For other control parameters, where shut down (S/D) has not been specified, action should be taken to bring the values to action level 2 within 24 hours, otherwise action should be initiated to shut down the reactor within the next 4 hours. However, if there is a significant improvement in these chemical parameters towards NRV, during the process of shut down, power operation can be continued. Technical review of the incident should be documented and discussed in SORC/COSWAC.

In general chemistry related failures do not suddenly cause collapse of the structural integrity of the system except in cases like stress corrosion cracking and the like. Hence there are no scrams proposed upon violation of chemistry parameters. Only planned shutdown is recommended. It is explicitly known that the field experience, R&D data and operating constraints have together led to the above classification. The action levels between NRV and S/D are on the conservative side and provide enough breathing time for the implementation of corrective actions.

Several chemistry parameters are inter-related and some of them are designated as diagnostic parameters. Usually the parameter which has highest sensitivity and quickest to respond to a perturbation is chosen as control parameter while the associated parameters are chosen as diagnostic parameters. Diagnostic parameters usually have only one range of values.

Conclusion

The chemistry domain of the operating nuclear power plant is complex because of the temperature domain, variety of materials of construction, nature of the coolant and the radiation field. Yet, management of the chemistry is made possible so as to operate the reactors effectively. Constant improvements in the chemistry control specifications are needed because of the improved understanding of the processes, materials and design. Specific problems encountered in operating nuclear reactors are due to unusual material, improper operating procedure etc. Most of these problems can be solved easily with a better understanding the chemistry of the domain and also the design of the operating plant. The prevailing conditions in India have so far led to successful operation of all nuclear power plants without any serious failures traceable to any violation in chemistry domain. In several cases the plant life extension is also made possible by maintaining good practices.

Chemical Decontamination Strategies

Dr. S. Velmurugan *of Water and Steam Chemistry Division, BARCF, Kalpakkam obtained his M.Sc(Chemistry) from Madurai-Kamaraj University and Ph.D from University of Madras and joined BARC through 28th Batch of training school. Since 1985, he has been carrying out R&D activities in the field of water chemistry as relevant to Pressurized Heavy Water Reactors(PHWRs). The objective of the work program is to control the radiation field built-up in the reactor coolant systems of Indian nuclear reactors. Extensive work to understand and optimize a chemical process for the decontamination of reactor coolant systems of PHWRs were carried out. This includes studies on oxide/oxide film dissolution, ion exchange studies with metal ions, activities and complexing agent pick-up on ion exchange resins, studies on corrosion behavior of reactor structural materials in the chemical formulations used for the decontamination, chemical cleaning etc. The chemical process thus evaluated has been applied ten times to decontaminate the Indian PHWRs. Currently he is engaged in studies on flow accelerated corrosion and in optimization of water chemistry to AHWRs. He has 33 Journal papers and 64 International/national conference papers to his credit.*
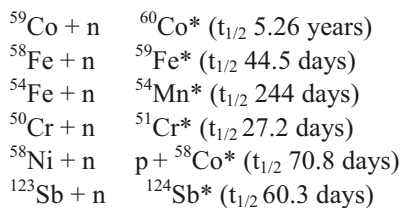
Introduction

The term 'Radiation' is synonymous with 'Nuclear'. Radiation field builds up in the nuclear coolant systems of nuclear reactors and causes exposure of personnel to radiation. Efforts are being made world over to reduce the radiation field that builds up in the reactor coolant systems. Radiation emanating from the fission of uranium and the decay of fission products are contained very well within the core by the multi level shielding provided to the calendria / reactor vessel. Thus, the radiation field observed around the coolant system arises mainly due to the radioactive contaminants deposited onto the out-of-core surfaces such as coolant system piping, pumps and steam generators etc. Deposition of radioactive contaminants takes place due to the transportation of corrosion products into and out of the reactor core. These corrosion products are made radioactive by the neutron flux present in the core. Fission products escaping the failed fuel elements contribute to some extent to the radiation field. Hence, the major contribution to the radiation field arises from the neutron activated corrosion products. Stainless steel, Inconel-600, Inconel-690, Incoloy-800, carbon steel, zircaloy-2 / 4 and Zr-2.5%Nb alloy are the major alloys used in the reactor coolant system. These structural materials of the reactor coolant system are made of iron, nickel, chromium and zirconium. Few reactors in the world use copper containing Monel-400 as steam generator tube material. Alloys containing cobalt such as stellite were used earlier as wear resisting materials in valves. All the above alloys interact with the high temperature (upto $320^{o}C$) water present in the coolant system and forms oxides (Fe_3O_4, Fe_2O_3, $NiFe_2O_4$, $FeCr_2O_4$ etc.) of elements constituting the alloys. The composition and nature of the oxides formed on the structural material surfaces of the coolant system depends on two main factors i) material composition of the structural material ii) chemistry of the water coolant. The corrosion product oxides thus formed on the surfaces of the structural materials incorporate the radioactive nuclides transported by the coolant by processes of adsorption, absorption and by chemical reaction. Among the several radioactive contaminants present in the system surfaces ^{60}Co, ^{59}Fe, ^{54}Mn, ^{51}Cr, ^{58}Co, ^{124}Sb and ^{110}Ag are important as they have relatively long half lives and the -rays emitted by them are having energy sufficient to penetrate the thickness of pipes to cause exposure of personnel manning the power plant to radiation. These radio active isotopes

Dr.S.Velmurugan, Water and Steam Chemistry Division, BARC Facilities, Kalpakkam, Tamil Nadu 603 102;
E-mail: svelu@igcar.gov.in

are formed by the following nuclear reactions involving neutron (n) and the parent inactive isotopes present in the corrosion products:

^{59}Co + n ^{60}Co* (t$_{1/2}$ 5.26 years)
^{58}Fe + n ^{59}Fe* (t$_{1/2}$ 44.5 days)
^{54}Fe + n ^{54}Mn* (t$_{1/2}$ 244 days)
^{50}Cr + n ^{51}Cr* (t$_{1/2}$ 27.2 days)
^{58}Ni + n   p + ^{58}Co* (t$_{1/2}$ 70.8 days)
^{123}Sb + n ^{124}Sb* (t$_{1/2}$ 60.3 days)
*indicates radioactive isotope

In recent years, the ^{124}Sb contribution has increased especially during shutdown owing to the use of antimony containing materials as seals and bearings in primary coolant pumps. In addition to these activated corrosion product isotopes, fission products such as ^{125}Sb, ^{95}Zr, ^{95}Nb, ^{103}Ru, ^{106}Ru, ^{137}Cs, ^{141}Ce and ^{144}Ce were also observed in the systems but their contribution to field is relatively less (< 10%) as compared to the activated corrosion products.

Efforts are being made to minimize the radiation field in the reactor coolant systems of nuclear power plants by careful selection of materials. As ^{60}Co is the most important radioactive contaminant because of its long half life (5.26 years) and hard gamma (1.17 and 1.33 MeV) emission, cobalt containing materials such as stellites are avoided and in its place nickel or iron based hard facing materials are chosen. In addition, the cobalt content in the alloys chosen for steam generator tube material or the alloy chosen for coolant piping are specified in such a way that it is kept as minimum as possible. Similarly antimony and silver containing materials are avoided to the extent possible. In order to reduce corrosion and activity pick-up on the system surfaces, some of the PWRs use components that are electropolished to get smooth surface.

The other option available to reduce the radiation field in the coolant system components is optimization of the chemistry of the coolant which in turn reduces the quantity and/or the release rate of the corrosion products. The reducing and alkaline chemistry conditions maintained in the PHWRs/PWRs primary coolant systems' ensure the formation of spinal type oxides. The protective nature of these oxides ensures that the rate of corrosion decreases as the oxide film grows. In BWRs, even though alkaline conditions are not maintained, the impurities in the water are kept at very low levels that corrosion of reactor materials and coolant system materials (stainless steel) are very low. In western BWRs, zinc is added at ppb levels to the coolant that modifies the oxide film formed over the structural material surfaces making it more corrosion resistant and adherent. Also, they keep the coolant condition reducing by adding hydrogen or hydrogen after noble metal treatment. Though hydrogen addition is practiced to prevent IGSCC failure of stainless steel, it also enables the formation of protective spinel type oxides on the system surfaces.

The efforts taken in choosing the right material for construction of coolant systems and in maintaining the right coolant chemistry have helped to significantly reduce the radiation field in the out-of-core surfaces of reactor/primary/moderator coolant systems of power reactors. But, as far as radiation exposure of plant personnel is concerned, the principle of `As low As Reasonably Achievable (ALARA)' is followed by the nuclear power stations. Hence, the stations look for other means to further reduce the radiation field. In this respect, chemical decontamination has proved to be an easy and efficient way of reducing the radiation field in the reactor coolant systems.

Fundamental principle involved in Chemical Decontamination

Nature of the oxide formed in Structural Materials

The chemicals added during chemical decontamination react with the oxide film present in the coolant system structural materials' surfaces and dissolve or dislodge the oxide film along with the radioactive contaminants. The metal ions, crud and the radioactive contaminants released from the surfaces are taken out of the system either by draining the decontaminating fluid and disposing off as liquid radioactive waste (rarely practiced) or by collecting the metal ions, activities on ion exchange resins and filters and disposing them as solid radioactive waste. The efficiency with which the radiation field is reduced by decontaminating reagent depends on so many factors. The most

Fig. 2   Dilute Chemical Decontamination (DCD) Process

Fig. 1   Oxide double layer structure

important factor is the nature of the oxide film. In most part of the system surfaces, the oxide film has a double layer structure (Fig. 1). The double layer structure of the oxide film was proposed by Potter and Mann. The oxide film consists of a fine grained inner layer and a coarse grained outer layer. The inner layer is grown on oxide and the outer layer is formed by precipitation of the oxides from the coolant saturated with the dissolved metal ions. Hence, the composition of the oxide between the two layers varies from each other. In multi element alloys such as stainless steel, Incoloy-800, Inconels etc., the composition varies within the layer itself.

In the case of boiling water reactors (BWRs), the reactor coolant system, the re-circulation lines, the steam generator tube are made of stainless steel. The reactor core is lined with stainless steel. Under the oxidizing chemistry conditions maintained in some of the BWRs (as in TAPS#1&2), hematite (α-Fe$_2$O$_3$) is the dominant corrosion product oxide. The top layer is expected to have less chromium because of the continuous removal of chromium(III) in the oxide to Cr(VI) and its subsequent dissolution by the water medium. However, the inner layer of the oxide film is expected to retain some of the chromium(III) formed by the corrosion process. In TAPS#1&2, it was reported that it contains more amount of chromium than that was expected for a BWR operated under oxidizing chemistry condition. This was attributed to the deposition of chromium(III) formed from the chromate added during shut down. However, this observation needs to be established by experimental investigations. In BWRs that adopt Zinc Ion Passivation (ZIP)
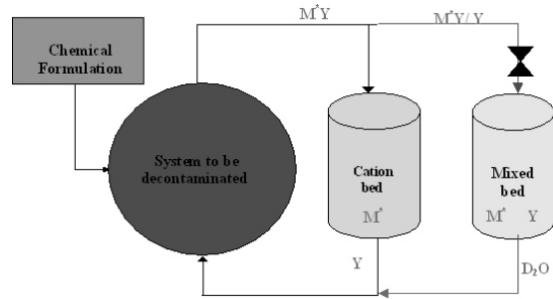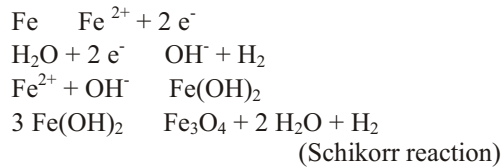
technique to reduce radiation field, zinc is incorporated in significant quantities on the oxide film making the film thinner and tenacious. In BWRs that follows hydrogen water chemistry with or without noble metal(Pt/Ir) chemical addition, the oxides formed are ferrites and chromites. The thickness of the oxide film is an important parameter as it decides the concentration and quantity of decontaminating reagent to be added. Under the oxidizing chemistry and neutral pH condition of the coolant, the stainless steel surfaces of the BWRs, forms a thick oxide film as hematite is not a protective oxide. Depending on the duration of power operation the thickness of the oxide film can grow upto 15 μm.

In PWRs and VVERs, the same stainless steel (304 or 316) is used as structural material of the primary coolant system. The light water coolant in these reactors is conditioned by alkalies (LiOH or KOH) to maintain a high temperature pH_T of 6.9 – 7.4. The concentration of lithium or potassium is adjusted according to the boron concentration to get the above high temperature pH. In addition, reducing condition is ensured by adding hydrogen (10 – 30 cm^3/kg) either directly or through the addition of ammonia. Under these conditions a thin adherent oxide film is formed. The oxide film is composed of mixed ferrites and mixed chromites (Fe$_{(1-x)}$Ni$_x$Fe$_2$O$_4$, Fe$_{(1-x)}$Ni$_x$Cr$_2$O$_4$, Fe$_x$Ni$_y$Cr$_z$Fe$_{[3-(x+y+z)]}$O$_4$ etc.).

In PHWRs, the mainstay of the Indian nuclear power program, carbon steel is extensively used. All the primary coolant system feeders and headers are made of carbon steel. The steam generator tube material is either Mone-400, an alloy of copper

(30%) and nickel (70%) or Incoloy-800 (an alloy containing 32% nickel and 22% chromium and remaining iron). The pressure tube and the fuel clad in the core are made of zircaloy or Zr-Nb alloy. The heavy water primary coolant, which is maintained at pHa 10-10.5 and hydrogen concentration of 3-10 ml/kg, interacts with the structural material forming corrosion product oxides. As carbon steel has a large surface area (1500 m^2 for 220 MWe PHWRs) and also because of its relatively high corrosion rate, the corrosion product formed on the carbon steel viz. magnetite (Fe_3O_4) dominates the corrosion product inventory in the system. Magnetite is formed by the following sequence of reactions:

$$Fe \longrightarrow Fe^{2+} + 2\ e^-$$
$$H_2O + 2\ e^- \longrightarrow OH^- + H_2$$
$$Fe^{2+} + OH^- \longrightarrow Fe(OH)_2$$
$$3\ Fe(OH)_2 \longrightarrow Fe_3O_4 + 2\ H_2O + H_2$$

(Schikorr reaction)

The thickness of the magnetite formed over the carbon steel under normal flow conditions can be determined by the logarithmic rate law. Thickness values of 20–40 m have been observed on carbon steel surfaces that has seen 10 years of operation. Some variation in thickness is expected because of the temperature difference within the system. In addition, the areas affected by flow accelerated corrosion would have very thin oxide film (< 2 m). The double layer magnetite (Fe_3O_4) film formed over the carbon steel surfaces undergoes dissolution and are transported as ferrous ions and as magnetite particulates and deposited over the steam generator and zircaloy surfaces in the core viz. fuel and pressure tubes. It has been reported that in nickel based steam generator tube surfaces, some conversion of the deposited magnetite (Fe_3O_4) to nickel ferrite ($NiFe_2O_4$) is possible. The parent oxide in Incoloy-800 formed at the primary coolant operating conditions would be the mixed ferrite and chromites ($Fe_{(1-x)}Ni_xFe_2O_4$, $Fe_{(1-x)}Ni_xCr_2O_4$, $Fe_xNi_yCr_zFe_{[3-(x+y+z)]}O_4$ etc.), but the x,y,z values are different from that formed on stainless steels.

In all the reactor types zircaloy-2 / 4 or Zr-Nb alloys are used as materials for in-core components such as fuel clad, pressure tube/channels etc. These zircaloy surfaces also undergo corrosion and form a thick oxide film (ZrO_2). As the zircaloy components are inside the core which is heavily shielded, no effort is made to remove the zirconium oxide film. However, the iron, nickel, chromium oxides transported to the core and deposited over the ZrO_2 film by the coolant require to be removed to avoid re-contamination after decontamination.

Activity incorporation in the Oxide Film

In the primary/reactor coolant systems of power reactors the concentration of cobalt ions in the coolant and the percentage composition of cobalt in the crud or deposits is insignificant as compared to iron, chromium and nickel etc. Hence, the chemical form in which cobalt is present in the oxide is very difficult to identify. However, it has been proved that the active cobalt isotope ([60]Co & [58]Co) along with the inactive precursor can get incorporated in the chromite matrix. Calculation of octahedral site stabilization energies for Fe^{2+}, Co^{2+}, Ni^{2+} indicated that the cobalt is stabilized in the tetrahedral sites of the chromites which has a normal spinel structure. This clearly shows that the cobalt chromite formation is thermodynamically favourable under the reactor coolant conditions. In addition to this mechanism of cobalt incorporation in the oxide lattice, other mechanisms such as cobalt adsorption by ion exchange over the surface hydroxyl groups of the oxides which act as inorganic ion exchangers is also proposed. The cobalt ion initially adsorbed over the surface can further react and can form part of the oxide. The mechanism of incorporation of ^{51}Cr and ^{59}Fe activities in the oxide lattice is obvious.

In view of the high contribution of antimony activities during shut down in some of the reactors including PHWRs, the mechanism by which antimony activities ([124]Sb and [122]Sb ($t_{1/2}$ 2 days) are picked up on the surfaces of primary coolant systems of PHWRs and PWRs is being debated. The antimony released from the pump seals and bearings is transported to the core and gets activated by the neutron flux present in the core. The high temperature pourbaix diagram indicate that the pH_T and the potential condition of the PHWR primary coolant lies in the interface between Sb [elemental (metalloid) form] and the Sb^{3+} form. Hence, the exact chemical form in which it resides in the core is not clearly established. There are indications that it exists in Sb^{3+} form either adsorbed or deposited over the ZrO_2 film in the in-core zircaloy surfaces.

Similarly, the chemical form of antimony activities in the out-of-core surfaces is also not known clearly. Possibility of Sb^{3+} adsorption on oxides, plating out on carbon steel surfaces and formation of antimony containing iron compound ($FeSb_xO_y$) are being postulated.

Chemical dissolution of the oxide

The radioactive contaminants causing the radiation field in the reactor / primary coolant system have got incorporated in the oxide film. Hence, in order to remove these radioactive contaminants, the oxide film itself has to be removed. This can be achieved by dissolving the oxide film using chemical reagents. Large numbers of chemical reagents are used for the removal of oxide film from the coolant system surfaces. These reagents are different from the ones used for removing floor or surface contamination which are meant for the removal of loosely held contaminants and are surfactant based. The chemical reagents meant for the removal of radioactive contaminants fixed onto the oxide film can be broadly classified into three categories:

1. Simple acids

2. Reducing agents and/or Organic complex forming acids

3. Oxidizing compounds

Dissolution of Oxides by Acids

Most of the corrosion products in the coolant system are iron containing oxides. The iron containing oxides can be dissolved by reacting with acids

$$Fe_3O_4 + 8\,H^+ \quad Fe^{2+} + 2\,Fe^{3+} + 4\,H_2O$$
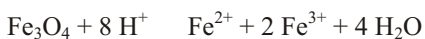
Thus, even mineral acids such as hydrochloric acid or sulphuric acid can be used for dissolving the oxide film containing iron. However, considering their high acidity and their incompatibility with the underlying metal, strong mineral acids are avoided. Organic complex forming acids such as

1. Ethylene di amine tetra acidic acid (EDTA),

2. Nitrilo Tri Acetic acid (NTA),

3. Picolinic acid (PA),

4. Citric aicd (CA)

are favoured because of their low acidity and compatibility with the system structural materials. Also, these acids do not contain sulphur which is avoided because of its incompatibility with nickel and copper based alloys. Under the low acidic conditions provided by these weak organic acids, the iron oxide dissolution reaction is expected to be low. This is partially compensated by the complex forming ability of these organic acids. The complex formation reaction drives the dissolution equilibrium to the right.

$$Fe_3O_4 + 8\,H^+ \quad Fe^{2+} + 2\,Fe^{3+} + 4\,H_2O$$
$$Fe^{2+/3+} + Y^{x-} \quad Fe^{(x-2/3)-}$$
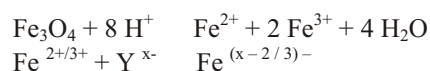
Yet, the high temperature formed oxides and especially oxides such as hematite and nickel ferrite resist dissolution by the organic complex forming acids. The dissolution rates of these oxides are quiet low with these organic acids. Experiments carried out with these oxides showed that reducing agents aid the dissolution of these oxides

Reductive dissolution of Oxides

$$Fe_3O_4 + 8\,H^+ + 2\,e^- \quad 3\,Fe^{2+} + 4\,H_2O$$
e^- is provided by the reducing agent
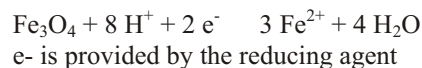
Reduction of ferric in the oxide lattice results in the formation of ferrous ion having a larger ionic size and hence destabilizes the lattice. Also, the ferrous ion formed in the lattice makes the oxide more soluble there by enabling faster dissolution of the oxide by the acid. Both organic and inorganic reducing agents are used for this purpose. Among them the following reagents are popular and extensively used:

(i) Oxalic acid

(ii) Ascorbic acid

(iii) Low oxidation state metal ions (LOMI) eg., V^{2+}(picolinate)

Apart from these reducing agents, the ferrous ion complexes formed insitu in the dissolution reaction eg., ferrous oxalate, ferrous-EDTA etc., can also act as a reducing agent. In the case of oxides formed over carbon steel, its dissolution is controlled by the underlying metal. The underlying

metal itself acts as a reducing agent by participating in the dissolution reaction

Base Metal Aided Dissolution

$$Fe_3O_4 + Fe + 8 H^+ \quad 4 Fe^{2+} + 4 H_2O$$

The participation of underlying base metal is so effective that it makes the externally added reducing agent ineffective.

Thus, dissolution by organic complex forming acids aided by an organic or inorganic reducing agents is a preferred method. Mixtures of complex forming acid and a reducing agent with or without a chemical inhibitor, normally constitute a chemical decontamination formulation. Some of the well known chemical decontamination formulations are:

1. Citric acid and Oxalic acid (CITROX)
2. EDTA, Citric acid, Oxalic acid (CANDECON)
3. V^{2+} (Picolinate), Picolinic acid (LOMI)
4. Pyridine di carboxylic acid, Ascorbic acid
5. EDTA, Ascorbic acid and Citric acid (EAC)
6. NTA, Ascorbic acid and Citric acid (NAC)

These chemical formulations, applied in concentrations of one to few gms/litre, have been proved to be effective in dissolving iron and nickel containing oxides and some of them have been applied in coolant system decontaminations achieving good decontamination factors

Decontamination factor (DF) =

$$\frac{\text{Radiation field before decontamination}}{\text{Radiation field remaining after decontamination}}$$

In systems which do not contain chromium, decontamination factors in the range 2 – 50 are obtained depending on the nature of the system and the material involved. However, these chemical formulations give very poor decontamination factors when they are applied to coolant system surfaces that contain significant amount of chromium.

Oxidizing reagents for the Dissolution of Chromium Containing Oxides

The chemistry of chromium containing oxides differs very much from the chemistry of iron oxides. The chromium containing oxides in the coolant system have varying composition such as Cr_2O_3, $Fe_xNi_yCr_zO_4$ etc. It is very difficult to reduce the Cr^{3+} in these oxides to Cr^{2+}. Chromium (VI) is highly soluble. Hence, instead of reducing the Cr(III), it is oxidized to Cr(VI) by using oxidizing agents such as permanganate.

$$Cr_2O_3 + MnO_4^- \quad 2 Cr(VI) + MnO_2$$

Permanganate as oxidizing agent, can be applied in three different forms:

1. Alkaline permanganate ($KMnO_4$ + NaOH) (AP)
2. Nitric acid Permanganate ($KMnO_4$ + HNO_3) (NP)
3. Permanganic acid ($HMnO_4$) (Used in CORD process)

All the three are effective as oxidizing pre-treatment reagents. However, their effectiveness varies with material to material. Inconel alloy was found to be effectively decontaminated by alkaline permanganate. Where as, stainless steel and Incoloy-800 has been found to be effectively decontaminated by acidic permanganate reagents.

Development of Chemical Decontamination processes

From the fore going discussion it is clear that the choice of chemical reagents for effecting decontamination of a system or a component is material and system specific. The knowledge of material composition, operating conditions and chemistry of the system/component is essential to predict the nature of the oxides formed and the activities present in the surfaces. The chemical reagent is chosen from the nature of the oxides to be dissolved. An oxidizing pre-treatment step is introduced if a system surface contains significant amount of chromium in its oxide film.

The reagents chosen are put to extensive material qualification tests by carrying out corrosion compatibility experiments with all the major and

minor structural materials that are present in the coolant system.

After establishing the compatibility of the chemical formulation and its effectiveness in removing the oxide film and radioactive contaminants from the system surfaces, the question of mode of disposal of the radioactive waste arising out of the decontamination process is addressed. The preferred mode of collecting the metal ions, radio activities and the chemicals, used for the decontamination, is by ion exchange.

The decontaminating chemicals added are re-circulated through a pump, heater and the component/system to be decontaminated. Depending upon the process requirement, the temperature of process is chosen. It is normally in the range $60 – 90^{o}C$. Some processes are applied at still higher temperatures. In the case of processes operated in regenerative mode, a cation exchange column is connected in the circuit. Finally, the added chemicals, the metal ions and activities released from the system surfaces are removed by a mixed bed ion exchange columns.

Full system decontamination of primary coolant systems of Pressurized Heavy Water Reactors (PHWRs)

Most of our reactors are of Pressurized Heavy Water Reactors (PHWRs). Unlike the PWRs and BWRs, the PHWRs are of tube type reactors. The primary heavy water (D_2O) coolant passes through zircaloy fuel channels and takes the heat to steam generator through carbon steel feeders and headers. Radiation field in the primary heat transport (PHT) system of PHWRs builds up over a period of time. A process has been developed to decontaminate the entire coolant system. This process called Dilute Chemical Decontamination (DCD) process is applied to the full system when the reactor is under shutdown. This process has the following advantages:

1. The decontaminating chemicals are added to the heavy water coolant without significant downgrading of heavy water

2. The decontamination is carried out with the fuel in the core

3. The metal ions, activities and the added chemicals are removed on ion exchange resins. Hence, only solid radioactive waste is generated.

4. The system is brought to normal operating condition within 3 – 4 days

The chemical formulation consisting of a chelating agent, acid and a reducing agent is added in concentration of 1 g/litre. The chemical is injected into the system as slurry. The system is kept under circulation using the primary pumps and the temperature is maintained in the range $80 – 85^{o}C$. The schematic of the process is given in Fig. 2. The process is carried out in a regenerative mode. As the concentration of chemical formulation is very low, the formulation tends to saturate because of its reaction with the oxides. The partially spent chemical formulation is continuously passed through cation exchange resin columns in the modified purification system which removes the metal ions and activities and regenerates the formulation constituents. The regenerated chemical formulation joins back the main system and continues the oxide dissolution/decontamination. After exhausting all the cation exchange resin columns, the decontamination process is terminated by valving-in the mixed bed columns consisting of cation and anion exchange resins. The mixed bed columns remove all the remaining metal ions, activities and all the decontamination chemicals thereby bringing back the coolant system to normal operating conditions.

This process has been applied ten times in Indian reactors (MAPS#1&2, RAPS#1&2 and NAPS#1&2) with varying degree of success. Chemical formulations based on EDTA or NTA have been used in these full primary system decontamination campaigns. Good decontamination factors in the range 2 – 30 were obtained on carbon steel components of the system. Where as on Monel-400 and other non carbon steel portions of the system the DF used to be in the range 2 – 7. This process works well in systems that have ^{60}Co and activities other than antimony (^{122}Sb and ^{124}Sb). The Fig. 3 gives the radiation field in various components of the primary coolant system before and after each of the three chemical decontamination campaigns carried out in MAPS#1.
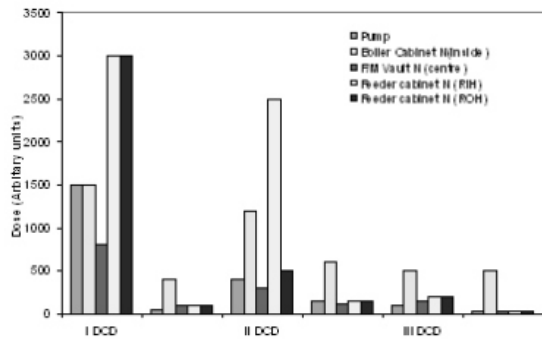
Fig. 3   Radiation field reduction observed in each decontamination campaigns in MAPS

In systems dominated by antimony activities, the above chemical decontamination process brings surprises. Radiation field on the system components does not reduce after decontamination, instead increased fields were observed in certain locations of the primary coolant system. This was attributed to the deposition of antimony activities on the system surfaces during decontamination. The antimony activities (^{122}Sb and ^{124}Sb) present in the core zircaloy surfaces were released during the chemical decontamination campaigns. These activities were existing in anionic form and hence were not removed on cation exchange resin. Under the acidic conditions prevailing in the formulation, these activities deposit on the out-of-core carbon steel and steam generator surfaces. This deposition of antimony activities offsets the field reduction achieved by removing other activities such as ^{60}Co, leading to little decrease in radiation level or in some components increase in radiation field were observed.

Modification of the DCD process to systems where antimony is the dominant activity

Detailed studies carried out on the adsorption behavior of Sb^{3+} indicated that it interacts directly with Fe^{2+} formed in the corrosion reaction and deposits there itself. This gave an indication that if corrosion process is inhibited the deposition of antimony on the surface also can be hindered. Experiment carried out on the deposition of antimony on carbon steel in medium containing chemical decontamination formulation and in the presence of corrosion inhibitor (Rodine 92B),

proved that antimony deposition can be prevented by the corrosion inhibitor.

Based on this study a modified chemical decontamination process is applied to primary coolant systems which are having significant quantities of ^{124}Sb activities. An additional antimony removal step is introduced before the normal decontamination process. A mixture of NTA (100 mg/l)+Citric acid (100 mg/l) + Rodine 92B (100 mg/l) is added to the system and circulated for about half an hour at 85°C under non-regenerative mode (without regenerating the formulation through cation exchange resin as it will remove the inhibitor). The antimony activities released from the core are finally removed on the mixed bed ion exchange columns.

After the antimony removal step and after removing all the added chemicals, activities and metal ions, the normal decontamination carried out in regenerative mode using cation exchange resin is carried out to remove other activities.

This process of removal of antimony activities is superior to the process that uses oxidizing agent. Hydrogen peroxide is used as the oxidizing reagent. It oxidizes Sb(III) to Sb(V), the antimony in the latter form does not deposit on the surfaces and hence all the antimony released from the core are removed on anion IX or the mixed bed. This method has the disadvantange of using an oxidizing agent. PHWRs/PWRs are normally maintained, both during operation and shutdown, under reducing condition.

Problem of `Hotpsots' in the moderator system of PHWRs and its removal

In the moderator systems of some of the PHWRs, `Hotspots' (localized high radiation fields) were observed. Systematic investigations of the 'Hotspots' indicated that they are due to the deposition of particulate activities in the low flow areas. Control rod drive assembly contains rollers made of stellite, a high cobalt (40 -60 %) containing material. Wear of this material result in the release of particulate. These particles are neutron activated in the core to give particles of high specific activity. These active particles settle down in low flow areas causing `Hotspots'.
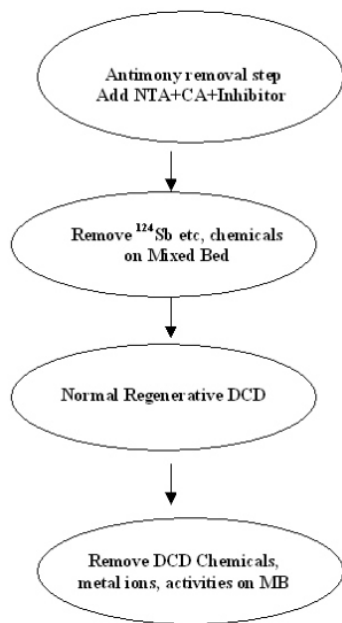
Fig. 4

The moderator system is a stainless steel system which is operated under low temperature conditions ($60 - 70^{o}$C). Hence, hardly any oxide film is expected on the stainless steel surface. Thus, attempt was made to develop a chemical formulation that is capable of dissolving the stellite particle itself. As stellite contains chromium along with cobalt, the reagents used for removing chromium containing oxide films were tested. Experiments carried out with alkaline permanganate, acidic permanganate and permanganic acid indicated that permanganic acid followed by a reducing formulation (EDTA based reducing formulation) is superior in dissolving the stellite particles. Oxidation by permanganic acid followed by reduction by reducing formulation has to be carried out at about 90°C and this cycle has to be repeated thrice to get good decontamination factors. This process has been demonstrated in a component removed from the moderator system of a PHWR. Decontamination factors as high as 11 was achieved on this component.

Decontamination process for stainless steel surfaces of BWRs

The reactor coolant system of BWRs is made mostly of stainless steel. At the high temperature operating condition and under the oxidizing chemistry condition, hematite oxide film containing nickel and chromium is expected to be formed. Permanganate under acidic condition followed by treatment with a reducing formulation is normally recommended. As the oxide film is thin and the redox cycle has to be repeated, the process is carried out under non regenerative mode.

Conclusion

From the knowledge of system structural material, operating condition and the chemistry condition of the coolant, it is possible to arrive at a suitable chemical decontamination process and to reduce the radiation field in the system.

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Removal of Turbidity from Coolant Systems using Electrochemical Filtration

Dr. G.Venkateswaran is a post-graduate in Chemistry from the University of Madras , a Ph.D. from University of Mumbai and is from the 14th batch of Bhabha Atomic Research Centre (BARC) Training School. His areas of specialization are: nuclear power reactor fuel performance evaluation, suspended corrosion product removal from reactor coolants, chemical decontamination of nuclear reactors, metal-ion passivation etc. Turbidity removal from the Dhruva coolant and TAPS Clean-up System Decontamination are his notable projects executed. He over 165 publications in international journals and conferences He is a recognized guide of the Ph.D. programme of Mumbai University and he is a Professor in the Homi Bhabha National Institute in Mumbai. He is currently heading the Analytical Chemistry Division of BARC.

Dr. A.G. Kumbhar is a M. Sc. (Inorganic Chemistry) from Shivaji University, Kolhapur and Ph. D. (Chemistry) from University of Madras, Chennai. He is Experienced in the area of Electrochemical Speciation, Condensate Polishing, Ion exchange, Chemical Decontamination and Health Physics. Currently working in the area of Radiolytic Hydrogen Generation, nano-size turbidity removal with modified ion exchanger and electrochemical filtration for water purification. He is a Post-graduate Teacher at the Homi Bhabha National Institute.

Introduction

In many aqueous coolant systems suspended sub-micron size particles in a low / medium concentration is referred as the turbidity of the coolant. At low concentrations parts per billion (ppb) level of metals, solution may apparently look clear, but at parts per million level (ppm) the coolant can appear very turbid. Turbidity itself or its deposition on surface can cause heat transfer problems to the nuclear power and other industries as well. Such problems were encountered in the form of aluminum turbidity in Dhruva reactor in 1985, in the form of radioactive indium turbidity in Rajasthan Atomic Power Station Unit # 2 (RAPS #2) moderator heavy water system and in the form of iron turbidity in the active process water system (APWS) of Kaiga Generating Station Unit # 1 (KGS # 1). In Dhruva and RAPS it resulted in high radioactivity in coolant which was addressed and in KGS fouling of moderator cooling intermediate heat exchanger was combated. Removal of turbidity due to its feeble particle charge and low concentration is problematic. Electro-deposition of particles on porous graphite/Carbon electrodes is one of the best-suited methods for such turbidity removal. Initially, a prototype electrochemical filter (ECF) was fabricated and tested for indium turbidity removal at RAPS #1. Subsequently a larger version of the ECF was designed and in house fabricated and was deployed for iron turbidity removal at Kaiga and for silica and iron turbidity removal at Kalpakkam. ECF showed 75-80% turbidity removal along with 50% capacity for non-reactive silica removal and near complete removal of microbes.

PZC of iron turbidity particles and ECF carbon felt

Turbidity in solution arises due to charge on the particles. Most of the suspended particles containing hydrours / hydrated or hydrous oxides or mixed oxides will have point of zero charge (pzc) For example, iron containing Fe in the Fe_3^+ or in $[Fe^{2+}+Fe^{3+}]$ state, will have PZC values in the range of 6.0 to 8.5: F_3O_4: 6.5, $-Fe_2O_3$: 6.7, Fe_2O_3 : 6.7, $-FeOOH$: 6.7, $-FeOOH$ 7.4, $Fe(OH)_3$ (amorph) :

G. Venkateswaran, Analytical Chemistry Division Bhabha Atomic Research Center, Trombay, Mumbai 400 085and A.G. Kumbhar, Water and Steam Chemistry Division, BARC Facility, Kalpakkam, Taml Nadu; E-mail:

8.5 [1]. At a particular solution pH particle surface charge ism governed by the equation:

$$= k \, (pzc - pH) \tag{1}$$

where ' ' is the zeta potential of the suspended particle, 'pzc' is its point of zero charge and pH is the solution acidity in pH units. The zeta potential of graphite felt particles suspended in distilled water was found to be -25 mV at neutral pH. Even at a pH of 1.5 the graphite felt particles were found to carry a negative surface charge. Hence by the natural zeta potential effect the hydrated / hydrous oxides of Fe^{3+} will be electrostatically repelled from the fibrous graphite felts. However, in the present study, these graphite felts are made anodic / cathodic with the help of an applied potential thus overcoming its natural zeta potential effect.

Turbidity in a large cooling water system, due to suspended micron or submicron size particles and at low particulate concentration, poses a problem for its removal by normal micron / sub-micron filtration or by ion exchange process. Surface modified ion exchangers resins i.e., precipitated ion-exchange (PIE) resins can be used for this purpose but this requires a back-up normal ion-exchange column to remove the soluble metal ions, resulting from the limited solubility of the precipitate from the PIE resin, which otherwise can enter the main system as impurities [2]. When the turbidity levels are low, this washing-out effect impacts on the throughput realizable by these precipitated ion-exchangers. Thus the use of PIE resins has limitations if one encounters large system volumes of dilute turbidity to be cleaned up. Commercial Zeta-potential filters on the other hand employ a special cartridge (housed in an outer shell), which has a thin coat of a material on a base matrix with zeta-potential opposite in sign to the zeta potential of the suspended particles. They are very suitable for treating very dilute turbidities {< 5 Nephelometric Turbidity Units (NTU)} but in the middle range (5-10 NTU) and high range (> 10 NTU) can give rise to problems of cartridge change which requires new filter procurement as these filters are once-use throw-away type [2].

Electro-deposition of suspended particles from a turbid solution on graphite felts is another method for this type of dilute turbidity removal from water [3]. The higher surface area (typically 10-12 m^2/g)

with a concomitant improved contact with flowing solution, high fluid permeability with free flow of the solution without back pressure to higher flows and chemical, electrochemical inertness, their regenerability and reuse makes the graphite felt electrochemical filter more suitable for dilute turbidity removal.

Indium Turbidity removal from RAPS # 1, Moderator Heavy water:

It is very difficult to remove metal ion based colloidal turbidity from water using normal filters, which can remove particles of up to a few micron size only. In nuclear power stations such a turbidity containing an element, which gets activated by neutrons, can create a radiation exposure problem to the operation and maintenance staff. For example, a leaky calandria Over Pressure Rupture Device (OPRD) of moderator system of Rajasthan Atomic Power Station (RAPS-I) was sealed using indium (In) metal in March 1998. Under normal operating conditions, moderator does not come in contact with this indium sealant. However, the condensing moisture on this sealing surface containing some radiolytically produced HNO_3 caused corrosion of this indium metal and introduced indium in the moderator heavy water. In the neutral pH regime of moderator the indium seemed to have formed colloidal indium turbidity. Due to a reasonably high neutron absorption cross section (170 barns) ^{115}In (95.7% isotopic abundance) got converted to radioactive In^{116m} ($t_{1/2} = 54$ min, E = >1 MeV). This created operational problems while handling moderator heavy water samples for analysis of chemistry parameters. Hence it was necessary to remove the indium turbidity from the moderator system. As the size of turbidity particles was very small (< 1 µm) and indium concentration was very low (100-150 ppb), it could not be removed by normal filtration or by the system purification ion exchangers. Two approaches were studied to remove this indium turbidity. A Mg-Mg(OH)$_2$ precipitated weak acid cation exchanger resin which was earlier demonstrated by us in laboratory as well as in the actual reactor system for removal of aluminum turbidity (2) was tried and found to satisfactorily remove this indium turbidity. Removal of indium turbidity was also attempted by
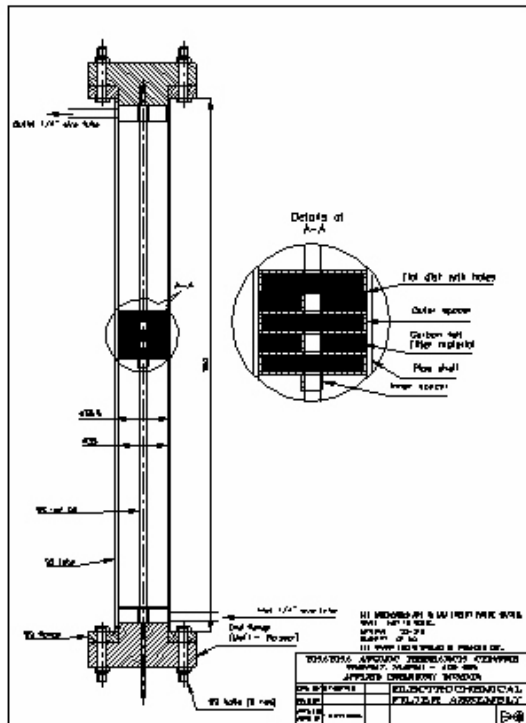
Fig. 1   Schematic of ECF

Fig. 2   Indium Turbidity Removal: from laboratory generated turbidity using Electrochemical filter

electrosorption on fibrous graphite. The results of electrosorption study are given bellow.

Fabrication of an Electrochemical Filter (Fig. 1)

The basic design of the electrochemical filter in this study is based on an earlier work reported in literature regarding removal of aluminum turbidity from D_2O in a nuclear reactor (4). The filter fabricated by us had 14 cathode anode pairs of fibrous graphite felt discs (each felt of ~6 mm thickness and of 35mm dia) The felt discs were separated and supported by 2 mm thick perforated polyethylene plates. A central SS rod connecting a set of 14 such felts and a outer SS cylinder connecting another set of 14 felts served as the electrode leads for impressing the potential in order to make the two felt sets as anodes and cathodes. The filter could be operated at a flow rate of 23 ml/min, so as to give a contact time of 2 min.

(i)   Lab generated turbidity removal

Results of a run performed on laboratory-generated turbidity with electrochemical carbon felt cell are shown in Fig. 2. At high (4.6 ppm In) and low (0.23 ppm In) indium inlet turbidity level, outlet indium was less than 0.001 ppm excepting the initial slip of 0.03 ppm at the beginning of low concentration run. Under closed circuit conditions applied field during low concentration run, 50 V emf was applied to cell and a current of 20 mA was observed. During the high concentration run 16.5 V emf was required to get 20 mA [5].

(ii)   Removal of moderator turbidity

A block diagram of the experimental setup as connected to the moderator sampling station as shown in Fig. 3. As shown, the filter was operated with the inlet moderator D_2O flowing from the bottom of the column to top and the exiting heavy water was collected in a plastic carboy. The valve arrangements made in the hook up of this column to the moderator sample point permitted a minimum flow rate of about 30-35 ml/min. A 1.2 m height semicircular lead screen mounted on a trolley was employed to isolate the experimental set up in the moderator sampling area. The turbidity removal was followed by monitoring the [116m]In radioactivity in the electrochemical filter column inlet and outlet solutions. The 2112.3 keV gamma (yield 15%) was chosen to minimize the compton scattering interference in the photo peak area determination of this isotope. HPGe (high purity germanium) detector coupled to a 4 K multichannel analyzer was used for the gamma counting. Additionally the dose rate
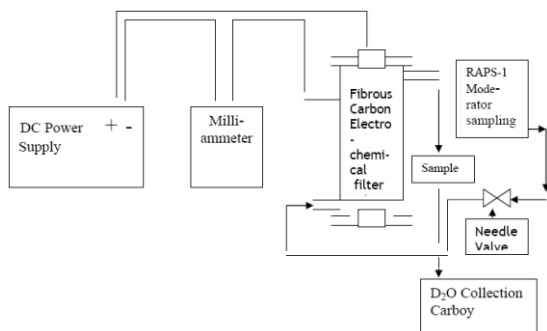
Fig. 3   Block diagram of Indium turbidity test removal setup connected to RAPS moderator sampling point

measurements near bottom (close to inlet), middle and top (close to outlet) zones of the column were carried out to assess the progress of Indium turbidity removal. This was done using an teletector dose monitor. Since the different zones of the column could not be shielded, a zone with a higher field (expected to be the bottom inlet zone) contributing to the dose measured at the upper lower dose zones (middle and top) is anticipated

In order to minimize the radiation exposure to personnel involved in the experiments it was felt prudent to connect the electrochemical filter to the system immediately after a shutdown of the reactor and monitor both inlet and outlet solution Indium

radioactivity levels at regular intervals of time on 4-12-01 at 1342 h. The electrochemical filter column was connected to the system within 90 minutes after reactor shutdown (i.e., 1510 h). Since reactor was shutdown, the normal ion-exchange inlet sampling point (SS#3) could not be made use of for providing the moderator D_2O to the electrochemical filter column and instead the adjuster rod moderator D_2O cooling water line sampling point was used for this trial removal study. Since it takes more than 40 minutes to get the heavy water flowing through this sample line from the core to the sampling point, the first column inlet and outlet samples were taken at 1620 h i.e., 70 minutes after valving-in the column. The electrochemical filter was operated at an applied potential of 40 V and a current of 0.8-1.4 mA could be realized. The temperature of the moderator was close to 303 K during this study.

Table 1 shows the performance of the electrochemical filter column in removing Indium from the moderator in terms of [116m]In radioactivity levels at the column inlet and outlet, percentage Indium removed, cell currents and cell voltage. As seen in the data of Table-1, the inlet activity was decreasing with time since the experiments began after the shutdown of the reactor. Except for the first inlet value (1620 h), the other values seem to follow closely the half life of [116m]In. The first value (3700 Ci / l) appears to be   20% lower than its expected value which is calculated from the second and

TABLE 1. Test removal of Indium from moderator of RAPS-1: Radioindium data

No	Sample time (minutes)	Cell Voltage (V)	Cell current (mA)	[116m]In activity (Ci / l)		Percentage Indium removal
				Column inlet	Column outlet	Removal Factor (RF)[*]
1	0	40	1.3	3700	200	94.6 / 18.5
2	72	40	1.0	2258	189	91.6 / 11.9
3	135	40	0.9	918	89	90.3 / 10.3
4	215	40	0.8	425	65	84.7 / 6.5
5	275	40	1.4	143	24	83.2 / 6.0

*Removal Factor (RF) = Column inlet activity / Column outlet activity
Percentage Removal = [{1 (1 / RF)}] 100

further activity values using the radioactive decay equation after applying the decay correction. The adjuster rod cooling water-sampling point is not normally used for moderator sampling during reactor operation. Hence the somewhat lower first value could possibly be because of some mixing of stagnant heavy water in the sample line with the actual moderator sample. The waiting period of 70 minutes after valving-in (at 1510 h) and before sample collection (at 1620 h) appears to be somewhat less than the actual time lapse required for a representative sample collection after valving-in the column. Once a steady flow of the actual moderator heavy water was established through the column, samples were collected at any time   from both the inlet and the outlet positions of the column. It may be noted that it takes about 6 minutes for the inlet water to come out of the column and in this period there could be   8 % reduction in the activity of outlet samples compared to sample entering the inlet. Hence any reduction in the outlet activity greater than 7.5% is to be attributed to the sorption capacity of the column. As such the activity of the outlet samples (Table 1) was not corrected for decay for this period of transit (6 min) through the column. However, the radioactivity values of inlet and outlet samples were decay corrected for the time elapsed between sample time and count time.

The percentage Indium removal can be expressed by the equation (1):

% removal = [{1 (1 / RF) }100]   (1)

where RF, the removal factor = Column inlet activity / Column outlet activity

Due to electroadsorption of colloidal Indium, the electrochemical filter column outlet activity values are lower by a factor (RF) ranging from 18.5 to 6. As seen from the table, the Indium removal has decreased from   95% in the initial stages to   83% at the end of about 6 h of run. It may be noted for this 12% decrease in removal, the RF value has decreased by 66%, i.e., from an initial value of 18.5 to the end of run value of 6. The decrease in % removal as indicated by radioactivity measurements may be arising due to decrease in the inlet activity values and not due to any reduction in the efficiency of column to sorb the Indium. It is well known in chemical decontamination operation that locations with higher initial radioactivity tend to show higher decontamination factors (higher % oxide removal) than those where the initial activity is lower. We thus infer that a 85-90 % removal efficiency can be assigned to the electrochemical filter column. We may also argue that the efficiency could have been higher than 90% had the column been operated at its designed flow rate of   20 ml / min against the minimum flow rate of 30-35 ml / min that could be achieved in this test removal experiment. We could ascribe this reason since in a pilot run conducted a day earlier when the reactor was operating at constant power of 90 Mwe and when the flow rate could only be adjusted to a minimum of 60-70 ml / min, no sorption of Indium activity by the column was observed.

Table 2 shows the radiation field accumulated on the column with the progress of the test removal run. The radiation field on the column at any time is a resultant of the earlier sorbed Indium activity decaying with time and freshly sorbed activity, the latter being at a lower value at   as compared to the value at an earlier time t -   t) . Accordingly the radiation field observed at the bottom of the column has shown a lower decrease with time than the decrease warranted by half-life. However, the radiation field at the column outlet had remained nearly steady at   300-400 mR / h (3-4 mSv/h) without showing a decrease similar to the bottom of the column. This is due to the background   shine from the bottom of the column contributing to the dose measurements at the top of the column. The high field at the bottom of the column shows that it is the initial 4-5 anode/cathode pairs, which essentially contributed to the sorption process. The cell current of   1 mA applied to the electrochemical cell induced a voltage of 40 V. Since the moderator had a conductivity of 0.5   S cm^{-1}, it is likely that most of the voltage drop occurs across the solution resistance and only a small portion of the applied voltage is experienced by the electrical double layer to drive the adsorption process. Unlike the experiment with laboratory generated turbidity, the present experiment with moderator Indium turbidity could be not be conducted without applying the field (since radioactivity in the moderator was decaying and the cell could only be operated in the desired applied field mode to collect the turbidity removal data) to

TABLE 2. Radiation field on the electrochemical filter during test removal of Indium from the moderator of RAPS-1

No	Sample time (min)	Radiation Field on Electrochemical Filter Column (mR / h)		
		Bottom (inlet) of column[@]	Middle of column	Top (outlet) of Column
1	0	> 10000	2000	400
2	72	5000	1800	350
3	135	3000	800	300
4	215	2500	700	300
5	275	1400	450	300

@The terms bottom, middle and top of the column refer to about 10-12 cm length of each of these portions of the column as seen by the sensor of the teletector monitor.
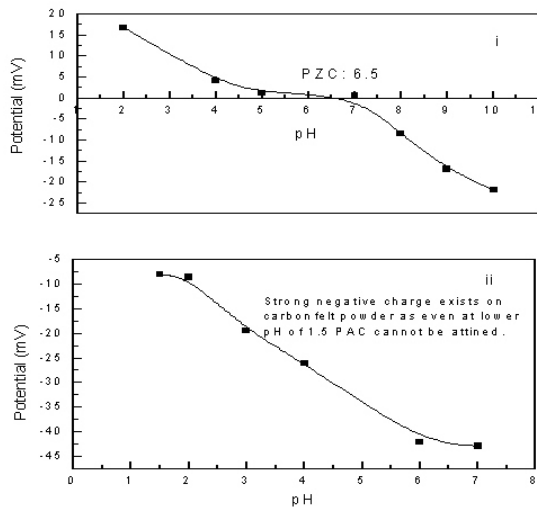
Fig. 4a (i) Plot of charge vs. pH for PZC of KGS#!1, APWS turbidity.
(ii) Plot of charge vs. pH for carbon felt powder used in ECF.

assess as to what extent the applied field has helped. In the case of laboratory generated Indium turbidity, the removal was quantitative even without applying the electrical field. However, it is reported that in the removal of aluminum turbidity (colloidal Al_2O_3) by this fibrous carbon electrode method, the application of electric field had helped in clearing the turbidity to the clean water level while without field about 90% reduction in turbidity was noticed (4).

Zeta potential of carbon felt particles suspended in distilled water was found to be <-25 (clost to 5mV) mV at neutral pH (Fig.4a) and was similar in sign to indium turbidity (-22 mV).

This indicates that during open circuit conditions turbidity removal is by physical adsorption and during close circuit condition by electrostatic attraction and physical sorption.

Microbes removal from RAPS #2 Moderator Heat exchanger Water

Significant sensitivity reduction was observed in online tritium monitor system of RAPS-2. This was identified as due to microbial fouling of surface of the plastic scintillation detector [6]. A twenty times reduction in microbial population was observed when the sample was passed though ECF under closed circuit condition (Fig.5a). Based on this work sample conditioner system modifications were suggested in existing online tritium monitoring facility at RAPS-2 (Fig.5 b)

Iron turbidity removal from APWS of KGS #1

The Active Process Water System (APWS) at Kaiga Generating Station (KGS) units-1&2 (Schematic-A) experiences iron turbidity to
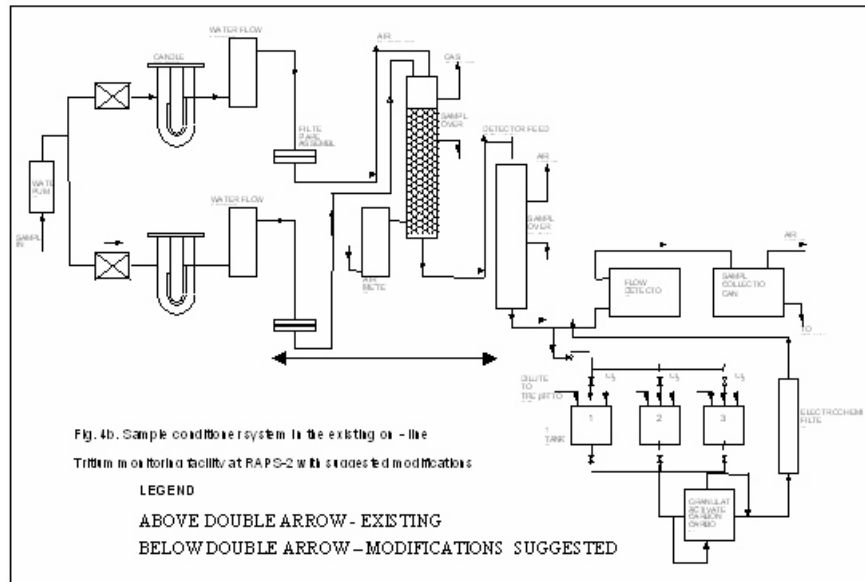
Fig. 4b. Sample conditioner system in the existing on – line

Tritium monitoring facility at RAPS-2 with suggested modifications

LEGEND

ABOVE DOUBLE ARROW - EXISTING

BELOW DOUBLE ARROW – MODIFICATIONS SUGGESTED

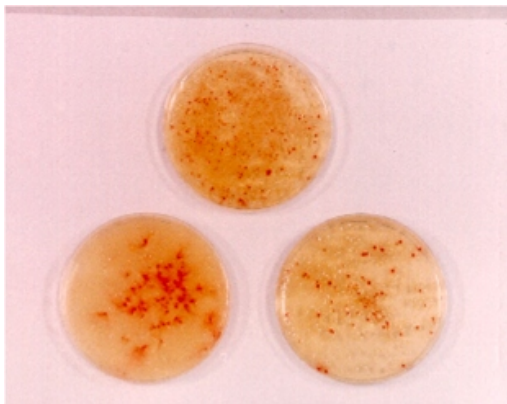*Fig. 4b   Sample conditioning system modifications for online monitoring Tritium monitoring system*

Fig. 5a   Macrographs of microbes grown in nutrient
Rich medium in process water sample of RAPS-2 collected after the sub-micron filter(top a), after passed through the electrochemical filter without field (left b) and after passed through the electrochemical filter with field (right c)
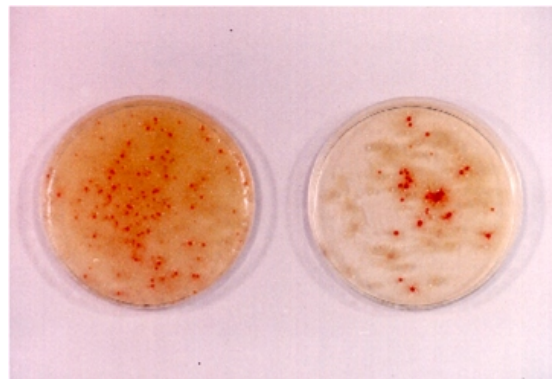
Fig. 5b   Macrographs of microbes grown in nutrient rich
Medium in process water collected directly (before the system Filter) passed through the electrochemical filter without field (left d) and with field (24V, 350 mA) (right e)

different levels during various operational periods of the system. The entry of iron corrosion products from the backup fire water system seems to be the cause for the observed turbidity levels in APWS. On the one hand, APWS cools the shell-tube type moderator heat exchanger [7] and on the other hand it rejects this heat to the Active Process Cooling Water System (APCWS) through plate type heat exchanger(s). The water in APCWS in turn gets cooled by the Induced Draft Cooling Tower (schematic-A). The continued operation of turbidity ridden APWS can result in fouling of the plate type
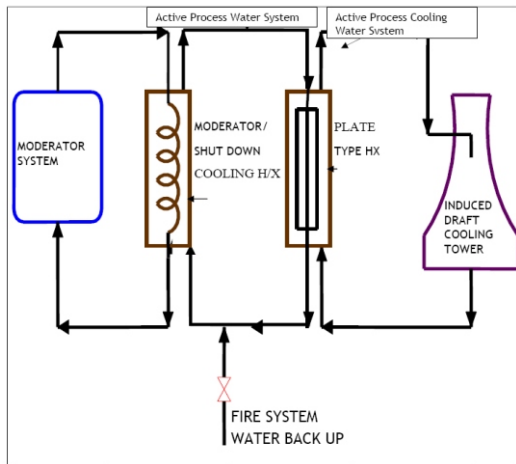
Scheme A: Active Process Water System (Apws) At Kgs

HXs through deposition of iron corrosion products. Such a fouling of the heat exchanger reduces the desired cooling efficiency of APWS to maintain the temperature of moderator water within the specified limits, which in turn will have safety implications.

An in-house designed and fabricated electrochemical filter (ECF) containing alternate array of 33 pairs of cathode and anode graphite felts was successfully tested for the removal of iron turbidity from Active Process Water System (APWS) of Kaiga Generating Station unit-1 (KGS # 1).

Electrochemical filter (ECF) fabrication

A cross-sectional view of the fabricated ECF is shown in Fig.6. The outer cylinder (integrated with flanges), central pipe leading the inlet turbid solution and the inlet / outlet connections of the filter are made of stainless steel. 33 pairs of circular graphite felt anode and cathode of about 6mm thickness 150 mm diameter supported on perforated polymethylmethacrylate (Perspex) plates were assembled inside the cylinder (clearance between SS shell and the felt housing made of Perspex is 13 6 ìm). Alternately, a set of 33 discs of graphite felt was contacting outer SS cylinder at periphery of the cylinder and was isolated from the central SS pipe using spacers and another set of 33 discs was contacting central SS pipe of the filter and was isolated from outer periphery of the cylinder using
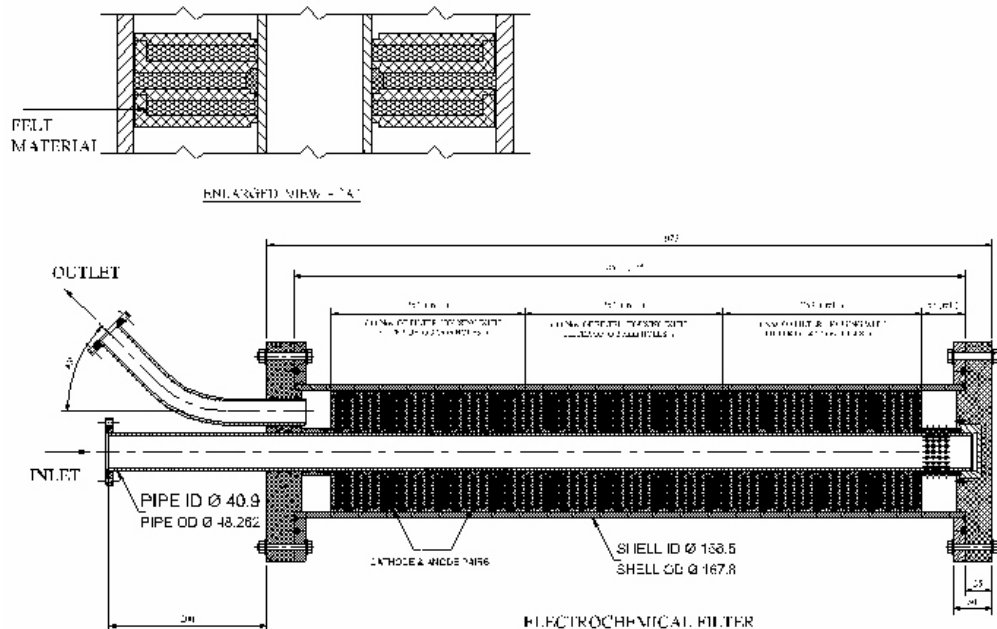

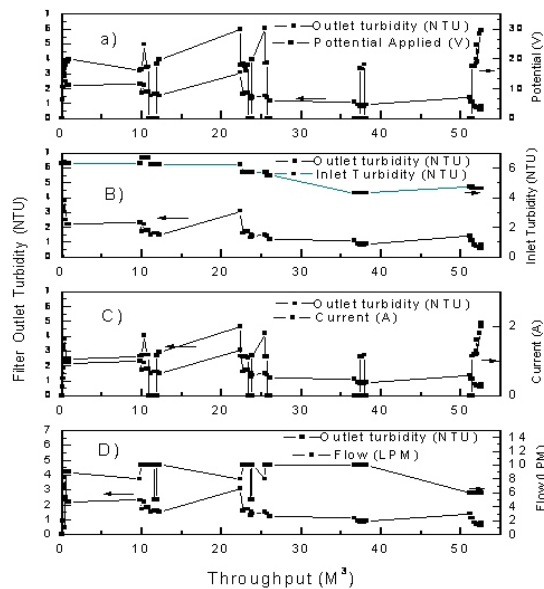*Fig. 6   Cross sectional view of electrochemical filter*

Fig. 7   ECF testing at KGS #1, APW system. : ECF Outlet turbidity as a function of potential applied, inlet turbidity, current and flow

box type cathode support perspex plates. Thus the electrodes could be used as alternate anodes and cathodes while applying potential. Both inlet and outlet of the filter were connected from top of the filter. The central stainless steel pipe served as inlet to the filter with water flowing down through the pipe and rising above from the bottom through a bottom end spacer, then through the perforated perspex plates holding the cathode/anode graphite felts before exiting. The inlet flange portion of the central SS pipe and the flange part of the main SS shell were used as contact points for imposing the electromotive force. The central SS pipe was Teflon coated from inside to avoid streaming currents due to flow. Graphite felts were activated by heating them in oven at 450ºC for 2 h in air oven prior to packing them in the ECF.

Effect of Potential, flow, and inlet turbidity variation on ECF outlet are shown in Fig.7. The operation of electrochemical filter has revealed the possible occurrence of three phenomena simultaneously: a) the settling of negatively charged oxide particles on the anode surface, b) the release of gravity settled particles causing turbidity possibly from the cathode surface, and c) the effect of O_2 and H_2 evolution on the settled oxide particles from the electrode (anodic and cathodic) surfaces. When the turbidity values are high, application of potentials of the magnitude of 20 V appears optimum for turbidity removal (75% removal). Once sufficient accumulation occurs on the fibrous felts, this efficiency is observed even when there is no applied potential. But once low levels of inlet turbidity are reached (< 5 NTU) then outlet turbidity could be suppressed further (1 NTU) by increasing the potential beyond 20 V i.e., 25 to 30 V. Hence for each application of turbidity removal an optimization of parameters like potential and flow vis- vis inlet turbidity requires to be carried out.

After flowing 40 m³ of APCW through the ECF, with the existing 0.5 hp pump, flow could not be maintained at 10 lpm and it decreased slowly to 6 lpm. This may be due to the clogging of the filter and hence the run was terminated. At this point the outlet ECF turbidity was 0.6 NTU indicating that the filter has still capacity to remove turbidity and it has not it reached to saturation. Towards the end of the run, the applied potential was 29 V, current was 1.4 A and the filter showed an efficiency of 87 %. As far as a submicron sized and low concentration turbidity removal is concerned such an efficiency exhibited by the ECF indicates its satisfactory performance. At the termination of the experiment, a throughput of > 2.08×10^5 NTU-liters could be realized and still the filter was working with about 85% efficiency. At the end of the experiment the internals of ECF were removed for observation. Only about 30% of the felts from the bottom of the filter were found to be used up and the rest appeared new and unused. Hence the throughput of this filter is expected to be much more than 2×10^5 NTU-liters.

Turbidity removal from Pond Water used for Cooling Heat Exchanger at Kalpakkam

Turbidity of HTHP cooling pond was 3-5 NTU. In case of APWS KGS #1, the water was DM water with additive to make pH to 9.0-9.5. But, in this case it was a open storage tank natural water, hence it contained both macro and micro turbidity. As, the ECF is exclusively for removing micro turbidity, the bottom felts of ECF were often getting choked due to macro turbidity. Out of two runs
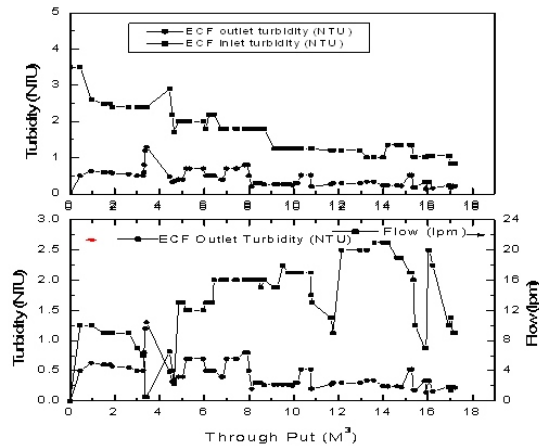
Fig. 8   Run No. 1: Effect of inlet turbidity and flow on ECF operation at WSCD Kalpakkam

Fig. 9   Run. No. 1: Effect of potential and current on ECF operation at WSCD, Kalpakkam.

conducted with this water in the first run 17.2 m^3 water was processed with 2.15 x 10^4 NTU-liters turbidity removal. In this run a clogged bottom carbon felt pairs were removed each time when 4.65, 12.14 and 15.92 m^3 of water was processed. At the end of 4.65 m^3 through put a cartridge filter was also incorporated in the before the inlet of ECF to take care of macro turbidity. After 12.14 m^3 throughput it looks like other 31 felts also might have got clogged with the turbidity and hence removing the third pair of bottom felts at the end of 15.92 m^3 did not help in extending the run further. Due to back pressure the run has to be terminated at 17.21 m^3 throughput.

At this point the storage pond turbidity was reduced from 3.6 NTU to 0.85 NTU (75 % turbidity removal).

With the average inlet turbidity of 1.67 NTU and outlet turbidity of 0.42 NTU. ECF efficiency of 74% was realized. The effect of applied potential, current, flow rate and inlet turbidity on ECF outlet turbidity are shown in Fig. 8 and 9. Flow rate of 10-20 lpm, potential of 5-8 V with current of ~ 1A and an attachment of a cartridge filter before inlet were the optimized as ECF operational conditions for the efficient turbidity removal of Kalpakkam water.

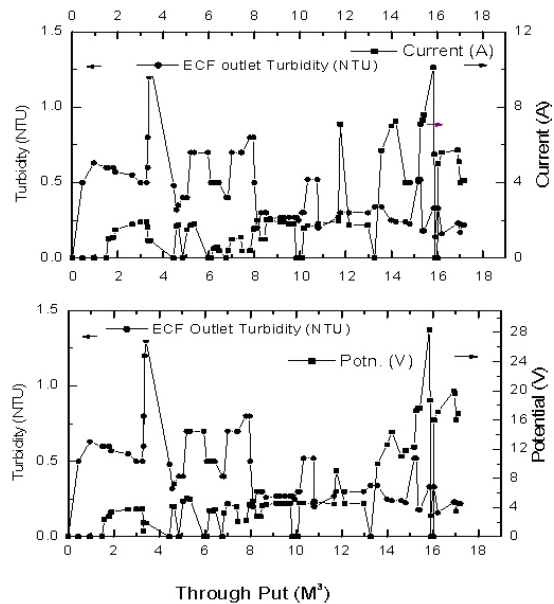In the second run ECF was packed with top 25 empty Teflon spacers followed by six cathode /

anode pairs and two bottom empty spacers. The cartridge filter was also attached before the ECF inlet. Effect of applied potential, current and flow rate is shown in Fig. 9. As, in the earlier first run earlier most of the macro turbidity was removed the inlet turbidity level in this was only 0.85 NTU. In this run most of the time ECF inlet and outlet turbidity level remained constant with a inlet value of 0.85 NTU and a outlet value of 0.27 NTU. Continuous decrease in flow rate (18.0-4.5 lpm) with increasing throughput was observed during the run, indicating the continuous loading of filter with turbidity. Optimum potential of 5.2 V and current of 1 A was established for efficient functioning of ECF. 6.65 m^3 of water was processed with 3.87 10^3 NTU-liter turbidity removal. The efficiency of 68 % was realized which is quite satisfactory for low level (> 1 NTU) and sub micron turbidity removal.

Silica (Si) content in Kalpakkam water was 19-29 ppm, of which 0.7-0.8 ppm was non- reactive Si. Non reactive Si is crucial to super critical steam generators as it passes through ion exchange purification system and then gets converted in the reactive Si resulting in silica deposits on the turbine blades. Table.3 shows Si analysis from WSCD,
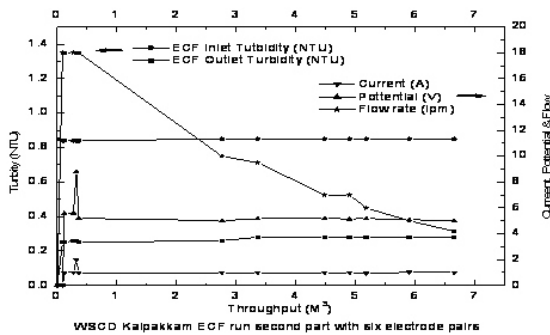
Fig. 10 Run No.2: Effect of Inlet turbidity, flow, potential on ECF operation at WSCD, Kalpakkam

Kalpaakm experiment. Although, no reactive Si removal was shown by ECF, 50 % efficiency for non reactive Si removal was observed. By considering low inlet non reactive Si concentration (0.6 ppm), the observed 50 % reduction in outlet (0.3 ppm) is quite effective. ECF also showed near complete removal of Coliform S microbs from water.

Conclusions

1. Prototype electrochemical filter shown to remove radioactive indium turbidity from RAPS # 2 moderator heavy water

2. The filter was also tested for microbes removal and a modification in tritium detector assembly was suggested for preventing fouling.

3. Test of the pilot plant scale electrochemical filter employing fibrous graphite felt electrodes with APWS of KGS #1 and WSCD Kalpakkam service water has shown that the fine turbidity from the system could be removed effectively.

4. Applied potential, flow rate and the effect of open-circuit conditions were evaluated for the turbidity removal. An applied potential of 20V and a flow rate of 10 lpm was found to be optimum for APWS, KGS #1, and applied potential of 5-8 V and flow rate of 10-20 lpm was optimized. In both the cases ECF showed an average efficiency of 75%.

5. Turbidity removal by ECF involves no addition / hookup of any chemical or chemically loaded ion-exchanger in the system and the method is independent of zeta-potential of the particles unlike in the case of commercial zeta-potential filters

6. ECF can also be used for microbes removal and non reactive Silica

Acknowledgements

TABLE 3. Effect of Applied potential and flow on turbidity and non reactive silica removal by ECF

Date	Time (h)	Th put (M³)	Flow (lpm)	Potential (V)	Current (A)	ECF Inlet			ECF Outlet		
						Reactive Si	Non reactive Si (ppm)	Turbidity (NTU)	Reactive Si (ppm)	Non reactive Si (ppm)	Turbidity (NTU)
03.06.08	17.35	00.45	10.0	0	0	19.2	0.85	2.6	18.8	0.54	0.63
	20.05	01.80	09.0	2.76	1.09	19.20	0.70	2.4	19.10	0.38	0.57
04.06.08	00.30	03.31	05.0	1.64	0.80	19.31	0.49	2.4	19.12	0.28	0.80
	11.00	04.50	06.5	0	0	19.20	0.70	2.9	19.10	0.20	0.48
05.06.08	11.20	04.85	13.0	0	0	19.00	0.50	2.0	18.80	0.30	0.40
06.06.08	11.00	14.20	21.0	14.35	7.25	18.90	0.40	1.4	19.10	0.10	0.24

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Corrosion of Primary Heat Transport System Carbon Steel Material in PHWR

Hariharan Subramanian *(M.Sc. Applied Chemistry, Cochin University of Science and Technology, India) joined Water and Steam Chemistry Laboratory of Bhabha Atomic Research Centre in the year 1997. His field of interest includes decontamination and high temperature aqueous corrosion.*

Structural materials in power plants interact with high temperature aqueous environment in the heat transport system. The main structural materials in the primary heat transport system are Carbon steel 106 Gr-B as piping, Incoloy-800/Monel-400 as the steam generator material and Zr-Nb/Zircaloy-2 in the core. Every effort is made to minimize the corrosion and its impact on operation of the plant. A major emphasis is given to maintain the chemistry of coolant water during operation of the reactor and its shutdown. This paper mainly deals with the corrosion behavior of carbon steel in the primary heat transport system of PHWR. Corrosion of carbon steel structural material contributes to the radiation field build up in out of core surfaces and leads to excessive wall thinning of carbon steel outlet feeders necessitating mid course en-masse replacement of feeders. Any attempt to inhibit corrosion would also address these two phenomena.

The Radioactive Deposit Problem

Radioactivity build-up in the primary heat transport (PHT) system, due to corrosion and activation of corrosion products in nuclear reactors; results in exposure of personnel to radiation field during maintenance work. Considerable R&D is being done to reduce the radiation field build-up in the primary coolant system. Radioactivity build-up in the primary heat transport system is due to corrosion and activation of corrosion products. World over attempt is being made to develop new structural materials and to frame strict chemistry control regimes to mitigate this problem. There is very little scope of tinkering with the structural materials in operating reactors except for minor refurbishment. However effective water chemistry control can help in taming this problem.

Structural materials used in primary heat transport system such as Carbon Steel, Stainless steel, Monel-400, Incoloy-800, Stellite etc corrode to form solubles, colloids and particulates which, are transported to the core and activated. These activated corrosion products are re-transported by the coolant and deposited on out of core surfaces. ^{60}Co is found to be one of the main contributors to the radiation fields existing on out of core surfaces. Most of the corrosion product oxides in the PHT system are spinel type of oxides. Effective pH and chemistry control, Hot-conditioning etc. minimize corrosion and corrosion product solubility whereas sub-micron filtration, Ion-exchange purification etc. reduces the inventory of corrosion products in the water coolant. Full system decontamination and component decontamination help in reducing this radiation field but the beneficial effect is available for short duration. A long-term remedy should address the root cause of the problem namely corrosion and corrosion release. All the external additives added to the PHT system aim at achieving this goal.

Protective Oxide Film on Metals

Controlling the corrosion and corrosion release of materials involve understanding the mechanism of formation and stability of the corrosion product films on them. Corrosion of structural materials like

Hariharan Subramanian, Water and Steam Chemistry Division, BARC Facilities, Kalpakkam, Tamil Nadu 603 102; E-mail: hsub@igcar.gov.in
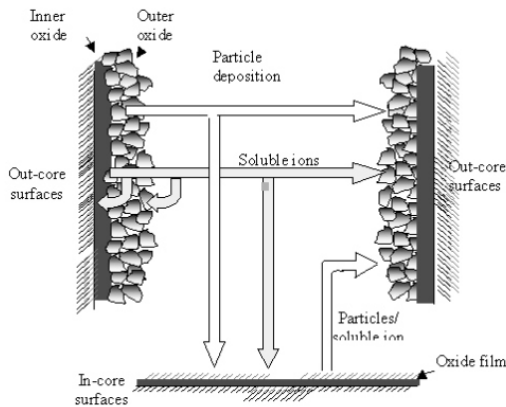
Fig. 1   Duplex film

Carbon steel, Stainless steel etc. in the PHT circuit results in the formation of duplex layers (Fig. 1). The inner layer is a few nanometers thick and fine grained. The outer layer can run in to a few microns and consists of large crystallites and is highly porous in nature. Growth of oxide film proceeds by ionic transport in the film. The composition and structure of the film determines the species that moves across the film. Build-up of oxide film on reactor structural materials is due to the transport of oxygen and cationic species to and from Oxide-Solution interface. Cation transport contributes to film growth, film dissolution and re-deposition. The driving force for this mobility is either a concentration gradient or a potential gradient. Metal Oxide to metal volume ratio (P.B ratio) for Iron Oxide Fe_3O_4 is ~2.1. This indicates that only ~50% of the iron (as oxide) corroding from the base metal is required to fill up the void created by its removal. The rest of the iron is transported to the oxide solution interface. This iron can deposit insitu as outer oxide or can be transported and removed by purification or deposited elsewhere in the PHT system. The growth stresses in the inner layer due to volume constraints creates micro pores which can act as access channels for the water to reach the base metal. In the case of availability of an external circuit for charge flow, the conversion of excess iron to oxide need not occur insitu. Depending on the constituents of the base metal, the inner and outer layer composition varies and it also affects the kinetics of the process.

Activity incorporation in Oxide

Many activity deposition mechanisms such as co-precipitation, adsorption, ion exchange are known which result in accumulation of ^{60}Co on these spinel oxides. The intake of activity in to this film can be in different ways. Activity as particulates can stick to these oxide surfaces. Activities in soluble form can be adsorbed or exchanged on the outer layer oxide. The activity can also be incorporated right during the formation of the outer layer. The inner layer porosity is very less, so ingress of activity in to this layer demands transport through grain boundaries or by transportation along lattice defects. In the point defect model the film grows by generation of cation vacancies at the oxide solution interface and their annihilation at the metal oxide interface. The resulting flow of vacancies is the basis of film growth in this model. These vacancies can pick up these active metal ions. An alternative to this is the transportation of activity along the grain boundaries. The diffusion constants indicate that the grain boundary diffusion is more (five orders of magnitude larger) feasible than volume/Lattice diffusion. Of course the pore diffusion constant does dominate, but as mentioned earlier the extent of porosity in the inner layer is extremely small. So ^{60}Co could migrate in to the pores under a concentration gradient. Electrical field in the oxide will counteract this and the rate will be reduced. At the end of a closed pore, grain boundary transport takes over and further incorporation in to the grain is by lattice diffusion. The latter step is a very slow one as compared to the other two. Hence, activity incorporation can take place both in the outer and inner layer of oxide.

The activity transport and hence radiation field build up are part of the corrosion phenomenon and hence can be controlled by controlling the corrosion of reactor structural materials. Corrosion can be controlled by the following ways:

1.   Pre conditioning of structural materials (like hot conditioning)

2.   Optimisation of water chemistry

3.   Metal ion passivation

Use of structural materials containing no or minimum cobalt and full system decontamination
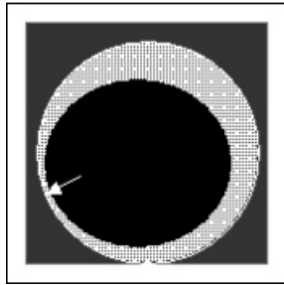
Fig. 2   FAC induced wall thinning

Fig. 3   Typical single phase FAC pattern

are other options available for reducing the radiation field.

Flow Accelerated Corrosion (FAC)

Flow accelerated Corrosion is a process by which the normally protective oxide layer on carbon or low alloy steel dissolves under the influence of a stream of flowing water or a water- steam mixture. Under the influence high flow velocity and turbulence of the coolant, the oxide layer becomes thinner and less protective. In some instances the oxide layer may be so thin as to expose bare metal surface[1]. The damage caused by this type of phenomena can lead to a general reduction of wall thickness rather than a local attack (Fig. 2). In a single phase flow (only water) FAC, when the corrosion rate is high, the metal surface has a scalloped appearance (Fig. 3). For two-phase flow, the surface will have 'tiger striped' appearance. The rate of FAC depends upon hydrodynamic factors such as flow velocity, pipe roughness and geometry of the flow path etc., In addition, the environmental factors like temperature, pH, reducing agent and oxygen concentration and metallurgical factors like the composition of steel also affects the rate at which the carbon steel undergoes FAC. Thus, metal loss due to this phenomenon occurs over a limited area of piping due to high turbulence.

FAC in PHWR Feeder

A schematic diagram of the PHWR primary coolant system is given in Fig. 4. The primary circuit of PHWR reactors contains considerable quantities of carbon steel as the material of the feeder pipes and headers that connect the reactor fuel channels to the steam generator. FAC leading to wall thinning of outlet feeders, was first observed in one of the
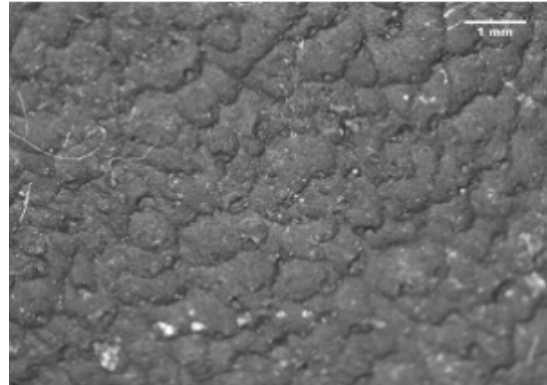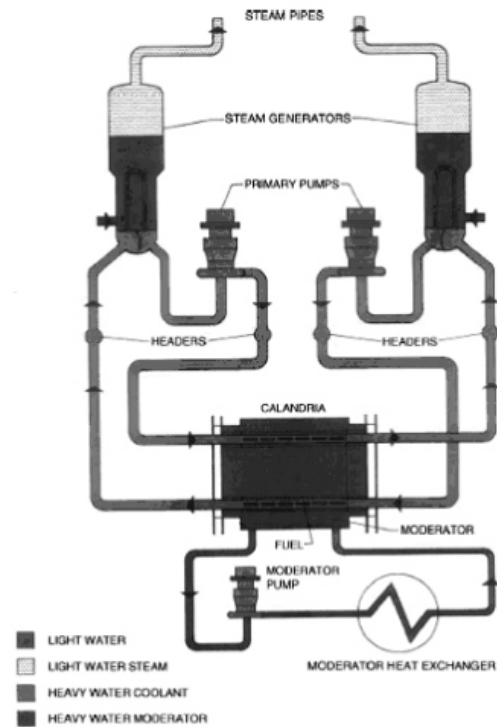

Fig. 4   Schematic of CANDU primary heat transport[4] system

CANDU reactor in 1994. Wall thickness measurements, especially at the extrados of the first bend, showed that this type of corrosion can reduce the wall thickness of the feeders to below the allowed limit within the reactor life time.
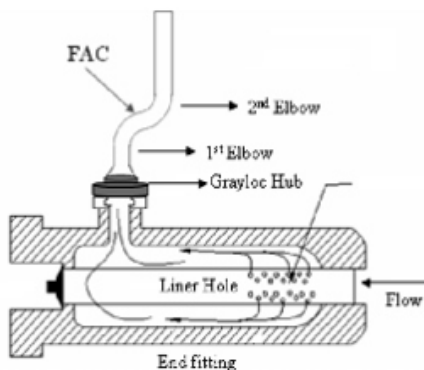
Fig. 5   Flow path of D₂O in the End fitting outlet feeder region

The susceptibility of outlet feeder for FAC can be understood by observing the D_2O flow path (Fig. 5). The D_2O leaves the end fitting annulus at a right angle and enters the Grayloc hub resulting in a disturbed turbulent flow at the entrance to the outlet feeder. The operating coolant velocities in coolant channels of PHWRs range from 8 to 18 ms^{-1}, yielding turbulent Reynolds number.in the range of 10^6 to 10^7. Steam quality in PHWRs is in the range 0 – 4 wt%.

The investigations carried out on the specimen taken out from the reactor showed a clear indication of single phase FAC in outlet feeders (seeing a temperature of 300 C and a coolant velocity of 15m/s) as its surface was having a scalloped appearance[4]. On comparison with the unused specimen, the corrosion rate of the outlet feeder was found to be 100 – 150 m/y which is much higher than the corrosion allowance provided during the design i.e. 75 m/y. Where as, the grayloc hub of the outlet feeder which joins the feeder to the end fitting and containing 0.13% Cr, showed corrosion rate of only 20 m/y.

Even though secondary side experiences show that FAC can occur at the temperature of 170 C also, no FAC was observed on inlet feeders where similar flow conditions exist as that of outlet feeders. The primary coolant loaded with iron enters the steam generator where the temperature drops from 300 to 250 C. This results in deposition of Iron in the steam generator tubes starting from the beginning of 180 bend near the hot leg and continues up to the core inlet. Coolant iron concentration drops to lower values during this transit. This fluid is again heated to 300°C across the core. The Iron saturation solubility is higher at 300°C as compared to 250°C at this temperature. The fluid under saturated in iron exits the reactor core and interacts with the carbon steel outlet feeders leading to excessive wear. This indicates that FAC is favoured when the coolant is under saturated with respect to dissolved iron. The Cr content in carbon steel was found to prevent FAC by forming a less soluble Cr rich oxide layer. Various loop studies showed that the threshold Cr concentration in Carbon steel to reduce FAC is 0.04%. Hence, it is expected that 0.2 % of Cr in CS will effectively reduce FAC.

Laboratory studies also indicated that lowering pH from 10.8 to 10.2 drastically reduced FAC rate. But the same effect was not observed in reactor, FAC rate decreased when pH was lowered from 10.8 to 10.4 but increased to its initial value when pH was further reduced to 10.2. Understanding the effect of pH on FAC is important from the point o view of reducing FAC in the operating plants, whereas switching over to Cr rich carbon steel could solve the problem for new reactors.

Optimisation of Water Chemistry

By efficient water chemistry control it is possible to control corrosion of these materials which in turn reduces the out-of-core contamination. In PHWRs, a pH_{300} of 7.4-7.6 is maintained using only LiOH and reducing condition is achieved by injecting 3- 10 cm^3/kg H_2 into the primary coolant. In all the reactors, utmost importance is given to purity of water with main emphasis on checking ingress of ionic impurities to minimise corrosion. Similarly dissolved oxygen is controlled (to <10 ppb) in order to protect the structural materials from general and localised corrosion like IGSCC etc.

Maintenance of pH is one of the main criteria for coolant chemistry control. The importance of water chemistry control can be understood by analysing the mechanism of activity transport brought about by both soluble as well as particulate corrosion product oxides. For practical purposes it is assumed that whatever passes through 0.45ìm filter constitutes soluble species. In PHWR, the dominant
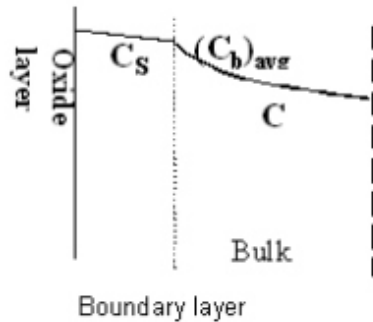
Fig. 6

corrosion product oxide is magnetite (Fe_3O_4) and nickel ferrite ($Ni_xFe_{3-x}O_4$).

Control of soluble species transport

The soluble ions along with the radionuclide get incorporated in the growing oxide layer through co-precipitation. The dissolution/crystallization of the oxide layer is a combination of two processes i.e. dissolution/crystallization of oxide crystal on the surface and mass transfer of dissolved ions across the boundary layer (Fig. 6).

The processes are mainly driven by the difference in concentration of iron in the bulk (C_b) and the solubility of iron in the corrosion product oxide (C_s) at the temperature of the surface film. Solubility for pure magnetite and nickel ferrite has been widely studied. Solubility of magnetite can be represented by the following equilibrium,
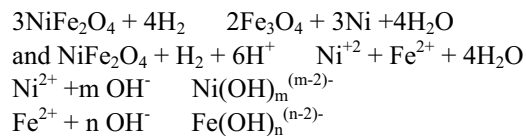
$$1/3\ Fe_3O_4 + (Z\text{-}b)\ H^+ + (4/3 - z/2)\ H_2$$
$$Fe(OH)_b^{(Z\text{-}b)+} + (4/3 - b)H_2O$$
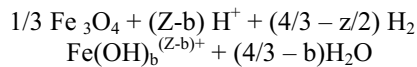
where z =2 refers to Fe^{2+} and Z=3 refers to Fe^{3+}, b=0 to 3 for Fe^{2+} and b=3 to 4 for Fe^{3+}

Solubility $Cs = [Fe(OH)_b^{(Z\text{-}b)+}]$

As can be seen from the above equation, solubility is controlled by pH (maintained by using LiOH), dissolved H_2 and hydrolysis constants of all the iron species and their dependence on temperature. The concentration of Fe^{2+} species is proportional to $p(H_2)^{1/3}$ and Fe^{3+} is proportional to $p(H_2)^{-1/6}$, indicating that the dependence of solubility on dissolved H_2 is fairly weak. pH_T can be calculated from the above equilibrium, by setting up charge balance equation for the system, and using best estimated K_w values at any given temperature. In cases where boric acid/ ammonia is present along with LiOH, their dissociation reactions are also included for pH calculation. The hydrolysis constants for various iron hydroxides are computed using principles of thermodynamics.

Similarly for Nickel ferrite, the equilibrium is given by

$$3NiFe_2O_4 + 4H_2 \quad 2Fe_3O_4 + 3Ni + 4H_2O$$
$$\text{and } NiFe_2O_4 + H_2 + 6H^+ \quad Ni^{+2} + Fe^{2+} + 4H_2O$$
$$Ni^{2+} + m\ OH^- \quad Ni(OH)_m^{(m\text{-}2)-}$$
$$Fe^{2+} + n\ OH^- \quad Fe(OH)_n^{(n\text{-}2)-}$$

To reduce radiation field build up in reactors the recommended pH should be such that, at that pH_T there is minimum corrosion release from structural materials and minimum deposition of corrosion products in the core. So, a pH of minimum solubility and zero temperature coefficient of solubility [TCS i.e. $(dS/dT)_{pH} = 0$] is desired. Numerous experimental studies of magnetite solubility have been carried out by different groups, in the range of 200 C to 300 C with H_2 in the range $10-20$ cm^3/kg. The pH_{300} of minimum solubility observed, ranged from 6 to 8. The variation of magnetite solubility with pH_{300} calculated (Tremaine and Leblanc) is given in Fig. 7 .These solubility studies show that at normal PHWR operating temperatures (~300 C) there is a negative temperature dependence of solubility of iron in acidic solutions, a zero temperature dependence in weakly alkaline solutions and a positive dependence in moderate and high alkaline solutions. Similar observations were made by Sandler and Kunig in their experiments measuring solubility of a variety of synthetic non-stoichiometric nickel ferrite from RT to 350 C, with H_2 10-20 cm^3/kg that yielded a pH_{300} of minimum solubility in the range of 5.0 to 8.5. Figure 7 demonstrates the variation of solubility of iron in magnetite with temperature for given pH_T. It shows that At pH_{25} <9.7 there is a negative temperature gradient for solubility, where as pH_{25} 10 has positive temperature gradient of solubility. It implies that at PWR and PHWR operating temperatures, the coolant traversing through the core sees driving force for dissolution if any oxide is present in coolant
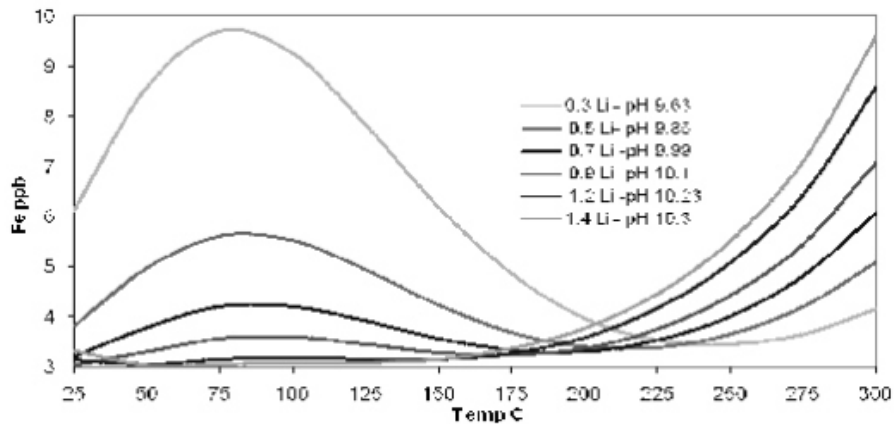
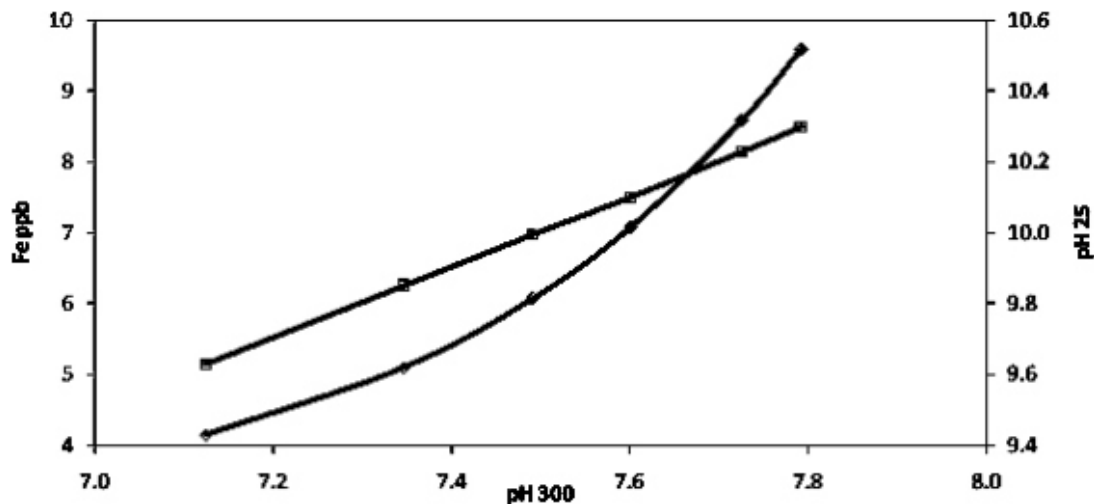*Fig. 7   Magnetite solubility variation with temperature and pH*

Fig. 8   Magnetite solubility as a function of High temperature pH

or on in-core surfaces. For the steam generator surfaces where temperature decreases from 320 C to 250 C, the solubility tends to decrease and the supersaturation of the coolant is relieved by oxide precipitation or crystallization on the surface. Hence pH_{25} of 10 and above are favourable for minimizing in-core deposition and it is the basis for the existing pH_{25} range of 9.5 – 10.5 (approximately equal to pH_{300} of 7.2 Fig. 8) in PHWR. These solubility studies are quite helpful in understanding the scientific basis involved in the phenomena. It should be noted that the stoichiometric composition of oxides formed in reactor systems are not well defined and so are different from whatever oxides are studied in laboratory experiments. Also lots of uncertainties exist because of the differences in the available correlations for K_w used for high temperature pH calculation. These factors lead to large standard deviation in pH of minimum solubility and large pH range for the occurrence of total corrosion product solubility co-efficient (TCS) 0.

Metal Ion Passivation

Once the transport of iron across the inner layer is altered, corrosion is reduced. This in turn reduces

the inventory available for activation in the core, which results in lowering of radioactivity build up. In the Metal Ion Passivation technique (MIP) a highly protective, tenacious film is formed on the metal by continuous injection of the modifying ion (in ppb levels). This film results in reduced activity build up and lower corrosion rates. It is still not fully known how this added metal ion helps in achieving lower radiation levels. The added metal ion has been found as ferrite on the metal, but the added amount is not sufficient enough to form a uniform protective coating over the metal. Its presence in grain boundaries, thus effectively blocking transport pathways have not been proved conclusively. Re-circulating loop experiments have demonstrated the effectiveness of this procedure, but conclusive proof is elusive.

Plant and loop experience

MIP methodology was first adopted by BWR's and is widely used now[1]. Zinc as depleted Zinc Oxide (to avoid ^{64}Zn) is the passivating agent used. Re-circulating loop and plant experience have amply demonstrated that Hydrogen water chemistry (reduces stress corrosion cracking of stainless steels) along with zinc injection reduces radiation field build up. In re-circulating loop experiments many other ions like (Mg, Mn, Ni) have been tried and were found to be effective. In PWR's also beneficial effects were found in loop experiments. It was found that on new metal surfaces, zinc addition results in thinner oxide layers and lower incorporation of cobalt in to the oxide. Depth profile studies have indicated presence of ^{60}Co and Zn in the outer layer. In Farley-2 reactor, channel head dose rates decreased considerably during Zinc addition. [2]

MIP in PHWR

Under PHWR chemistry conditions only some re-circulating loop experiment data is available. In the case of 410SS, the ^{60}Co activity deposited reduced by a factor of 10 and for carbon steel it reduced by a factor of 2 at 10ppb Zn concentration.[3] Similarly iron release rates for carbon steel came down by a factor of 18 and corrosion by a factor of 2.5 and for SS410 it reduced release by a factor of 16 and corrosion by a factor of 8. Some studies carried out with Mg have also shown reduction of Corrosion and corrosion release in Carbon steel and Monel.

The beneficial effects of passivating metal ion were found at lower concentrations and it did not improve on further addition. This indicates that the protective behaviour is not due to the formation of films ie Zinc ferrite, but may be the presence of these ferrites or oxides in the grain boundaries and thus blocking them. The role of zinc ion in reducing the radiation field build-up in the stainless steel surfaces of BWRs and PWRs is being studied to understand the mechanism of its action. Alternative metal ions such as Mg^{2+} can be a substitute for zinc ion especially in PHWR primary coolant systems. Hence, an in depth study to understand the effect of passivating metal ions for a system dominated by carbon steel such as the PHWR primary coolant system is necessary.

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Role and Responsibilities of a Station Chemist in a Nuclear Power Station – A Perspective

Dr.K.S.Krishna Rao is from the 14th Batch of BARC Training School and joined in the Chemistry Division, BARC in 1971. Subsequently he was transferred to RAPS in 1974 and then to MAPS as Station Chemist in 1976. He has rich experience of 37 years in the field of Power Reactor Water Chemistry. He obtained his Ph.D degree from the University of Madras in 1989.

The job of a Station Chemist in a Nuclear Power Station is multidisciplinary in nature and he has a major role to play in the smooth, safe and efficient operation of the Power Station. The prime responsibilities of the Station Chemist are :

1. Optimisation of Chemical Control parameters to minimise corrosion related problems in the reactor / conventional systems and in the various heat-exchangers of the process systems.

2. To maintain the chemical parameters in all the systems well within limits as required by the Technical Specification Documents of the Stations. Any deviations/off-normal values of the chemical parameters are to be brought to the notice of the Station Management and also to be reviewed by the Station Operations Review Committee (SORC).

3. To minimise the build-up of radiation fields on the out-of-core surfaces of the Primary Heat Transport / Coolant System so as to reduce man-rem / person-sievert expenditure of the station during maintenance works.

4. Active participation in the ageing management and PLEX programmes of the Station.

5. To ensure the reliability of the analytical data generated in the Chemical Control Laboratory.

6. Upgrading the analytical facilities of the laboratory and to ensure the reliable performance of the laboratory analytical instruments as well as that of the on-line analysers of the process systems to take prompt corrective actions as and when required.

7. Adoption of fast and reliable analytical techniques.

8. Updating the professional knowledge of the chemists by proper coordination with R&D laboratories and making available the literature/ reports related to the latest developments in the Power Reactor Water Chemistry.

9. Implementation of the good practices.

10. Strict chemical control measures to be adopted in the water cooled systems of reactor safety related equipment like Diesel Generators.(Ex: Jacket cooling water circuits)

11. Chemical and biofouling control in the tertiary circuits of the Power Station (Ex: Cooling Towers, Condenser Cooling Systems). In the coastal-based stations, macrofouling control in the sea water cooling circuits assumes utmost importance for the efficient performance of the Station.

12. Preservation of process circuits/systems during shutdown periods.

In order to fulfill the above objectives and discharge the responsibilities/duties in an efficient manner the Station Chemist should have the knowledge of following .

1. Understanding the Operational & Engineering aspects of all the systems of the Station.

Dr.K.S. Krishna Rao, Station Chemist & HW Manager, Madras Atomic Power Station, Kalpakkam 603 102; E-mail:

2. Metallurgical aspects of the structural materials of the circuits /systems with reference to corrosion control.

3. Knowledge of the laboratory analytical/on-line instruments.

4. Radiological & Industrial Safety aspects.

5. Chemical and Physical properties of the lubricating / insulating oils used in Station Electrical Equipment and their testing procedures.

6. Biological aspects of corrosion

7. Spectroscopy techniques viz., Infrared, Atomic Absorption, UV –Visible, Radiochemical & Gamma spectral analyses etc;

The normal routine analytical works carried out in the Chemical Control Laboratory of the Power Station(PHW type) are:

1. Isotopic analyses of heavy water samples in the range of 0.01% to 99.98% D_2O

2. Determination of the concentration of ionic and metallic impurities at ppb/ppm levels in light &heavy water samples.

3. Analyses of ion-exchange resins.

4. Radiochemical analysis for fission and corrosion products.

5. Analyses of insulating and lubricating oils for critical parameters.

6. Analyses of cover gas samples of Moderator, PHT& Turbogenerator systems by Gas Chromatography and also checking the purity of the gases in cylinders procured by the Station

The following significant chemistry related jobs carried out at MAPS illustrate the above viewpoints / importance of chemical control and gives a perspective of the role of the Station Chemist.

1. A total number of six Dilute Chemical Decontamination Campaigns (three in each reactor) were carried out in the Primary Heat Transport (PHT) Systems of MAPS-1&2 during the period 1993-2003 in order to reduce the out-of-core radiation fields mainly due to Co-60 activity in collaboration with /guidance

of WSCD/ BARC, COSWAC and NPCIL -HQ after getting approvals from safety bodies. The objectives of the campaigns carried out during 2001 in MAPS-2 and during 2003 in MAPS-1 were to reduce the man-rem / person- sievert expenditure during the Enmass Coolant Channel Replacement (EMCCR) jobs. The high Co-60 activity in the PHT systems encountered during the initial period of operation of the reactors was due to use of stellite (Cobalt - based alloy) coated primary seals in the Primary Coolant Pumps. Subsequently, the seals have been replaced with Cobalt free alloys. Hence by reducing the source term of cobalt 59 and with DCD Campaigns, the radiation fields on the out-of-care surfaces had got reduced significantly. During 1993 (i.e., before the first DCD campaign of MAPS-1) the total man-rem(external) consumption in both reactors was 822 whereas it was 118 in 2007 after the six DCD campaigns and taking the corrective measures as mentioned in this article.

2. The cover gas in the PHT storage tank was changed from costly helium to nitrogen in MAPS-2 during the initial operation of the reactor in 1985 on an experimental basis. After ensuring the satisfactory performance of nitrogen gas with respect to Chemical Control and also from the operations viewpoint , nitrogen was continued as the PHT cover gas. Subsequently the cover gas in the PHT Systems in all the Indian PHWRs had been changed over to nitrogen. This change over had proved to be cost effective and also beneficial from the chemistry view point. However the PHT cover gas in PHWRs abroad continued to be helium. (Maximum limit for nitrogen : 6% V/V).

3. MAPS has twin PHW- type reactors that uses sea water for cooling the main steam condensers of the Turbines. In the case of leaks from the condenser tubes during the period 1983 to 1989, the sea water contaminated condensate/feed water used to go directly to the Boilers/Steam Generators, resulting in high specific conductivity and low pH (due to hydrolysis of $MgCl_2$ present in sea water) in the

Boiler water, highly conducive for corrosion phenomena. The congruent phosphate treatment used to be carried out during the ingress occasions of the sea water has not been found satisfactory. Hence full flow Condensate Polisher Plant (CPP) with macroporous resins was retrofitted in 1989 in the condensate and feed water circuits of both the reactors.

Morpholine has been used as the alkalizing agent to maintain the pH of the secondary circuit (Boiler feed water) in the range of 8.8 to 9.2 in all PHWRs. It gets uniformly distributed in the circuit as the distribution ratio between steam and water is 1.3 at 250^0C. Since the cation resin of the CPP removes morpholine as morpholinum ion, booster dosing is done at the down stream of the ion-exchange (CPP) beds. As the cation gets saturated with morpholine, leaching of sodium ion increases from CPP beds resulting in the pH variations and high ionic conductivity in the SG/Boiler water. In addition, sulphate leaching has also been observed from the macroporous CPP resins when condensate temperature was high ($>45^o$c) resulting in reduction in pH of Boiler Water. The increase in morpholine concentration has not been found to improve the situation. In fact it has been observed that the leaching of ionic impurities from the saturated beds used to increase with the morpholine concentration. Hence vigorous efforts have been made to identify a superior amine to replace morpholine. Based on the published reports and the R&D work carried out at WSCD, BARCF, it has been decided to use Monoethanolamine (ETA) in the secondary circuits of both MAPS-1&2 after getting necessary approvals from COSWAC and safety bodies. The advantage with ETA is that the pH in the secondary circuit increases progressively from hot well (8.5-8.6) to Boilers/ Steam Generators (9.3-9.5) and the quantity of chemical required is also less (One-third of morpholine) due to higher basicity. As the concentration of ETA is minimum (~1 ppm) at CPP inlet (unlike morpholine which will have concentration of 6-8 ppm due to the uniform distribution), the service cycle of the beds is prolonged before

saturation and hence minimises the leaching of ionic impurities. Apart from better Chemical Control in SGs, the change over from morpholine to ETA at MAPS resulted in the overall savings of ~ Rs.25 lakhs per annum mainly due to the lower consumption of chemicals and also reduced frequency of regeneration of CPP ion-exchange beds. After the good experience at MAPS, the other Indian PHWR stations switched over to ETA.. The cost effective chemical treatment in the secondary circuit at MAPS has been selected as a good practice by CANDU OWNERS GROUP (COG) and put on their website as COG-GP-20. MAPS-1 was the first PHWR to effect this change.

4. Colloidal activity contributes 20-30% to the radiation fields on out-of-core surfaces of the PHT system and the major contributors are Co-60 & Zr-Nb- 95. In order to reduce the radiation fields due to colloidal activities, sub-micron filters (1.1 micron size absolute filters) have been installed in the PHT system of MAPS-1 since 1998 and in MAPS-2 from 2003 onwards. The normal cellulose based filters used in the PHT system remove particles of 10 microns and above only.

5. The performance of the heat-exchangers play a major role in Heavy Water Reactors. Any pinhole leak in the tube of a heat-exchanger, results in the tritium and radioactivity release and contamination of cooling water on the shell side. In RAPS-1&2 lake water is used (once-through) for cooling these heat–exchangers and from MAPS onwards this has been designed as closed loop system with chemically treated demineralised water. This change helped significantly in minimising the corrosion related problems in the heat-exchangers. It is gratifying to note that the performance of these HXs at MAPS has been extremely good and the percentage of plugged tubes in the past 25 years of operation was very low. (< 5%)

6. The growth of small sized barnacles (Balanus reticulatus) has been found to be high in the Process-Sea water Heat-Exchangers as the temperature was conducive for their growth

and as a result the heat transfer was affected. Further it has been found difficult to clean these HXs during shutdown periods as the fouling calcareous deposits were hard in nature. Actibromide Treatment has been started in these HXs since 1995 to control the growth of barnacles and the treatment was found to be effective in minimising the fouling and improved the performance of the HXs. Further it has been found easy to clean these HXs in short time during shutdown periods as these deposits were found loose and less in quantity with actibromide treatment.

Thus the Station Chemist plays a major role in minimising corrosion related problems, reduction in manrem expenditure, PLEX programmes and efficient performance of the Station by optimisation / maintenance of good chemistry control in various process systems.

Gamma spectrometric measurements on PHT and Moderator systems of PHWRs

Dr. B.S.Tomar *obtained his M.Sc. Degree in chemistry from Garhwal University, Srinagar in 1979. He joined the 25th batch of the BARC Training School in 1981 and won the Homi Bhabha Prize for securing the academic excellence. Subsequently he joined the Radiochemistry Division in 1982. He obtained his Ph.D. degree in Chemistry from Bombay University in 1990. His areas of research include Nuclear Chemistry in general and Nuclear Fission, Nuclear reactions, Perturbed Angular Correlation, Ion Beam Analysis and Speciation of actinides and fission products in particular. He is a Ph.D. guide of University of Mumbai as well as professor of Homi Bhabha National Institute and has a large number of publications in the international journals. He is a member of the IAEA expert panel on Radiation Detection and Measurement. Presently he is heading the Actinide Chemistry Section of Radiochemistry Division, BARC.*

Shri Sumit Kumar *joined the Radiochemistry Division, BARC, in 2003 after graduating one-year training program on Nuclear Science and Technology of BARC Training School. His research interests are application of Radio-analytical techniques in various scientific problems and Actinide Speciation in environment.*

Shri T.P. Chaturvedi, *an electronic engineer, joined Radiochemistry Div, BARC in 1981. He has extensive experience in radiation detector systems and nuclear instrumentation. He has developed computerized data acquisition systems for fuel pin scanner and LVDT microscanner for post irradiation examination of reactor components. He interfaced and automated the cryogenic temperature controllers for positron annihilation spectrometry and data acquisition system for photo acoustic spectrometer. His current interests include development of magnetic barkhausen noise acquisition system for the study of stresses in reactor components, digital signal processing for zero dead time spectrometers and assessment of the high radiation field at power reactors. He is a member of The Institution of Engineers (I).*

Dr. V.K. Manchanda

Dr. B.S. Tomar, Shri Sumit Kumar, Shri T.P. Chaturvedi and Dr. V.K. Manchanda, Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085; E-mail:

Introduction

Minimising radiation field buildup in the primary heat transport system (PHT) has been the focus of water chemistry maintenance in water-cooled nuclear power plants. Identification and quantification of the radionuclides responsible for the high radiation levels in the PHT system helps in planning the decontamination strategies, in predicting the rate of build up and in evaluating the effectiveness of water chemistry domain. This requires on-line gamma ray spectrometric measurements at various locations of the PHT, where the radiation levels may vary from a few mR/h to a few hundred mR/h. Further the ambient temperature in some areas may be as high as 40 C at which conventional high resolution HPGe detectors are extremely difficult to use. HPGe detectors require the cooling to liquid nitrogen temperature and need the associated electronic set up. Further the large volume (50-100cm^3) of the Ge detector, commonly available in radiochemical laboratories, leads to high-count rates and hence high dead time/ pile up effects. NaI(Tl) detector, though can be operated at room temperature, but suffers from the limitations of poor energy resolution (~7% at 661 keV) with which it is not possible to resolve the close lying gamma lines in the gamma ray spectrum. In view of this a small volume (0.5cm^3) CdZnTe detector connected to a portable multi-channel analyzer (MCA) was used for gamma ray spectrometric measurements. The present article gives a brief description of some of the measurements carried out at the PHT and moderator systems of PHWRs at Narora (NAPS#1 &2), Rawatbhata (RAPS#3 &4) and Kakrapar (KAPS1&2).

Detection System

The detector is based on high band gap semiconductor (CdTe) with small amount of Zn to increase the resistivity of the detector material. The high band gap (1.6 eV) enables it to be operated at room temperature. At the same time the relatively better energy resolution (~2% at 661 KeV) compared to NaI (Tl) detector is sufficient to resolve the gamma lines of interest. The small volume of the detector helps in using it in high radiation fields without any dead time/ pile up effects, which was
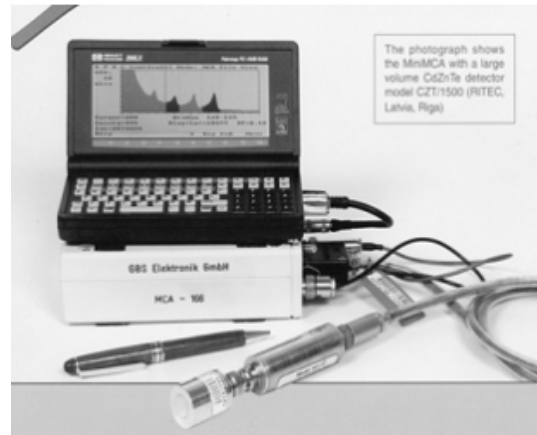

Fig. 1   CdZnTe detector system

further taken care of by shielding the detector with a 75mm thick lead shield. The details of the detector system can be found in [1]. Figure 1 gives the photograph of the CdZnTe detector system. Since the dimensions of the source of gamma rays are large compared to that of the detector, the measured activity is the sum total of all the activity due to radionuclides deposited through out the pipelines in the vicinity of the detector system. In order to minimise the contribution from surroundings, the detector was housed in a cylindrical lead shield having OD=75 mm, ID=30 mm with a collimator in the front having OD=75 mm, ID=10 mm and length= 100 mm. The entire assembly was housed in an aluminum casing so as to make the shield and the collimator concentric. Figure 2 shows the schematic of the collimator.

Gamma Ray Spectrometric Measurements

The first set of Gamma ray spectrometric measurements were carried out on PHT, Moderator, End-shield and Calandria Vault of NAPS Unit # 2 during May 24-25, 2005. Subsequently measurements were carried out on PHT and moderator lines of both the units of Narora Atomic Power Station (NAPS) during May 15-18, 2006. These were followed by measurements on the PHT system of RAPS3 during September 8-9, 2006 and at KAPS1&2 during November 30- December 1, 2007. The length of the collimator for measurement at KAPS was reduced in view of the lower levels of radioactivity. The efficiency calibration of the
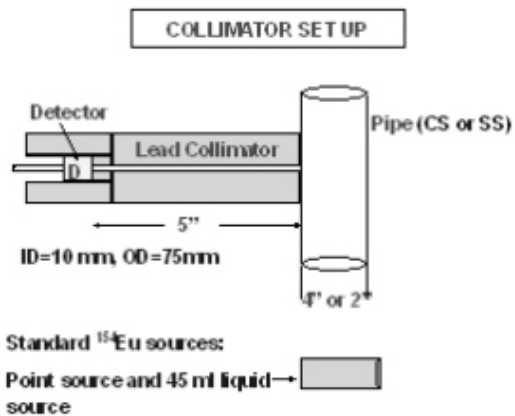
Fig. 2   Collimator set up

Fig. 3   Gamma ray spectra of PHT system of NAPS-2 (a) line (100s), (b) fluid (300 s)
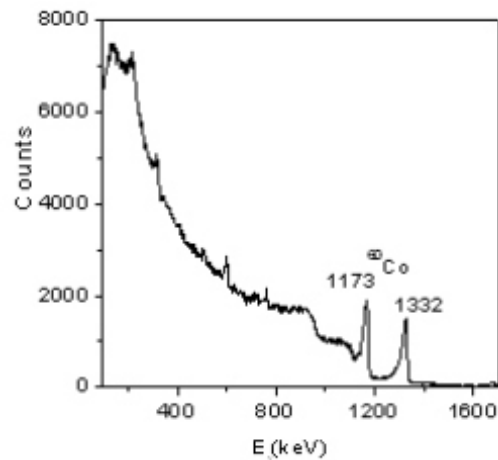
Fig. 4   Gamma ray spectrum of Moderator line of NAPS-2

detector was carried out by counting the standard source of ^{154}Eu in the desired geometry of a point source as well as an extended source in the form of a polypropylene tube of length 100mm and diameter 30mm. Correction factors for contributions from sideways to the spot of measurements were also determined by measuring the count rate from intense sources of ^{137}Cs and ^{60}Co kept at a varying distance from the center of the collimator.

Results and Discussion

Figure 3 shows the gamma ray spectra of PHT purification by-pass lines as well as the PHT fluid sample of NAPS-2, which suggests much higher concentrations of fission and activation products in the pipelines as compared to the fluid samples. The spectra show that the major activity in both the samples is due to ^{124}Sb. Figure 4 shows the gamma ray spectra of moderator pipelines in the purification building and the moderator fluid sample. In this case the dominant activity is due to ^{60}Co. Figures 5 shows the typical gamma ray spectrum recorded at RAPS-3 FM Vault (North) in the Reactor Building, where the activity levels were maximum. The gamma ray spectra of CdZnTe detector were analysed using the peak fitting program, PHAST, developed by Electronics Division, BARC. The program employs nonlinear least square fitting of the gamma peaks with a function comprising a Gaussian with lower exponential tail and polynomial background. The shape parameters of the peaks as a function of gamma ray energy were obtained using the gamma
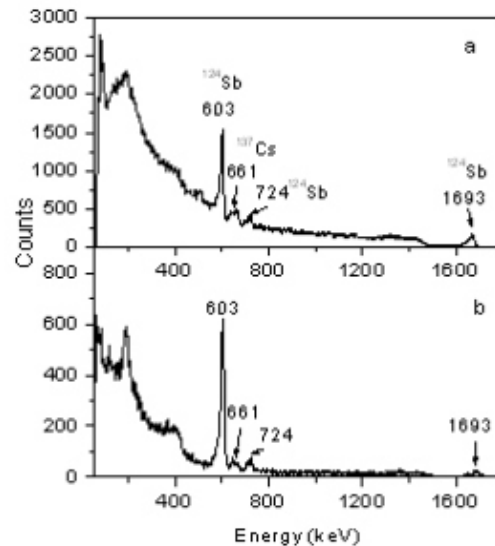
ray spectra of ^{154}Eu, which was also used for efficiency calibration of different geometry samples and energy calibration of the MCA. The lower exponential tail is a significant feature of the gamma ray peaks in CdZnTe detector due to large number of electron trapping centers present in the crystal. The activity of radionuclides deposited in the pipe lines were obtained from the measured count rates after correcting for the detection efficiency, contribution

from sideways and the activity deposited on the opposite side of the pipe.

Table 1 and 2 give a comparative data of activity of ^{124}Sb and ^{60}Co (in Ci/cm^2) fixed on the
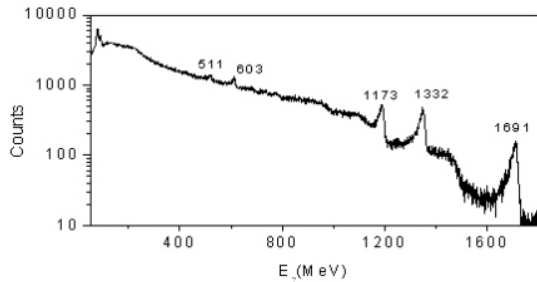

Fig. 5   Gamma ray spectrum of EM vault (N) of RAPS-3

PHT piping and other locations in Reactor Building and Reactor Auxiliary Building of NAPS#1, RAPS#3 and KAPS#2.. As can be seen from the tables, PHT pipelines of all the reactors are contaminated with ^{124}Sb at certain locations, which has a half life of 60 days and has a large number of gamma rays ranging from 603 KeV to 2.09 MeV. The spectra recorded on other parts of PHT lines also revealed some fixed activity due to ^{60}Co though the PHT fluid sample did not show any activity due to ^{60}Co. The activity of ^{124}Sb in the PHT fluid sample was found to be very small compared to that observed in the PHT lines and hence was not corrected for in the in-situ measurements. The gamma spectrometric survey, from PHT bleed circuit up to purification inlet line, indicated presence of ^{124}Sb along with contribution from ^{60}Co. Comparison of the activity in pipe lines and fluid samples revealed that most of the gamma activity

TABLE 1. Comparison of activity (Ci/cm^2) of ^{124}Sb at different power stations

Location	NAPS1	NAPS2	RAPS3	KAPS2
Shut down start date →	15.10. 2005	14.05.2006	29.08.2006	01.11.2006
Measurement date →	15.05.2006	16.05.2006	08.09.2006	30.11.2006
Bleed Condenser		8.4	2.5	2.0
PHT Bleed Condenser Inlet		5.8		
PHT Bleed Condenser outlet		8.4	2.5	
Up stream BCD CV		8.2		
Regenerative HX			6.6	
SG Hot leg		0.4	0.9	
SG cold leg		1.4		
Shutdown HX-I				1.2
Down stream of primary pressurising pump			2.8	
PHT PCP	0.7			
PHT purification inlet	2.8	12.2	7.9	
PHT purification outlet	1.8	9.8	2.1	
FM Vault (S) Close position			34.5	7.2
FM Vault (N) close position			55.8	7.3

TABLE 2. Comparison of activity (Ci/cm2) of ^{60}Co at different power stations

Location	NAPS1	NAPS2	RAPS3	KAPS1	KAPS2
Shut down start date →	01.11.2005	14.05.2006	29.08.2006	—	01.11.2006
Measurement date →	15.10.2006	16.05.2006	08.09.2006	01.12.2006	30.11.2006
Bleed Condenser		1.4	2.5		0.7
Moderator lines in purification building	18	36			
Moderator pump	165	180			
Moderator HX inlet	61	32			
Moderator HX drain		284			
SSS Tank -4		8	3	3.4	2.5
ALPAS Tank		6		3.4	
Down stream of primary pressurising pump				26	
FM Vault (S) lose			82		22
FM Vault (N) close			54		55
FM (S) outlet feeder	9.2				30

observed in the pipe lines of PHT system has got fixed in the pipelines. In comparison to other locations inside Reactor Building, the observed activities are higher in FM Vault areas, which is mainly due to ^{124}Sb and ^{60}Co.

In the case of KAPS#2 the FM vault (N) was observed to have higher radiation levels than that in FM vault (S). The difference was found to be due to ^{60}Co, while the ^{124}Sb activity was same in both the locations.

Conclusions

The measurement of gamma activity of radionuclides present in the PHT and moderator lines were carried out using a small size CdZnTe detector. It is now established that such measurements can be easily made in power plants for quantification of radioactive contamination. The data showed significant activity of ^{124}Sb in PHT lines and that of ^{60}Co in moderator lines. Comparison of the on line measurement data with that of the fluid

samples revealed that most of the activity was fixed on the pipe lines. Measurements were also carried out on the feeder pipes in FM Vault, which showed significant activity mainly because of ^{124}Sb and ^{60}Co.

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3. Identification and estimation of radionuclides responsible for high radiation dose in the PHT/Moderator pipe lines of NAPS#2, B.S.Tomar, T.P.Chaturvedi, S.K.Upadhyay and V.K.Manchanda, INS Annual Conference, Nov. 15-18, 2005, Mumbai.

Roundup

The 66th BRNS-IANCAS "National Workshop on Radiochemistry and Applications of Radioisotopes" (NWRAR) was inaugurated by Prof. Diwakar Shastri, President, Banasthali University on February 7, 2008

Prof. Rekha Govil

The workshop was being jointly organized by the "Indian Association of Nuclear Chemists and Allied Scientists" (IANCAS) and Department of Physics, AIM&ACT, Banasthali University during 7-15 Feb. 2008. Prof. Rekha Govil, Dean, AIM & ACT and Convener of the workshop welcomed all the resource persons from BARC, participants and students.

Dr. V.K. Manchanda, President, IANCAS and Head, Radiochemistry Division, BARC emphasized the need for energy in general and nuclear energy in particular. The association celebrated its silver jubilee in January 2008 and has been playing an important role in popularizing nuclear science in general and discipline of radiochemistry in particular. Shri S.K. Chande, Vice-chairman, Atomic Energy Regulatory Board (AERB) discussed about the Indian nuclear power programme. He stressed that the safety standards of nuclear industry worldwide as well as in India are very high. He mentioned that whereas in the history of nuclear industry, there have been only 2 major accidents when compared to many more in the same period. However, the nuclear industry worldwide has further enhanced the safety standards and the regulatory aspects to ensure that this industry is safe. Shri Chande was very appreciative of the culture developed in Banasthali in the staff as well as the students.

There were 5 special lectures delivered by Shri Chande of AERB, Dr.Manchanda, Dr.Meera Venkatesh, Shri Kanwar Raj and Shri B.K. Sen respectively on topics 1.Safety Standards in nuclear power plants, 2. DAE activities at a glance, 3. Applications of Radioisotopes for the societal benefit, 4. Nuclear waste management and 5. Production & Applications of Radioisotopes in Industry.

Shri B.K. Sen, Head, Produuct Development Division, BARC was the Chief Guest during the valedictory function and handed over the equipment to the host institute to encourage them to continue the work initiated by IANCAS in popularising the subject of Nuclear Chemistry.

In addition to the main workshop there was a lecture cum demonstration programme for the students of 11th, 12th and B.Sc./M/Sc in schools.

Dr.Veena Sagar and Dr.K.V.Lohitakshan are the coordinators and Dr.P.K.Pujari, Shri K. Sudersan, Dr.Y.P. Naik, Smt. Sashikala Ojha, Dr.D.G.Phal from BARC and Shri Chandan Kumar from BRIT were the other resource persons.

IANCAS deeply regrets the sad demise of Prof. Rekha Govil, Ex- BARC, and also Coordinator of the recently held BRNS-IANCAS National Workshop at Banasthali on 10-09-2008